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Methane and Carbon Monoxide Production, Oxidation, and Turnover Times in the Caribbean Sea as Influenced by the Orinoco River

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The surface distribution of CH₄, photoproduction capacity of seawater for CO, and CH₄ and CO microbial oxidation rates and turnover times were determined for the surface waters of the southeastern Caribbean Sea and Gulf of Paria as affected by the Orinoco River. Measurements were made during the spring (low river flow) and the fall (high river flow) in order to determine the influence of Orinoco River discharge on these parameters. Methane concentrations were generally lower in the fall than in the spring. Low CH₄ oxidation rates and similar surface distributions were observed during both seasons. Methane oxidation in the river plume was significantly higher in the fall. Potential CO photoproduction and CO oxidation rates were generally higher during the fall. Possible effects of the Orinoco River on potential CO photoproduction capacity were observed as far as Puerto Rico. Turnover times for CH₄ were in the order of years, whereas CO turnover times were in the order of hours. The Orinoco River has a significant impact on the consumption of CO and CH₄ and the photoproduction of CO in the southeastern Caribbean Sea, presumably resulting from inputs of riverine carbon and nutrients.

INTRODUCTION

The Orinoco River contributes approximately $86 \times 10^6$ tons of suspended material per year to the Caribbean Sea through its estuarine-deltaic system [Salazar, 1989]. Maximum water flow occurs in August, when precipitation is highest (127 mm) and minimum flow occurs in March, when precipitation is lowest (19 mm), with an average flow of $34 \times 10^3$ m$^3$ s$^{-1}$ [Salazar, 1989]. Measurements of pigment concentration in the Caribbean Sea show that the influence of the Orinoco River on the Caribbean Sea during the high flow season reaches Puerto Rico [Müller-Karger and Varela, 1988]. Thus, the Caribbean Sea/Orinoco River system presents an opportunity to study the effects of terrestrial freshwater inputs on marine biological and chemical processes, particularly those affecting carbon and nutrient cycling.

Rivers often contain high levels of CH₄ resulting from both natural [de Angelis and Lilley, 1987; Wilkness et al., 1978] and anthropogenic [Brooks and Sackett, 1973; Butler et al., 1987] sources. For example, de Angelis and Lilley [1987] observed high natural levels of CH₄ in undisturbed forest streams and rivers from the Oregon coast. Furthermore, mixing between high CH₄-containing river water and low CH₄-containing seawater end-members appeared to control CH₄ concentrations in estuaries [de Angelis and Lilley, 1987].

Rivers also contain supersaturated concentrations of CO [Butler et al., 1987], but their contribution to CO levels found in estuarine and sea waters is unclear. The largest source of CO in surface waters appears to be abiotic photoproduction of dissolved organic material [Wilson et al., 1970; Conrad and Seiler, 1980; Conrad et al., 1982; Redden, 1983]. Consumption of CO is primarily a bacterial oxidation process [Conrad et al., 1982].

Methane concentration and CO production, and oxidation and turnover times for these gases were measured in the surface waters of the southeastern Caribbean Sea, the Gulf of Paria, and the Orinoco River in order to determine the influence of river inputs on these parameters in seawater.

MATERIALS AND METHODS

Water Samples

Surface water samples were collected during two cruises to the southeastern Caribbean Sea and the Orinoco River in Venezuela during April and October 1988 (Figure 1). Additional cruise details are presented in the paper by Bonilla et al. [this issue]. Water samples were collected using a teflon-lined bow pumping system connected to the inlet of an automated gas chromatographic/stripping system (described below). Samples for CH₄ and CO concentration measurements were collected automatically every 30 min while the ship was underway and every 60 min when the ship was on station. The fixed sampling stations for both the spring and fall cruises are shown in Figure 1. Samples for determination of microbial activities were collected using the same pumping system and placed in 500-mL polyethylene bottles. All microbiological and photochemical assays were conducted within 4 hours of sample collection.

Methane and Carbon Monoxide Concentration

Methane and CO concentrations were measured from the same water sample using an automated version of the gas chromatograph/stripper described by Redden [1983] and Butler et al. [1987]. Two hundred and fifty milliliters of sample were automatically drawn from the bow pumping system into an evacuated stripping flask (500 mL) and stripped for 10 min with purified helium flowing at 100 mL min$^{-1}$ through a scinttered glass disk. The stripped gases and the helium carrier were passed through traps containing Drierite (10/20 mesh) and Ascarite (8/20 mesh) and onto a...
Methane and Carbon Monoxide Oxidation

