

Emission of hydrogen from deep and shallow freshwater environments

H. SCHÜTZ,¹ R. CONRAD,² S. GOODWIN³ & W. SEILER¹

¹Fraunhofer Institut für Atmosphärische Umweltforschung, Kreuzteckbahnstrasse 19, D-8100 Garmisch-Partenkirchen, FRG; ²Universität Konstanz, Fakultät für Biologie, POB 5560, D-7750 Konstanz, FRG, (requests for offprints); ³Dept. of Microbiology, University of Massachusetts, Amherst, MA 01003, USA

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Abstract. In-situ partial pressures of hydrogen in anoxic profundal lake sediments reached values of up to 5 Pa which were more than 5 orders of magnitude lower than the partial pressures of methane. Analysis of gas bubbles collected from anoxic submerged paddy soil showed H₂ partial pressures in the range of 1.8 ± 1.3 Pa being ca. 4 orders of magnitude lower than the CH₄ partial pressures. H₂ emission rates, on the other hand, were less than 3 orders of magnitude lower than the CH₄ emission rates indicating that H₂ and CH₄ were oxidized to a different extent in the rhizosphere of the soil before they reached the atmosphere, or that H₂ was produced by the plants. More than 70% of the emitted H₂ reached the atmosphere via plant-mediated flux. The rest was emitted via ebullition from the anoxic soil and, in addition, was produced in the paddy water. A significant amount of H₂ was indeed found to be produced in the water under conditions where thallic algae and submerged parts of the rice plants produced oxygen by photosynthesis. Very little H₂ was emitted via molecular diffusion through the paddy water; in addition, this amount was less than expected from the degree of supersaturation and the diffusional emission rate of CH₄ indicating a relatively high rate of H₂ consumption in the surface film of the paddy water. The total H₂ source strength of rice paddies and other freshwater environments was estimated to be less than 1 Tgyr⁻¹, being negligible in the atmospheric budget of H₂.

Introduction

While the microbial production, turnover and emission of methane in oxic or anoxic aquatic environments has been studied by many researchers, (e.g. reviews by Rudd & Taylor 1980; Hanson 1980; Seiler 1984) that of hydrogen has received relatively little attention. Hydrogen is produced in anoxic methanogenic or sulfidogenic environments by fermentative bacteria. However, its partial pressure is kept at a very low value through consumption by methanogenic or sulfidogenic bacteria which thus make the decomposition of organic matter possible for the anaerobic microbial community (Zehnder 1978; Zeikus 1983; Nedwell 1984). Because of the low H₂ concentrations in

aquatic sediments, it is generally believed that these environments are only a marginal source for atmospheric H_2 (Koyama 1964; Seiler 1978; Seiler & Conrad 1987).

From profundal sediments both H_2 and CH_4 can escape into the atmosphere by ebullition and by diffusion through the water column. During diffusional transport most of the CH_4 may be utilized by pelagic bacteria and thus, is not released into the atmosphere (Fallon et al. 1980). A similar situation exists for sedimentary H_2 (Conrad et al. 1983). Hence, the only significant escape mechanism of H_2 would be ebullition concomitantly with CH_4 according to their relative partial pressures in the sediment. Mainly because of analytical problems there is a marked lack of data on in-situ H_2 partial pressures which has just recently been overcome by development of analytical techniques (Conrad et al. 1983, 1985; Scranton et al. 1984).

Littoral sediments are completely different from profundal sediments, since they are usually vegetated with higher plants which mediate the exchange of reduced gases from the sediments into the atmosphere (DeBont et al. 1978; Dacey & Klug 1979; Sebachner et al. 1985). Hence, three different transport processes may contribute to the flux of H_2 from shallow aquatic environments into the atmosphere:

- diffusion through the water column,
- ebullition, and
- plant-mediated flux.

In this paper, we will describe field measurements in freshwater lakes and in rice paddy fields which were conducted to characterize and quantify the flux of H_2 from sediments into the atmosphere. For this purpose, we determined the concentrations of dissolved H_2 in the water column and the sediment of different lakes. In paddy fields, we used the static box technique to determine diffusional and plant-mediated flux of H_2 and CH_4 , and used funnels to determine ebullition rates and to measure the mixing ratios of H_2 and CH_4 in the trapped gas as well as in gas bubbles stirred out of the submerged soil. H_2 production was also studied by in-situ incubation of algal and plant material collected from the rice paddy.

Methods

Analysis of lake water and lake profundal sediments

Loclat is a eutrophic dimictic lake located in Switzerland (Conrad et al. 1983). Lake Mendota is a eutrophic dimictic lake in Madison, Wisconsin,

which has been intensively studied by Brock and coworkers (Brock 1985). Knaack Lake is a eutrophic meromictic lake in the center of Wisconsin (Parkin et al. 1980) and Lake Mary is an oligotrophic meromictic lake in the lake district of Northern Wisconsin (Weimer & Lee 1973). The oligotrophic Lake Allequash and Sparking Lake are also located in this district (Goodwin et al. 1988).

