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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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# 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 CH<sub>4</sub>, photoproduction capacity of seawater for CO, and CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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  $34 \times 10^3 \text{ m}^3 \text{ s}^{-1}$  [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 CH<sub>4</sub> 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 CH<sub>4</sub> in undisturbed forest streams and rivers from the Oregon coast. Furthermore, mixing between high CH<sub>4</sub>-containing river water and low CH<sub>4</sub>-containing seawater end-members appeared to control CH<sub>4</sub> 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 photo-oxidation 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].

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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 CH<sub>4</sub> 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  $100 \text{ mL min}^{-1}$  through a scintered 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

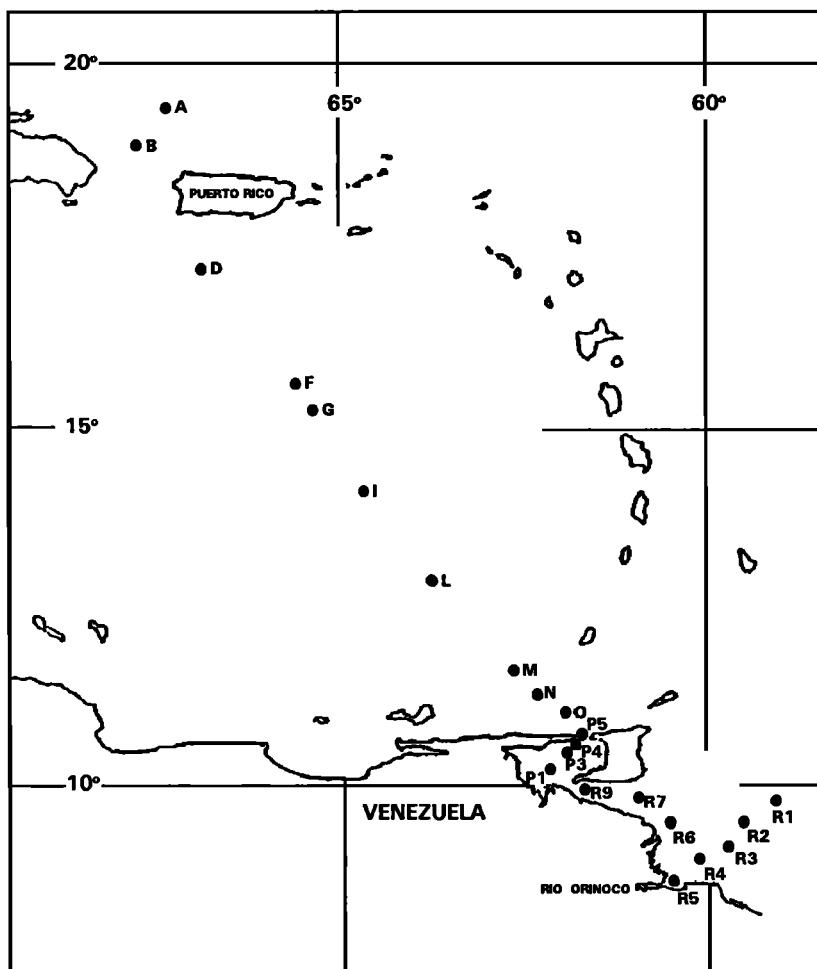


Fig. 1. Location of sampling stations for spring and fall cruises.

liquid nitrogen-cooled molecular sieve trap (MS-5A) that retained and partially separated the CO and CH<sub>4</sub>. The molecular sieve trap was removed from the liquid nitrogen bath and heated to 200°C. The carrier gas containing the CO and CH<sub>4</sub> was sent to the gas chromatograph (model HP5890, fitted with a MS-5A molecular sieve, 60/80 mesh, column, 0.318 cm ID × 2 m long), mixed with a stream of H<sub>2</sub> gas, and the resulting mixture passed over a heated (320°C) Ni catalyst to reduce CO to CH<sub>4</sub>. Methane and CO were quantified using a flame ionization detector. Additional details of the gas chromatograph/stripping system configuration and standardization procedures can be found in Jones [1991].

