Sources Of Atmospheric Methane: Measurements in Rice Paddies and a Discussion

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We have made field measurements of methane fluxes from rice paddies, fresh water lakes, and saltwater marshes to infer estimates of the size of these sources of atmospheric methane. The rice-paddy measurements, the first of their kind, show that the principal means of methane escape is through the plants themselves as opposed to transport across the water-air interface via bubbles or molecular diffusion. Nitrogen-fertilized plants release much more methane than unfertilized plants but even these measured rates are only one fourth as large as those inferred earlier by Koyama and on which all global extrapolations have been based to date. We also compare our measured methane fluxes from lakes and marshes to similar earlier data and find that extant data and flux-measurement methods are insufficient for reliable global extrapolations.

In 1978 the tropospheric concentration of methane was about 1.72 ppm by volume in dry air in northern mid-latitudes and 1.62 ppm in southern mid-latitudes [Heidt et al., 1980]. While the first unambiguous detection of methane in the atmosphere appears to be that of Migeotte [1948], who observed its infrared absorption bands in the solar spectrum there has been very little sustained effort to observe its temporal and spatial variations. In the 1960's and 1970's a number of workers have conducted a sizable number of methane measurements mostly by flame-ionization gas chromatographic analysis of air sampled directly or stored in flasks. Absolute calibrations for CH₄ mole fraction in clean air differ slightly; Bush et al. [1978] reported 1.63 ± 0.12 for a 1978 worldwide average while Rasmussen and Khalil [1981] were closer to 1.60 in clean northern hemisphere air in 1978. At these concentrations methane is important in atmospheric chemistry and radiation: The oxidation of methane initiates key tropospheric reaction chains [Levy, 1971; McConnell et al., 1971; Wofsy, 1972; Crutzen, 1973; Chameides and Walker, 1973] that produce CO and H₂ and strongly influence tropospheric chemistry. Also, the stratospheric oxidation of methane leads to approximately 50% of the water vapor and H₂ found there and CH₄ itself serves as the dominant terminator of chlorine-atom chains that destroy stratospheric ozone [Stolarski and Cicerone, 1974]. Further, the 7.7 μ band of CH₄ traps a significant amount of outgoing planetary radiation so that increases in atmospheric CH₄ levels would lead not only to chemical perturbations such as those mentioned by Chameides et al. [1977] and Sze [1977] but also to surface temperature increases [Wang et al. 1976].

From the ¹³C content of atmospheric methane, Ehhalt [1974] and Ehhalt and Schmidt [1978] have estimated that about 80% of it is produced biogenically and have tabulated various CH₄ sources, source strengths, and annual sinks. This annual methane cycle shows sources of 5 to 11 × 10⁻¹⁴ g/yr and atmospheric residence times of 4 to 7 years. An acute lack of field data forced Ehhalt to base his methane source estimates on a few laboratory simulations (with rice paddy soils) and on isolated other data. While abiogenic sources are clearly possible (e.g., from natural gas releases and from geological faults [Gold, 1979]) the view that most of atmospheric methane is biogenic is strongly supported by arguments such as those of Lovelock and Margulis [1974] who showed that a purely abiogenic thermodynamic equilibrium would predict 29 orders of magnitude less CH₄ in the air than is observed.

From Ehhalt's methane source surveys one can see that a large fraction of the biogenic sources are wholly or partly under man's control through his agricultural practices (mostly rice cultivation) and domestication of cattle, as are several other methane sources: natural gas handling, coal mining, etc. Coupled with possible anthropogenic influence on methane sinks [Chameides et al., 1977] these factors could lead to man-induced changes in atmospheric methane levels. Rasmussen and Khalil [1981] are measuring a methane increase in clean background air.

To provide a better data base on methane sources and to develop techniques for measuring fluxes of other largely biogenic gases we decided to devise field experiments to measure methane fluxes from several areas in California. These areas included several key environments of the type that influenced Ehhalt's surveys: rice paddies, freshwater lakes, and saltwater marshes.