Water samples were taken by means of hydrocasts (Loclat) or peristaltic pumps (other lakes) and were transferred into glass vials as described by Conrad et al. (1983). The microorganisms were inactivated by addition of HgCl_2 solution (final concentration $100 \mu\text{g ml}^{-1}$) and the samples were transported in ice chests into the laboratory within 3–10 h. There, the dissolved H_2 and CH_4 were extracted from the water by using H_2 and hydrocarbon-free air (Conrad & Seiler 1982; Conrad et al. 1983) and were analyzed by means of an H_2 analyzer based on the HgO -to- Hg vapor conversion technique (Seiler 1978; Seiler et al. 1980) and of a gas chromatograph detecting CH_4 with a flame ionization detector. Sediment samples were taken by means of an Ekman grab. Sediment samples were taken from the top 5 cm layer by using a 60-ml plastic syringe to which latex tubing (length, 7 cm; inside diameter, 5 mm) was connected instead of a needle. The samples were transferred into glass flasks (100 ml) flushed with H_2 -free nitrogen. The transfer was done in a way that gas bubbles contained in the sediment accumulated in the top of the syringe and were not transferred. Dissolved H_2 and CH_4 were extracted immediately at in-situ temperature, transported into the laboratory, and analyzed as described recently (Conrad et al. 1985). Partial pressures were calculated from the concentrations of dissolved gases by using their Bunsen solubility coefficients at the temperature observed in-situ.

The detection limits for H_2 were 2.5 nl per liter of water and 10 nl per liter of sediment, corresponding to partial pressures of ca. 13 and 50 mPa, respectively. The precision of repeated extraction and analysis was within $\pm 10\%$. The detection limit for the analysis of the H_2 mixing ratio in gas bubbles was 2 parts per billion or 0.2 mPa. H_2 contamination by corroding materials was avoided by using glass and plastic equipment which has been checked for inertness with respect to H_2 by tests in the laboratory. The detection limit for CH_4 was 25 μl per liter of sediment, equivalent to a partial pressure of ca. 60 Pa. The detection limit for the analysis of the CH_4 mixing ratio in gas bubbles was 10 parts per billion or 1 mPa.

Flux measurements in rice paddies

The studies were done in the rice paddy fields of the Italian Rice Research

Institute in Vercelli which is located in the valley of the River Po in Northern Italy. A few data were also obtained during field measurements in Andalusia, Spain (Seiler et al. 1984). Fluxes were measured by a static box system as described in detail (Seiler et al. 1984; Holzapfel-Pschorn & Seiler 1986). The detection limits for H_2 and CH_4 emission rates were $10 \text{ nl m}^{-2} \text{ h}^{-1}$ and $100 \mu\text{l m}^{-2} \text{ h}^{-1}$, respectively. Fluxes were measured in the presence of intact rice plants as well as after the plants had been cut below the water surface and the soil surface had been covered with a nylon screen ($100 \mu\text{m}$ mesh) to prevent plant-mediated gas flux as well as the escape of gas bubbles. H_2 and CH_4 fluxes were determined by using rectangular glass boxes (18–65 cm height, 800 cm^2 area). CH_4 fluxes were in addition measured by using rectangular plastic boxes (ca. 110 cm height, 3600 cm^2 area) which were automatically and continuously operated (Schütz & Seiler, in prep.). Temperatures were routinely measured in ambient air, in different soil depths, and in the paddy water. Soil and water temperatures in soil and water did not change significantly when the box was placed over the field plot.

Bubbles from the submerged paddy soil were trapped by using glass funnels with an effective trapping area of 375 cm^2 . The funnels were installed ca. 1 cm above the sediment-water interface. Bubbles were trapped either after forcing them out of the soil by stirring or by collecting them over periods of at least 2 hours as they were released by natural ebullition (Holzapfel-Pschorn et al. 1986). H_2 and CH_4 were analyzed at the field site with the instruments described above. Gas samples were also transferred into bottles filled with saturated Na_2SO_4 solution and were transported as a gas bubble to our laboratory in Mainz, Germany, as described by Conrad et al. (1985). There, the gas bubbles were retrieved and analyzed for O_2 , N_2 and CH_4 by using a gas chromatograph with a thermal conductivity detector.

Gas production in samples of algae and plant material

Thallic green algae (in form of filaments and leaf-like material) were collected by hand from the paddy water and transferred into glass syringes (50–200 ml) which were completely filled with paddy water. Controls were made by filling the syringes with unfiltered paddy water and paddy water filtered through $0.45 \mu\text{m}$ cellulose acetate filters. Plant material was sampled from the aquatic weed *Alisma plantago* and from rice (*Oryza sativa*) phyllosphere. The leaf material was transferred into glass syringes filled with water. The syringes were incubated in the rice paddy water until a sufficient amount of gas bubbles had developed through photosynthetic activity of the in-

Table 1. H_2 and CH_4 concentrations of the profundal sediments of freshwater lakes in July 1983.

