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A Methane Budget for the Hudson River and Estuary

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Abstract

Methane distributions and CH₄ oxidation rates were surveyed throughout the Hudson River Estuary in March and August of 1991. Methane concentrations ranged from 50 to 940 nM (saturation factors of 18 to 376) with generally higher CH₄ values in the lower, saline portion of the Estuary. Despite presumably higher CH₄ production in the warmer summer months, little seasonal variation in CH₄ levels was observed. This is most likely due to significantly higher CH₄ oxidation rates in summer than in winter. Microbial methane oxidation was found to remove up to 70% of ambient CH₄ per day in August in the freshwater portion of the river. Maximum removal rates of 13% were observed in March. Methane oxidation activity decreased rapidly as salinity increased in the estuarine portion of the river, oxidizing less than 2% of ambient CH₄ by salinities of 25‰. Additions of NaCl to freshwater samples resulted in severe inhibition of methanotrophic activity. Salt and temperature effects were found to account for most seasonal and spatial variations in CH₄ oxidation in the lower half of the river. A seasonally averaged diffusive flux to the atmosphere from the Hudson River was estimated to be 0.5 mg CH₄ m⁻² day⁻¹, or a total annual flux of CH₄ to the atmosphere of 61 X 10⁶ g CH₄ yr⁻¹ (3.8 X 10⁶ moles CH₄ yr⁻¹). Comparison of major sinks for CH₄ in the Hudson River indicated that microbial CH₄ oxidation was the most important removal mechanism for riverine CH₄ in the summer when temperatures were high. In winter, lower temperatures and more frequent wind events made evasion to the atmosphere the most significant sink for CH₄. Budget calculations showed that high CH₄ production in the sediments in the Lower Estuary must be supplying large quantities of CH₄ to the overlying water column throughout the year. The results of this study suggest that CH₄ budgets for discrete sections of rivers may serve as a useful monitor of sites of high sedimentary CH₄ production due to anthropogenic carbon loadings. Microbial methane oxidation was estimated to contribute 254 kg day⁻¹ of organic carbon in the form of bacterial biomass throughout the entire river in August.

Introduction

Methane levels reported in rivers are 1 to 3 orders of magnitude greater than that found in open ocean waters or that predicted to be in equilibrium with the atmosphere (Lamontagne et al., 1973; Brooks and Sackett, 1973; Wilkniss et al., 1978; de Angelis and Lilley, 1987; Richey et al., 1988; Lilley et al., 1992). As a result, rivers serve as sources of CH₄ to both the atmosphere and nearshore ocean regions. Large CH₄ concentrations of up to several micromolar also suggest that rivers could be sites of high microbial CH₄ oxidation activity (methanotrophy) due to high substrate concentrations. Yet, few studies have examined the role of CH₄ oxidation in controlling CH₄ distributions in rivers.

Methane has been sampled for a variety of rivers ranging from heavily impacted rivers (Lamontagne et al., 1973) Brooks and Sackett, 1978) to relatively pristine rivers (Wilkniss et al., 1978) and mountain streams (de Angelis and Lilley, 1987; Lilley et al., 1992). Despite comparable CH₄ levels of hundreds to thousands of nanomolar CH₄ in most of the rivers studied to date, multiple CH₄ sources have been identified. However, the primary source of CH₄ has been found to vary from river to river. For example, elevated CH₄ concentrations of 1700 nM CH₄ for the Potomac River (Lamontagne et al., 1973) and 107 to 366 nM CH₄ for the Mississippi River (Brooks and Sackett, 1973) were attributed to the effects of sewage input and oil pollution. In both the Hudson River (Hammond et al., 1975) and Columbia River (Lilley et al., 1992) locally elevated CH₄ levels due to point source sewage input have been observed. Wilkniss et al. (1978), however, reported CH₄ concentrations of 87 to 133 nM CH₄ for a pristine river in New Guinea. These values, while lower than those observed in rivers impacted by man, are well in excess of that expected with respect to equilibrium with the atmosphere (approximately 2 to 3 nM CH₄). Richey et al. (1988) found an average concentration of 50 nM CH₄ for the mainstream of the Amazon. These data suggested that CH₄ supersaturations occur naturally in rivers. This is consistent with the observation of CH₄ concentrations of up to 79 nM CH₄ in small mountain streams

of the Cascade Range of Oregon (de Angelis and Lilley, 1987) and the Olympic Peninsula (Lilley et al., 1992) where anthropogenic impact is believed to be negligible.