**METHODOLOGY**

Several problems arise in measuring fluxes of gases into the air from water bodies and soils. Though not completely documented, many problems associated with gas collectors are notorious, including those of perturbing the turbulence fields in air or water, perturbing the thermal environment, or gaseous composition and introducing artificial gradients [see e.g., Hitchcock, 1979]. Flux-measurement techniques based on meteorological gradient or correlation techniques offer advantages in many cases but we decided to use gas-collection methods (described below) largely because methane transport across water-air interfaces can proceed through bubble breaking [see e.g., Martens and Klump, 1980]. Still more considerations arise when one attempts to measure fluxes of biogenic gases: living systems, be they microbes or plants, exhibit spatial patchiness, and they are susceptible to many perturbations such as physical manipulations and thermal changes. Accordingly, we experimented with several different gas-collecting systems.

In open water situations we used a glass carboy collector, a closed chamber of volume 11 l with 50 ml stainless steel...
To minimize damage to the plants, we employed a flexible saran bag collector that had ~ 1 l/min of ambient air drawn through it by a portable Bendix pump. The air passed from the collector directly to a portable gas chromatograph for immediate analysis. The procedure was to analyze a standard, analyze an ambient air sample, then a sample from the collector and repeat this several times. The flowing collector was used to maintain a near ambient environment around the rice plants beneath the collector. When the bag collectors were employed in rice paddies, no attempt was made to shade the bags from direct sun because in the collection interval (10-20 min), no appreciable heating occurred. Indeed, no significant day-night differences were evident, as reported below. With the glass-carboy collector we shaded (usually but not as assiduously) the sunward side of the collector with an aluminum foil wrap.

In the field, sample analysis was accomplished on an A.I.D. portable gas chromatograph equipped with a flame-ionization detector and gas-sampling valve. Three ml air samples were separated on a 5' x 1/8" Spherocarb column held at 100°C with 25 ml/min N₂ carrier flow. The methane retention time was about 3 min. Signals were fed to a 1mV recorder, and concentrations were calculated by using peak heights. The system minimum detectable methane concentration was 50 ppb and precision for repeated analysis was about 1%. Samples were compared to a standard prepared by Matheson of methane in zero air and calibrated in our laboratory by using a feedback flow system [Stedman et al., 1978]. When samples were returned to our laboratory at Scripps from saltwater marshes and lakes, analysis was performed on a Perkin Elmer Sigma 4 flame-ionization detector gas chromatograph configured as described above. System precision on this chromatograph was very good; standard deviations were 0.2-0.4% of the mean for repeated analyses. Careful tests in which air samples were dried with a Drierite desiccant showed that the principal effect of water vapor was to degrade column performance (after many moist-air injections). Samples were dehumidified through Drierite in most cases but not in the rice paddy studies where bag collectors were used. Sample moisture was, in fact, of no concern.

To enable us to run repeated analyses the atmospheric pressure samples were pressurized with 10 psig (68.9 kPa) of pre-
purified N₂ that had been previously checked for methane content. This dilution factor was applied to calculate the final methane concentrations. Once these concentrations were determined, the flux could be calculated by using the collector volume, the area covered by the collector, and the elapsed time. Dissolved oxygen was measured with an Orion Research model 399 A/F meter equipped with a model 97-08 oxygen electrode. The range was nominally 0–14 ppm (438 µM) with accuracy of ± 0.05 ppm.

RESULTS

Rice paddy flux measurements were made in an experimental rice field located on the grounds of the University of California at Davis, (40.2øN, 122.1øW). The work was done in late summer with daytime temperatures ranging from 26ø–32øC dropping to 17ø–20øC at night. Several parameters were measured with each collection. The water, which was 10–18 cm deep over the 350 m² area of the test paddy, was being replaced at a rate of ~3 l/min. It had a pH range of 6.9–8.1, while its temperature ranged from 18ø–26øC. The dissolved oxygen exhibited a cyclic diurnal behavior as was expected with daylight values supersaturated (off scale, over 440 µM) and nighttime values as low as 95 µM. Soil temperature was relatively stable at 28ø–29øC.

By placing a collector over a test area and sampling the gas inside the collector after measured time intervals, we deduced the methane flux across the plane defined by the collector orifice. Figure 2a displays the rates of increase of methane concentration under two glass-carboy collectors, one placed over rice plants and one placed over nearby, adjacent open paddy water with no rice plants in it. Note the nearly linear rates of increase under both collectors. After 4 hours the collector over rice plants contained 290 ppm methane and the collector over open water contained 3.80 ppm methane. Figure 2b displays similar data but with both collectors over rice plants, one group unfertilized and one group fertilized with (NH₄)₂SO₄ at a rate of 120 kg nitrogen per hectare per year. Fertilized rice plants consistently released more methane as discussed below.