Lake	Depth of water column (m)	H_2^a (Pa)	CH_4^a (kPa)	H_2/CH_4 ($\times 10^{-4}$)
Lake Mendota	24	3.6 ± 1.5	190 ± 68	0.19
Knaack Lake	18	4.7 ± 3.5	175 ± 37	0.27
Lake Mary	17	0.6 ± 0.1	230 ± 26	0.03
Lake Allequash	8	0.9 ± 0.1	80 ± 15	0.11
Sparkling Lake	19	1.1 ± 0.2	205 ± 29	0.05
Average \pm SD		2.2 ± 1.8	176 ± 57	0.13 ± 0.10

^a Mean values \pm SD of triplicate sediment samples.

cubated material. The gas was completely removed from the syringe and was analyzed for H_2 , CH_4 , O_2 and N_2 . After removal of the gas bubbles incubation of the syringe was continued.

Results

H_2 flux from water and profundal sediments of freshwater lakes

The partial pressures of H_2 and CH_4 which were measured in the anoxic sediments of different freshwater lakes are shown in Table 1. Aqueous systems are in equilibrium with atmospheric H_2 and CH_4 at partial pressures of ca. 0.05 and 0.17 Pa, respectively. The H_2 partial pressures in the various lake sediments were on the average of 2.2 Pa. Methane, on the other hand, was heavily supersaturated. Owing to the hydrostatic pressure, the CH_4 partial pressures were lower in Lake Allequash (8 m depth) than in the other, deeper lakes (17–24 m depth), and on the average reached a value of 176 kPa. The ratio of H_2 to CH_4 partial pressures were in the relatively low range of 0.13×10^{-4} so that any gas bubble escaping from the profundal sediment into the atmosphere would result in an H_2 flux being approx. 10^5 times smaller than the CH_4 flux.

The distribution of dissolved H_2 with depth in 4 different lakes during summer stratification is shown in Fig. 1. At the time of observation, the lakes were characterized by an oxic epilimnion and metalimnion and by an anoxic hypolimnion. The profundal sediments were completely anoxic and were actively producing methane. A gradient of H_2 diffusing from the anoxic sediment into the water column was not observed, so that the diffusional loss

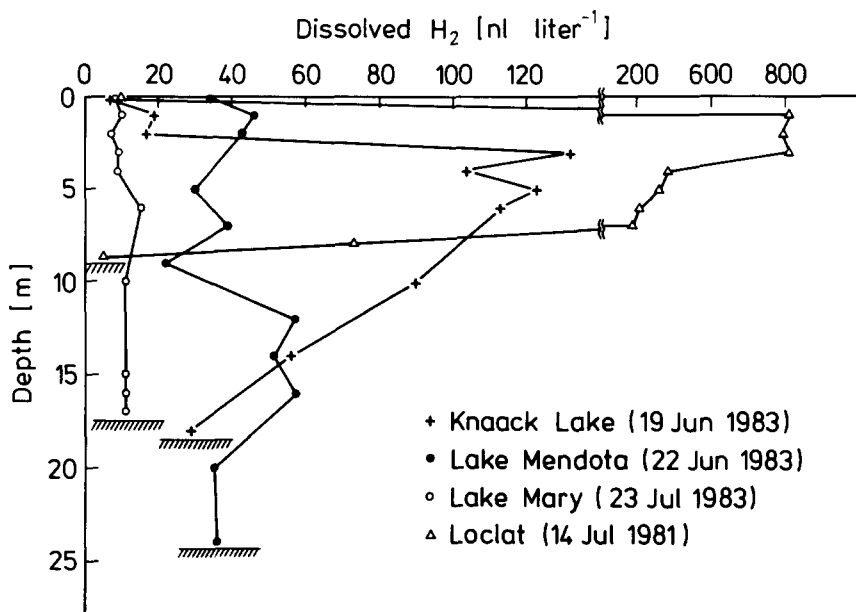


Fig. 1. Vertical profiles of dissolved H_2 in the water column of different freshwater lakes during summer stratification. The oxyclines were in 4 m depth (Knaack L.), 5 m depth (Loclat), 6 m depth (L. Mary) and 12 m depth (L. Mendota).

