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NITROUS OXIDE IN FRESH WATER SYSTEMS:

AN ESTIMATE FOR THE YIELD OF ATMOSPHERIC N_2O

ASSOCIATED WITH DISPOSAL OF HUMAN WASTE

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Abstract

The N_2O content of waters in the Potomac and Merrimack Rivers was measured on a number of occasions over the period April to July 1977. The concentrations of dissolved N_2O exceed those which would apply in equilibrium with air by factors ranging from about 46 in the Potomac to 1.2 in the Merrimack. Highest concentrations of dissolved N_2O were associated with sewage discharges from the vicinity of Washington, D. C. and analysis indicates a relatively high yield, 1.3 to 11%, for prompt conversion of waste nitrogen to N_2O. The yield could be even higher if bubbles originating in sediments should contain as little as 0.3% N_2O. Measurements of dissolved N_2O in fresh water ponds near Boston demonstrate that aquatic systems may provide both strong sources and sinks for atmospheric N_2O.

1. Introduction

Oxides of nitrogen play an important role in stratospheric chemistry. Ozone in the natural environment is thought to be removed mainly by catalytic reactions involving NO and NO_2 (Crutzen, 1970; Johnston, 1971). Nitric oxide is formed in the stratosphere by reaction of $O(^1D)$ with N_2O (Crutzen, 1971; McElroy and McConnell, 1971; Nicolet and Vergison, 1971). Nitrous oxide is believed to originate as a by-product of micro-biological activity at and near the earth's surface (Bates and Witherspoon, 1952; Bates and Hays, 1967), and concern has arisen in recent years that a variety of human activities might lead to a significant increase in the net global source of atmospheric N_2O (Crutzen, 1974; McElroy, 1974; Pierotti and Rasmussen, 1976; Weiss and Craig, 1976).

Recent interest has focussed on perturbations associated with agriculture. Quantitative assessment is hampered however by major gaps in our understanding of the global nitrogen cycle, and by specific difficulties which arise in the description of the human influence.

One possible approach to the problem has been outlined by McElroy (1976) and by McElroy et al. (1977). Under conditions appropriate to North American agriculture, approximately 70% of nitrogen applied as chemical fertilizer may be recovered in crops. Approximately 6% of crop nitrogen is consumed directly by the human population. A much larger fraction, 67%, is fed

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to animals. The remainder, 27%, is lost to a variety of factors including processing waste, spoilage, fire, insects, and plant pathogens. The human population obtains 30% of its nitrogen requirement directly from plants. The remainder is supplied indirectly through the animal food chain as meat, eggs, and dairy products.

Human waste per person in the developed world amounts to some 5.4×10^3 grams of fixed nitrogen per year (National Academy of Sciences, 1972), equivalent to some 1.14×10^6 tons N per year for the human population of the United States. The comparable figure for the world population is estimated at 1.5×10^7 tons N per year, using data from a variety of sources (Deevey, 1970; National Academy of Sciences, 1977). Animals in the United States excrete an estimated 3.7×10^6 tons N per year. By way of comparison, we might note that photochemical processes in the stratosphere represent a sink for N_2O of magnitude 10^7 tons N per year. It is clearly important that one should define the magnitude of the anthropogenic contribution to atmospheric N_2O.

This paper offers a preliminary account of results obtained in a series of measurements intended to explore the distribution of dissolved N_2O in a variety of aquatic systems. The paper includes results for two rather different river systems which receive human wastes, the Merrimack in Massachusetts and the Potomac near Washington, D. C. The Merrimack provides an example of a fast moving stream with few tributaries, draining

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a large industrial area with a population of about 500,000 persons. The Potomac is relatively sluggish at sites sampled here, receiving wastes from a concentrated population in excess of 2 million. In addition, data are presented for a number of shallow fresh water ponds in Massachusetts.

2. Experimental procedures

Waters deeper than a meter were sampled by hydrocast using 1.7 liter Niskin bottles. Each bottle was equipped with a self-reversing thermometer triggered by the Niskin messenger unit. A waiting period between 7 and 10 minutes was observed at depth in order to allow the thermometer and sample bottle to equilibrate with their environment.

After retrieval of bottles, bubble-free water samples were removed by slow gravity feed to permit analyses for salinity, pH, dissolved oxygen and nitrous oxide. Dissolved oxygen, salinity and pH were measured immediately using a Yellow Springs Instruments Model 57 oxygen meter, a Yellow Springs Instruments Model 33 conductivity/salinity meter, and an Orion Model 407A pH meter respectively.

Samples for N_2O determination were transferred from the Niskin bottles to 300 ml BOD bottles. Microbial activity was inhibited by addition of 1 ml of a saturated $HgCl_2$ solution. Samples were cooled to a temperature between 5 and 10°C until analyzed.

Measurements of N_2O were usually performed within 1 to 2 days of sample acquisition. Analyses were performed using a Perkin-Elmer 3920B electron capture gas chromatograph equipped with an 8' by 1/8" OD column of Porapak Q held at a temperature of 40°C. The ^{63}Ni detector was operated at a temperature of 350°C with a standing current of 3.5×10^{-9}

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amps. This procedure allowed excellent separation of N_2O

from possible contaminating gases as illustrated in Figure 1.

We verified experimentally that samples treated with $HgCl_2$

exhibit no significant gain or loss of N_2O during storage

intervals employed here (Elkins et al., 1977).

