Title
Nitrous oxide in Michigan waters and in U.S. municipal waters

Journal
Geophysical Research Letters, 5(3)

ISSN
0094-8276

Authors
Cicerone, Ralph J
Shetter, James D
Liu, Shaw Chen

Publication Date
1978-03-01

DOI
10.1029/gl005i003p00173

VOL. 5, NO. 3 GEOPHYSICAL RESEARCH LETTERS MARCH 1978

NITROUS OXIDE IN MICHIGAN WATERS AND IN U.S. MUNICIPAL WATERS

Ralph J. Cicerone, James D. Shetter, Shaw Chen Liu

Space Physics Research Laboratory, The University of Michigan, Ann Arbor, Michigan 48109

Abstract. We have measured dissolved nitrous oxide (N_2O) concentrations in Michigan surface waters by equilibration of the water samples with ambient air followed by gas chromatographic analysis of the air. Two rivers and one lake show significant N_2O supersaturations (factors of five or more) directly traceable to sewage treatment plant effluents. Municipal tap water samples from 19 U.S. cities also show supersaturations. Our data indicate that chlorination of river water and of wastes might be a key step in N_2O production. To measure N_2O fluxes from water to air we employ a gas collection device; two initial flux measurements from supersaturated waters are reported.

Introduction

Nitrous oxide is important in the atmosphere because $N_2O + O(^1D) \rightarrow NO + NO$ is a major source of stratospheric nitrogen oxides [Crutzen, 1971] which in turn partially control ozone-layer photochemistry. Changes in N_2O concentrations can thus affect the O_3. Large increases in N_2O can also lead to appreciable extra trapping of outgoing planetary IR radiation [Yung et al., 1976]. For these reasons the possibility of atmospheric N_2O increases due to nitrogen fertilizer usage [Crutzen, 1974] has been studied recently by McElroy et al. [1976], Liu et al. [1976], Crutzen [1976], Sze and Rice [1976], McElroy et al. [1977], Liu et al. [1977] and Hahn and Junge [1977]. The fact that combustion produces N_2O has also been uncovered [Pierotti and Rasmussen, 1976; Weiss and Craig, 1976]. Interest in N_2O also results from renewed attention to the earth's nitrogen nutrient cycle and because great improvements in instrumentation have facilitated measurement [see e.g., Pierotti and Rasmussen, 1977].

In this paper we turn to N_2O in water bodies strongly influenced by man. There have been several suggestions that N wastes in fresh water should be examined [Bolin and Arrhenius, 1977; Crutzen and Ehhalt, 1977; McElroy et al., 1977], and work is underway in several laboratories to determine through measurements whether such waters are significant N_2O sources. Preliminary 1971 data indicated that the Rhine River is one such source [Hahn and Junge, 1977].

Analytical Techniques and Instrumentation

Water samples were collected in 1 liter Nalgene flasks with screw top polypropylene caps. Laboratory tests showed the ability of these flasks to store undersaturated water and greatly N_2O-supersaturated samples for at least two weeks; analyses of samples were usually performed within two days. Parallel tests with a glass vessel capped by stainless steel with an "O" ring compression fitting gave results similar to the Nalgene flask tests. Through each lid a Swagelock bulkhead union was affixed with a Neoprene gasket seal. Each flask was filled with about 700 ml water sample and about 300 ml of ambient air, sealed, and the water temperature recorded. Equilibrium between the air and water sample was attained by shaking the flask vigorously for a total of 15 minutes spaced over a two-hour period. By observing the asymptotic approach of chromatographic responses to a time sequence of 10 ml air samples taken during this equilibration procedure from the head spaces of prepared test flasks we monitored the progress of equilibration. In these tests and after equilibration of actual samples an air sample was withdrawn by syringe through the stainless steel fitting mounted in the cap and was injected into a gas chromatograph. Each sample was then stored at room temperature, shaken, and re-analyzed one day later. Temperature-dependent N_2O solubilities used in data reduction were taken from Wilhelm et al. [1977].

Separation and detection of N_2O was by electron-capture gas chromatography. Our system is described in Cicerone et al. [1978]. For this study a 10 ft., 1/8" Porapak Q Column at 50°C was used; to cross-check for N_2O identification a similar 3/16" column of Molecular Sieve 5A at 275°C was employed. In several chlorine-addition tests the equilibrated sample gases were run through a cold trap at -79°C to remove other volatiles.