of H_2 from the sediment was apparently negligible. In two of the lakes, (Knaack Lake & Loclat), however, there was a maximum of dissolved H_2 in the oxic epilimnion indicating that H_2 was produced in this water layer which also exhibited a bloom of phytoplankton (Conrad et al. 1983). The H_2 concentrations were lower in the oligotrophic Lake Mary compared to the other, eutrophic lakes. The differences among the lakes may also be due to the timing of sampling, or to spatial or hydrographic differences. In general, however, surface water exhibited H_2 concentrations in the relatively narrow range of 10–40 nl liter^{-1} (ca. 0.055 – 0.220 Pa partial pressure) corresponding to a slight supersaturation with respect to atmospheric H_2 by a factor of about 1–4. Hence, the diffusional loss of H_2 from the water into the atmosphere is very small. It may roughly be estimated by the stagnant film model (Broecker & Peng 1974; Liss & Slater 1974) applying a transfer velocity (K_L) of $3 \times 10^{-3} \text{ cm s}^{-1}$ which corresponds to a film thickness (z) of about 200 μm (Torgerson et al. 1972; Wanninghof et al. 1985). The resulting H_2 flux would be in the order of $0\text{--}3.2 \mu\text{l m}^{-2} \text{ h}^{-1}$.

H_2 flux from submerged paddy soil

The partial pressures of H_2 and CH_4 in gas bubbles which were stirred out

Table 2. H₂ and CH₄ mixing ratios of gas bubbles stirred out from submerged rice paddy fields.

Location and date	H ₂ (Pa)	CH ₄ (kPa)	H ₂ /CH ₄ ($\times 10^{-4}$)
Spain, August 1982	1.3	42	0.3
Italy, June 1984	4.1 \pm 0.4	56 \pm 23	0.7
Italy, June 1985	1.3 \pm 0.3	15 \pm 8	0.9
Italy, July 1985	1.0 \pm 0.5	12 \pm 8	0.8
Italy, August 1985	1.1 \pm 1.2	14 \pm 12	0.8
Average \pm SD	1.8 \pm 1.3	28 \pm 20	0.7 \pm 0.2

^a Mean values \pm SD of at least triplicate samples.

of the submerged anoxic paddy soil are shown in Table 2. The samples were taken during the growing season from fields which were covered with rice vegetation. The average H₂ partial pressure was 1.8 Pa which is in the same range as the value observed in profundal lake sediments. CH₄ mixing ratios showed an average value of 28 kPa which is one order of magnitude lower than the values measured in profundal lake sediments. The difference is most probably due to the fact that CH₄ can escape by plant-mediated transport and thus does not accumulate as in deep sediments, where ebullition and diffusional loss are the only escape mechanisms. Accordingly, the ratio of H₂ and CH₄ mixing ratios had an average value of 0.7×10^{-4} which is almost one order of magnitude higher than the ratio in the profundal sediments.

The emission rates of H₂ and CH₄ which were measured in rice paddy fields during the main growing season are shown in Table 3. It is interesting to note that compared to the flux of CH₄, the flux of H₂ was more than one

Table 3. Emission rates of H₂ and CH₄ from rice paddy fields in Italy.

Experiment ^a	H ₂ emission (F _{H2}) ($\mu\text{l m}^{-2} \text{h}^{-1}$)	CH ₄ -Emission (F _{CH4}) ($\text{ml m}^{-2} \text{h}^{-1}$)	F _{H2} /F _{CH4} ($\times 10^{-4}$)
Plot A; 9 July 85	76.0	21.8	34.9
Plot B; 10 July 85	28.9	10.3	28.0
Plot C; 12 July 85	126.9	54.0	23.5
Plots C, D, E; 11 July 85 ^b	50.5	12.5	40.4
Average \pm SD	70.6 \pm 42.2	24.6 \pm 20.2	31.7 \pm 7.5
Flux [$\mu\text{g m}^{-2} \text{h}^{-1}$]	5.88	16,400.0	

^a The fluxes of H₂ and CH₄ were measured simultaneously in the same glass box (Height = 15 cm).

^b Measurement of 9 fluxes of H₂ on plot C from 11 July, 7 a.m. to 12 July, 10 a.m., and of 2 fluxes of CH₄ over the same period but on plots D and E being approx. 5 m distant from plot C. Different boxes were used, glass box (H = 15 cm) for H₂ and plastic box (H = 85 cm) for CH₄.

