ISOTOPIC COMPOSITION OF METHANE RELEASED FROM WETLANDS: IMPLICATIONS FOR THE INCREASE IN ATMOSPHERIC METHANE

Paul D. Quay, Stagg L. King, John M. Lansdown, and David O. Wilbur

School of Oceanography, University of Washington, Seattle

Abstract. Measurements of the $\delta^{13}C$ of methane released from tropical, temperate, and arctic wetland sites are reported. The mean $\delta^{13}C$ values (relative to PDB) for methane emitted from the Amazon floodplain, Minnesota peat bogs and Alaskan tundra are $-53 \pm 8$, $-66 \pm 5$ and $-64 \pm 5^\circ/_{oo}$, respectively. These measurements combined with methane flux estimates yield a flux-weighted global average $\delta^{13}C$ value of $-59 \pm 6^\circ/_{oo}$ for methane released from wetlands, a major natural methane source. The agreement between the measured $\delta^{13}C$ for methane emitted from wetlands and the calculated steady state value of approximately $-60^\circ/_{oo}$ for the $\delta^{13}C$ of preindustrial methane sources suggests that methane was predominantly produced biogenically in the preindustrial era. The industrial era time rate of change of the $\delta^{13}C$ of the global methane flux is calculated from estimates of the growth rate of the major anthropogenically derived methane sources and the $^{13}C$ composition of these sources, and compared to the measured change in the $\delta^{13}C$ of methane during the last 300 years. Based on these results, we estimate that $13 \pm 8\%$ of the current global methane flux is derived abioiogenically from natural gas and biomass burning, whereas the remainder is derived biogenically primarily from wetlands, rice paddies, and livestock.

INTRODUCTION

Methane in the atmosphere has more than doubled over the last 300 years [Khalil and Rasmussen, 1985]. This increase is due to increases in the CH$_4$ source strengths coupled with a possible decrease in CH$_4$ oxidation rates [Khalil and Rasmussen, 1985; Thompson and Cicerone, 1986]. The current input rate of CH$_4$ to the atmosphere has been estimated at 400 to 600 Tg/yr [Khalil and Rasmussen, 1985; Seiler and Conrad, 1987; Binger and Crutzen, 1987; Stevens and Engelkemeir, 1988], (see Table 1). The variability in these estimates results primarily from the uncertainty in extrapolating a few site specific measurements to global scales. Recent atmospheric methane budgets suggest that rice paddies, livestock, natural gas, and biomass burning are the major anthropogenic CH$_4$ sources. Although the total current emission rate from these four sources is generally estimated to be $\approx 300 \pm 50$ Tg/yr, estimates of the proportion of CH$_4$ derived from each of the major sources varies by up to a factor of 3 (Table 1). The release rate of CH$_4$ from thermal destabilisation of sedimentary gas hydrates, although potentially enormous, is essentially unknown [Revelli, 1983].

Three hundred years ago the CH$_4$ concentration was 0.7 $\pm$ 0.1 ppm [Craig and Chon, 1982; Khalil and Rasmussen, 1985; Stauffer et al., 1985], in contrast to the present (1984) concentration of 1.63 ppm [Steele et al., 1987]. The preindustrial CH$_4$ concentration, when combined with a tropospheric lifetime for CH$_4$ of 7–10 years [Khalil and Rasmussen, 1983; Mayer et al., 1982], yields a preindustrial CH$_4$ source strength of 190–269 Tg/yr. If the preindustrial lifetime of CH$_4$ was shorter than at present by $\sim 30\%$ [Khalil and Rasmussen, 1985], then the preindustrial source strength was 270–384 Tg/yr. However, the natural sources of CH$_4$ have not been clearly identified, and global CH$_4$ balances have not always accounted for the importance of natural sources of CH$_4$ (see Table 1). Wetlands are considered to be the largest natural source of CH$_4$, yet Matthews and Fung [1987] recently estimated the current global CH$_4$ release rate from wetlands.

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TABLE 1. Estimates of the CH$_4$ Source Strengths in 1980

<table>
<thead>
<tr>
<th>Source</th>
<th>CH$_4$ Flux (Tg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural sources</td>
<td>285$^{+35}_{-25}$</td>
</tr>
<tr>
<td>Anthropogenic sources</td>
<td></td>
</tr>
<tr>
<td>Rice paddies</td>
<td>95</td>
</tr>
<tr>
<td>Livestock</td>
<td>110</td>
</tr>
<tr>
<td>Natural gas and coal mining</td>
<td>40</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>25</td>
</tr>
<tr>
<td>Solid wastes</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>555$^{+115}_{-45}$</td>
</tr>
</tbody>
</table>

$^{a}$This flux includes CH$_4$ released from rice paddies.

$^{b}$Percentage of total CH$_4$ flux derived from natural gas, coal mining, and biomass burning.

at 110 Tg/yr, which falls short of the required preindustrial source strength.

Neither the anthropogenic nor natural CH$_4$ source strengths are known precisely enough to tightly constrain a global CH$_4$ balance. Additionally, uncertainty in the magnitude of the anthropogenic perturbation of chemical interactions between CH$_4$, CO, NO$_x$, and OH in the troposphere makes it difficult to quantify the preindustrial CH$_4$ lifetime [Thompson and Cicerone, 1986]. Thus because of the uncertainty about the rates of input and loss of atmospheric CH$_4$, other methods must be used to quantify the global CH$_4$ cycle.

Here we present an additional constraint to the global CH$_4$ balance by examining the $\delta^{13}$C of CH$_4$ released from anthropogenic and natural sources as well as the change in the $\delta^{13}$C of atmospheric CH$_4$ that occurred over the last 300 years. The $\delta^{13}$C (per mil, $\%_{oo}$) is defined as the relative difference between the $^{13}$C/$^{12}$C of the sample and the PDB carbonate standard [Craig, 1957]. Only recently have enough $\delta^{13}$C measurements become available to begin to establish a global isotopic CH$_4$ balance [Stevens and Engelkemeier, 1988]. In this study we present the following: (1) measurements of the $\delta^{13}$C of CH$_4$ released from tropical, temperate, and arctic wetlands, (2) a calculation of a global mean $\delta^{13}$C of wetland derived CH$_4$, (3) the $\delta^{13}$C balance for atmospheric CH$_4$ in preindustrial times, and (4) an estimate of the time rate of change of the $\delta^{13}$C of atmospheric CH$_4$ over the last 300 years. On the basis of these results, we determine the current amount of CH$_4$ produced biogenically and emitted from sources like wetlands, rice paddies, and livestock versus that produced abiotically and emitted from natural gas release and biomass burning.