Nitrous oxide was removed from water·samples using the

static gas partitioning method described by McAuliffe (1969,

1971). A 100 ml glass syringe with a locking input orifice

(Precision Sampling Corporation) was flushed with N_2O-free

helium. A 50 ml sample of water was displaced from the BOD

bottle into the empty syringe again using helium. This pro-

cedure was devised in order to minimize contamination by out-

side air. Finally 50 ml of helium was introduced

into the syringe and the syringe barrel was isolated,leaving

a 1:1 volume ratio of helium and water. The syringe was

placed on a wrist action shaker for 10 minutes to equilibrate

the two phases. Gas from the syringe was then passed through

the sample loop of the gas chromatograph and a 1 ml

sample was injected for analysis. Residual helium was released

and 50 ml of fresh helium were added. This process was repeated

2 or 3 times. A plot of log N_2O peak area versus

number of equilibrations yields a straight line. The y inter-

cept of this line is a function of the initial N_2O concentration,

as discussed by McAuliffe (1969, 1971).

Air samples obtained at the same time as the water samples

were analyzed for atmospheric N_2O. Samples were acquired using

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a 12V DC portable Speedaire compressor and were stored in 1 liter Whitey 304 stainless steel cylinders. Sample cylinder pressure delivered air to the chromatograph through a six port Carle Model 5518 valve equipped with a 1 ml sample loop. Column and detector parameters were identical to those used for water measurements. Two or three injections of synthetic air standards with known N_2O concentration (209, 326 or 420 ppb) were measured prior to analysis of each unknown. Standards were obtained from Scott Environmental Technology Incorporated, who certified their N_2O concentrations to an accuracy of $\pm$ 2%. An absolute pressure gauge was used to achieve equal sample loop pressures of unknowns and standards. Chromatographic peaks from both air and water samples were integrated using a Hewlett Packard 3380 A electronic integrator. Replicate analyses of air and water samples were used to establish overall precisions of 1% and 3% respectively.

3. Results

Figure 2 summarizes the N_2O data obtained for the Merrimack River on April 13, 1977 and June 29, 1977. ly. Samples were acquired in the order indicated by the station numbers, 1 through 14. The inital measurements were taken when the flow rate in the river was high, 466 m^3 sec^{-1}, corresponding to a linear flow speed of about 50 cm sec^{-1}. Flow rates were smaller during the June sampling period, 131 m^3 sec^{-1}, corresponding to a flow speed of about 14 cm sec^{-1}. Stations 9 and 14 were occupied at approximately the same position and give a direct indication of temporal variability of dissolved N_2O.

Results for N_2O in Figure 2 are quoted as saturation ratios for dissolved gas with respect to the measured air concentration of 294±3 ppbv. Solubility data were taken from Markham and Kobe (1941). Fresh water sections of the river show at most small spatial variations in the concentration of dissolved N_2O for either measurement period. Other measured properties of the water, pH, O_2 and temperature, are also spatially uniform. Concentrations of dissolved N_2O are spatially variable near the mouth of the river, downstream from station 4, consistent with a model in which fresh waters of high N_2O content are admixed with salt waters containing relatively little N_2O, as illustrated in Figure 3. Average properties of the river as measured for all 14 stations are summarized in Table 1.

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Selected profiles for dissolved N_2O in the Potomac River are shown in Figures 4 and 5. Measurements were taken over the time period July 16, 1977 to July 23, 1977. Exceedingly high concentrations of N_2O were observed in waters near and downstream from the Alexandria and Blue Plains Wastewater Treatment Plants. As indicated in Figure 5, the water at station 12 was supersaturated in N_2O with respect to ambient air by a factor in excess of 40 on July 16, 1977. The concentration of N_2O in surface waters at station 11, closer to the Treatment Plants, was larger than that at station 12 by a factor of 1.2 . The influence of the Treatment Plants extends approximately 25 km downstream, as may be seen from the data in Figure 5. Lowest concentrations of N_2O, approximately 150% of saturation with respect to ambient air, were measured upstream of the Treatment Plants at stations 4, 5 and 6. The surface concentration of N_2O at station 16, near Quantico, Virginia, was somewhat higher than that at stations 4-6, about 200% of saturation with respect to ambient air. In mid-stream where the Potomac River enters Chesapeake Bay, the surface concentration of N_2O had a value equivalent to a supersaturation of 164% with respect to ambient air on July 18, 1977. At Harpers Ferry, 60 miles northwest of Washington, D. C. the surface concentration of N_2O was equivalent to 119% of saturation on July 17, 1977.

A significant, factor of 1.8, change in the concentration of dissolved N_2O was detected in waters near the Wastewater treatment plants between July 16 and July 23, 1977. The change

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may be attributed to the influence of strong winds associated with the passage of a storm through the Washington area on July 21 and July 22, 1977, as indicated in Figure 6. The rate for gas exchange across an air-water interface is known to depend in a fairly sensitive fashion on wind speed (Broecker and Peng, 1974; Emerson, 1975), and we shall return to this matter later. The Blue Plains Plant releases approximately 2×10^4 kg of N per day with trivial variation in outflow rate over the period covered by these measurements. The nitrogen source from the Alexandria Plant is approximately 10% of that from Blue Plains.

Dissolved oxygen concentrations showed substantial undersaturations ($\sim 40\%$) near the bottom of the Potomac River. Surface waters were generally close to equilibrium, or slightly supersaturated, with respect to atmospheric oxygen.