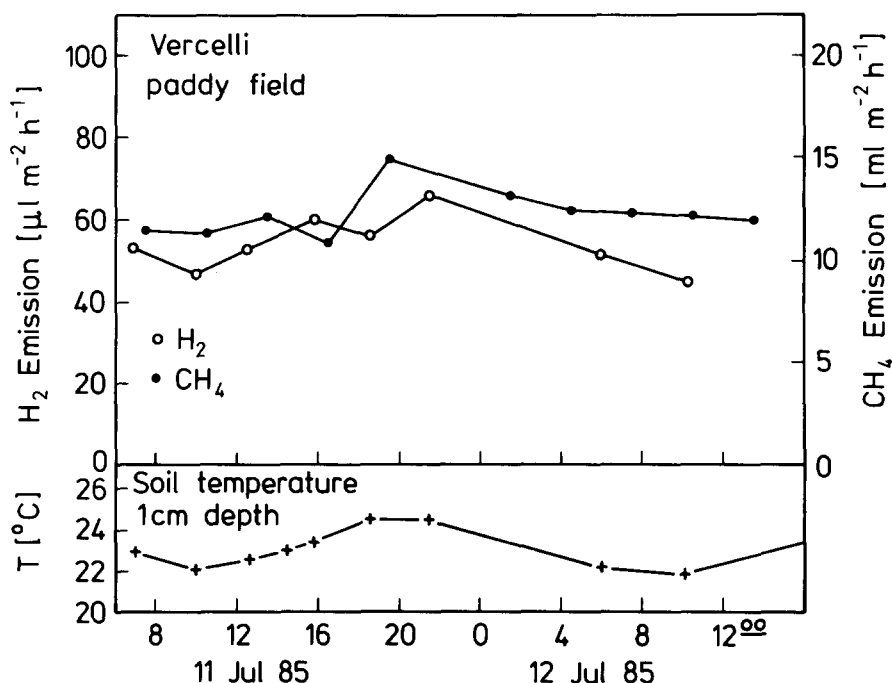


Fig. 2. Diurnal change of H₂ and CH₄ emission rates and soil temperature in a paddy field.

order of magnitude higher than expected from the ratio of H₂ and CH₄ in the soil gas. The average H₂ flux showed a value of $70 \mu\text{l m}^{-2} \text{h}^{-1}$ which was 30×10^{-4} times the flux of CH₄.

Figure 2 shows the emission rates of H₂ and CH₄ over a period of one day. The emission rates of that day showed only a small diurnal change which was parallel to the soil temperature. Diurnal changes of CH₄ emission rates were generally low during the first half of July, but were much more pronounced in June and August (Schütz et al., in prep.). Hence, it is possible that H₂ fluxes also exhibit steeper changes at other times of the year.

Transport of H₂ from the paddy soil into the atmosphere

To find out if H₂ emission was mediated by transport through the inter-cellular gas space system of rice plants, H₂ fluxes were measured before and after the rice plants were cut. Figure 3 shows that cutting the plants below the water surface resulted in a dramatic decrease to 26% of the H₂ flux that was observed with intact plants or plants cut above the water surface. If all of the H₂ transported by the plant had originated in the sediments, this would account for at least 74% of the sedimentary H₂ flux.

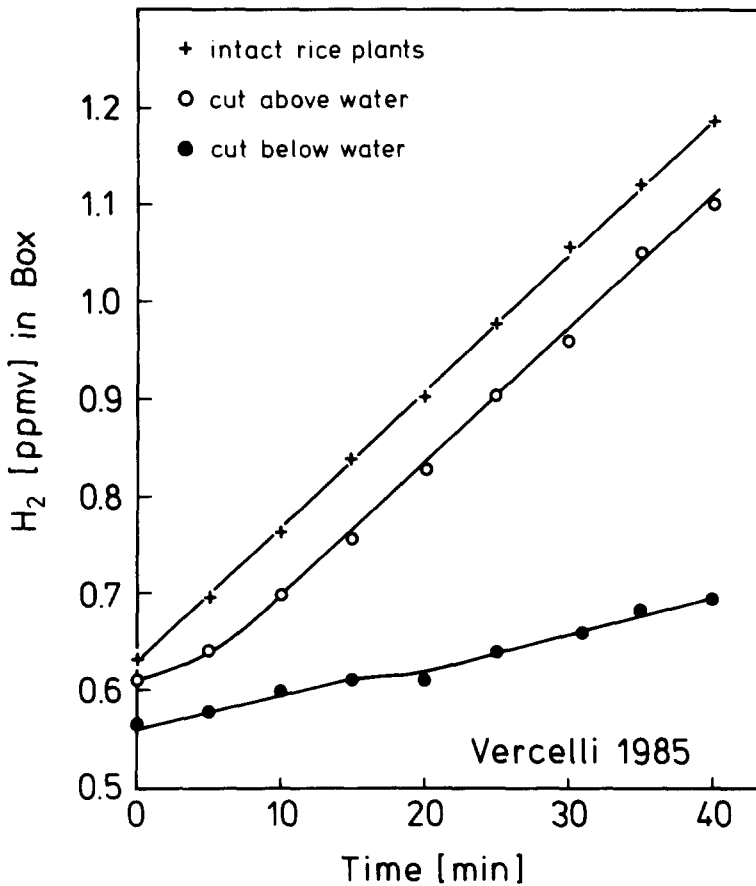


Fig. 3. Effect of cutting the stems of rice plants on the emission of H_2 from a paddy field.