#### Methane and Carbon Monoxide Oxidation

Methane and CO oxidation rates were measured using <sup>14</sup>C-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 <sup>14</sup>CO diluted in nitrogen (0.5 μCi mL<sup>-1</sup>; 56 mCi mmol<sup>-1</sup>; Amersham Corp., Arlington Heights, Illinois) or 1.0 mL of <sup>14</sup>CH<sub>4</sub> diluted in nitrogen (1.0 μCi mL<sup>-1</sup>; 59 mCi mmol<sup>-1</sup>; Amersham) was injected into the headspace. Degassing with filtered air reduced dissolved CH<sub>4</sub> and CO concentrations so they represented <0.05% of the labeled substrate, thus assuring no discernible isotope dilution ef-

fects. 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 (<sup>14</sup>CO) or 24 hours (<sup>14</sup>CH<sub>4</sub>) 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 <sup>14</sup>CO<sub>2</sub> was released, trapped, and assayed using the methods described by Griffiths et al. [1982]. The equilibrium concentrations of <sup>14</sup>CH<sub>4</sub> and <sup>14</sup>CO in solution were determined by multiplying the Bunsen solubility coefficient (Schmidt [1979] for CO; Yamamoto et al. [1976] for CH<sub>4</sub>). Both salinity and temperature effects on solubility were taken into account when calculating oxidation rates. CH<sub>4</sub> and CO oxidation rates were normalized to rates at a CH<sub>4</sub> concentration of 11.93 nM and a CO concentration of 2.23 nM, thus allowing comparison with previous work. No significant incorporation of <sup>14</sup>C into cellular material was detected in any of the <sup>14</sup>CO samples and only samples from stations R3, R4 and R5 demonstrated significant <sup>14</sup>C incorporation from <sup>14</sup>CH<sub>4</sub>. These samples incorporated between 3 and 5% of the label. Since incorporation was so limited only <sup>14</sup>CO<sub>2</sub> production was used in both CH<sub>4</sub> 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

Station	Spring			Fall		
	Ambient Concentration, nM	Oxidation Rate, pmol L <sup>-1</sup> h <sup>-1</sup>	Turnover Time, years	Ambient Concentration, nM	Oxidation Rate, pmol L <sup>-1</sup> h <sup>-1</sup>	Turnover Time, years
A	—	—	—	2.7	0.04	38.8
B	1.6	0.04	37.3	—	—	—
D	—	—	—	2.8	0.04	31.5
F	1.7	0.05	30.1	—	—	—
G	—	—	—	3.3	0.02	63.6
I	2.0	0.30	4.6	—	—	—
L	—	—	—	3.6	0.02	71.5
M	2.1	0.18	7.4	12	0.02	56.1
N	5.2	0.15	8.8	—	—	—
O	—	—	—	33	0.40	3.4
P5	18	0.33	4.1	36	0.27	5.0
P4	—	—	—	31	0.24	5.8
P3	40	0.38	3.6	34	0.55	2.5
P1	66	0.85	1.6	37	0.34	4.0
R9	176	3.47	0.4	—	—	—
R7	39	0.45	3.0	48	0.47	2.9
R6	68	0.36	3.8	61	0.94	1.5
R5	103	2.23	0.6	13	168.7	0.007
R4	138	—	—	25	119.7	0.008
R3	37	6.63	0.2	9.0	2.27	0.06
R2	27	—	—	3.0	0.19	7.2
R1	46	0.24	5.7	3.2	0.13	10.4

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<sup>-2</sup> irradiance.

## RESULTS AND DISCUSSION

### Methane

Surface concentrations of CH<sub>4</sub> 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 CH<sub>4</sub> were on the order of 45 nM. The highest concentrations of CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub> 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 CH<sub>4</sub>, in addition to the Orinoco River itself. Similar seasonal effects on distribution of CH<sub>4</sub> 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 CH<sub>4</sub> oxidation rates. Methane oxidation rates were extremely low during both the spring and fall, with similar surface distributions (Table 1). However, significantly higher CH<sub>4</sub> oxidation rates were observed during the fall in the Orinoco River plume. The higher rates of CH<sub>4</sub> oxidation may have contributed to the decrease in surface CH<sub>4</sub> concentration in the fall, particularly in the area of the river plume (Northwest to the Gulf of Paria). Higher rates of CH<sub>4</sub> 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].