Scranton and McShane (1991) postulated that the extremely high CH₄ levels they estimated for the Rhine and Western Scheldt Rivers were due primarily to eutrophication and subsequent CH₄ production in anoxic sediments. Hammond et al. (1975) concluded that for portions of the Hudson River Estuary, methane concentrations of 200 to 600 nM CH₄ were sustained principally by production in organic rich anaerobic sediments and subsequent diffusion into the water column. This is similar to what has been shown to occur in lakes (Strayer and Tiedje, 1978). However, de Angelis and Lilley (1987) reported similar levels of CH₄ in Oregon Coast Range streams with rock streambeds and no sediment cover. Other riverine sources of CH₄ which have been found to be significant include runoff from waterlogged organic-rich forest soils (de Angelis and Lilley, 1987), runoff from agricultural and grazing lands (de Angelis and Lilley, 1987; Lilley et al., 1992), and possibly input by groundwater (Lilley et al., 1992). Partial dissolution of bubbles from methane-saturated anaerobic sediments can serve as an additional source of water column CH₄. The relative magnitude of these sources to any particular river in most cases cannot be readily predicted and indicates the need for more extensive study of CH₄ in rivers.

In addition to direct sources, CH₄ levels in any environment are dependent on the magnitude of sink or loss terms as well. For rivers, diffusive flux across the air/river interface, advection to nearshore waters and CH₄ oxidation are the most significant sink terms. Variable flux rates and microbial CH₄ oxidation rates are potentially as important in determining CH₄ levels in rivers as are the source terms. Yet few studies address either or both of these terms. Flux rates can be estimated by surface CH₄ concentrations and estimates of wind speed or turbulence. Lilley et al. (1992) found that extremely large amounts of CH₄ can be lost to the atmosphere in turbulent portions of rivers and mountain streams.

Microbial CH_4 oxidation is the only process occurring within the water column which can prevent eventual loss of CH_4 to the atmosphere, yet few studies have examined this process in rivers. In the lower reaches of the Hudson River, Hammond et al. (1975) measured disappearance of CH_4 in stored samples over time and concluded that CH_4 oxidation was insignificant. However, Lilley et al. (1992) measured CH_4 oxidation rates in several Pacific Northwest Rivers and reported that up to 25% of the ambient CH_4 was oxidized per day. These data indicate that CH_4 oxidation cannot be neglected in riverine environments and that more study is needed to quantify the importance of this process.

This paper presents the results of an extensive survey for CH_4 and microbial CH_4 oxidation for the Hudson River and Estuary for both winter and summer. From these data, we estimate the relative importance of diffusive flux across the air/river interface versus microbial CH_4 oxidation along the entire length of the river including freshwater and saline portions of the estuary for these two seasons. In addition, methane budgets are determined for various sections of the river.

Study site and sampling locations

The Hudson River Estuary runs in a north-south direction and empties into Upper New York Bay (Figure 1). The Hudson River supplies approximately 85% of the fresh water to the Bay. Locations along the length of the Hudson River are designated by river miles (rm) north (+) or south (-) of The Battery at the southern tip of Manhattan Island. The Hudson Estuary is classified as a partially mixed estuary and is tidal as far upstream as the Green Island Dam near Troy at rm 154 with a mean tidal amplitude of approximately 1 meter (Hammond et al., 1975). Salt intrusion (0.01‰ isohaline) ranges from rm 25 during the winter to rm 65 during periods of low flow, particularly in the late summer. Bottom salinities in the lower estuary are typically 2 to 4 ‰ greater than surface salinities.

Precipitation is fairly uniform throughout the year. However, snowmelt results in a major increase in freshwater discharge in spring. Average flow for March, 1991 was approximately $850 \text{ m}^3 \text{ sec}^{-1}$ and $150 \text{ m}^3 \text{ sec}^{-1}$ for August, 1991 (REF). Typically, approximately 50 to 70% of the fresh water

supplying the Hudson River comes from above the Green Island Dam at rm 154. Further downriver, there are no major tributaries entering the Hudson. Below rm 90, additions to the Hudson drainage basin area is relatively small, with a few minor tributaries supplying the river (Garvey, 1990). Groundwater input is believed to be small (Hammond et al., 1975).

The Hudson River Estuary can be divided into 5 distinct sections based on their geometries (Figure 1, Table 1). The Upper Estuary, which runs from rm 154 to rm 56, is relatively narrow with a mean depth of 8 meters. The Hudson Highlands (rm 56 to 40) is also relatively narrow but deepens to an average depth of 12.8 m while the Tappan Zee (rm 40 to 20) is wide and shallow (mean depth of 5.3 m). The Lower estuary extends from rm 20 to 0 where the river again narrows and deepens (10 m). Upper New York Bay, located immediately below the river, is wide and shallow (3 to 5 meters depth).