Methane and CO oxidation rates were measured using 14C-labeled gases, as described by Jones and Morita [1983a, b] and Jones et al. [1984]. Water samples (25 mL) were placed in 60-mL serum bottles, degassed for 8 min with activated carbon-filtered air, sealed with serum stoppers, and 0.5 mL of 14CO diluted in nitrogen (0.5 μCi mL−1; 56 mCi mmol−1; Amersham Corp., Arlington Heights, Illinois) or 1.0 mL of 14CH4 diluted in nitrogen (1.0 μCi mL−1; 59 mCi mmol−1; Amersham) was injected into the headspace. Degassing with filtered air reduced dissolved CH4 and CO concentrations so they represented <0.05% of the labeled substrate, thus assuring no discernible isotope dilution effects. All bottles were prepared in triplicate and acidified controls were incubated along with samples from each series. Bottles were incubated in the dark for either 12 hours (14CO) or 24 hours (14CH4) at 26°C. The reaction was terminated by injection of 1.0 mL of 5 N NaOH. Bottles were then transported to the laboratory where 14CO2 was released, trapped, and assayed using the methods described by Griffiths et al. [1982]. The equilibrium concentrations of 14CH4 and 14CO in solution were determined by multiplying the Bunsen solubility coefficient (Schmidt [1979] for CO; Yamamoto et al. [1976] for CH4). Both salinity and temperature effects on solubility were taken into account when calculating oxidation rates. CH4 and CO oxidation rates were normalized to rates at a CH4 concentration of 11.93 nM and a CO concentration of 2.23 nM, thus allowing comparison with previous work. No significant incorporation of 14C into cellular material was detected in any of the 14CO samples and only samples from stations R3, R4 and R5 demonstrated significant 14C incorporation from 14CH4. These samples incorporated between 3 and 5% of the label. Since incorporation was so limited only 14CO2 production was used in both CH4 and CO oxidation rate determinations.

Potential Photoproduction Capacity for Carbon Monoxide

Potential photoproduction capacity of the water for CO was determined using surface water samples. The water...
TABLE 1. Methane Concentrations, Oxidation Rates, and Turnover Times

<table>
<thead>
<tr>
<th>Station</th>
<th>Spring</th>
<th>Fall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ambient</td>
<td>Oxidation</td>
</tr>
<tr>
<td></td>
<td>Concentration</td>
<td>Rate,</td>
</tr>
<tr>
<td></td>
<td>nM</td>
<td>pmol L⁻¹ h⁻¹</td>
</tr>
<tr>
<td>A</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>1.6</td>
<td>0.04</td>
</tr>
<tr>
<td>C</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>D</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>E</td>
<td>2.0</td>
<td>0.30</td>
</tr>
<tr>
<td>F</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>G</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>H</td>
<td>5.2</td>
<td>0.15</td>
</tr>
<tr>
<td>I</td>
<td>3.3</td>
<td>0.02</td>
</tr>
<tr>
<td>J</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K</td>
<td>66</td>
<td>0.38</td>
</tr>
<tr>
<td>L</td>
<td>176</td>
<td>3.47</td>
</tr>
<tr>
<td>M</td>
<td>39</td>
<td>0.45</td>
</tr>
<tr>
<td>N</td>
<td>68</td>
<td>0.36</td>
</tr>
<tr>
<td>O</td>
<td>103</td>
<td>2.23</td>
</tr>
<tr>
<td>P1</td>
<td>138</td>
<td>—</td>
</tr>
<tr>
<td>R4</td>
<td>37</td>
<td>6.63</td>
</tr>
<tr>
<td>R2</td>
<td>27</td>
<td>—</td>
</tr>
<tr>
<td>R1</td>
<td>46</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Station designations refer to Figure 1. Oxidation rates normalized to a concentration of 11.93 nM. Turnover time is defined as the inverse of the first-order rate constant.

samples (160 mL) were drawn into quartz tubes (30 cm long × 2.6 cm diameter) fitted with polypropylene valves and syringe plungers covered with teflon. The tubes containing the water were placed in a circulating water bath and irradiated in full sunlight on the deck of the ship between 1000 and 1500 LT. Samples wrapped with aluminum foil to prevent light penetration were exposed to the same conditions as controls (time-zero blanks). Carbon monoxide concentrations were measured as described above. Total solar irradiance was measured using a radiometer fitted with a bandpass filter that limits the spectral response of the photocell to wavelengths between 300 and 700 nm, and all samples were normalized to 1000 Wh m⁻² irradiance.