Measurements for a variety of shallow ponds in the Boston area are summarized in Table 2. The data from Concord Town Forest are perhaps most intriguing, in that they illustrate the remarkable spatial heterogeneity of N_2O in fresh water systems. Measurements were carried out in two ponds separated by an embankment approximately 5 meters wide by about 0.5 meters high. The larger pond (Fairyland Pond) is approximately 60 meters long by 30 meters wide and is drained from its lower end through a small dam. It is choked with a variety of aquatic plants at its upper reach. Stations 1-4 are situated along the mid section of the pond beginning at its upper end. Surface concentrations of

N_2O range from 650% of saturation with respect to ambient air in the upper region, to about 150% of saturation in clear waters near the center of the pond. Surface waters of the pond are super-saturated with respect to atmospheric O_2 by about a factor of 2, reflecting the influence of photosynthesis. The vertical profile for N_2O at station 2 suggests that the source for N_2O may occur at depth, and that it may be largest in areas of highest biological productivity. In contrast the adjacent Concord bog which has no surface outlet, appears to act as a vig-orous sink for N_2O. Waters there were undersaturated in N_2O with respect to ambient air by factors which varied between about 2 and 5. Water samples from this system were incubated for five days under a variety of conditions in the laboratory. Samples treated with $HgCl_2$ showed at most small changes in the concen-tration of dissolved N_2O over this period. The concentration of N_2O in untreated samples dropped below detectable limits, about 10 ng l^{-1}. This behavior was observed for both light and dark incubations. Oxygen was also consumed in untreated samples. Its concentration was reduced to 0.4 mg l^{-1} and 0.25 mg l^{-1} for light and dark incubations respectively.

The data for Great Meadows National Wildlife Refuge were taken from a system of two ponds each about 200 meters square, separated by a dike. The upper pond, fed with treated sewage from the town of Concord, exhibited patches of floating algal growth apparently absent from the lower pond. Dissolved oxygen concentrations were relatively high in the upper pond. The

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N_2O concentration was relatively low however, though samples were not taken close to the sewage outflow region. The data suggest that the upper pond may be slightly undersaturated in N_2O, although the discrepancy could be attributed to experimental error.

4. Discussion

The data described above may be used to place quantitative limits on the yield for N_2O associated with disposal of human waste in rivers. The results for the Potomac are especially relevant in this regard, in that the Blue Plains and Alexandria Treatment Plants may be considered point sources for anthropogenic nitrogen. The discharges have a major influence on the river, providing as much as 20% of the total stream flow over the period covered by our measurements. In addition, the temporal variability observed for N_2O allows us to make a direct estimate for the magnitude of the N_2O flux to the atmosphere.

Figure 7 illustrates the spatial distribution of N_2O as measured in the river near the treatment plants between July 16, 1977 and July 23, 1977. The N_2O plume associated with the plants is relatively extensive. Flow conditions in the stream were such that a period of approximately 40 days would be required for waters to traverse a distance of 25 km in the interval prior to July 23, 1977. The change in N_2O detected between July 16 and July 23 might be attributed to dilution associated with the higher flow rates which occured on July 23 after the storm. The time and space scales exhibited in Figure 7 would not appear, however, to support this conjecture. It seems more probable that the variation in N_2O should be attributed to a change in the rate for gas exchange across the river surface associated with

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passage of the storm on July 22. Future measurements may be expected to resolve possible ambiguities about the mechanism for temporal variations of N_2O.

Gas exchange across an air-water interface is frequently described using a simple diffusion model (Broecker and Peng, 1974), in which gas flux is given by

$$\phi = \frac{D}{Z} (C_L - C_E) ,$$

where D is a molecular diffusion coefficient, Z is an empirical parameter which defines the thickness of a hypothetical molecular boundary layer, C_L is the observed concentration of gas in the liquid phase, and C_E is the concentration of dissolved gas which should apply if the liquid were in equilibrium with the atmosphere. The parameter Z may be estimated using an empirical relationship between Z and wind speed developed by Emerson (1975) from studies of radon and CO_2 in a variety of aquatic systems. Following his data, we derive a value for Z of approximately 75 μ for the period 0900 July 21 to 0600 July 23 (see Figure 6). The river has a mean depth of about 4 meters over the spatial domain of interest here. A film thickness of 75 μ would imply therefore a residence time for dissolved gas of about 2 days.

Other factors, in addition to those included by the simple wind-driven model, could contribute to the rate for gas exchange across the air-water interface in the Potomac. We might note that the river carries a significant traffic in moderate-sized power

boats. Tour boats from the Wilson Line, for example, have an underwater cross section of approximately 10 m^2. These boats pass through the waters sampled here on an average of 6 times per day, displacing as much as 1% of the total water mass per day, at least 7% of the river encountered during the sampling interval, or 40% of the river during the 40 day residence time of water in the polluted area. It would appear that boat traffic could have a significant influence on gas exchange, at least during periods of relatively low wind speed and summer flow conditions.

The observed variation in N_2O may be used to place empirical limits on the rate for N_2O exchange. It appears that the N_2O content of the river downstream from Blue Plains decreased by approximately 580×10^3 g (N) over the period July 16 to July 23. If we assume that the storm represented the dominant environmental change in this interval, and ignore sources of N_2O during the storm, we may place a lower bound on the N_2O release rate equivalent to 290×10^3 g N day^{-1}, or 1.3% of the total nitrogen released from the wastewater treatment facilities over this period. Alternatively, we might suppose that the waters were entirely depleted of excess N_2O due to the influence of the storm, and that the concentration of disequilibrium N_2O observed on July 23, 6 hours after storm passage, indicates the recovery rate of the water system. This assumption would imply an upper limit to the prompt source strength for N_2O of magnitude 2460×10^3 g N day^{-1}, or a yield of about 11% for conversion of wastewater N to N_2O. A source strength for N_2O of 290×10^3 g

N day^{-1} could be rationalized on the basis of the diffusive exchange model if the film thickness, Z, were taken to have an average value of about 200 μ during the storm. A source strength as high as 2460 x 10^3 g N day^{-1} would require a film thickness of about 30 μ.