In an unfertilized area of the paddy we compared data obtained with the three collectors by deploying the glass-carboy collector, the saran-bag collector, and the flowthrough bag collector near each other, each over rice plants. Table 1 shows the results of nine individual collections designed to compare collection methods. The individual collectors were deployed near each other over unfertilized rice, and fluxes were determined from measured rates of changes of methane versus time such as those exemplified in Figures 2a–2c. As Table 1 shows, the three methods compared rather well considering the different perturbations introduced by each collector, the spatial patchiness of the rice paddy, and other sources of error, (e.g., inaccuracies in bag volumes owing to variable deformations in the bags between deployments). In any case, the differences in fluxes measured by these different collectors are much smaller than (1) the interesting differences between fluxes from open paddy water (no plants) and from rice plants, and (2) the differences between fluxes from fertilized and unfertilized rice plants.

Table 2 summarizes our quantitative data on methane fluxes from rice paddies. These data strongly suggest that the major mechanism for CH₄ release is not upward transport from the sediments by rising bubbles or by gaseous molecular diffusion, but, instead, by direct passage from the sediment/soil through the rice plants. Further, nitrogen-fertilized plants release more methane. Adjacent collectors over open water and over rice plants gave fluxes of 0.0035 and 0.18 g CH₄/m²/
ment/soil through the rice (as opposed to being produced in tions where bubbles were excluded from one collector by plac-

unfertilized rice plants, some intact and others cut down opening. The data appear in Table 5. In each case the collec-
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We have also measured methane fluxes from several saltwater marshes and lagoons in southern California. These measurements were made with the glass-carboy collectors in standing water and are summarized in Table 3. Collections were often over 24-hour periods but always over one hour long. The increase in methane concentration versus time was determined by sampling at intervals of 30 min to 1 hour in the initial stages of each collection, then usually at 4, 8, and 16 hours later. Graphs similar to Figures 2a and 2b were thus generated. Straight-line segments were drawn through the individual data points and an overall best fit line through all data points. The slopes and thus the fluxes for each time interval were almost always within ± 25% of the slope of the overall line. The observation of nearly linear increase in methane concentration in the collector over 24-hour periods rules out back diffusion as a serious concern in these measurements. Nonetheless, this technique is still susceptible to problems such as those mentioned earlier. The Batiquitos location is a shallow, several km2 saltwater lagoon with a thick organic muck base. It is covered by surface waters except in the end of the dry season, typically August and September. The Penasquitos location is similar but with much more swamp-grass vegetation. At Batiquitos the average flux was 2.16 × 10−2 g CH4/m2/d for the five dates shown, while at Penasquitos the average flux was 3.65 × 10−2 g CH4/m2/d for the 17 dates shown in Table 3.

With similar methods we made 10 flux measurements at three southern California freshwater lakes, as summarized in Table 4. Excluding the largest flux (7.86 g CH4/m2/d on August 31, 1979, at Lake Hodges) the remaining nine points averaged 0.13 g CH4/m2/d. The influence of bubbles on these experiments was evident; rising bubbles were often apparent. Methane concentrations inside bubbles from freshwater and coastal sediments are typically 35–85% [Martens and Klump, 1980; Dacey and Klug, 1979; Baker-Blocker et al., 1977] as we found. In an attempt to determine how much of our measured fluxes arose from bubble ebullition we did side by side collections where bubbles were excluded from one collector by placing a fine stainless steel mesh (100 micron holes) over the opening. The data appear in Table 5. In each case the collector without the screen showed a bigger flux, suggesting that bubble ebullition is often the dominant means of escape for methane from the water column into the air. It can be suggested that the screen is impeding eddy transport in the water column, but in the stagnant areas where this work was done eddy transport would be weak anyhow. Further, in the course of similar studies we have done on N2O release from Michigan rivers and lakes we found that varying the depth to which the collector rim penetrates the water leads to only ~ 10% decreases in measured fluxes when the rim penetrates twice as far into the water. This suggests that our bubble-deflecting screen did not interfere materially with those eddies that deliver gases from below.