After cutting the plants below the water surface, H_2 emission can only be due to ebullition or diffusion. The diffusional transport of H_2 accounted for only 0.03% of the total flux. This is seen from the results of an experiment (Table 4) in which the plants had been cut and the soil surface had been covered by a screen to prevent transport of gas bubbles through the water column. Therefore, the observed flux was exclusively due to diffusional gas transport across the air-water interface. The values of flux and dissolved gas concentrations were used to determine the transfer velocity (K_L) and the laminar film thickness (z) according to the stagnant film model (Broecker & Peng 1974; Liss & Slater 1974). The experiment showed that the diffusional H_2 flux was much lower than expected from the concentration of dissolved H_2 by applying the transfer velocity measured for CH_4 . In fact, the transfer velocity for H_2 apparently was 20 times lower than that of CH_4 and the

Table 4. Diffusional emission of H_2 and CH_4 from the paddy water into the atmosphere (10 July 85).

Parameter	H_2	CH_4
D ($10^{-5} \text{ cm}^2 \text{ s}^{-1}$)	5.8	2.8
α (20 °C)	0.018	0.035
Atmospheric mixing ratio (m) (ppmv)	0.54	1.81
Concentration in water (C) ($\mu\text{l l}^{-1}$)	0.130	45.3
Flux (F) ($\mu\text{l m}^{-2} \text{ h}^{-1}$)	0.040	285.0
Transfer velocity (K_L) ^a (cm s^{-1})	8.5×10^{-6}	1.7×10^{-4}
Laminar film thickness (z) ^b (μm)	67850	1600

^a Calculated from $K_L = F/(C - \alpha m)$.

^b Calculated from $z = D/K_L$. Gas diffusivities (D) and solubilities (α) are tabulated values, the atmospheric mixing ratios (m), concentration in water (c), and fluxes (F) of H_2 and CH_4 were measured at the same time.

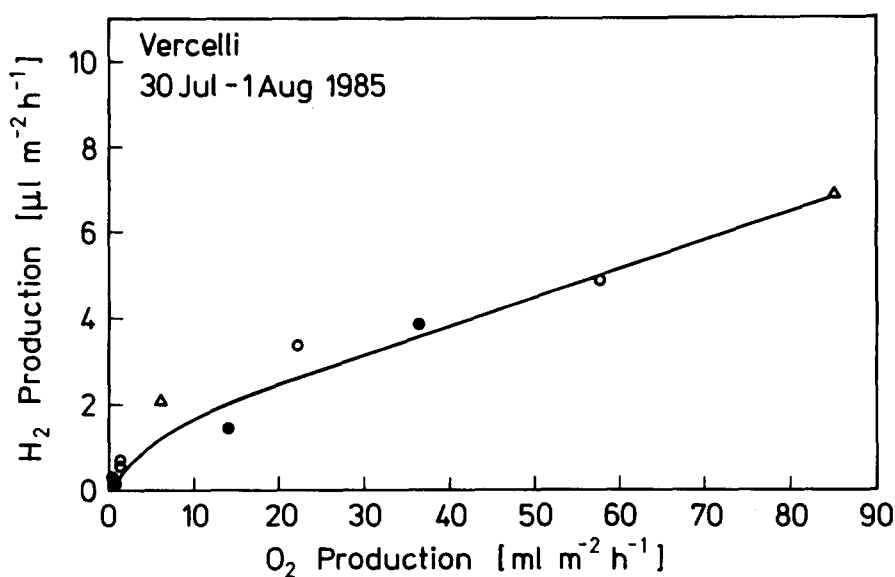


Fig. 4. Relation of H_2 to O_2 trapped as ebullition gas in a submerged paddy field. The figure summarizes H_2 and O_2 production rates determined at different daytimes and different field plots by measuring the rates of ebullition and the mixing ratios of H_2 and O_2 in the trapped gas.

Table 5. Production rates of H₂ and total gas in water incubated with thallic algae or other plant material under in-situ conditions in the paddy field.

Experiment ^a	H ₂ production (nl h ⁻¹ g ⁻¹ d.w.)	Total gas production (ml h ⁻¹ g ⁻¹ d.w.)	H ₂ /Total gas (× 10 ⁻⁶)
Unfiltered or filtered paddy water	0	0	0
Thallic algae ^b	37 ± 31	1.3 ± 1.6	28
Oryza sativa ^b	4 ± 7	0.5 ± 0.3	8
Alisma plantago	0.7	0.3	2

^a Plant material was collected from rice paddies in Vercelli, Italy, during August 1985 and incubated for 8–10 h under in-situ conditions in the paddy water.

^b Average values ± SD of 3–5 replicates experiments.

calculated laminar film thickness was about 40 times larger for H₂ than for CH₄.

Gas ebullition was directly measured by trapping the slowly emerging gas bubbles in funnels. Beside CH₄, which sometimes reached mixing ratios of > 50%, N₂ and O₂ were the major gas compounds to a total of 95–105%. The H₂ mixing ratios were on the order of 10–40 ppmv thus being higher than expected from the partial pressure observed in the submerged soil. During daytime the ebullition gas contained relatively high amounts of O₂ (27–35%) which was most probably due to photosynthesis of algae growing in the paddy water and releasing the produced O₂ into the gas traps. During the night the ebullition gas contained little O₂ (4–7%). The results shown in Fig. 4 indicated that the amount of trapped H₂ gas was related to the release of O₂ gas bubbles. Hence, it appears that H₂ was produced in the oxygenated paddy water in addition to the H₂ released from the anoxic paddy soil.