Sampling was conducted along the length of the Hudson River Estuary from Albany, NY (rm 143) to the Narrows (rm -8) at the entrance to Upper New York Bay from March 19 to 22 and August 21 to 24, 1991. Surface samples for both CH_4 concentrations (March and August) and CH_4 oxidation rate determinations (August only) were obtained on an upstream transit from Nyack (rm 30) to Albany (rm 143) carried out on a single day. More detailed profiles were obtained on the downstream transit from Albany (rm 143) to Pier 26 in lower Manhattan (rm 2) in March or to the Narrows (rm -8) in August. Transects consisting of profiles obtained mid-channel and near both banks were carried out at rm 125, 39, 33 and 11 to test for lateral differences in CH_4 and CH_4 oxidation parameters. In addition, surface water samples were obtained in May, 1991 from Cold Spring, NY (rm 52) and in August, 1991 off Kingston (rm 91) for experiments to test for the effects of salt and nutrient additions on CH_4 oxidation in river water.

Methods

Samples on the upriver transit were collected approximately every 5 river miles while the ship was underway. Methane concentration samples were collected using the ship's hull pump while samples for CH_4 oxidation were obtained off the stern of the ship. Water temperature was determined using a laboratory

mercury thermometer with divisions of 0.1°C. For downstream transits, profiles were obtained in the middle of the channel approximately every 10 to 15 river mile. Water for CH₄ and CH₄ oxidation determinations were collected from the surface, mid-depth and 1 meter off the bottom using a rosette sampler equipped with Niskin bottles and a CTD. At selected downriver stations, surface water samples only were drawn using the hull pump.

Methane concentrations were determined using a McAuliffe extraction (McAuliffe, 1971) and flame ionization detection (FID) gas chromatography. Thirty ml samples for CH₄ concentrations were drawn into 60 ml syringes. Care was taken to ensure that no bubbles were present in the syringe or any connecting tubing. The sample was allowed to equilibrate to room temperature without a headspace. Immediately before analysis, 30 ml of N₂ was drawn into the syringe which was then shaken for 2 minutes. In March, multiple re-extractions on selected samples indicated that this technique resulted in 98% of the CH₄ being partitioned into the headspace for a single extraction. In August, extraction efficiencies were lower with a mean value of 90 %. The headspace of the syringe was passed through a 10/20 mesh Drierite column (0.64 cm X 10 cm nylon) directly into a 1.4 ml calibrated sample loop. The sample was then manually injected using a Carle 6-port valve into a 60/80 mesh Porapak R column (0.32 cm o.d. X 0.9 m stainless steel) in a Carle AGC 211 gas chromatograph equipped with a FID. Fifteen ml of extracted sample was found to be sufficient to completely flush the sample loop and prevent contamination between samples. Therefore, each 60 ml syringe yielded duplicate samples. Air samples were collected at all stations and injected in an identical manner for use in flux calculations. For some samples, 30 ml syringes with 15 ml water and 15 ml air were used. Duplicate 30 ml syringes were drawn for these samples.

Surface samples for CH₄ oxidation on the upstream transits were collected directly from the ship's stern by opening a 250 ml wide mouth polyethylene bottle just beneath the surface. Water for CH₄ oxidation determinations for profile samples were drawn from the rosette mounted Niskin bottles directly into autoclaved

250 ml wide mouth polypropylene bottles. For some Lower Estuary samples on the downriver transit below rm 30, nonsterile bottles were used. For these samples, bottles were rinsed three times before filling. In all cases, a headspace was left in the bottle and each bottle was shaken vigorously and the cap removed 3 to 5 times over a 3 minute interval to remove any ambient CH_4 originally present. Laboratory experiments indicated that this treatment removed >98% of the original CH_4 at the concentrations present in Hudson River water.

Samples for CH_4 oxidation determinations were incubated in 14 ml septum vials (Pierce) sealed with teflon-faced silicone septa with no headspace. Twenty-four hours before each sample incubation, filter-sterilized (0.22μ) fresh water was placed in 10 ml gas-tight syringes with no headspace. A known volume of $^{14}\text{CH}_4$ (specific activity = 32.5 or 51.5 mCi mmol^{-1}) was then drawn into the syringe and the syringe stopcock closed. The $^{14}\text{CH}_4$ was allowed to equilibrate with the seawater overnight in the dark at 5°C until immediately before sample inoculation. The bubble was then removed. Syringes which retained any visible gas bubbles were not used. The amount of equilibrated $^{14}\text{CH}_4$ within each syringe was calculated from the volume of CH_4 added and the solubility tables of Wiesenburg and Guinasso (1979). Previous analyses of seawater so equilibrated showed good agreement with calculated values. The stock $^{14}\text{CH}_4$ was assayed by flame ionization gas chromatography at the beginning and end of each cruise.