DISCUSSION AND CONCLUSIONS

Our rice paddy measurements are the first such field studies of methane release to the atmosphere. An earlier study by Koyama [1963, 1964] was performed by incubating rice paddy soils in the laboratory. On the basis of Koyama’s estimate of an annual global average methane flux of 206 g/m2/yr, Ehhal and Schmidt [1978] concluded that rice paddies account for 2.8 × 1014 g CH4/yr globally or 33–49% of all biogenic atmospheric methane and 26–47% of all atmospheric methane from

| Flux From: | Number of Trials | Range (g CH4 m−3 d−1) | Average (g CH4 m−3 d−1) |
|-----------|------------------|----------------------|------------------------|
| Open water (no rice plants) | 3 | 1.26 × 10−2 to 7.42 × 10−3 | 3.5 × 10−3 |
| Rice plants (adjacent to open paddy water, see above) | 6 | 7.5 × 10−3 to 3.0 × 10−1 | 0.18 |
| Unfertilized rice plants | 9 | 1.32 × 10−2 to 6.82 × 10−2 | 3.2 × 10−2 |
| Fertilized rice plants | 11 | 5.3 × 10−2 to 3.0 × 10−1 | 0.15 |
| Cut off rice plants (unfertilized) | 2 | (4.78, 5.85) × 10−2 | 5.3 × 10−2 |
| Intact rice plants (unfertilized) | 2 | (3.85, 5.07) × 10−2 | 4.4 × 10−2 |
| Day, fertilized rice plants | 3 | 7.5 × 10−2 to 0.30 | 0.173 |
| Night, fertilized rice plants | 3 | 0.13 to 0.24 | 0.186 |

* With 140 kg N ha−1 yr−1 as (NH4)2 SO4.
TABLE 3. Methane Flux Measurements From a Southern California Saltwater Marsh (Penasquitos) and From a Shallow Southern California Lagoon (Batiquitos)

| Date       | Depth, cm | Water Temperature, °C | Flux (g CH₄ m⁻² d⁻¹) |
|------------|-----------|-----------------------|----------------------|
| **Penasquitos** |           |                        |                      |
| May 24, 1979 | 40        | 26                    | 8.44 x 10⁻⁴          |
| May 30, 1979 | 29        | 23                    | 5.11 x 10⁻⁴          |
| June 4, 1979 | 18        | 21                    | 9.82 x 10⁻⁴          |
| June 6, 1979 | 38        | 20                    | 1.35 x 10⁻⁴          |
| June 14, 1979 | 25       | 30                    | 5.20 x 10⁻⁴          |
| June 19, 1979 | 16.5     | 27                    | 8.67 x 10⁻⁴          |
| June 20, 1979 | 16.5     | 23                    | 9.25 x 10⁻⁴          |
| June 27, 1979 | 21.5     | 23                    | 2.36 x 10⁻⁴          |
| July 12, 1979 | 10       | 27                    | 6.27 x 10⁻⁴          |
| July 18, 1979 | 5         | 31                    | 1.98 x 10⁻⁴          |
| July 18, 1979 | 114      | 26                    | 9.33 x 10⁻⁴          |
| July 30, 1979 | 9         | 28.5                  | 5.46 x 10⁻⁴          |
| Aug. 2, 1979  | 13        | 25                    | 5.92 x 10⁻⁴          |
| Aug. 13, 1979 | 5         | 30.5                  | 2.46 x 10⁻⁴          |
| **Batiquitos** |           |                        |                      |
| Aug. 14, 1979 | 23        | 27.5                  | 6.22 x 10⁻⁴          |
| Aug. 22, 1979 | 25        | 27                    | 1.07 x 10⁻⁴          |
| Nov. 29, 1979 | 41        | 15                    | 3.30 x 10⁻⁴          |
| Jan. 25, 1980 | 46        | 16.5                  | 3.51 x 10⁻⁴          |
| March 14, 1980 | 7         | 25                    | 6.38 x 10⁻⁴          |
| April 28, 1980 | 13        | 23                    | 7.88 x 10⁻⁴          |
| May 30, 1980  | 25        | 24.5                  | 2.32 x 10⁻⁴          |
| June 29, 1980 | 32        | 26                    | 4.59 x 10⁻⁴          |

At these locations, water pH ranged from 7.0 to 9.9 with highest pH values in daytime, lowest at night typically. Dissolved oxygen was near or supersaturated (>284 µM at 20°C) on bright days and went as low as 95 µM at night.