The $\delta^{13}$C of atmospheric CH$_4$ has been measured at $-47.7^\%_{oo}$ in 1980 [Stevens and Engelkemeier, 1988], $-46.5^\%_{oo}$ in 1985 [Tyler, 1986], $-47.4^\%_{oo}$ in 1987 [P. Quay, unpublished data] and $-46.8^\%_{oo}$ in 1986–1987 [Wahlen et al., 1987]. The range in the measured $\delta^{13}$C values for atmospheric CH$_4$ is likely derived from differences in sampling sites and sample preparation procedures. These $\delta^{13}$C values primarily represent air samples collected in the northern hemisphere. In contrast, 300 years ago the $\delta^{13}$C of atmospheric CH$_4$ was $-49.7^\%_{oo}$, as measured from air trapped in Greenland ice [Craig et al., 1986; Stevens and Engelkemeier, 1988]. Thus the $\delta^{13}$C of atmospheric CH$_4$ has increased by 2–3$^\%_{oo}$ since preindustrial times.

Methane production pathways can be categorized as either biogenic or abiotic. Biogenic CH$_4$ is derived from anaerobic microbial fermentations. Biogenic CH$_4$ sources include wetlands, rice paddies, termite mounds, freshwater and marine sediments, and solid wastes. Some natural gas reservoirs (~20%) contain biogenic methane [Rice and Claypool, 1981]. Major sources of biogenic CH$_4$ have mean $\delta^{13}$C values which vary from −70 to −50$^\%_{oo}$ (see Table 2). Abiogenic CH$_4$ is derived from abiological reactions such as incomplete combustion or thermal alteration of buried organic matter. Sources of abiotic CH$_4$ include most natural gas reservoirs, CH$_4$ associated with petroleum, coal, and lignite, and CH$_4$ produced during biomass burning. Abiogenic methane derived from natural gas sources has a mean $\delta^{13}$C of ~−40 ± 7$^\%_{oo}$, and CH$_4$ produced during biomass burning has a mean $\delta^{13}$C of ~−27 ± 3$^\%_{oo}$, significantly higher than the $\delta^{13}$C of biogenic CH$_4$ (see Table 2).

The $\delta^{13}$C of atmospheric CH$_4$ depends on the proportion of CH$_4$ input from biogenic versus abiogenic sources. Abiogenic CH$_4$ sources are almost exclusively derived from
<table>
<thead>
<tr>
<th>Source</th>
<th>Range $\delta^{13}C$</th>
<th>Mean $\delta^{13}C$</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td><strong>Biogenic Sources</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Wetlands</td>
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<td>Alaskan tundra</td>
<td>-73 to -55</td>
<td>-64</td>
<td>This work</td>
</tr>
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<td>Minnesota peat bog</td>
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<td>-66</td>
<td>This work</td>
</tr>
<tr>
<td>Minnesota peat bog</td>
<td>-71 to -64</td>
<td>-67</td>
<td>Stevens and Engelkemeir [1988]</td>
</tr>
<tr>
<td>West Virginia peat bog</td>
<td>-56</td>
<td>-56</td>
<td>Wahlen et al. [1987]</td>
</tr>
<tr>
<td>Florida Everglades</td>
<td>-58 to -53</td>
<td>-55</td>
<td>Stevens and Engelkemeir [1988]</td>
</tr>
<tr>
<td>Amazon floodplain</td>
<td>-73 to -41</td>
<td>-53</td>
<td>This work</td>
</tr>
<tr>
<td>Rice Paddies</td>
<td>-68 to -66</td>
<td>-67</td>
<td>Stevens and Engelkemeir [1988]</td>
</tr>
<tr>
<td>California</td>
<td>-58</td>
<td>-58</td>
<td>Tyler [1987]</td>
</tr>
<tr>
<td>Kenya</td>
<td>-63</td>
<td>-63</td>
<td>Wahlen et al. [1987]</td>
</tr>
<tr>
<td><strong>Ruminants</strong></td>
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<tr>
<td>Cows (C3 diet)</td>
<td>-76 to -62</td>
<td>-64</td>
<td>Rust [1981]</td>
</tr>
<tr>
<td>Cows (C2 diet)</td>
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<td>Rust [1981]</td>
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<tr>
<td>Cows (diet?)</td>
<td>-75 to -65</td>
<td>-64</td>
<td>Tyler [1986]</td>
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<tr>
<td>Termites</td>
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<td>Tyler [1986]</td>
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<tr>
<td>Termites</td>
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<td>Wahlen et al. [1987]</td>
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<td>Oona and Deevey [1960]</td>
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<td>-52 to -48</td>
<td>-50</td>
<td>Games and Hayes [1976]</td>
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<tr>
<td>Solid wastes</td>
<td>-55 to -50</td>
<td>-53</td>
<td>Tyler [1986]</td>
</tr>
<tr>
<td>Solid wastes</td>
<td>-55 to -50</td>
<td>-53</td>
<td>Tyler [1986]</td>
</tr>
<tr>
<td><strong>Abiogenic Sources</strong></td>
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<td></td>
</tr>
<tr>
<td>Thermogenic natural gas</td>
<td>-76 to -21</td>
<td>-42</td>
<td>Deines [1980]; Schoell [1980]</td>
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<tr>
<td>Oil-associated gas</td>
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<td>Schoell [1980]</td>
</tr>
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<td>Biomass burning</td>
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<td>-28</td>
<td>Stevens and Engelkemeir [1988]</td>
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<tr>
<td>Biomass burning</td>
<td>-24</td>
<td></td>
<td>Wahlen et al. [1987]</td>
</tr>
</tbody>
</table>

anthropogenic activities. Biogenic CH$_4$ sources are both naturally occurring and anthropogenically derived. Therefore since preindustrial times there has been an increase in the proportion of CH$_4$ input from abiogenic sources. The $\delta^{13}C$ of atmospheric CH$_4$ has changed during the industrial era in response to the increase in abiogenic CH$_4$ input, because abiogenically produced CH$_4$ has a $\delta^{13}C$ composition which is typically 20–30‰/oo greater than biogenic CH$_4$. We use current estimates of the $\delta^{13}C$ of the major CH$_4$ sources and the change of the $\delta^{13}C$ of atmospheric CH$_4$ over the last 300 years to calculate the proportion of CH$_4$ derived from biogenic and abiogenic sources.