Indeed, significant amounts of H₂ were produced under in-situ conditions in water when algae or plant material was present (Table 5). No H₂ was produced by unfiltered or filtered paddy water. In all other samples, however, significant amounts of gas were produced as soon as the plant material was incubated in submerged condition. The gas emerged as small bubbles from the plant surface. Gas production reached a maximum during noon light and was zero during night. The production of H₂ amounted to a fraction of 2–28 × 10⁻⁶ of the total gas production.

Discussion

We have shown that H₂ production in freshwater aquatic ecosystems occurs in the oxic part of the water column as well as in anoxic sediments. H₂

production in the water occurred simultaneously with the photosynthetic release of oxygen by phytoplankton, thallic algae and submerged parts of higher plants. Relatively high H_2 concentrations or H_2 production activities in oxic water layers have also been observed in other freshwater lakes (Dahm et al. 1983; Schink & Zeikus 1984), in Big Soda Lake (Oremland 1983), and in ocean water (see review by Conrad & Seiler 1986). The observed H_2 production under oxic conditions may be explained by three conceivable metabolic processes:

- Photometabolic H_2 production to regulate the redox state of the photoelectron transport chain (see reviews by Hallenbeck & Benemann 1979; Bishop & Jones 1978),
- H_2 production by nitrogenase in N_2 -fixing cyanobacteria (see reviews by Bothe et al. 1980; Lambert & Smith 1981).
- H_2 Production by fermentative bacteria associated with algae or material of higher plants (Oremland 1983).

At the moment it is not possible to decide by which mechanism H_2 is produced in the epilimnion of lakes and the water of paddy fields.

In anoxic sediments, H_2 production is a well documented process. Our data show that H_2 dissolved in profundal sediments does not reach the atmosphere by diffusion through the water column. Apparently H_2 is cycled within the anoxic sediments or the hypolimnion, or is oxidized by H_2 -oxidizing bacteria or enzymatic activities in the oxic part of the water column (Conrad et al. 1983). The only possibility that profundal H_2 may reach the atmosphere is by ebullition in bubbles formed by the active methanogenesis. There are reports of methane ebullition from some hypereutrophic profundal lake sediments (Molongoski & Klug 1980; Strayer & Tiedje 1978), however, in most lakes the hydrostatic pressure is too high and the methanogenic activity too low to allow the escape of bubbles.

The ratio of H_2 to CH_4 partial pressures in profundal lake sediments was on the order of 0.1×10^{-4} . This low range makes lakes an insignificant source for atmospheric H_2 even if gas evasion would occur via ebullition. Since freshwater lakes constitute only a very low source for atmospheric methane with values of ca. 5 Tg yr^{-1} (Ehhalt & Schmidt 1978; Seiler 1984, 1985), the source strength for atmospheric H_2 should be on the order of less than 0.025 Tg yr^{-1} . In addition to this amount, H_2 is produced in the oxic part of the water column and diffuses through the water-air interface. Using an average H_2 emission rate of $0.5 \mu\text{l m}^{-2} \text{ h}^{-1}$ as indicated by the data presented in this paper and a global lake surface area of $2.5 \times 10^6 \text{ km}^2$ (Hutchinson 1948), we arrive at a source strength of ca. 0.001 Tg yr^{-1} . The total source strength of lake ecosystems including sediment and water thus is certainly less than 0.05 Tg yr^{-1} .

Higher H_2 emission rates may be expected in those environments where CH_4 emission is high. These areas are rice paddy fields and swamps which together constitute the largest source for atmospheric CH_4 (Seiler 1984, 1985). These areas are characterized by shallow water depth and by the presence of aquatic plants. Under these conditions gas evasion from the anoxic sediment may occur via plant transport or ebullition (Cicerone & Shetter 1981; Seiler et al. 1984; Sebacher et al. 1985; Holzapfel-Pschorn et al. 1986). Methane is certainly one of the dominant gas species which are emitted into the atmosphere via these transport processes. In paddy soil the CH_4 partial pressure in gas bubbles was by a factor of ca. 10^4 higher than that of H_2 . A similar ratio has been observed by Koyama (1964) during incubation experiments with submerged soil samples. Our results show that H_2 is in principle emitted by the same transport pathways as methane. Thus, > 70% of the total H_2 was emitted by plant mediated transport and the rest by bubble release. Diffusional transport of H_2 through the water column was of minor importance. In fact, our data indicate that the diffusional resistance of the air-water interface was much higher for H_2 than for CH_4 , indicating that a significant proportion of the dissolved H_2 may be consumed in the surface film possibly by microorganisms associated with this layer. Similar observations were made for gas exchange across the ocean-atmosphere interface, where H_2 , CO, CH_4 and N_2O exhibited different transfer velocities and exhibited lower values for the emission than for the deposition flux (Conrad & Seiler 1988).