TABLE 4. Methane Flux Measurements From Three Freshwater Lakes in Southern California

| Location | Date, 1979 | Depth, cm | Water Temperature, °C | Flux, g CH₄ m⁻² d⁻¹ |
|----------|------------|-----------|-----------------------|---------------------|
| Lake Miramar | Aug. 7  | 91        | 27.5                  | 3.39 x 10⁻³          |
| Lake Guajome  | Aug. 23  | 122       | 22.5                  | 3.81 x 10⁻³          |
| Lake Hodges  | Aug. 31  | >150      | 26                    | 2.32 x 10⁻¹          |
| Lake Hodges  | Aug. 29  | 46        | 28                    | 2.55 x 10⁻¹          |
| Lake Hodges  | Aug. 31  | 12.7      | 30                    | 7.86                |
| Lake Hodges  | Sept. 26 | 91        | 31                    | 4.43 x 10⁻¹          |
| Lake Hodges  | Oct. 18  | 122       | 24                    | 8.40 x 10⁻²          |
| Lake Guajome  | Oct. 24  | 46        | 27                    | 3.65 x 10⁻³          |
| Lake Hodges  | Nov. 8   | 25        | 21                    | 5.03 x 10⁻²          |
| Lake Hodges  | Nov. 15  | 46        | 16                    | 2.71 x 10⁻²          |

Water pH ranged from 7.2 to 9.0. In the shallower water nighttime dissolved oxygen values decreased to 60-90 µM while daytime values were near or supersaturated (284 µM at 20°C).
forces atmospheric oxygen to water lily roots and delivers CO₂ to the plant leaves and methane to the atmosphere through the leaves. Contrary to earlier ideas, Dacey [1980] found significant mass flows through plant lacunae.

Our freshwater lake data (Table 4) gave typical methane fluxes of 0.13 g CH₄/m²/d, although a much higher flux was observed on 1 day. Including all the data points in Table 4 raises the average flux to 0.89 g CH₄/m²/d. Clearly, extrapolating from these data is perilous. Previously, four swamp-gas samples analyzed by Conger [1943], as interpreted by Ehhalt and Schmidt [1978], implied a flux of 0.32 g CH₄/m²/d from a location in Maryland. Baker-Blocker et al. [1977] trapped rising bubbles below the water surfaces of two farm ponds in Michigan and deduced fluxes between 0.09 and 1.1 g CH₄/m²/d. As Baker-Blocker et al. and Ehhalt and Schmidt [1978] have discussed, it is desirable to deduce a temperature dependence for the methane evolution (and escape). It is questionable whether there are enough data at present to permit an accurate temperature dependence to be inferred. Further, because bubbles dissolve rapidly under some conditions [Marten and Klump, 1980], the methane escape rate to the atmosphere is likely to be less than the rate of methane release from the sediments. Additional complexities arise from the recent recognition [Dacey and Klug, 1979] that substantial amounts of methane escaping from lakes rises through plants like water lilies. Dacey and Klug [1979] measured escaping methane fluxes of 0.35 g CH₄/m²/d (2.2 × 10⁻² moles/m²/d) from a small, eutrophic Michigan lake in August. Half or more of this flux came directly through plants; Dacey and Klug measured open-water contributions to the methane flux by static closed chamber trapping. The fact that methane can be oxidized as it rises [see discussion of Ehhalt and Schmidt, 1978; Martens and Klump, 1980], whether in bubbles or in dissolved form, especially in waters deeper than 2 m, combined with the transport-through-plants mechanism makes it difficult to know if the present data base is adequate for reasonable extrapolations. Our average flux, 0.13 g CH₄/m²/d (Table 4), although it arises from fairly warm water samples, is lower than the above-quoted figures. Over 365 days our figure would yield 47 g CH₄/m²/yr, slightly below Ehhalt and Schmidt's [1978] lowest estimate. Further, the higher fluxes reported by Baker-Blocker et al. [1977] might be overestimates because they trapped bubbles below the water surface; subsequent oxidation might have led to a lower actual escape flux of methane. On the other hand, the role of plants as escape conduits for methane from lakes could lead to higher actual methane release than we have measured or Ehhalt and Schmidt [1978] have estimated. For purposes of global extrapolation, one must know the fraction of lake surfaces participating in methane release. This fraction, taken to be 0.01 to 0.1 by Ehhalt [1974], is very uncertain owing to lack of data and also owing to the great potential of plants to control the release. As a last note on freshwater lakes, we saw no evidence of diurnal variability in the methane release rate from open waters in several day and night measurements. Dacey and Klug [1979] and Dacey [1980] have reported a daytime maximum in the methane flux from plants in a small Michigan lake.