We should caution that the efficiency for prompt conversion of waste nitrogen to N_2O could be even larger than values quoted here. The measured profiles for dissolved N_2O suggest that the gas may originate at or below the sediment-water interface. Bubbles were observed to reach the surface at station 11 at a rate of approximately 3.5 ft^{-2} min^{-1}. These bubbles had an average diameter of about $\frac{1}{4}$". If we assume that the bubbles originate in the sediment and are composed primarily of CH_4, reasonable assumptions based on dissolved CH_4 data reported by Swinnerton, Linnenbom and Cheek (1967) (see also Hammond et al. (1975)), we may estimate a CH_4 source strength of magnitude 2 x 10^8 g C day^{-1} over the polluted stretch of the Potomac. Bubbles containing a ratio of N_2O to CH_4 as small as 0.3% could provide an additional source for atmospheric N_2O which might exceed even the largest value derived above.

Flow rates in the Merrimack River are much higher than those measured for the Potomac. It is unlikely that transport of gas across the air-water interface in the Merrimack should be described by the thin film model given above for the relatively placid Potomac. A model outlined by Fortescue and Pearson (1967) provides an alternate description for gas exchange across the boundary of a turbulent liquid.

The flux is given in this case by

$$\phi = 1.46 \ (\frac{Du}{L})^{1/2} \ (C_L - C_E)$$

where u is the root mean square speed for the river, L is the
average depth of the liquid, and other symbols are as described
above. The turbulent model suggests a lifetime for dissolved
gas in the Merrimack of about a day for conditions encountered
during the initial measurements on April 13, 1977, and is
approximately twice as long for the measurements taken in June.

Flow rates in the Merrimack are such that the water would
be expected to travel a distance in excess of 40 km over the
one day residence time inferred here for dissolved N_2O in April,
or 25 km for conditions encountered in June. We may note in
this context that the Merrimack River is dammed near Lawrence
and that it subsequently traverses a 1 km stretch of rapids
located about 46 km upstream from the mouth of the river. One
would not expect, therefore, any direct contribution to the excess
concentrations of N_2O measured near the river mouth due to export
of N_2O from regions of the river above Lawrence. Indeed, the resi-
dence time for dissolved N_2O estimated above, when combined
with measured flow speeds for the river, suggest that the excess
N_2O measured in April must be generated in close proximity to our
sampling stations, in any event within an upstream displace-
ment of 40 km. Supporting this view, we may note that the concen-
tration of excess dissolved N_2O at Nashua, 80 km from the river

mouth is approximately half that measured in the estuary.
Nitrous oxide should be a conservative property of the river
over the 15 km interval sampled in April. A similar conclu-
sion holds for the measurements made in June.

The measurements in April may be used to obtain a direct
estimate for the quantity of N_2O released to the ocean by the Merri-
mack in this period. We find in this manner that the river exported
a quantity of N_2O equivalent to 2×10^4 g N day^{-1} at that time.

It would seem reasonable to suppose that a major fraction
of the excess N_2O measured in the Merrimack should reflect
denitrification of N associated with diffuse sources of human
waste. If the efficiency for conversion to N_2O were similar
to that observed for the Potomac, the excess concentrations of
N_2O in the Merrimack could be attributed to prompt denitrifica-
tion of waste from a population of between 10,000 and 100,000
persons, with the lower value corresponding to a conversion
efficiency of 11%. The river over its bottom 40 km drains an
area occupied by a total population of about 180,000 people.
The fraction of this population which exhausts its human waste
directly into the Merrimack is somewhat undertain. Moreover,
a significant fraction of waste nitrogen entering the river is
likely to be exported directly to the ocean as NO_3^- during the
high flow conditions encountered during our measurements (U. W.
Geological Survey, unpublished). Within the accuracy of the
present analysis we may conclude that the April data for N_2O
in the Merrimack are consistent with the range of yield factors

inferred earlier from the Potomac for prompt conversion of human waste nitrogen to N_2O, and a similar analysis may be made for the Merrimack data taken in June.

5. Concluding remarks

The data presented here allow us to estimate the magnitude of N_2O source associated with one component of the anthropogenically perturbed nitrogen cycle. If yields for N_2O inferred from the Potomac are representative, human wastes could provide a global source for N_2O of between 2×10^5 and 1.6×10^6 tons N per year, or between 2% and 15% of the rate at which the gas is consumed photochemically today in the stratosphere. We should note that these estimates reflect prompt sources for N_2O. They do not account for N_2O formed on a delayed basis following export of nitrogeneous material. They omit also possible sources of atmospheric N_2O associated with bubble transport of gas from polluted sediments.

Extrapolation to global scale is hazardous, however, for several reasons. Results for the Potomac reflect sources of N_2O associated with one particular method for waste disposal at one particular time. Results from the Merrimack are consistent with a relatively high prompt yield for N_2O, but our understanding of the Merrimack system is not sufficiently complete to allow more definitive conclusions.

Animal wastes contain additional sources of nitrogen which exceed those for the human population of the developed world by more than a factor of 3. We are unable from the present study to offer any quantitative estimate for the corresponding yield of N_2O from this source. It could however be significant.

Our understanding of processes affecting atmospheric N_2O remains deficient. The limited data on rivers and ponds described here indicate that biological processes may offer both sources and sinks for the gas. Further observational data are clearly needed in order to quantify the overall budget of atmospheric N_2O.