The release of H_2 in the form of bubbles is less important than plant mediated transport. However, the bubbles trapped in a funnel were relatively enriched in H_2 compared to the gas bubbles which were stirred out of the anoxic soil, so that the ratio of H_2/CH_4 by ebullition flux may be up to one order of magnitude higher. The difference is probably due to H_2 production in the water and to photosynthetic release of O_2 bubbles by thallic algae and submerged plants, which increase H_2 and decrease the fraction of CH_4 in the trapped gas bubbles. Hence, the total ebullition flux apparently consists of two fractions, the bubbles generated in the submerged soil and the bubbles generated by photosynthetic oxygen production in the water. The latter fraction obviously contains significant amounts of H_2 in addition to oxygen. This result partially explains our observation that the flux of H_2 is a factor of 43 higher than expected from the ratio of H_2/CH_4 content in the gas bubbles contained in the anoxic soil.

However, this explanation may not be sufficient, as the plant-mediated H_2 emission ($30\text{--}110\ \mu\text{l m}^{-2}\text{ h}^{-1}$; Table 3) is much higher than the emission by ebullition ($1\text{--}7\ \mu\text{l m}^{-2}\text{ h}^{-1}$; Fig. 4). Since the gas transport process via plants should have no effect on the H_2/CH_4 ratio, the discrepancy between H_2/CH_4

content of sediment gas bubbles and H_2/CH_4 flux requires other explanations. There are two conceivable explanations:

- H_2 is produced not only by thallic algae and submerged parts of rice plants but also by the phyllosphere of rice. The produced H_2 would add to the H_2 which originates from the anoxic soil, but is emitted via the phyllosphere. So far, however, H_2 production by the phyllosphere of plants has to our knowledge not been reported. Unpublished in-situ experiments on forest trees (see Seiler et al. 1978) did not show any significant release of H_2 by the tree leaves.
- The H_2 present in the submerged soil is consumed in the rhizosphere to a smaller extent than CH_4 . Up to 80% of the CH_4 produced in anoxic paddy soil is oxidized in the rhizosphere of the paddy soil and does not reach the atmosphere (Holzapfel-Pschorn et al. 1985; Schütz et al. in prep.). Hence, the ratio of H_2/CH_4 emitted would considerably increase relative to the ratio of the mixing ratios in the gas bubbles, if H_2 oxidation in the rhizosphere would be less than CH_4 oxidation. CH_4 oxidation most probably occurs by methanotrophic bacteria which accumulate in the shallow oxic layer around the root surface (De Bont et al. 1978). H_2 oxidation should also be possible, since H_2 -oxidizing bacteria are present in the endorhizosphere and H_2 potentially stimulates N_2 -fixation in excised roots (Gowda & Watanabe 1985). However, since CH_4 concentrations are 3 orders of magnitude higher than H_2 concentrations, methane-oxidizing bacteria may be supported in growth, whereas H_2 -oxidizing bacteria may not have sufficient substrate (Conrad 1984). This is mainly because CH_4 concentrations are significantly higher than the half-saturation constants of methane-oxidizing bacteria, while H_2 concentrations are significantly lower than the half-saturation constants of H_2 -oxidizing bacteria. Hence, CH_4 may be oxidized to a greater extent than H_2 resulting in relatively higher H_2 emission rates as expected from the H_2/CH_4 ratios in the soil gas bubbles.

The H_2 source strength of rice paddy fields and other littoral-like aquatic systems may be estimated by using the data of CH_4 source strengths. Using a ratio of H_2/CH_4 emission rates of as high as 3×10^{-3} and a total CH_4 source strength of 40–170 Tg yr^{-1} for paddy fields (Cicerone & Shetter 1981; Holzapfel-Pschorn & Seiler 1986; Seiler 1984, 1985), plus 45–106 Tg yr^{-1} for waterlogged tundra areas (Sebacher et al. 1986), plus 25–70 Tg yr^{-1} for swamps and other shallow freshwater ecosystems (Seiler 1985; Seiler & Conrad 1987), the H_2 emission would amount to 0.3–1.0 Tg yr^{-1} . This source strength may be overestimated, since not all of the shallow freshwater ecosystems are covered with plants and thus, emit lower fractions of H_2 to

CH₄. Together with freshwater lakes, the total source strength for H₂ would therefore be in the range of < 1 Tg yr⁻¹ which is negligible in the total budget of atmospheric H₂, which amounts to 50–110 Tg yr⁻¹ (Seiler 1978; Seiler & Conrad 1987).

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