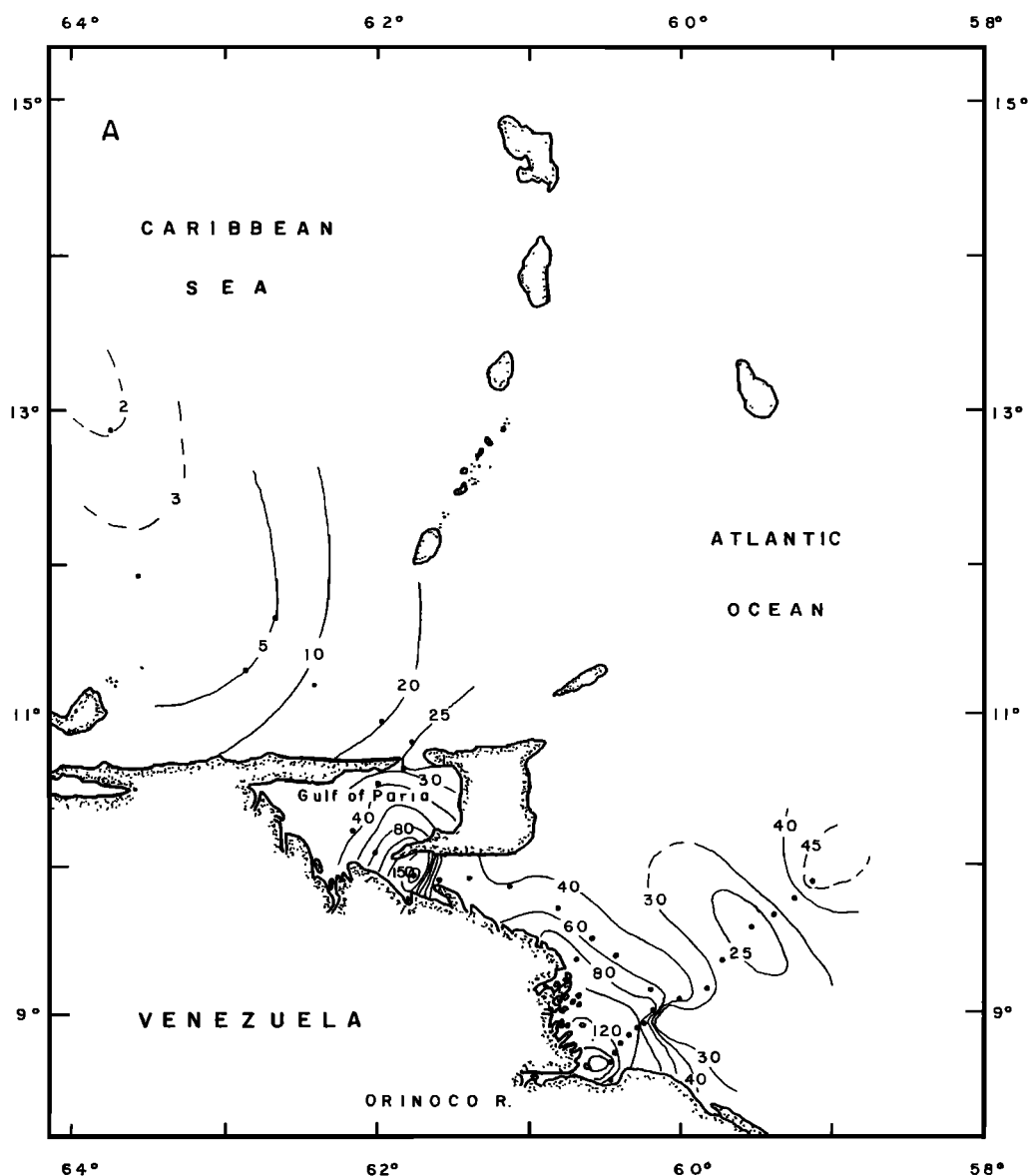


Fig. 2. Distribution of surface  $\text{CH}_4$  concentrations during the (a) spring and (b) fall in the Caribbean Sea and Orinoco River. Sampling was continuous while the ship was underway; not all sample collection points are indicated.