Acknowledgement

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Table I

Merrimack River Station Average Data

April 13, 1977 Mean air concentration 295 ± 5 ppbv N_2O Mean River Flow 466 m³ sec⁻¹

Station #	Dissolved N_2O (mg m⁻³)	Excess N_2O (mg m⁻³)	pH (range)	O_2 (ml/l)	O_2 Saturation ratio (%) (range)	Salinity (‰) (range)	Total Depth (m)	# Depths Sampled	Temp (°C) (range)	Remarks
1	0.65	0.14	8.0-8.2	6.31	64-97%	24.8 (16.1-28.0)	17.8	(5)	5.0 (3.4-6.8)	River plume to 3m with high N_2O. River temp. 7.5-8.5 °C, ocean 3.5 °C.
2	0.684	0.15	7.97-8.16	5.57	55-63	24.5 (17.8-27.8)	10.7	(5)	5.0 (3.7-5.9)	
3	0.822	0.28	7.80-7.98	6.06	71-83	12.7 (11.2-16.8)	16.2	(5)	6.6 (6.4-6.7)	
4	0.876	0.34	7.4-7.7	6.01	69-81	7.5 (4.5-8.9)	16.2	(5)	7.6 (7.5-7.8)	
5	0.984	0.42	7.0-7.6	6.32	70-84	0	4.9	(4)	7.65 (7.6-7.75)	
6	1.05	0.49	6.9-7.0	6.37	71-82	0	6.1	(4)	7.73 (7.6-7.8)	
7	1.05	0.49	6.9-7.0	6.30	73-79	0	4.6	(3)	8.0 (7.9-8.1)	
8	1.07	0.52	6.8	6.45	65-73	0	9.8	(5)	8.3 (8.1-8.8)	Incubated samples (1 week) grew in 0.07 µg/1 N_2O (average of 3).
9	1.04	0.49	6.9	6.66	72-76	0	8.2	(5)	8.25 (8.2-8.3)	
10	1.03	0.47	6.9	6.0	70-76	0	6.1	(4)	8.2 (8.1-8.4)	
11	0.63	0.09	8.1-8.2	5.2	64-73	28.0 (25-30)	11.6	(5)	4.2 (3.3-6.9)	River plume above 3.5 m.

June 29, 1977 Mean air concentration 291 ± 4 ppbv N_2O Mean River Flow 131 m³ sec⁻¹

Station #	Dissolved N_2O (mg m⁻³)	Excess N_2O (mg m⁻³)	pH (range)	O_2 (ml/l)	O_2 Saturation ratio (%) (range)	Salinity (‰) (range)	Total Depth (m)	# Depths Sampled	Temp (°C) (range)	Remarks
12	1.50	1.17	7.5-8.1	6.22	105-107%	0	3.0	(2)	24.0	
13	1.40	1.09	8.2-8.3	7.0	120	0	2.0	(2)	24.5	
14	1.44	1.12	7.8-8.0	6.87	115-120	0	8.5	(5)	24.2	Approx. same location as Station 9 of 4/13/77.

Table 2

Concord Town Forest: Concord Bog   (6/9/77)

Location	Time	N_2O (mg m^{-3})	% N_2O Saturation	°C	O_{2-1} (ml l^{-1})	% O_2 Saturation	pH
I	6/9/77	0.152	36.5	15.5	6.9	98.9	6.5
II	6/9/77	0.214	51.4	15.5	6.9	98.9	6.5
III	6/16/77	0.205	54.3	19.9	6.2	103	6.7
IV	6/16/77	0.078	20	19.2	6.5	100	6.7
V	6/16/77	0.227	57.2	18.5	3.9	59.6	6.5

Table 2 (cont.)

Concord Town Forest: Fairyland Pond   (6/9/77)

f_{N_2O} = 285 ppb

Location	N_2O (mg m^{-3})	% N_2O Saturation	°C	O_2 (ml l^{-1})	% O_2 Saturation	pH
1, < 8"	2.59	650	16.8	12.3	181	6.7
2, surface	0.958	225	14.9	11.8	167	6.6
2, 2.5'	1.249	292	14.7	13	183	6.6
3, surface	0.624	156	16.7	13.1	192	6.5
3, 2.5'	0.645	159	16.4	11.7	171	6.6
4, surface	0.753	181	15.5	12.2	175	6.8
4, 2'	0.775	197	17.2	11.9	177	6.8

Table 2 (cont.)

Great Meadow National Wildlife Refuge

6/9/77

Station	N_2O (mg m^{-3})	% N_2O Saturation	°C	O_2-l (ml l^{-1})	% O_2 Saturation	pH
Algal mat I	0.367	99.1	19.0	12.6	194	6.9
Algal mat II	0.387	104	18.9	18.0	277	7.4
III	0.353	95.3	19	8.4	129	6.6
IV	0.338	90.7	18.8	10.1	149	6.8
V	0.348	93.3	18.8	10.1	149	6.8

Figure Captions

Figure 1.   Chromatograms showing response of the ECD to O_2 and N_2O.   Chromatogram A is an air sample containing 295 ± 3 ppbv N_2O. Chromatograms B and C are successive extractions of N_2O from a water sample using the technique of McAuliffe (1969).   This water sample contained 1.404 µg N_2O/liter.