The $^{14}\text{CH}_4$ -equilibrated seawater was added to the incubation vials using a sideport needle to give final $^{14}\text{CH}_4$ concentrations in the vials of 234 to 767 nM CH_4 . Vials were run for each of 3 time points in addition to controls killed at time zero. Samples were incubated in the dark at 5 to 7°C in March and 24 to 27°C in August for times ranging from 3 to 12 hours. At the end of each incubation period, uptake of CH_4 was stopped by addition of 0.25 ml 6N NaOH to give a final pH of >10. Controls consisted of replicate samples to which NaOH was added at the beginning of each incubation period immediately after addition of $^{14}\text{CH}_4$. Killed samples were transferred to 40 ml vials which were sealed with poly-seal caps and stored for up to 1 week before analysis.

Kinetic studies were carried out on selected samples by adding three different $^{14}\text{CH}_4$ concentrations to replicate sample vials. Uptake of CH_4 was found to be linear over the range of CH_4 concentrations observed throughout most of the river. Only 2 samples (Staats Point, August; Pier 26, March) exhibited CH_4 concentrations which exceeded the range of CH_4 levels tested for linearity of CH_4 oxidation.

Any $^{14}\text{CO}_2$ produced was recovered by acidifying the samples with 10N H_2SO_4 to a final pH of 2 and stripping with a stream of helium (60 ml/min) for 5 minutes. The stripped $^{14}\text{CO}_2$ was trapped in a series of 2 scintillation vials each containing 0.25 ml Carbosorb (Packard), which retains CO_2 but does not trap CH_4 . Efficiency of $^{14}\text{CO}_2$ trapping was greater than 98% using $\text{NaH}^{14}\text{CO}_3$ (ICN; 55 mCi/mmol) standards. After stripping was complete, 6 ml of Permafluor V (Packard) scintillation cocktail was added to each vial which was then counted on a Packard model 1600CA liquid scintillation counter. The sum of the counts for both vials was taken as equal to the total counts for each sample. Blanks were run frequently to check for contamination between samples. Acidified and stripped samples were filtered through 0.22 μm filters (Millipore GSWP) to test for incorporation of label into cell carbon. Filters were air dried, dissolved in 10 ml Omnifluor and counted in the liquid scintillation counter. Extremely low oxidation rates (approximately $0.0001 \text{ nM hr}^{-1}$) have been detected using this methodology (de Angelis, unpublished data).

Oxidation rates of $^{14}\text{CH}_4$ were calculated from the sum of the production of both $^{14}\text{CO}_2$ and cell- ^{14}C and were determined from the linear portion of the incubation plots of $^{14}\text{CH}_4$ oxidized vs incubation time. These measured $^{14}\text{CH}_4$ oxidation rates were converted to actual rates occurring in the Hudson River Estuary as described below. Two kinds of CH_4 oxidation rates were calculated and are used throughout this paper: specific CH_4 oxidation rates and ambient CH_4 oxidation rates. Microbial CH_4 oxidation is first order with respect to CH_4 concentration (Ward et al., 1987). The specific CH_4 oxidation rate is the first order rate constant for this reaction and is independent of CH_4 concentration. The specific CH_4 oxidation rate has units of

day⁻¹ and is equivalent to the fraction of available CH₄ which can be utilized per day. The turnover time for CH₄ is determined as the inverse of specific oxidation rate. For example, a specific CH₄ oxidation rate of 0.5 day⁻¹ means that 50% of the ambient riverine CH₄ at that location can be oxidized per day by microbial CH₄ oxidation or that the turnover time for CH₄ for this sample is 2 days. Specific oxidation rates are useful since they are a measure of CH₄ oxidation activity and, being independent of CH₄ concentration, can be used to compare relative CH₄ oxidation activities among samples containing much different CH₄ levels or from different locations. Ambient rates of CH₄ oxidation were calculated by multiplying specific oxidation rates determined at any one location by the measured ambient CH₄ concentration at that location. Ambient CH₄ oxidation rates represent the actual rates of CH₄ oxidation (in units of nM day⁻¹) occurring in the environment.

The effect of additions of salt, seawater and nitrogen nutrients was tested on samples collected in the freshwater portion of the river. Salt additions were made by adding a preweighed amount of NaCl to a known volume of sample. Seawater of known salinity (34⁰/₀₀) was obtained from 15 m depth in Long Island Sound and was filter sterilized through 0.22 μ filters prior to addition to river samples. All rates obtained for seawater addition experiments were corrected for dilution. Nitrogen nutrient supplements of either nitrate (up to 60 μ M) or ammonium (up to 30 μ M) were made from 0.25 to 2 ml additions of 6 mM KNO₃ or 2 mM (NH₄)₂SO₄ stock solutions.

Experiments to test for possible associations of CH₄ oxidizers with specific size fractions of particles were carried out on river samples collected at rm 92 in October, 1991. Water was filtered at low pressure (<10 psi) with a hand vacuum pump. Filters were changed frequently to prevent changes in nominal pore size due to clogging. The filters used and their nominal pore sizes were GF/F (0.7 μ m), GF/B (1.0 μ m), GF/C (1.2 μ), GF/A (1.6 μ m), Whatman #1 (11 μ m) and Whatman 541 (20-25 μ m). After filtration, samples were added to 14 ml incubation vials and

tested for $^{14}\text{CH}_4$ uptake using the previously described method. Replicate unfiltered samples were run at the same time under the same conditions.