**METHODS**

**Wetland Sampling Sites**

Methane samples for analysis of carbon isotopic composition were collected during 1985–1987 from three different wetland environments: Amazon floodplain, Minnesota peat bogs, and Alaskan tundra (Figure 1). Methane samples were collected on the Amazon River floodplain, which covers $\sim10^5$ km$^2$ within the Amazon basin, as part of the Amazon Boundary Layer Experiment (ABLE) 2A and 2B programs [Devol et al., 1988]. Peat bogs in Marcell Experimental Forest, located near Grand Rapids, Minnesota, were sampled in conjunction with a group from NASA/Langley [Harries et al., 1985; Grill et al., 1987]. Bo- real peatlands, of the type sampled in northern Minnesota, have a global area of $\sim10^6$ km$^2$ [Harries et al., 1985]. The Alaskan tundra was sampled (following the Alyeska pipeline) between the Brooks Range and the Arctic Ocean at Prudhoe Bay. Tundra regions of northern Canada, the USSR, and Scandinavia cover $>10^6$ km$^2$ [Matthews and Fung, 1987].

**Sampling Techniques**

Samples collected for isotopic analysis consisted of chamber flux samples, bubble samples, water samples, and ambient air samples. The chambers used in Alaska were 1 m$^2$ and either 0.3 or 0.5 m high and constructed of sheet aluminum. Each chamber had two sampling hoses of 3 m length and an inside mounted fan which completely mixed the chamber within 1 min. The chambers used in Minnesota and the Amazon were 0.5 m$^2$ and 0.4 m high of the design described by Sebacher et al. [1987]. Circular chambers $\sim13$ cm high and 50 cm in diameter were also used in the Amazon, as described by Devol et al. [1988]. Collars were used to seal the chambers at some of the Minnesota
sites, while surface water provided a seal at most waterlogged sites. At sites without standing water the chamber was sealed at the subsurface water level by cutting the chamber into the soil to a depth of 5 to 10 cm. Methane flux rates were calculated from the time rate of change of CH₄ concentration during the first 30 min. Methane concentrations were measured by gas chromatography (± 1% precision). When the methane concentration reached 10 parts per million by volume (ppmv), typically 1–2 hours after deployment, a sample was collected for δ¹³C analysis by drawing air from the chamber into an evacuated 500-mL glass flask and then pumping the flask up to a pressure of...
2 atm using a metal bellows pump (Biospherics Research Corporation).

Bubble samples from all three sampling sites were collected by disturbing the soil with a steel rod and displacing water from inverted funnels. In addition to the collection of forced bubbles, naturally occurring bubbles in Amazon floodplain lakes were collected during ABLE 2A and 2B. Bubble samples were stored in evacuated serum bottles. During ABLE 2A, samples of methane dissolved in anoxic lake water were extracted by equilibration of equal volumes of lake water and air, as discussed by Devol et al. [1988].

We also used the naturally occurring containment provided by nocturnal atmospheric inversions to trap CH₄ released from wetland soils. During nighttime periods of elevated atmospheric methane concentrations, air samples were collected by opening an evacuated 15- or 35-L flask. Samples of this nighttime air integrate CH₄ sources over much greater spatial scales than individual flux chambers.

**Extraction Procedures**

Chamber flux samples collected in 500-ml bottles were analysed for δ¹³C composition of CH₄ following a procedure similar to the one described by Stevens and Rust [1982]. Air was pulled (50 mL/min) through a sequence of (1) two dry ice/isopropanol traps to trap out water, (2) a liquid nitrogen trap to collect the CO₂, (3) iodine pentoxide (Shutze Reagent) to convert CO to CO₂, which was trapped in a second liquid nitrogen trap, (4) a quartz tube containing ~50 g platinumized silica at ~850°C to combust the methane to CO₂, H₂O, and some CO and a liquid nitrogen trap to collect CO₂ and H₂O, and (5) a second bed of Shutze Reagent to oxidize CO to CO₂ and a liquid nitrogen trap to collect CO₂. The methane-derived CO₂ was cryogenically separated from water and transferred to a manometer for measurement (± 0.2% precision). Our extraction efficiency was 99 ± 1%, yielding a δ¹³C accuracy of ± 0.1‰. Bubble samples used the same procedure as above with the following exceptions: (1) an aliquot of the gas sample was transferred from the serum collection bottle to the inlet using a gas-tight syringe, (2) the volume of gas was recorded and ultrapure oxygen was added in excess as oxidant, and (3) the oxygen mixture was then treated like a flux sample, the flow regulated to <20 mL/min.

The CO₂ derived from CH₄ combustion was analysed for δ¹³C on a Finnigan MAT 251 isotope ratio mass spectrometer. Methane samples collected during ABLE 2A were prepared for isotopic analysis using a CuO oxidation procedure described by Devol et al. [1988]. These samples were measured with a precision of ± 0.3‰ on a Nuclide 6-60 mass spectrometer, intercalibrated with the Finnigan MAT 251.