Figure 2.   Merrimack River N_2O profiles are shown for April 13, 1977 and June 29, 1977.   Data are given as saturation ratios of N_2O with respect to air containing 294 ± 3 ppbv N_2O.   The distance between stations 3 and 9 is 12 km.   Stations 14 and 9 are located at the same site.   The extent of tidal influence in the river is approximately 10 km from the mouth of the river.
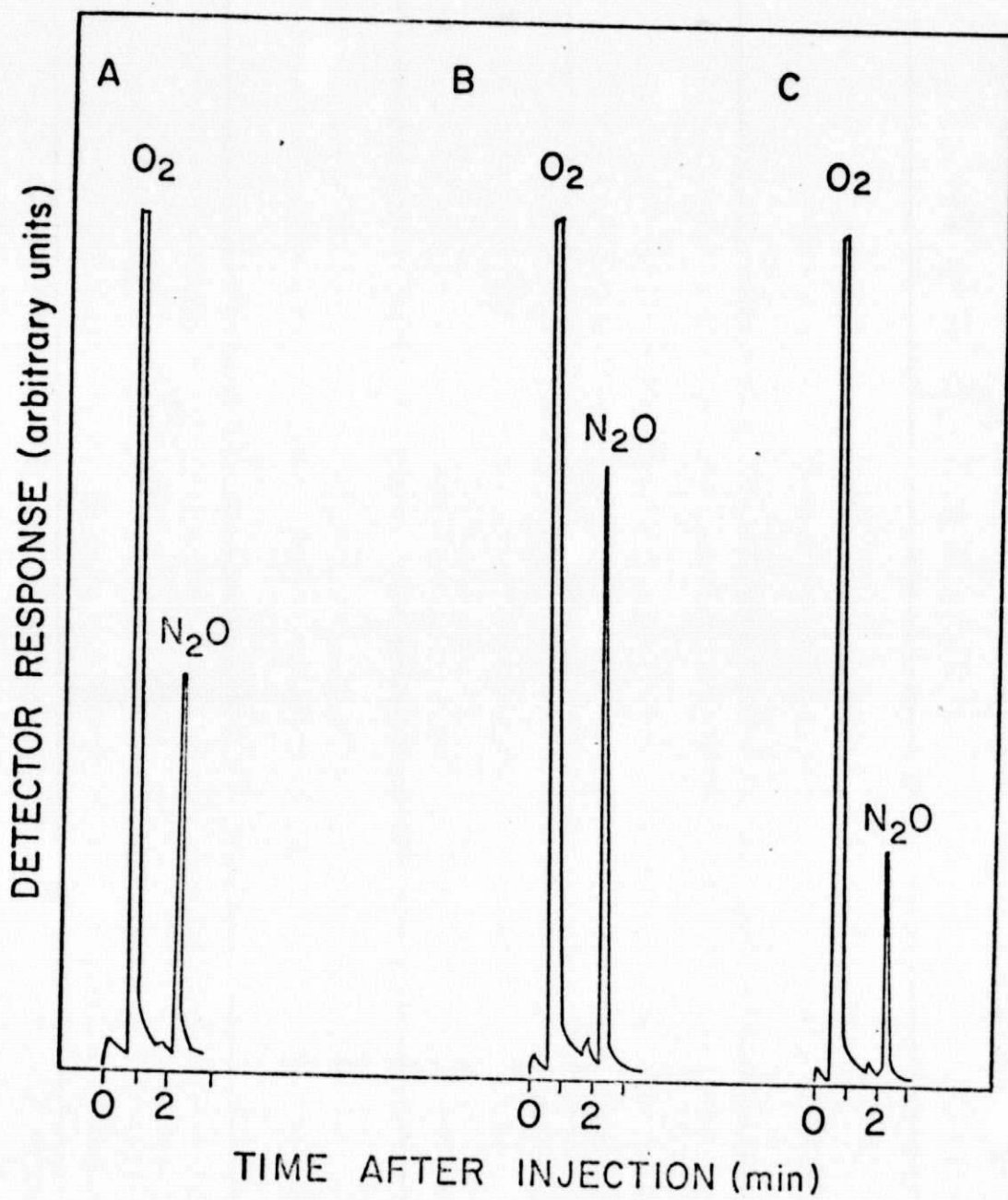
Figure 3.   Dissolved N_2O is plotted against salinity in a 12 km segment of the Merrimack River for the data from April 13, 1977.
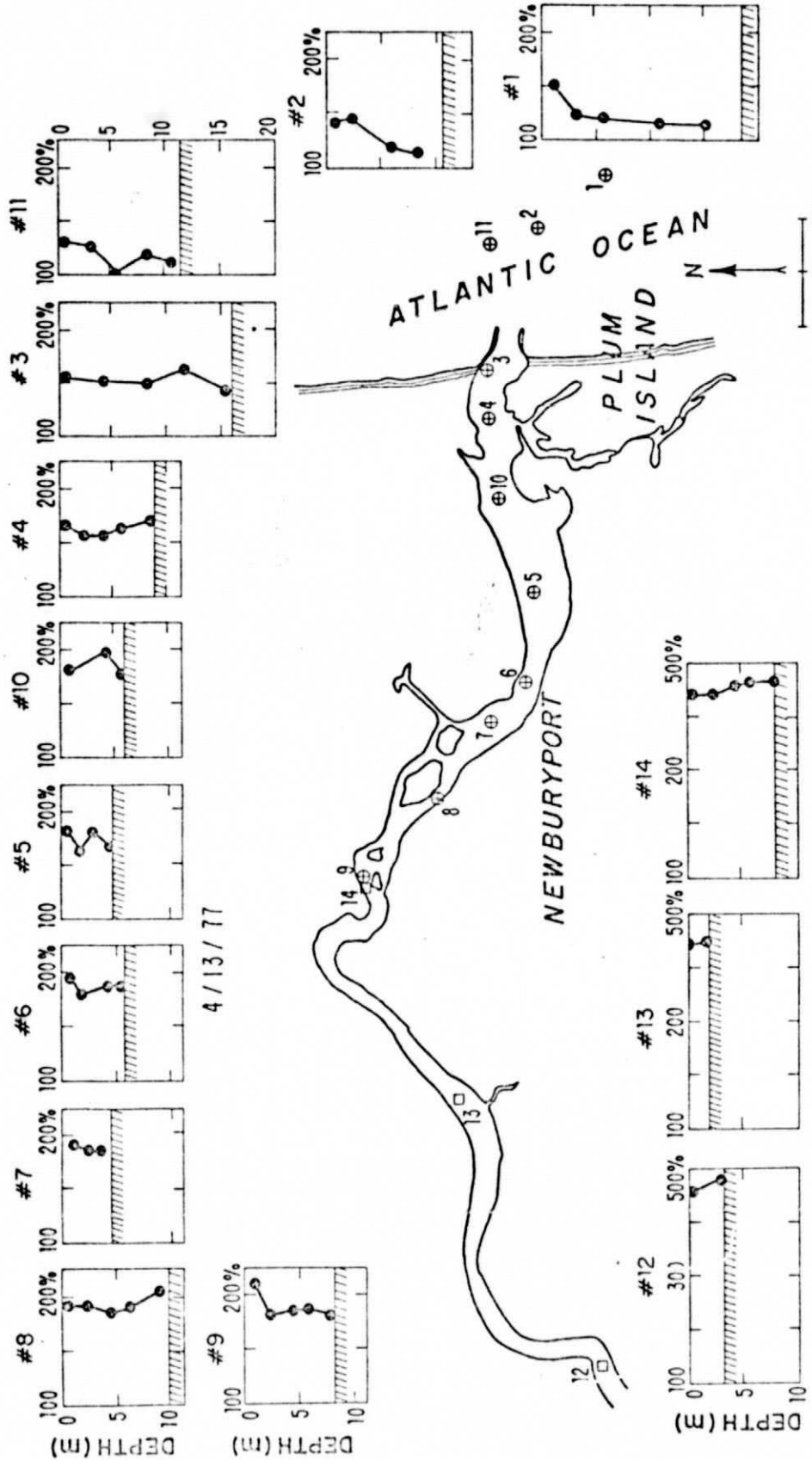
Figure 4.   Locations of sampling stations 1-16 are illustrated for the Potomac River between Washington, D. C. and Quantico, Va.