Analysis of total suspended matter (TSM) was carried out on the upriver transit in August by filtering 250 ml of surface water through preweighed combusted 47 mm GF/C filters. Samples were collected off the stern of the ship in 250 ml polyethylene bottles. Samples were shaken thoroughly and measured out in a 250 ml graduated cylinder immediately before filtration. Filters were dried at 110°C for 3 hours prior to final weighing.

Results

Methane concentrations

In March, 1991, salt intrusion to the $0.01^\circ/\text{oo}$ isohaline occurred between rm 39 and 52. In August, 1991, salt intrusion occurred to at least rm 65. Surface salinities at the Narrows (rm -8) were 20 and $25^\circ/\text{oo}$ in March and August, respectively. Differences between surface and bottom water (1 meter off the bottom) were 5 to $7^\circ/\text{oo}$ below rm 20 in March and between 2 and $5^\circ/\text{oo}$ at and below rm 33 in August. Surface to bottom water differences at points further upriver to the extent of salt intrusion were less than $1.5^\circ/\text{oo}$.

Methane concentrations, and CH_4 oxidation parameters for all Hudson River stations sampled in March and August, 1991 are given in Table 2. Surface CH_4 concentrations did not vary significantly between the upriver and downriver transits from rm 30 to rm 143 in either March or August (Figure 2). During the March sampling period, CH_4 concentrations throughout the estuary ranged from 95 nM to 858 nM CH_4 with a surface CH_4 concentration of 227 nM at the furthest station upriver (rm 143) (Figure 3a). Methane levels increased further downriver to 303 nM CH_4 at rm 120 and then decreased gradually with increasing distance downstream until a minimum value of 95 nM was reached at Nyack (rm 30). Past this point, CH_4 concentrations increased rapidly with a maximum surface CH_4 level of 679 nM at rm 2. Methane concentrations were not measured below rm 2 in March.

In August, CH₄ concentrations ranged from 48 nM (at rm 62) to 938 nM CH₄ (at rm 140) (Figure 3b). Maximum values of CH₄ ranging from 766 nM to 938 nM were observed far upriver between rm 140 and 143. Methane levels dropped rapidly downriver reaching surface values of 353 and 227 nM CH₄ at rm 134 and rm 125, respectively. Thereafter, CH₄ levels decreased very gradually to minimum values of 48 to 55 nM CH₄ from rm 62 to 74. Further downriver, between rm 55 and 20, surface CH₄ levels fluctuated between 80 and 129 nM CH₄. For all depths, CH₄ concentrations ranged from 80 to 202 nM CH₄ in this region. Below rm 20, CH₄ values again increased sharply, reaching a surface concentration of 675 nM at the Narrows (rm -8).

Depth profiles of CH₄ through the water column were generally uniform in the Upper Estuary for both sampling months (Table 2). In some cases, CH₄ increased slightly towards the bottom, while in others, a small decrease was detected. No trends with respect to CH₄ concentration and depth were apparent in this part of the river. For some stations in the Tappan Zee and Lower Estuary, increases of 55 to 82% from surface to bottom were noted, although at the Narrows (rm -8), CH₄ concentration decreased with depth. The most significant increase of CH₄ with depth occurred, for both March and August, at rm 10 off of the Upper West Side Sewage Treatment Plant. Methane levels increased from an average surface value of 430 nM CH₄ to 769 nM in March and 651 nM in August at a depths of 12.6 and 14.2 m, respectively. No significant differences in CH₄ profiles was observed at any of the cross-river transects with the exception of the station at rm 10. Methane levels in samples collected from the east side of river, directly off the Sewage Treatment Plant, were generally higher than for samples obtained from similar depths on the west side.

Methane concentrations followed similar trends towards salinity for both March and August (Figure 4). In the freshwater (S⁰/₀₀) portion of the river, a broad range of relatively low CH₄ values was observed. In March, CH₄ concentrations in these samples varied from 101 to 303 nM CH₄. In August, the majority of the freshwater samples fell within the range of 48 to 353 nM CH₄. Five samples obtained from rm 140 to 143 formed another

cluster of points at higher CH_4 levels (Figure 4b). Fairly constant CH_4 concentrations of 95 to 177 nM occurred within the salinity range of $0.015^\circ/\text{oo}$ to $6^\circ/\text{oo}$ in March and to $11^\circ/\text{oo}$ in August. At higher salinities, CH_4 levels for both sampling periods increased systematically to values in excess of 500 nM by $20^\circ/\text{oo}$.