For surface water-to-air flux measurements we have used a 13 liter Pyrex carboy with its glass base removed by cutting. To the carboy neck we affixed a stainless plate and Nupro valve with an "O" ring compression fitting. In place at a water surface the assembly is suspended, partially submerged, by a large ring stand.

$HgCl_2$ was used as a sample preservative (0.5 to 2.0 ml, 3% solution) in all Detroit River and Lake Erie samples. Virtually no N_2O differences were seen between $HgCl_2$-treated and untreated samples.

Results and Discussion

Municipal water supplies appeared to invite examination for possible excesses of dissolved N_2O caused by man's activities. Table 1 shows results from 19 U.S. municipalities sampled between August and December, 1977. Numbers labeled "Saturation Factor" are the ratios of the amounts of N_2O dissolved in the water sample divided by the amount of N_2O that would have been dissolved in the sample if it were in equilibrium with ambient air. N_2O concentrations in ambient air were actually measured for several of the Ann Arbor entries in Table 1 but for other locations we assumed a concentration of 3.27×10^{-7} by volume. Based on the relatively small (one standard deviation ≃ 1.0%) spatial variability in tropospheric N_2O (seen by Goldan et al. [1978] and ourselves) as compared to the large entries

Paper number 8L0086.
0094-8276/78/038L-0086$02.00

Table 1. N_2O in Municipal Tap Water

City, Date (1977)	N_2O Saturation Factor[a]
Ann Arbor, MI, 11/17	22.4
New Orleans, LA, 11/10	8.8
Denver, CO, 11/10	18.7
Seattle, WA, 11/8	3.8
Ypsilanti, MI, 11/4	89.2
Houston, TX, 10/30	1.8
Dallas -Ft. Worth Airport, 10/28	24.4
San Francisco, CA, 10.27	3.4
Los Angeles, CA, 10.25	5.9
Ann Arbor, MI, 10/18	7.4
Pasadena, CA, 10/13	8.7
Huntsville, AL, 10/13	6.2
Boulder, CO, 10/13	3.3
Chicago, IL, 10/13	3.3
Lanham, MD, 9/28	28.0
Washington, DC, 9/26	7.4
New York, NY, 9/19	6.7
Pittsburgh, PA, 9/16	9.6
Ann Arbor, MI, 9/16	42.3
Syracuse, NY, 9/12	4.1
Brockton, MA, 9/11	8.1
Ann Arbor, MI, 9/8	11.4
Rochester, MI, 9/5	3.3
Ann Arbor, MI, 8/30	40.9
Ann Arbor, MI, 8/29	16.7
Ann Arbor, MI, 8/23	25.0

[a] An entry of 1.0 would mean that the water sample was in equilibrium with atmospheric N_2O. An entry of 3.3 means that the dissolved N_2O was 3.3 times more concentrated than in equilibrium with the atmosphere, etc.

of Table 1, this assumption is of little concern. The smallest and largest N_2O concentrations in Table 1, are 1.8 and 89.2 times the value in equilibrium with the atmosphere, respectively. Seven samples from Ann Arbor range from 7 to 42. If one assumes a saturation factor of 25 characterizes the entire U.S. and that all of the dissolved N_2O escapes to the atmosphere, one deduces an annual source of the order of 10^3 metric tons from U.S. water usage; this flux is too small to be significant globally [cf., Liu et al., 1977].

Although we extrapolate the results of Table 1 to a relatively insignificant annual release of N_2O the finding of N_2O supersaturations in municipal tap water is still interesting for several reasons. First, a question is raised: what process produces N_2O in water treatment (presumably from NH_4^+, NO_3^- and possibly organic N)? Second, those scientists who perform soil studies that involve adding water to soils should be alerted of this possible source of error from the use of municipal water. Third, it is possible that N_2O in municipal water will be strongly correlated with NH_4^+ and NO_3^- in the intake water and that seasonal and regional variations in stream N contents would be so indicated.