Turnover times for  $\text{CH}_4$  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  $\text{CH}_4$  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 ( $36.6 \text{ nmol L}^{-1} \text{ h}^{-1}$ , station P3) and on a transect northeast of the mouth of the Orinoco River ( $43.5 \text{ nmol L}^{-1} \text{ h}^{-1}$ , station R1).

Values for CO potential photoproduction capacity during the fall ranged from  $22.8 \text{ nmol L}^{-1} \text{ h}^{-1}$  near Mona Passage (station A) increasing with proximity to the Orinoco River to  $88.3 \text{ nmol L}^{-1} \text{ h}^{-1}$  at station R3 near the mouth of the Orinoco. Potential photoproduction capacity for CO was

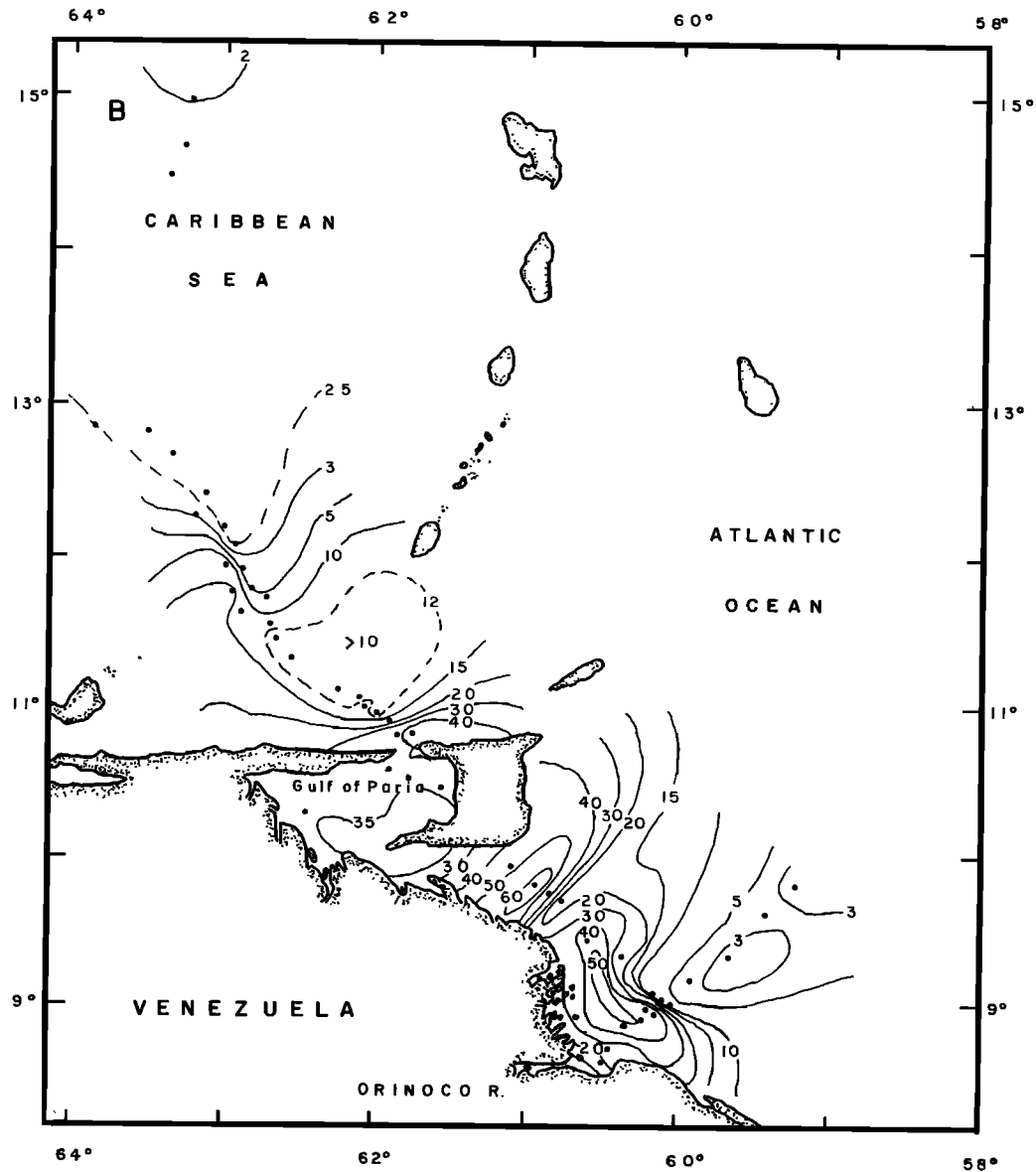


Fig. 2. (continued)

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 during the spring followed a pattern similar to that for CO photoproduction capacity. The rates were lowest near the Mona Passage (station B) ( $25 \text{ pmol L}^{-1} \text{ h}^{-1}$ ), increased with proximity to

the Orinoco River, and were highest at station R5 near the mouth of the river ( $976 \text{ pmol L}^{-1} \text{ h}^{-1}$ ) (Table 2). Intermediate values of CO oxidation rates were observed in the Gulf of Paria ( $118\text{--}143 \text{ pmol L}^{-1} \text{ h}^{-1}$ ).

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  $663 \text{ pmol L}^{-1} \text{ h}^{-1}$  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

TABLE 2. Carbon Monoxide Concentrations, Oxidation Rates, Turnover Times, and Potential Photoproduction Capacities

Station	Spring				Fall			