Methane oxidation rates

Specific oxidation rates (in units of day^{-1}) vs river mile for all samples are shown in Figure 5a and b for March and August, respectively. In August, specific CH_4 oxidation rates were 20 to 134 times higher in the Upper Estuary than those measured in March. In the Tappan Zee portion of the river, the seasonal difference was much lower, with August specific oxidation rates being 2 to 9 times higher than in March. In the Lower Estuary, August rates were 12 to 330 times higher in late summer than in early spring/late winter.

In March, the specific CH_4 oxidation rate at the station furthest upriver (rm 140) was 0.0072 day^{-1} (0.72% ambient CH_4 oxidized per day; turnover time = 139 days). Specific oxidation rates exhibited a gradual increase with distance downriver, reaching a maximum value of 0.13 day^{-1} (turnover time = 8 days) at West Point (rm 52). Below rm 52, specific CH_4 oxidation rates dropped sharply and reached very low levels of 0.006 to 0.017 day^{-1} by rm 30 to 33. With the exception of a single point (0.026 day^{-1}) at rm 10 off the Sewage Treatment Plant, specific CH_4 oxidation rates further downriver remained low at less than 0.005 day^{-1} (turnover time > 200 days) and reached extremely low values of less than 0.0001 day^{-1} at rm 2 and -8.

In August, at rm 141 to 143, specific CH_4 oxidation rates averaged 0.12 day^{-1} (12% ambient CH_4 oxidized per day; turnover time = 8.7 days). Specific CH_4 oxidation rates exhibited a sharp increase to a value of 0.47 day^{-1} by rm 134. Further downriver, specific oxidation rates remained high between 0.33 and 0.70 day^{-1} (1.4 to 3 day turnover time) to rm 55. Specific oxidation rates then decreased rapidly to rates of less than 0.05 day^{-1} at rm 33. These low rates persisted to rm 0. Below this point, extremely low specific rates of less than 0.02 day^{-1} were observed in Upper New York Bay (rm -4) and the Narrows (rm -8).

In March, no trend was apparent between specific CH_4 oxidation rate and depth for stations along the length of the river. Maximum differences of 0.03 day^{-1} were observed between surface and bottom water. In August, however, with the exception of a uniform profile obtained at rm 141, all profiles taken above the Lower Bay exhibited increases in specific oxidation rate with depth. In the Upper Estuary, from rm 53 to 125, specific CH_4 oxidation rates were 0.06 to 0.29 day^{-1} greater in bottom waters than at the surface. In the Tappan Zee portion of the river, differences between bottom and surface ranged from 0.008 to 0.03 day^{-1} . In the Lower Estuary, at rm 2 and -4, specific CH_4 oxidation rates decreased from the surface to the bottom. No differences in specific oxidation rates were observed between the sides and middle of the river at transect stations.

Specific oxidation rates for both sampling periods showed a distinct trend when plotted against salinity (Figure 6). In the freshwater portion of the river ($S^{\circ}/_{\text{OO}} = 0$), specific oxidation were generally high with a wide range of values. At the onset of salt intrusion to salinities of $>1 \text{ }^{\circ}/_{\text{OO}}$, specific oxidation rates begin to decrease, reaching consistently low levels by $8 \text{ }^{\circ}/_{\text{OO}}$.

In March, ambient CH_4 oxidation rates followed a similar trend as specific oxidation rates with distance downriver (Figure 7a). At rm 141 the ambient oxidation rate was $1.3 \text{ nM } \text{CH}_4 \text{ day}^{-1}$. Ambient rates generally increased with distance downriver, reaching maximum values of 10.3 to $13.4 \text{ nM } \text{CH}_4 \text{ day}^{-1}$ at rm 52. Rates then decreased rapidly to low values of 0.5 to $2.7 \text{ nM } \text{CH}_4 \text{ day}^{-1}$ between rm 10 and 33. An exception to these low rates was the single point of $10.9 \text{ nM } \text{CH}_4 \text{ day}^{-1}$ observed off the Sewage Treatment Plant at rm 10. This point corresponds to the anomalously high specific oxidation rate at the same location described above. At the furthest downriver station for which CH_4 concentrations are available for March, ambient CH_4 oxidation rates dropped to very low levels of $<0.1 \text{ nM } \text{day}^{-1}$.

In August, maximum ambient CH_4 oxidation rates of 115 to $167 \text{ nM } \text{day}^{-1}$ occurred from rm 125 to 140 (Figure 7b). Slightly lower rates of 87 to $104 \text{ nM } \text{CH}_4 \text{ day}^{-1}$ were obtained upriver at rm 141 and 143. Below rm 125, ambient oxidation rates decreased with increasing distance downriver to minimum values of 1.6 to 4.2 nM

CH₄ day⁻¹ by rm 20. Further downriver, rates increased slightly and remained in the range of 4.3 to 32.9 nM CH₄ day⁻¹ between rm 13 and rm -8.