**RESULTS AND DISCUSSION**

The δ¹³C of CH₄ from Wetlands

**Tropical wetlands: Amazon floodplain.** The δ¹³C of CH₄ from the Amazon floodplain was measured on samples taken during July–August 1985 and May 1987 over a 1600-km stretch along the main channel of the Amazon River between Vargem Grande and Obidos, Brasil (Figure 1). The 1985 sampling period was during the falling water portion of the hydrograph; the results from this survey during the ABLE 2A program [Devol et al., 1988] are shown in Figure 2 (sites 1 and 2). These data have been reported previously by Devol et al. [1988] who describe
in detail the sampling methods, sites, and CH₄ flux data. Briefly, the samples taken for isotopic analysis represent CH₄ dissolved in floodplain lake waters and CH₄ in both natural and forced bubbles. The δ¹³C of the dissolved CH₄ ranged from -66 to -41‰ with a mean of -55 ± 6‰/oo. For bubbles, the δ¹³C of CH₄ ranged from -73 to -47‰/oo with a mean of -61 ± 8‰/oo. At any given site the dissolved CH₄ had higher δ¹³C values than the CH₄ in bubbles and was interpreted to reflect isotope fractionation associated with methane oxidation [see Devol et al., 1988; Coleman et al., 1981].

In May 1987, during the rising water portion of the Amazon River hydrograph, a second set of CH₄ samples was obtained for isotopic analysis during the ABLE 2B program. These data are also presented in Figure 2 (sites 3 and 4). The data from 1987 represent the CH₄ collected in flux chambers and both natural and forced bubbles. The δ¹³C of CH₄ obtained from flux chambers ranged from -72 to -41‰/oo with a mean of -50 ± 8‰/oo. For bubbles the δ¹³C of CH₄ ranged from -60 to -44‰/oo with a mean of -51 ± 6‰/oo. The close agreement between the δ¹³C of CH₄ in bubbles and collected in flux chambers likely results from the observation that ~80% of the CH₄ flux from the Amazon floodplain is derived from bubble ebullition [Devol et al., 1988].

During the May 1987 sampling period, nighttime samples of air exhibiting elevated CH₄ concentrations were taken for isotopic analysis of CH₄ in order to determine the δ¹³C of CH₄ released from a larger source area. Vertical profiles of concentration along with other parameters associated with the inversion layer are needed to calculate flux rates [see Wofsy et al., 1988]. However, single point isotopic analysis of boundary layer air provides an estimate of the δ¹³C of source methane if one assumes that the methane in the nighttime boundary layer is a mixture of tropospheric methane and methane released from the source. Under these conditions a regression analysis of a plot of δ¹³C of CH₄ versus the reciprocal of the CH₄ concentration yields an intercept which represents the δ¹³C of the CH₄ source [Keeling, 1958, 1961]. For the air samples collected during ABLE 2B, a plot of δ¹³C of methane versus the reciprocal of the methane concentration yields an intercept of -52 ± 1‰/oo (Figure 3). This value agrees well with the mean δ¹³C obtained from the flux chamber and bubble samples collected during the 1987 sampling period suggesting that our flux chamber and bubble samples yield δ¹³C values that accurately reflect the δ¹³C of methane emitted from the Amazon floodplain.

The mean δ¹³C of all methane samples obtained in 1985 and 1987 from the Amazon floodplain is -53 ± 8‰/oo (n = 47). These results represent the most extensive determination of the δ¹³C of CH₄ released from tropical wetlands currently available. The CH₄ flux from the Amazon floodplain has been recently estimated at 200-400 mg CH₄/m²/d on the basis of the flux measurements made by Devol et al. [1988] during ABLE 2A. This CH₄ flux yields a total emission rate of 8–13 Tg/yr [Devol et al., 1988]. Previously, two measurements of the δ¹³C of CH₄ bubbles trapped beneath floating vegetation on the Amazon floodplain by Tyler [1986] indicated a δ¹³C of -65 and -63‰/oo, at the lower limit of the range of our results.

Temperate wetlands: Minnesota peat bogs. Forested and nonforested bogs represent by far the largest wetland environments in the northern temperate latitudes both in terms of areal extent and CH₄ emission rates [Matthews and Fung, 1987]. During April–June 1986 we made measurements of the δ¹³C of CH₄ released from five bogs in the Marcell Experimental Forest in northern Minnesota (Fig-
Our $\delta^{13}C$ measurements were made in conjunction with CH$_4$ flux measurements made by the group at NASA/Langley [see Crill et al., 1987]. Twenty-nine samples were collected from flux chambers for isotopic analysis. The $\delta^{13}C$ of CH$_4$ ranged from $-76$ to $-56^{/oo}$ (Figure 2, site 5) with a mean of $-66 \pm 4^{/oo}$. The $\delta^{13}C$ of CH$_4$ in bubbles collected at these sites ranged from $-86$ to $-50^{/oo}$ with a mean of $-66 \pm 10^{/oo}$ (see Figure 2, site 6). Two air samples were collected during nighttime inversions when the CH$_4$ concentrations were 1.89 and 2.06 ppm. These two samples yielded a $\delta^{13}C$ of source CH$_4$ of $-69^{/oo}$, in excellent agreement with the $\delta^{13}C$ measured from flux chamber and bubble samples.

The mean $\delta^{13}C$ of all CH$_4$ samples obtained from May-June 1986 in northern Minnesota was $-66 \pm 5^{/oo}$ similar to the value of $-67.2 \pm 1^{/oo}$ measured in this region by Stevens and Engelkeimeir [1988]. Methane fluxes measured by Crill et al. [1987], using the same chambers from which the isotopic samples were obtained, ranged from 14 to 711 mg CH$_4$/m$^2$/d with a mean of 230 mg CH$_4$/m$^2$/d. These flux estimates are derived from the linear increase with time of CH$_4$ in the chambers over the first 10-15 min of chamber deployment. Although chamber flux samples for $\delta^{13}C$ measurements were collected after 1-2 hours, isotopic analysis of a time series of chamber samples indicated there was no measurable change in the $\delta^{13}C$ of the source CH$_4$ during this time.

Arctic wetlands: Alaskan tundra. Arctic tundra represents a large but poorly known component of the wetland sources of atmospheric methane. Recent flux measurements [Sebacher et al., 1986] together with better areal estimates [Matthews and Fung, 1987] suggest that arctic wetlands may account for up to 25% of the wetland flux of CH$_4$ to the atmosphere.