RESULTS AND DISCUSSION

Methane

Surface concentrations of CH₄ during the spring ranged from less than 2 nM in the middle of the Caribbean Sea to 138 nM (station R4) near the mouth of the Orinoco (Table 1 and Figure 2a). Methane concentration decreased sharply with distance from the Orinoco River on a northeasterly direction towards the Atlantic Ocean, where surface concentrations of CH₄ were on the order of 45 nM. The highest concentrations of CH₄ were observed near the Serpents Mouth (station R9), at the southern entrance to the Gulf of Paria, and decreased sharply towards the Caribbean Sea (Table 1 and Figure 2a). During the fall, surface CH₄ concentrations had a narrower range, from 3.3 nM in the central Caribbean to 61 nM northeast of the mouth of the Orinoco near the coast (Figure 2b). The area of highest CH₄ concentration near the mouth of the Orinoco during the spring was found further out to sea and to the northwest during the fall. Changes in CH₄ concentration with distance from the Orinoco were less abrupt during the fall, with a fairly even surface distribution in the coastal area from the mouth of the Orinoco to the Gulf of Paria. There was little difference in the concentration of CH₄ between the Atlantic Ocean and the Caribbean Sea. However, these differences were of sufficient magnitude that the influence of the Orinoco was detected as far as Puerto Rico in the fall (Table 1) (see paper by Moore and Todd [this issue]).

The range of surface CH₄ concentrations was generally narrower during the fall than in the spring; however, the area of the southeastern Caribbean Sea with elevated concentrations was much larger (Figure 2) in the fall. Lower CH₄ concentrations during the fall may be due to dilution of the riverine source resulting from increased river flow, particularly in the estuarine-deltaic area of the Orinoco. These results indicate that the delta area and Gulf of Paria are potential sources of CH₄, in addition to the Orinoco River itself. Similar seasonal effects on distribution of CH₄ concentration concurrent with changes in river flow have been observed in Yaquina Bay, Oregon [Butler et al., 1987]. Alternatively, these differences may be accounted for by seasonal differences in CH₄ oxidation rates. Methane oxidation rates were extremely low during both the spring and fall, with similar surface distributions (Table 1). However, significantly higher CH₄ oxidation rates were observed during the fall in the Orinoco River plume. The higher rates of CH₄ oxidation may have contributed to the decrease in surface CH₄ concentration in the fall, particularly in the area of the river plume (Northwest to the Gulf of Paria). Higher rates of CH₄ oxidation may result from the large input of nutrients and sediments from the Orinoco River during the fall [Bonilla et al., this issue]. Methane oxidation has been shown to increase with increasing general microbial activity and ammonia concentration [Griffiths et al., 1982].
Fig. 2. Distribution of surface CH$_4$ concentrations during the (a) spring and (b) fall in the Caribbean Sea and Orinoco River. Sampling was continuous while the ship was underway; not all sample collection points are indicated.

Turnover times for CH$_4$ were in the order of years and were generally longer in the fall than in the spring (Table 1). Turnover times were shortest near the mouth of the Orinoco during both seasons, with a low value of 0.005 yr (about 2 days) at station R5 during the fall. The highest turnover times were observed in the Caribbean Sea during the fall (Table 1). The CH$_4$ turnover times were comparable to those observed previously in the Caribbean Sea by Ward [1987].

**Carbon Monoxide**

Surface CO concentrations ranged from 0.9 nM near the Mona Passage (station B) to 4.9 nM near the mouth of the Orinoco River (station R5) during the spring (Table 2). In the fall surface CO concentrations were significantly higher at stations R1 and R2 with values of 31.6 nM and 21.3 nM, respectively (Table 2 and Figure 1). Due to the nonconservative nature of CO in surface waters, it is difficult to interpret this data without additional information. Factors such as photoproduction capacity, light intensity and microbial oxidation (turnover times) can cause surface CO concentrations to vary 1 to 2 orders of magnitude over a 24-hour period [Conrad et al., 1982; Butler et al., 1987; Jones, 1991]. Therefore, values reported in Table 2 indicate only the concentration at the time of sample collection.

Potential photoproduction capacity for CO during the spring was lowest in the vicinity of Mona Passage (station B) and increased in the vicinity of the Orinoco River and Gulf of Paria (Table 2). The highest values for CO photoproduction capacity were observed in the Gulf of Paria (36.6 nmol L$^{-1}$ h$^{-1}$, station P3) and on a transect northeast of the mouth of the Orinoco River (43.5 nmol L$^{-1}$ h$^{-1}$, station R1).

Values for CO potential photoproduction capacity during the fall ranged from 22.8 nmol L$^{-1}$ h$^{-1}$ near Mona Passage (station A) increasing with proximity to the Orinoco River to 88.3 nmol L$^{-1}$ h$^{-1}$ at station R3 near the mouth of the Orinoco. Potential photoproduction capacity for CO was
generally higher in the fall than in the spring, with higher values observed particularly in the northern and central Caribbean Sea and the mouth of the Orinoco River.