Discussion

Methane can be supplied to rivers from a number of sources. For example, for any point in a river, CH₄ is being continually advected in from upstream portions of the river. A number of other potentially important CH₄ sources to the water column of a river exist which are summarized in Figure 8. The range of CH₄ concentrations (48 to 960 nM) observed in the Hudson River in this study are, at least in part, the result of contributions from one or more of these sources.

Depending upon the magnitude, many of the sources depicted in Figure 8 can be identified from CH₄ distributions, particularly in lotic systems such as the Hudson River. For example, large quantities of CH₄ can enter rivers from point sources such as sewage outfalls or polluted tributaries. Such point sources can usually be readily identified by sudden and localized increases in CH₄ levels, CH₄ maxima or isolated anomalously high CH₄ values. Gradual and consistent increases in CH₄ levels with distance downplume have been cited as evidence for a major contribution from runoff from adjacent land (de Angelis and Lilley, 1987; Lilley et al., 1992). Diffusion of CH₄ from anaerobic sediments usually is manifested by increasing CH₄ concentrations with depth from surface to bottom, with sharp increases near the sediment/water interface. An additional source of water column CH₄ comes from dissolution of bubbles rising from CH₄-supersaturated sediments. Since bubbles rising through a longer water column have more time to dissolve, Hammond et al. (1975) argued that this source could be identified by higher CH₄ concentrations in deeper sections of a river relative to a shallower section with a similar sediment regime.

An examination of the distribution of CH₄ concentrations determined in this study may provide information on important sources of CH₄ to the Hudson River for the seasons sampled. The extensive survey of CH₄ concentrations along the length of the river should permit identification of significant point sources of CH₄ as well as contributions from runoff to the river. A

strong point source was apparent at rm 10 at all depths for both March and August sampling periods (Figure 3). This site is adjacent to the Sewage Treatment Plant on the Upper West Side of Manhattan, which is the most likely candidate for the source of the elevated CH_4 levels. Advection of this CH_4 -rich water downriver, as well as tidal advection upriver most probably is responsible to some degree for the high CH_4 concentrations present from rm -2 to rm 20. Hammond et al. (1975) reported sewage outfalls off New York City to be a strong source of CH_4 in the Lower Estuary. This is also consistent with the findings of Lamontagne et al. (1975) for the Potomac River and Lilley et al (1992) for discrete stations in the Columbia River.

In August, an additional strong source as indicated by a CH_4 maximum, was noted upriver at rm 141 (Figure 3b). This station is located immediately off a fuel storage and loading facility, which is the most likely source of the elevated CH_4 levels at this location. Brooks and Sackett (1973) attributed high concentrations of CH_4 in the Mississippi River Delta to similar facilities. A small CH_4 maximum observed in March and centered approximately around rm 120 may be due to input from Kinderhook Creek, which enters the river near rm 122. This source cannot be verified since samples were not obtained from the creek. This maximum was not present in August, when tributary flows were much lower.

For the remainder of the river between rm 130 and 30, no evidence of strong point sources for CH_4 was found for either month. Rather, methane concentrations decreased gradually (approximately 1 to 1.5 nM CH_4 per river mile) downriver. This is in contrast to increasing CH_4 levels with distance downstream observed in Pacific Northwest rivers and streams (de Angelis, et al., 1987; Lilley et al., 1992) attributed to accumulating direct runoff from forested or agricultural land or input of CH_4 from tributaries. This is consistent with the relatively small contribution of tributaries to the Hudson River below Albany and the lack of agricultural or grazing lands directly adjacent to the river throughout most of its length.

Determining if diffusive flux of CH_4 to the water column from the sediments is a strong source at any location in the Hudson is complicated by the fact that the deepest water samples in this study were obtained from at least 1 meter off the bottom in a rapidly flowing system. In addition, in portions of the river where salt intrusion occurred, salinity differences from surface to bottom indicated the advection upriver along the bottom of CH_4 -rich saline waters. Therefore, it is difficult to identify the importance of this source from this data set, unless the signal is very strong, as in the case of the station at rm 10. Sediments off sewage outfalls are likely to be organically enriched and sites of elevated CH_4 production. At rm 10, CH_4 concentrations increased from surface to bottom by 230 nM in August and 330 nM in March compared to less than 110 nM for the rest of the river on all sampling dates.

Diffusion from sediments is likely to be an important source in other locations as well. Gilmour et al. (1987) found extremely high CH_4 concentrations in Hudson River sediments of the Lower Estuary, particularly off Manhattan Island and with higher production during the warmer summer months than in winter. High rates of sedimentary CH_4 production were also observed by these authors on some occasions at selected sites in the Tappan Zee and Hudson Highlands, indicating that diffusive flux and/or bubbling from sediments is likely to be an important source of CH_4 to the water column in certain areas of the Hudson River Estuary. However, the presence of CH_4 production within sediments does not necessarily mean that this CH_4 will reach the water column. Methane oxidation within aerobic surface sediment layers may remove some or all of this sedimentary CH_4 .