There are few data on fluxes from salt water marshes probably because it was established early on [Koyama, 1963] that the presence of salts inhibits methanogenesis. King and Wiebe [1978] show a wide range of 0.44-51 g CH₄ m⁻² yr⁻¹ in Georgia salt marshes. Their measurements were made over soil with plant material and showed a seasonal dependence. The measurements we made in southern California yielded a 0.28 g CH₄/m²/yr average flux but were made in areas of standing water of 15 cm, which probably allowed a considerable amount of oxidation before the methane was released to the atmosphere. We saw no seasonal changes, but it should be noted that seasonal temperature changes are small in southern California (see Table 3). The possibility that methane and other gases escape from salt marshes directly through reed-like grasses remains to be investigated. Indeed, it seems clear that all future investigations of gas evolution from marshes, lakes, and rice paddies must recognize that areas covered with plants can be as important as open-water areas.

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REFERENCES

Baker-Blocker, A., T. M. Donahue, and K. H. Mancy. Methane flux from wetlands areas, Tellus, 29, 245-250, 1977.

Bush, Y. A., F. C. Schmeltekopf, F. C. Fehsenfeld, D. L. Albritton, J. R. McAffee, P. D. Golden, and E. E. Ferguson. Stratospheric measurement of methane at several latitudes, Geophys. Res. Lett., 5, 1022-1029, 1978.

Chameides, W., and J. G. Walker, A photochemical theory of tropospheric ozone, J. Geophys. Res., 78, 8751-8760, 1973.

Chameides, W., S. C. Liu, and R. J. Cicerone, Possible variations in atmospheric methane, J. Geophys. Res., 82, 1795-1798, 1977.

Claypool, G., and I. R. Kaplan, The origin and distribution of meth-

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TABLE 5. Results of Six Carboy Collections to Estimate the Contribution of Bubbles to Methane Fluxes Across the Water-Air Interface

| Location           | Date, 1980 | Flux Without Screen | Flux With Screen | Depth, cm |
|--------------------|------------|---------------------|------------------|-----------|
| Lake Hodges        | Sept. 25   | 4.45 × 10⁻¹         | 6.29 × 10⁻³      | 90        |
| Batiquitos Lagoon  | July 24    | 4.43 × 10⁻⁴         | 6.11 × 10⁻⁴      | 15        |
| Batiquitos Lagoon  | July 18    | 4.33 × 10⁻⁴         | 1.77 × 10⁻⁴      | 15        |
| Batiquitos Lagoon  | July 31    | 5.79 × 10⁻⁴         | 1.91 × 10⁻⁴      | 15        |
| Batiquitos Lagoon  | Aug. 7     | 1.65 × 10⁻¹         | 2.18 × 10⁻⁴      | 10        |
| Batiquitos Lagoon  | June 20    | 5.30 × 10⁻³         | 2.48 × 10⁻³      | 36        |