During August 1987 we made measurements of both the $\delta^{13}C$ and the flux of methane over a 200-km transect of Alaskan tundra following the Alyeska pipeline from the northern foothills of the Brooks Range to the Arctic Ocean at Prudhoe Bay (Figure 1). The $\delta^{13}C$ of 17 flux chamber samples collected at 10 sampling sites ranged from $-70$ to $-59^{/oo}$ with a mean of $-64 \pm 4^{/oo}$ (see Figure 2, site 7). The mean $\delta^{13}C$ of CH$_4$ in five bubble samples collected at these sites was $-60 \pm 7^{/oo}$. The flux of methane determined from 27 chamber deployments ranged from $-1$ to $+145$ mg CH$_4$/m$^2$/d with a mean of $30 \pm 14$ mg CH$_4$/m$^2$/d. This mean flux includes six chamber deployments showing zero methane flux, and two chamber deployments in which significant methane consumption was observed. Our flux measurements follow the pattern of and fall within the range of values recently reported by Sebacher et al. [1986]. Generally, we measured higher CH$_4$ fluxes at wetter sites. However, the $\delta^{13}C$ of the CH$_4$ did not show any significant correlation with methane flux.

The $\delta^{13}C$ of Methane Released From Global Wetlands

A globally averaged $\delta^{13}C$ value for methane emitted from wetlands is needed to determine the $^{13}C$ composition of the global source of CH$_4$ input to the atmosphere. Our $\delta^{13}C$ measurements for CH$_4$ released from a tropical floodplain and arctic tundra isotopically characterize two important wetland sources of CH$_4$ for which virtually no isotopic data had existed. Our three sampling sites are representative of major wetland regions with global areas of $\sim 10^8$ km$^2$. The observed $\delta^{13}C$ range of $-65$ to $-53^{/oo}$ for the Alaskan tundra, boreal peatlands, and Amazon floodplain, encompasses the range of most previously reported values for CH$_4$ released from wetland environments (see Table 2). Earlier measurements of the $\delta^{13}C$ of CH$_4$ released from wetland environments varied from $-55^{/oo}$ for the Florida Everglades [Stevens and Engelkeimeir, 1988] to $-60^{/oo}$ for marsh gases in the USSR [Ovayannikov and Lebedev, 1967]. The processes yielding this range in $\delta^{13}C$ of CH$_4$ released from natural wetlands have not been identified. However, possible explanations include the proportion of C$_3$ versus C$_4$ plant material undergoing anaerobic decomposition, with C$_4$ plants having $\delta^{13}C$ values $\sim 14^{/oo}$ greater than C$_3$ plants [Bender, 1971], and the degree of microbial oxidation of CH$_4$, which fractionates the $\delta^{13}C$ by 15 to 24$^{/oo}$ [Coleman et al., 1981; S. King, submitted manuscript, 1988].

Since we observed significant differences in the $\delta^{13}C$ of methane from tropical versus high northern latitude wetlands, our calculation of a globally averaged $\delta^{13}C$ for methane emitted from wetlands must incorporate methane flux-weighted $\delta^{13}C$ values for each wetland type, as described below. We calculate this global $\delta^{13}C$ value by assuming a $\delta^{13}C$ for methane emitted from wetlands in any given latitudinal belt. Next we weight the isotopic values for CH$_4$ flux primarily on the basis of the recently published data of Matthews and Fung [1987] concerning the areal distribution of natural wetlands and the estimated mean annual fluxes of methane from these wetlands.

The measured $\delta^{13}C$ for methane from Minnesota peat bogs (47$^\circ$N) and Alaskan tundra (68$^\circ$-70$^\circ$N) clustered tightly around a value of $-55^{/oo}$. We assume $-56 \pm 6^{/oo}$ to be the mean $\delta^{13}C$ of methane emitted from wetlands located poleward of 40$^\circ$ latitude, i.e. forested and nonforest bogs [see Matthews and Fung, 1987]. Our mean $\delta^{13}C$ for CH$_4$ emitted from the Amazon floodplain was $\delta^{13}C = -53^{/oo}$ ($n = 47$); thus we use this value for the mean $\delta^{13}C$ of methane emitted from tropical wetlands located between 20$^\circ$S and 20$^\circ$N. For wetlands in subtropical (20$^\circ$-40$^\circ$S) locations where only a few scattered $\delta^{13}C$ measurements varying from $-69$ to $-55^{/oo}$ have been reported (summarized in Stevens and Engelkeimeir [1988]), we assume the methane has a $\delta^{13}C = -59^{/oo}$, an intermediate value between $-65$ and $-53^{/oo}$.

We use the global CH$_4$ flux estimates of Matthews and Fung [1987] to weight the various latitude-dependent $\delta^{13}C$ values for wetland methane. Matthews and Fung [1987] present the most comprehensive estimates of the global areal distribution and growing season of natural wetlands, but they admittedly base their methane emission rates on a very limited number of measurements. Therefore we determined the sensitivity of the calculated globally averaged $\delta^{13}C$ value to assumptions about the CH$_4$ flux rate while using their areal distributions and lengths of growing season. We assumed the CH$_4$ flux estimates used by Matthews and Fung [1987] had an uncertainty of $\pm 50\%$ and the mean $\delta^{13}C$ of CH$_4$ released from tropical, subtropical, and temperate/arctic (poleward of 40$^\circ$) wetlands were uncer-
tain to ± 8, ± 6 and ± 5°/oo, respectively. We calculated a flux-weighted mean δ13C value of −59°/oo for the global wetland CH4 flux, with an uncertainty of ± 6°/oo.

Source of CH4 in Preindustrial Times

The preindustrial atmospheric CH4 concentration of ~0.7 ppm [Khalil and Rasmussen, 1985; Stauffer et al., 1985] was sustained by CH4 released from natural sources at 190–384 Tg/yr. Wetlands were likely to have been the major natural source of CH4. Thus the δ13C of atmospheric CH4 in preindustrial times depended, to a large degree, on the δ13C of CH4 released from wetlands. In this section we compare our estimate of −59 ± 6°/oo for the δ13C of CH4 released from wetlands to a calculated value for the δ13C of CH4 released from natural sources required to yield the measured preindustrial atmospheric CH4 δ13C value of −49.7°/oo [Craig et al., 1986; Stevens and Engelkeimer, 1988].