Dissolution of CH_4 bubbles within the water column is another possible source of CH_4 to the Hudson River Estuary. Hammond et al. (1975) reported higher CH_4 levels in the narrow, deep Hudson Highlands than in the shallow, wider Tappan Zee portion of the river and higher CH_4 levels in March, 1974 than in August of the same year in both these regions. These authors explained the first observation as the result of differential CH_4 bubble dissolution within the water column. More CH_4 would dissolve during the longer transit through the deeper water

column of the Hudson Highlands resulting in higher CH_4 levels in this section than in the shallower Tappan Zee. Hammond et al. (1975) attributed higher March CH_4 concentrations to higher CH_4 solubilities in the colder water column in winter. We observed neither seasonal nor regional differences in CH_4 concentrations for the Hudson Highlands and Tappan Zee sections of the river. One explanation for this discrepancy is that additional sources of CH_4 were present in 1974, particularly to the Hudson Highlands region, that were not present or important in 1991. This may reflect efforts to clean up the Hudson in the last 20 years.

Sinks or loss terms cannot be neglected when discussing controls on CH_4 distributions in the Hudson River. Besides advection further downriver and eventually out of the estuary, there are 2 potentially major sinks for water column CH_4 in rivers: microbial CH_4 oxidation and diffusive flux to the atmosphere across the air/river interface (Figure 8).

Microbial CH_4 oxidation represents a potentially important sink for riverine CH_4 , but few studies have measured rates of this process. Hammond et al., (1975) measured CH_4 loss in stored Hudson River samples and concluded that CH_4 oxidation was insignificant for this river. However, their samples were taken only from the lower part of the river. Lilley et al. (1992) reported that CH_4 oxidation was insignificant in some Pacific Northwest rivers but could account for removal of up to 25% of available CH_4 on a daily basis in others.

Specific CH_4 oxidation rates of up to 0.13 day^{-1} in March and rates that ranged from 0.35 day^{-1} to 0.70 day^{-1} (35 to 70% available CH_4 oxidized per day) in August throughout most of the Upper Estuary (Table 2, Figure 5b) indicate that microbial CH_4 oxidation is an important sink term for CH_4 in the Hudson River that is likely to be a factor in controlling CH_4 distributions in this system. Specific CH_4 oxidation rates showed an inverse relationship with CH_4 concentrations in both March and August throughout the Hudson River (Figures 3 and 5). In both early spring and late summer, maxima in specific CH_4 oxidation rates coincided with minima in CH_4 concentration. In addition, below $\text{rm } 30$, CH_4 oxidation activity decreased sharply as CH_4 concentrations increased rapidly. It is also interesting to note

that in August the anomalously high CH_4 concentrations at rm 141 and 143 were matched by correspondingly low specific CH_4 oxidation rates relative to the rest of the upper river. These trends strongly suggest that microbial CH_4 oxidation is a major process controlling CH_4 distributions in the Hudson River.

Specific CH_4 oxidation rates were observed to decrease sharply below approximately rm 30 in both March and August to values close to those reported for the open ocean (Ward et al., 1987). This loss of CH_4 oxidation activity begins at or near the point of salt intrusion and becomes more severe with increasing salinity (Figure 6). This suggested that a salt effect might account for the precipitous drop in CH_4 oxidation in the lower part of the river.

To test this hypothesis, river water of 0‰ salinity collected at rm 92 in August was incubated in the presence of preweighed amounts of NaCl or seawater of known salinity. Results of this experiment, shown in Figure 9, revealed that salt additions to final salinities as low as 0.25‰ have an inverse effect on microbial CH_4 oxidation. No significant difference was observed between addition of NaCl or seawater to the same salinity. Similar results were obtained for river water collected in May from the vicinity of Cold Spring (rm 50). When the rates from the August salt addition experiment are plotted vs salinity along with the rates determined for the August river samples (Figure 10), all the data points fall on the same curve. From these results, it appears that the drop in specific CH_4 oxidation rates in the saline portion of the estuary can be attributed almost entirely to the effects of salt. The large and rapid increase in CH_4 concentrations in this portion of the river is likely due to the combination of a large input of CH_4 at rm 10 and the concurrent loss of CH_4 oxidation as a significant sink. An important consequence of this is the export to the nearshore ocean of large quantities of CH_4 which is eventually lost to the atmosphere through flux across the air/sea interface.

Strong seasonal differences were observed in CH_4 oxidation activity with much lower specific CH_4 oxidation rates in March than in August (Figure 11). For example, the highest oxidative loss of CH_4 observed in March was $13\% \text{ day}^{-1}$ compared to a maximum