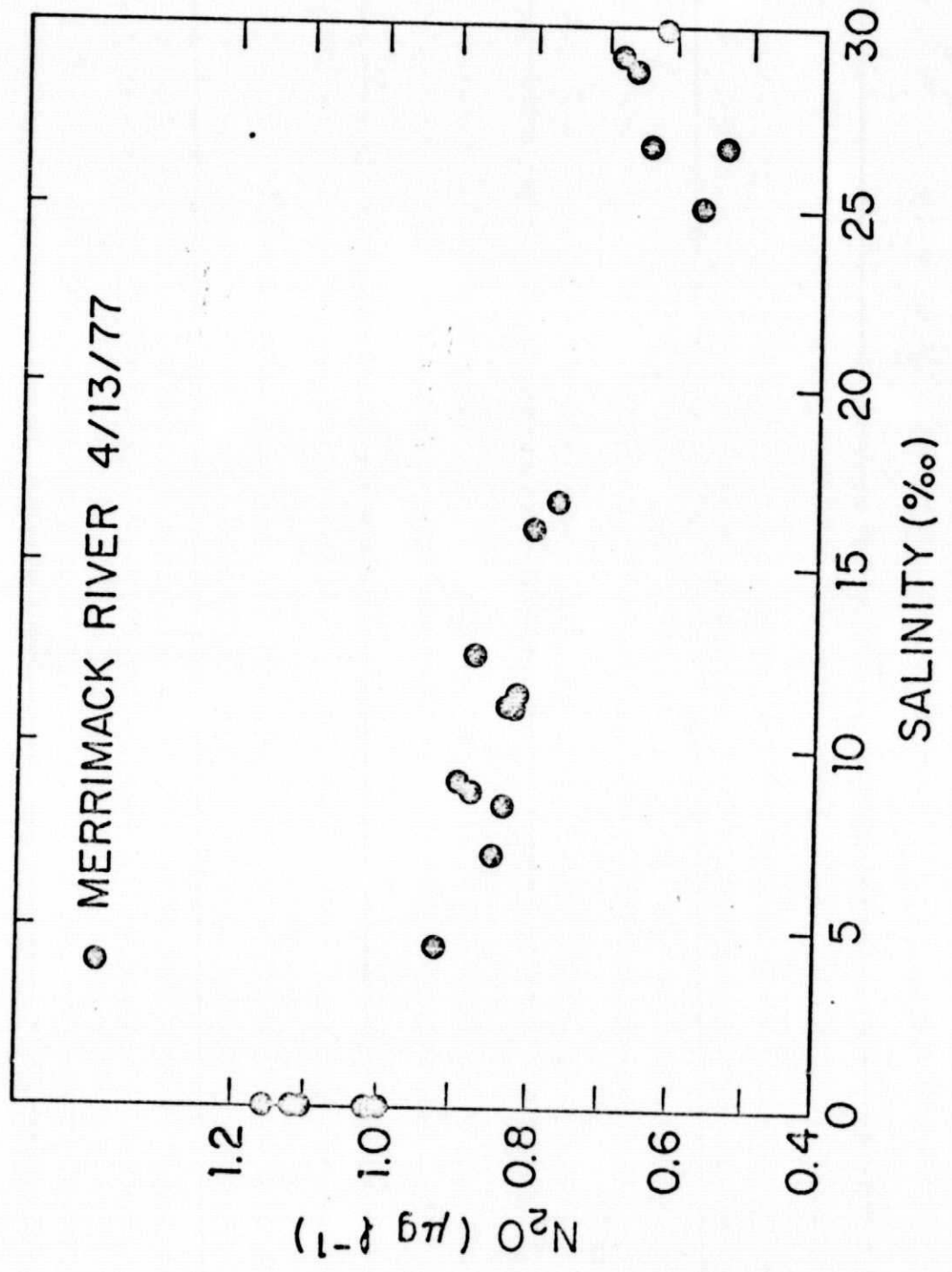
Figure 5. Selected depth profiles of N_2O in the Potomac are presented in terms of supersaturation with respect to ambient air. Station numbers refer to sites given in Figure 4.
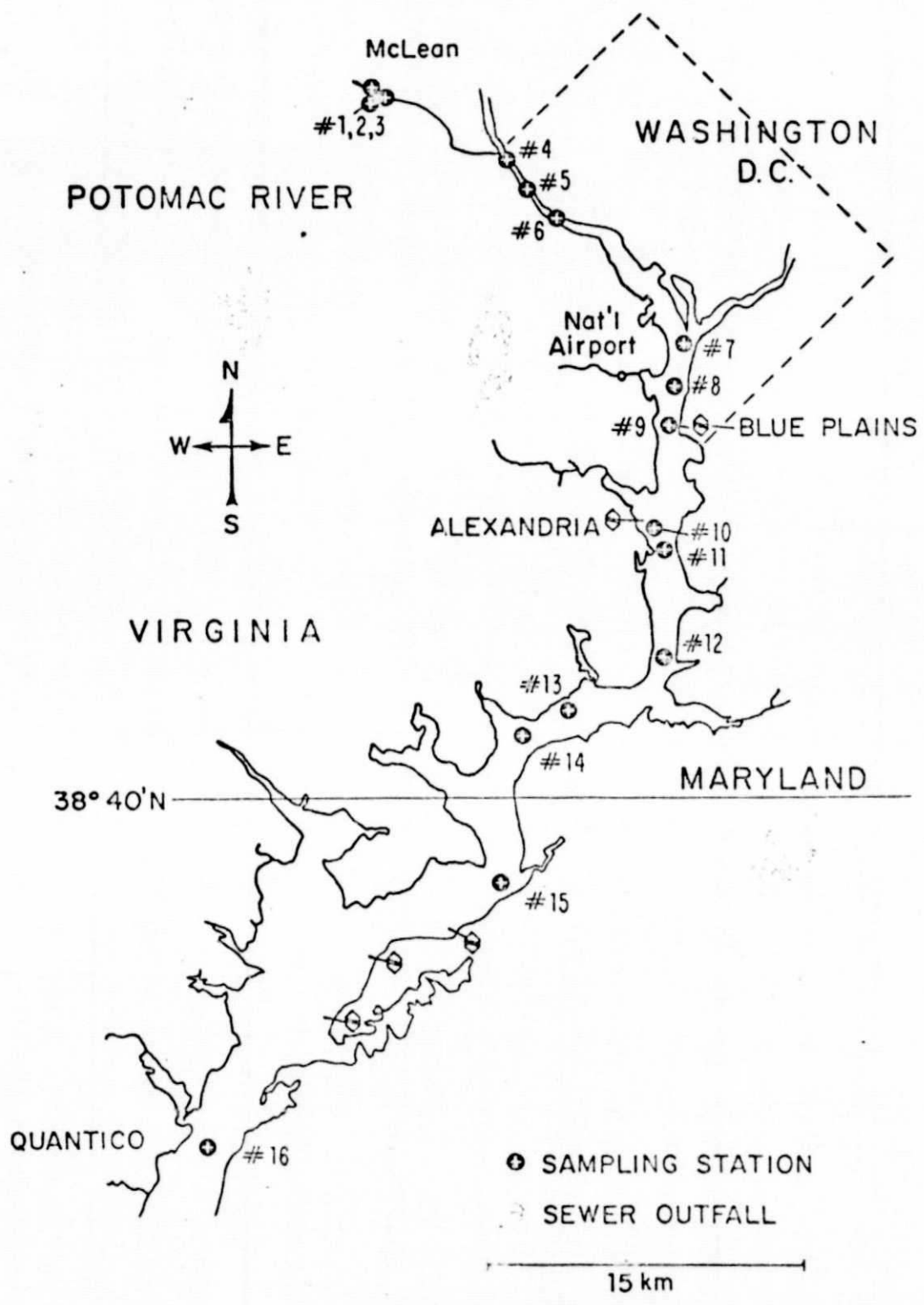
Figure 6. Surface wind data from Washington National Airport are given for the period July 21-23, 1977. The passage of a cold front is indicated by the arrow. Effective film thicknesses Z (Broecker and Peng, 1974) are shown which correspond to the various wind speeds. If the wind data were extrapolated to 10 cm elevation (cf. Emerson, 1975), the film thicknesses would be increased by about a factor of 2.

Figure 7. Mean concentrations of N_2O (mg m^{-3}) are plotted versus distance along the Potomac from the D. C. boundary (Chain Bridge), for various times during the week 16-23 July 1977. Stations where only surface data were acquired are marked by an asterisk (*). The location of the Blue Plains and Alexandria sewage discharges are indicated by the arrows.

MERRIMACK RIVER 4/13/77

Date   7/19/77   7/19/77   7/16/77
Station   #4   #6   #8

DEPTH (m)

SATURATION RATIO (%)

Date   7/16/77   7/23/77   7/23/77   7/23/77
Station   #12   #14   #15   #16

DEPTH (m)

SATURATION RATIO (%)

7

EXCESS N₂O (μg ℓ⁻¹) vs RIVER DISTANCE FROM CHAIN BRIDGE (km)

BLUE PLAINS   ALEXANDRIA

△ 7/16/77
⊡ 7/19/77
⊙ 7/23/77