If we assume the δ13C of atmospheric CH4 was in isotopic equilibrium with its sources in preindustrial times, the mass and isotopic balance for the preindustrial atmospheric CH4 are expressed as follows:

\[ S = KC \]

\[ S(13C/12C) = KC(13C/12C)R \]

where S is the total CH4 source strength, K is the first-order reaction constant for CH4 loss, C is the atmospheric CH4 concentration, \((13C/12C)S\) is the average \(^{13}C/^{12}C\) of the CH4 source, \((13C/12C)C\) is the \(^{13}C/^{12}C\) of atmospheric CH4, and R is the isotopic fractionation effect during CH4 loss. At steady state in preindustrial times the input of CH4 from its sources was balanced by CH4 loss. CH4 loss occurs primarily (~90%) via OH oxidation of CH4 and to a lesser extent via microbial CH4 oxidation in soils (~10%). Likewise, at steady state \((13C/12C)S = (13C/12C)C\)R. The fractionation effect during OH oxidation of CH4 is 0.990 ± 0.003 (~1%), as reported by Davidson et al. [1987], whereas for microbial oxidation the fractionation effect is 0.974 to 0.985 [Coleman et al., 1981; S. King, submitted manuscript, 1988]. An average value for the isotopic fractionation during CH4 loss (R) is -0.989 ± 0.004, weighted for the loss via each pathway.

Assuming a preindustrial atmospheric CH4 with δ13C = -49.7 ± 0.4°/oo [Stevens and Engelkeimer, 1988] and an R value of -0.989 ± 0.004, yields an average value of -60 ± 4°/oo for the δ13C of CH4 released from preindustrial sources. This calculated preindustrial source δ13C value agrees well with our estimate of -59 ± 6°/oo for the δ13C of CH4 released from wetlands, as expected if wetlands were the major natural CH4 source. Additionally, these results suggest that in preindustrial times there was little input of abiotogenically produced methane derived, for example, from naturally occurring forest fires or natural gas seepage.

Anthropogenically Derived Changes in the Concentration and δ13C of Atmospheric Methane

The increase in atmospheric CH4 concentrations over the last 300 years likely resulted from an increase in CH4 source strengths and, possibly, a decrease in OH oxidation rates. However, because of the uncertain estimates of individual CH4 source strengths (Table 1) and the industrial era change in atmospheric CH4 lifetimes [Khalil and Rasmussen, 1985], it is difficult to unambiguously determine the specific contribution of each methane source to the increase in atmospheric CH4. Here we reduce this ambiguity by examining the change in the δ13C of CH4 over the last 300 years. Because atmospheric CH4 in preindustrial times was predominantly biogenic, as discussed above, the subsequent change in the δ13C of CH4 is most sensitive to the input of CH4 produced abiotogenically. The largest sources of abiotic CH4 input to the atmosphere are natural gas release and biomass burning. In the following discussion we refer only to the abiotic portion of CH4 derived from natural gas release.

To determine the input of abiotogenically produced CH4 over the last 300 years, we need to determine how the time rate of change of the δ13C of atmospheric CH4 varied as a function of the proportion of biogenic versus abiotic CH4 source strengths. Therefore we first determine a CH4 source scenario that explains the observed industrial era time rate of change of CH4 concentration. Next we use this source scenario to show that the calculated time rate of change of δ13C significantly constrains the CH4 input rates from natural gas and biomass burning.

Methane concentration. To calculate the time rate of change of CH4 concentration we need to estimate the current (1980) methane source strength and loss rate and the time rate of change of the source strength and loss rates.

We chose the source scenario by Stevens and Engelkeimer [1988] to estimate the global CH4 source strength in 1980 (Table 1). This scenario has several advantages: it incorporates recent estimates of individual CH4 source strengths, it accounts for the "natural" CH4 sources required to explain the observed preindustrial concentration of 0.7 ppm [Khalil and Rasmussen, 1985], and it has a CH4 source strength allocation that explains the change in concentration and δ13C of atmospheric CH4 observed between 1978 and 1983. Stevens and Engelkeimer [1988] estimate the total CH4 source strength in 1980 to be ~504 Tg/yr, assuming a constant CH4 lifetime of 7.3 years. Of this total CH4 input rate, Stevens and Engelkeimer [1988] estimate that 348 Tg/yr are released from anthropogenic sources including rice, cattle, natural gas, organic waste, and biomass burning (Table 1).

To determine the industrial time rate of change of the CH4 release rate from anthropogenic sources, we follow the line of reasoning used by Khalil and Rasmussen [1985], who assumed that the CH4 released from anthropogenic sources increased at rates that follow the global population growth. Thus we assume that the CH4 released from anthropogenic sources increased at 0.3%/yr between 1650 and 1750, 0.39%/yr between 1750 and 1850, 0.86%/yr between 1850 and 1900 and 1.9%/yr after 1930 [Ehrlich et al., 1977]. Khalil and Rasmussen [1985] used their estimates of total CH4 emission rate in 1980 of 555 Tg/yr (Table 1) and the above emission growth rates between 1650 and 1980 to calculate a time rate of change of CH4 concentration that agrees well with the ice core data.

We chose an atmospheric lifetime (τ) for CH4 of ~7
years in 1980, to agree with the estimate of Stevens and Engelkeimir [1988]. This estimate falls within the 7 to 10 year range derived from the interhemispheric gradients of methylchloroform [Mayer et al., 1982] and methane [Khalil and Rasmussen, 1983]. A preindustrial CH4 concentration of 0.7 ppm coupled with a τ of 7 years yields a preindustrial, natural CH4 source strength of ~250 Tg/yr [Stevens and Engelkeimir, 1988].