Fluxes are g CH₄/m²/d. In all cases the collector with a bubble-excluding screen (see text) recorded a lower methane flux.
ane in marine sediments, in Natural Gases in Marine Sediments, edited by I. Kaplan, Plenum, New York, 1974.
Conger, P. S., Ebullition of gases from marsh and lake waters Publ. 59, pp. 1-42, Chesapeake Biol. Lab.,Solomons Island, Maryland, 1943.
Crutzen, P. J., A discussion of the chemistry of some minor constituents in the stratosphere and troposphere, Pure Appl. Geophys., 106-108, 1385-1399, 1973.
Dacey, J., Internal winds in water lilies: An adaption for life in anaerobic sediments, Science 210, 1017-1019, 1980.
Dacey, J., and M. J. Klug, Methane efflux from lake sediments through water lilies, Science, 203, 1253-1255, 1979.
Danckwerts, P. V., Gas-Liquid Reactions, McGraw Hill, New York, 1970.
Ehnhalt, D. H., The atmosphere cycle of methane, Tellus, 26, 58-70, 1974.
Ehnhalt, D. H., and U. Schmidt, Sources and sinks of atmospheric methane, Pure Appl. Geophys., 116, 452-464, 1978.
Gold, T., Terrestrial sources of carbon and earthquake outgassing, J. Petrol. Geol., 1, 3-19, 1979.
Heidt, L. E., and D. H. Ehnhalt, Corrections of CH₄ concentrations measured prior to 1974, Geophys. Res. Lett., 7, 1023, 1980.
Hitchcock, D. R., A problem with flux chamber measurements of biogenic sulphur emissions, Rep. EPA-600/3-70-033, Environ. Sci. Res. Lab., U.S. Environ. Prot. Agency, Research Triangle Park, North Carolina, 1979.
King, G. M., and W. J. Wiebe, Methane release from soils of a Georgia salt marsh, Geochim. Cosmochim. Acta., 42, 343-348, 1978.
Koyama, T., Gaseous metabolism in lake sediments and paddy soils and the production of hydrogen and methane, J. Geophys. Res., 68, 3971-3973, 1963.
Koyama, T., Biogeochemical studies on lake sediments and paddy soils and the production of hydrogen and methane, in Recent Researches In The Fields Of Hydrosphere, Atmosphere, and Geochemistry, edited by T. Miyake and T. Koyama, pp. 143-177, Murucen, 1964.
Kozuchowski, J., and D. L. Johnson, Gaseous emissions of mercury from an aquatic vascular plant, Nature, 274, 466, 1978.
Levy, H., Normal atmosphere: Large radical and formaldehyde concentrations predicted, Science, 173, 141-143, 1971.
Lovelock, J. E., and L. Margulis, Atmospheric homeostasis by and for the biosphere: The GAIA Hypothesis, Tellus, 26, 2-9, 1974.
Martens, C. S., and R. A. Berner, Methane production in sulphate-depleted marine sediments, Science, 185, 1167-1169, 1974.
Martens, C. S., and J. R. Klump, Biogeochemical cycling in an organic-rich coastal marine basin, J. Marine sediments-water exchange processes, Geochim. Cosmochim. Acta, 44, 471-490, 1980.
McConnell, J. C., M. B. McElroy, and S. C. Wofsy, Natural sources of atmospheric CO, Nature, 223, 187-188, 1971.
Migeotte, M. V., Spectroscopic evidence of methane in the earth's atmosphere, Phys. Rev., 73, 519-520, 1948.
Rasmussen, R. A., and M. A. K. Khalil, Atmospheric methane (CH₄): Trends and seasonal cycles, submitted to J. Geophys. Res., 1981.
Stedman, D. H., T. Kelly, R. E. Shetter, J. D. Shetter, and R. J. Cicerson, Feedback flow and permeation systems for the calibration of very low gas concentrations, paper presented at Proceedings ASTM Conference on Air Quality Meteorology and Atmospheric Ozone, Boulder, Colo., 1978.
Stolarski, R. S., and R. J. Cicerson, Stratospheric chlorine: A possible sink for ozone, Can. J. Chem., 52, 1610-1615, 1974.
Szé, N. D., Anthropogenic CO emissions: Implications for the atmospheric CO-CH₄ cycle, Science, 195, 673-675, 1977.
Wang, W. D., Y. L. Yung, A. A. Lacis, T. Mo, and J. E. Hansen, Greenhouse effects due to manmade perturbations of trace gases, Science, 194, 685-690, 1967.
Wofsy, S. C., J. C. McConnell, and M. B. McElroy, Atmospheric CH₄, CO, and CO₂. J. Geophys. Res., 77, 4477-4493, 1972.
Zeikus, J. G., and J. C. Ward, Methane formation in living trees: A microbial origin, Science, 184, 1181-1183, 1974.
Zeikus, J. G., and M. R. Winfrey, Temperature limitation of methanogenesis in aquatic sediments, Appl. Environ. Micro., 31, 99-107, 1976.

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