The Orinoco River waters appear to affect CO photoproduction as far as the Mona Passage near Puerto Rico during the fall (Table 2). Higher concentrations of dissolved organic matter are observed in the Caribbean Sea during the fall than in the spring, evidenced by higher optical densities of the water during this season [Zika et al., this issue], possibly increasing the concentration of precursor molecules for CO photoproduction. Higher microbial activity during the fall may also contribute to higher CO photoproduction rates by increasing the concentration of humic substances, known to contain carbonyl moieties, that are precursors for CO photoproduction [Redden, 1983; Mopper et al., 1991].

Carbon monoxide oxidation rates followed a pattern similar to that for CO photoproduction capacity. The rates were lowest near the Mona Passage (station B) (25 pmol L\(^{-1}\) h\(^{-1}\)), increased with proximity to the Orinoco River, and were highest at station R5 near the mouth of the river (976 pmol L\(^{-1}\) h\(^{-1}\)) (Table 2). Intermediate values of CO oxidation were observed in the Gulf of Paria (118–143 pmol L\(^{-1}\) h\(^{-1}\)).

Carbon monoxide oxidation rates were generally higher in the fall, particularly in the Caribbean Sea and the Gulf of Paria (Table 2). However, CO oxidation rates were lower in the vicinity of the Orinoco River in the fall than in the spring, with a maximum value of 663 pmol L\(^{-1}\) h\(^{-1}\) at station R4.

Carbon monoxide oxidation in the Caribbean Sea during the spring may be limited by nutrient availability [Bonilla et al., this issue]. This limitation could possibly be removed with the influx of higher concentrations of nutrients transported by the Orinoco River during the fall, resulting in increased microbial CO oxidation rates. The lower CO oxidation rates observed during the fall near the mouth of the Orinoco River are puzzling. Carbon monoxide oxidizing bacteria may be inhibited by the high concentrations of CO in the water resulting from higher photoproduction of CO in
this area during the fall. Nitrifying bacteria and carboxydo-
bacteria are both believed to have a role in oxidizing CO in
the oceans [Conrad and Seiler, 1980], and high concentra-
tions of CO are inhibitory of marine nitrifying bacteria
[Jones and Morita, 1983a, b].

Turnover times for carbon monoxide were in the order of
hours (Table 2). During the spring, turnover times in the
Caribbean increased with distance from the mouth of the
Orinoco, ranging from 2 hours at station R5 to 108 hours at
station A north of Puerto Rico. Carbon monoxide turnover times were consistent with those observed in similar environments [Jones, 1991].

These results indicate that the Orinoco River and deltaic
system may contribute large amounts of CH₄ and precursor
molecules for CO photoproduction, thus influencing the
chemical and biological processes that control the concen-
tration of these gases in the surface waters of the Caribbean
Sea.

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tended to Captain Robert Morgan and the crew of the R/V Columbus
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\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Station & Spring & Autumn & Fall & Winter \\
\hline
A & --- & --- & --- & --- \\
B & 0.9 & 25 & 38 & 18.5 \\
C & --- & --- & --- & --- \\
D & 1.9 & 58 & 39 & 18.5 \\
E & --- & --- & --- & --- \\
F & 1.2 & 66 & 34 & --- \\
G & --- & --- & --- & --- \\
H & 0.9 & 42 & 53 & --- \\
I & 2.8 & 32 & 70 & --- \\
J & --- & --- & --- & --- \\
K & 2.8 & 143 & 16 & 32.5 \\
L & --- & --- & --- & --- \\
M & 6.3 & 136 & 16 & 36.6 \\
N & 2.4 & 118 & 19 & --- \\
O & 3.8 & 247 & 7 & 23.7 \\
P & 2.5 & 159 & 14 & --- \\
Q & 1.7 & 145 & 15 & --- \\
R & 4.9 & 976 & 2 & 19.1 \\
S & --- & --- & --- & --- \\
T & 4.4 & 342 & 7 & 23.7 \\
U & 4.1 & 318 & 7 & 23.7 \\
V & 3.2 & --- & --- & --- \\
W & 2.3 & 21 & 108 & 43.5 \\
X & --- & --- & --- & --- \\
Y & 1.7 & 145 & 15 & --- \\
Z & 2.5 & 159 & 14 & --- \\
\hline
\end{tabular}
\caption{Carbon Monoxide Concentrations, Oxidation Rates, Turnover Times, and Potential Photoproduction Capacities}
\end{table}

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