Estimates of current atmospheric CH4 lifetimes may not apply, however, in preindustrial times. There is uncertainty regarding the preindustrial rate of CH4 loss via OH oxidation because of the complexity of the chemical interactions between CH4, CO, NOx, and OH and the anthropogenic perturbation of these interactions [Khalil and Rasmussen, 1985; Thompson and Cicerone, 1986]. Estimates of the decrease in the rate of CH4 oxidation rates by OH over the last 300 years vary from 0 to 40% [Khalil and Rasmussen, 1985; Thompson and Cicerone, 1986]. The uncertainty in the preindustrial CH4 lifetime results in estimates for natural CH4 source strength that range from 200 to 300 Tg/yr.

We chose not to set the preindustrial CH4 lifetime (τ0); rather we determined a value for τ0 that yielded the measured CH4 concentration of 1.56 ppm in 1980 [Khalil and Rasmussen, 1983] given an initial concentration of 0.7 ppm in 1550. This approach resulted in a CH4 lifetime of ~6 years in 1650 which then increased at ~0.1% yr to yield a lifetime of ~7 years in 1980. A preindustrial lifetime of 6 years implies a steady state natural CH4 source strength of 276 Tg/yr (see (1)), within the 260–320 Tg/yr range estimated by Khalil and Rasmussen [1985]. We assumed the natural CH4 source remained constant between 1650 and 1980 and when combined with a current anthropogenic source strength of 348 Tg/yr [Stevens and Engelkeimir, 1988] yields a total CH4 source strength of 624 Tg/yr in 1980.

To calculate the time rate of change of CH4 concentration over the last 300 years, we numerically integrated the following expression:

\[
\frac{dC}{dt} = S_o + S_a \exp(-nt) - CK \exp(-qt)
\]

where t is time, So is the preindustrial CH4 source strength, Sa is the anthropogenic CH4 source strength, n is the growth rate of anthropogenic sources, K is the first order reaction rate constant for CH4 loss and q is the time rate of change of the reaction rate constant for CH4 loss.

The results of our calculated time rate of change of CH4 concentration (Figure 4) fit well to the ice core data of Khalil and Rasmussen [1985] and the CH4 concentration in 1951 estimated from spectral data by Rinsland et al. [1985]. Given the uncertainties in natural and anthropogenic CH4 source strengths and the atmospheric CH4 lifetime, a unique CH4 budget cannot be derived from the ice core record. For example, Khalil and Rasmussen [1985] showed that the measured atmospheric CH4 increase between 1650 and 1980 could be explained by CH4 source strengths and atmospheric lifetimes that varied by up to 30% from their best estimates.

The source/sink scenario we derived to explain the time rate of change of CH4 concentration since 1650 is not unique. However, it does serve to test the sensitivity of the industrial era time rate of change of the δ13C of CH4 to the proportion of abiotic vs biogenic CH4 input, because the relative abiotic and biogenic CH4 fluxes, rather than the total CH4 flux, determine the δ13C of atmospheric CH4.
The δ¹³C of methane. The δ¹³C of atmospheric methane has increased by ~2‰/yr over the last 300 years, assuming the best estimate of the δ¹³C change is derived from measurements made by the same laboratory [Stevens and Engelkemeir, 1988] on air trapped in ice (~49.7‰/∞) and air collected in 1980 (~47.7‰/∞). The industrial era 2°/∞ increase in δ¹³C likely resulted from increased input of abiotic methane from natural gas release and biomass burning. The mean δ¹³C values of CH₄ released from natural gas and biomass burning are ~40‰/∞ and ~27‰/∞, respectively (see Table 2). Industrial era increases in biogenic CH₄ input from livestock and rice paddies are unlikely to have changed the δ¹³C values of atmospheric CH₄ because the δ¹³C values of CH₄ released from these sources (Table 2) and preindustrial CH₄ sources are similar.

We determined the time rate of change of the δ¹³C of atmospheric CH₄ since 1650 using the δ¹³C values for the CH₄ sources (Table 2) and the source strength scenario we derived to explain the time rate of change of CH₄ concentration. Following the procedure used for calculating the change in atmospheric CH₄ concentration, we calculated the time rate of change of the δ¹³C of CH₄ by numerically integrating the following expression:

\[
dt{\delta^{13}C}{[CH_4]} = S_{a} (13C/12C)_{s} + S_a (13C/12C)_{s} \exp (nt) - CK \exp (-Kt) (13C/12C)
\]

where (13C/12C)ₘₙₐₜ is the 13C/12C of the preindustrial CH₄ source and (13C/12C)ₚₐₜ is the flux-weighted mean 13C/12C of the anthropogenic CH₄ sources.

We assumed the CH₄ concentration is approximated by 12CH₄ and the δ¹³C of the preindustrial sources was ~60‰/∞, in isotopic equilibrium with an atmospheric δ¹³C = ~49.7‰/∞ [Stevens and Engelkemeir, 1988]. A δ¹³C of ~60‰/∞ for natural CH₄ sources is in good agreement with the ~59 ± 6‰/∞ value we determined for the δ¹³C of CH₄ released from wetlands, as discussed above. We used a value for the average isotopic fractionation during CH₄ loss (R) of 0.989 ± 0.004/∞, as discussed above. For the anthropogenic components we assumed the δ¹³C values for CH₄ released from rice paddies, livestock, natural gas, biomass burning, and solid wastes be ~63 ± 5‰/∞, ~60 ± 5‰/∞, ~40 ± 7‰/∞, ~27 ± 3‰/∞, and ~50 ± 5‰/∞, respectively, based on the compilation of data presented in Table 2. We estimate the uncertainties in these mean δ¹³C values to represent ±1σ. The growth rate of each anthropogenic CH₄ source was assumed to follow the global population growth rate, as discussed above.

The time rate of change of the δ¹³C of CH₄ since 1650 calculated for the source/sink scenario we derived to explain the time rate of change of CH₄ concentration yields a δ¹³C value of ~47.1‰/∞ in 1980. This calculated δ¹³C increase with time reflects the increased proportion of abiotic CH₄ input from biomass burning and natural gas which increased from 9% of the total CH₄ source in 1650 to 16% in 1980. The calculated δ¹³C of atmospheric CH₄ in 1980 is sensitive to the relative strengths of biogenic and abiotic CH₄ sources.