	Ambient Concentration, nM	Oxidation Rate, pmol L <sup>-1</sup> h <sup>-1</sup>	Turnover Time, hours	Production, nmol L <sup>-1</sup> h <sup>-1</sup>	Ambient Concentration, nM	Oxidation Rate, pmol L <sup>-1</sup> h <sup>-1</sup>	Turnover Time, hours	Production, nmol L <sup>-1</sup> h <sup>-1</sup>
A	—	—	—	—	1.7	20	98	22.8
B	0.9	25	88	18.5	—	—	—	—
D	—	—	—	—	1.2	88	25	—
F	1.9	58	39	18.5	—	—	—	—
G	—	—	—	—	0.9	156	14	25.5
I	1.2	66	34	—	—	—	—	—
L	—	—	—	—	1.6	275	8	—
M	0.9	42	53	—	2.7	292	8	—
N	2.8	32	70	—	—	—	—	—
O	—	—	—	—	0.7	372	6	—
P5	2.8	143	16	32.5	0.6	814	3	—
P4	—	—	—	—	6.1	636	4	—
P3	6.3	136	16	36.6	5.7	432	5	—
P1	2.4	118	19	—	2.8	313	7	—
R9	3.8	247	9	29.0	—	—	—	—
R7	2.5	159	14	—	1.0	365	6	—
R6	1.7	145	15	—	1.2	497	4	—
R5	4.9	976	2	19.1	0.7	540	4	63.6
R4	4.6	—	—	—	2.4	663	3	76.8
R3	4.1	342	7	23.7	0.7	602	4	88.3
R2	3.2	—	—	—	21.3	339	7	28.1
R1	2.3	21	108	43.5	31.6	366	6	22.9

Station designations refer to Figure 1. Oxidation rates normalized to a concentration of 2.23 nM. Turnover time is defined as the inverse of the first-order rate constant. CO photoproduction capacities are normalized to 1000 Wh m<sup>-2</sup> of total solar irradiance.

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 concentrations 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 R1. Turnover times were generally lower during the fall, and ranged from 3 hours at station R4 near the mouth of the Orinoco River to 98 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 CH<sub>4</sub> and precursor molecules for CO photoproduction, thus influencing the chemical and biological processes that control the concentration of these gases in the surface waters of the Caribbean Sea.

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