Magnitudes of Abiotic CH₄ Sources

Currently, the magnitude of abiotic CH₄ input from biomass burning and natural gas is uncertain. Estimates of the abiotic CH₄ flux in 1980 vary from 65 to 148 Tg/yr for the four scenarios listed in Table 1, representing from 12 to 36% of the total CH₄ flux. To test whether the magnitude of abiotic CH₄ source can be determined from the historical era change in the δ¹³C of atmospheric CH₄, we calculated the time rate of change of δ¹³C as a function of the abiotic source strength. We used the CH₄ source/sink scenario derived to explain the time rate of change of the CH₄ concentration and varied the abiotic source strength in 1980 from 62 to 156 Tg/yr while maintaining a constant total source strength of 624 Tg/yr. In practice, a portion of the biogenic CH₄ flux with a δ¹³C of ~60‰/∞ was replaced with an equivalent CH₄ flux from natural gas and biomass burning sources which had δ¹³C values of ~40‰/∞ and ~27‰/∞, respectively.

The calculated time rate of change of the δ¹³C of CH₄ is sensitive to the proportion of CH₄ input derived abiotically (Figure 5). The calculated δ¹³C in 1980 varies from ~48.4 to ~45.1‰/∞ for an abiotic source strength which varies from 10 to 25%, respectively, of the total CH₄ flux (i.e., 62 to 156 Tg/yr). The best fit to the ~47.1‰/∞ value measured in 1980 [Stevens and Engelkemeir, 1988] is obtained when the abiotic CH₄ source in 1980 is ~13% of the total CH₄ flux.

We determined the sensitivity of the estimated abiotic CH₄ input to the uncertainties (± 1σ) in the δ¹³C values in the calculation (see (4)). The industrial era change in the δ¹³C of CH₄ is known to ± 0.5‰/∞ [Craig et al., 1986; Stevens et al., 1985]. We estimate the uncertainties in the mean δ¹³C of the CH₄ sources to vary from ± 3‰/∞ to ± 7‰/∞ and in the isotopic fractionation effect during CH₄ loss (R in (4)) to be ± 4‰/∞, as discussed above. The uncertainties in the δ¹³C terms result in a range in the calculated time rate of change of the δ¹³C of atmospheric CH₄.

The error in the abiotic CH₄ flux estimate depends on the uncertainty in the calculated time rate of change of the δ¹³C. The error in the δ¹³C time rate of change was determined using a "bootstrap" procedure [Efron, 1992]. For this procedure 200 sets of values for the δ¹³C of each source and R were randomly selected from the Gaussian distribution described by the mean and standard deviation of each input variable. The time rate of change of δ¹³C was calculated for each set of input variables; on the basis of this set of calculations the mean and standard deviation of the δ¹³C in 1980 were determined. The results of our error analysis indicate the calculated δ¹³C time rate of change between 1650 and 1980 is uncertain to ± 1.7‰/∞, corresponding to a ± 8% uncertainty in the proportion of abiotic CH₄ input. Thus industrial era CH₄ input from natural gas and biomass burning likely contributed 13 ± 8% of the total CH₄ flux, which yields an abiotic CH₄ flux of 65 ± 42 Tg/yr in 1980 assuming a total CH₄ flux of 500 ± 100 Tg/yr (see Table 1). This calculated abiotic CH₄ flux agrees well with the 65 Tg/yr estimated by Khalil and Rasmussen [1985] but is lower than the three other estimates presented in Table 1.
The time rate of change of δ¹³C depends on the proportion of the abiotic CH₄ which is derived from biomass burning versus natural gas, as CH₄ from the former source has a δ¹³C of ~−27‰, significantly higher than the −40‰ for natural gas. The CH₄ source/sink scenario we used to calculate the time rate of change in δ¹³C has biomass burning and natural gas sources that contribute 45 and 55%, respectively, of the abiotic CH₄ flux. For comparison, the other scenarios listed in Table 1 estimate the CH₄ flux from biomass burning to contribute from 38 to 53% of the abiotic CH₄ flux. Allowing the proportion of abiotic CH₄ derived from biomass burning to vary from 25 to 75% in our source/sink scenario increases the uncertainty in the abiotic CH₄ source strength estimate to ± 47 Tg/yr.

CONCLUSIONS

The δ¹³C of CH₄ released from wetlands has a global average value of −59 ± 6‰. This value agrees with the preindustrial δ¹³C of −49.7‰ [Stevens and Engelkemeir, 1988] for atmospheric CH₄ and an isotopic fractionation of ~−0.989 during CH₄ loss [Davidson et al., 1987]. These results indicate that in preindustrial times CH₄ in the atmosphere was predominantly biogenic. There exists a significant difference between the δ¹³C of CH₄ released from the Amazon River floodplain (−53 ± 8‰) and from Minnesota peat bogs and Alaskan tundra (−65 ± 6‰). This difference in the δ¹³C of CH₄ released from tropical versus temperate and arctic wetlands possibly results from the proportion of C₄ versus C₃ plant matter or the degree of CH₄ oxidation in the soils.

The recent estimate of 110 Tg/yr for the CH₄ flux from wetlands [Matthews and Fung, 1987] is significantly lower than the preindustrial CH₄ source strength of 190–384 Tg/yr required to yield a CH₄ concentration of 0.7 ppm, given a preindustrial CH₄ lifetime of 5–10 years [Khalil and Rasmussen, 1985]. This discrepancy suggests that either the preindustrial wetland CH₄ flux was 2 to 3 times greater than at present, the current wetland CH₄ flux is substantially underestimated, or other natural CH₄ sources are as important as the wetlands.

The 2‰ increase in the δ¹³C of atmospheric CH₄ during the last 300 years determined by Stevens and Engelkemeir [1988] indicates that current abiotic CH₄ input from natural gas and biomass burning likely contributes 13 ± 8% of the total CH₄ source, equivalent to 65 ± 42 Tg/yr for a total CH₄ flux of 500 ± 100 Tg/yr in 1980.

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S. L. King, J. M. Lansdown, P. D. Quay, and D. O. Wilbur, Department of Oceanography, WB-10, University of Washington, Seattle, WA 98195.

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