Although municipal water treatment procedures are not uniform we decided to seek the key step(s) in the production of N_2O at the Ann Arbor Water Treatment Plant. We sampled the water at each step in the treatment sequence beginning with unadulterated river water. Two principal results emerged: (i) the addition of chlorine causes immediate and large N_2O increases, and (ii) N_2O concentrations increase while in reservoir storage. On two separate occasions we found the intake water (Huron River) to be within 5% of equilibrium and the concentrations rose by at least 500% after chlorine addition. While NH_4^+ and NO_3^- were not measured simultaneously we are now studying mechanisms to explain N_2O formation from NH_4^+. We have added chlorine to river water in laboratory tests and have found more evolved N_2O in those water samples to which the most chlorine was added, and no excess N_2O from control samples to which no chlorine was added. When the apparent chlorine demand was approached smaller increases were seen. Adding chlorine to distilled water gave virtually no N_2O. Evolution of N_2O is not unheard of in the literature of NH_4^+ oxidation by hypohalites. Further experiments are underway and mechanisms involving chlorine intermediates are being sought.

Two rivers in southeastern Michigan also appear to be strongly influenced by man's activities with respect to N_2O. Figure 1 shows a

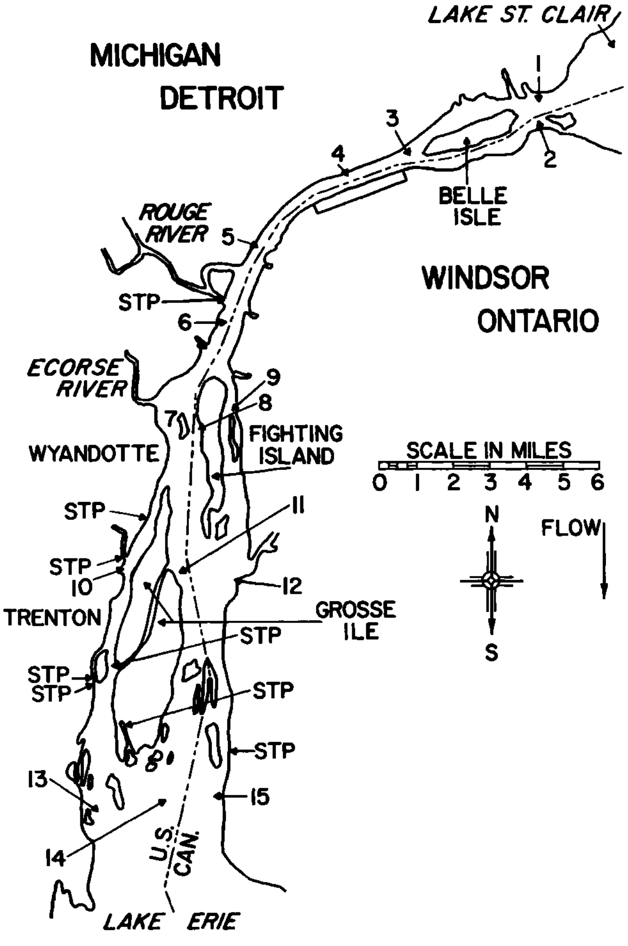

Figure 1. Sketch of the Detroit River with locations of sewage treatment plants (STP) and fifteen stations at which surface waters were sampled on October 4, 1977.

sketch of the Detroit River. Superimposed numbers represent 15 stations at which we sampled surface water (0.5 m) on October 4, 1977 and the letters "STP" indicate locations of sewage treatment plant discharges. N_2O concentrations at these 15 stations are shown in Table 2 as ratios of measured values to the equilibrium values. N_2O excesses at Stations 6, 7, 10, 11, 13 and 14 appear closely related to sewage treatment plant discharges. More compelling data from the Huron River are also in Table 2. Samples were gathered at 13 stations along the river. Station 1 was along shore 2 km upstream from the first municipal STP. Stations 2, 3, 4, spanned the river channel about 1 km upstream from the first STP. Station 5 was in the effluent stream of the first STP. Station 8 was 8 km downstream, southeast of Ypsilanti, Michigan, about 0.7 km upstream from the second municipal STP. Stations 9, 10 and 11 were within 15 m of this plant's discharge pipe, just into the northern basin of Ford Lake. Thus, the N_2O saturation factor was about unity upstream from the first STP, over 100 in the effluent stream and 13 downstream 1.1 km. Downstream from the second STP (which discharges into the north basin of Ford Lake) five samples across the north basin (area: 1 km^2) gave almost identical saturation factors of 5.4. Three more samples from November and December, 1977 from the lake's north basin and main basin (area: 3.5 km^2) had saturation factors from 3.5 to 5.7.

At its southeastern end Ford Lake feeds the continuation of the Huron River which flows to Erie. On September 19 we cruised across the western basin of L. Erie (directly south of the Detroit River, Figure 1) and gathered samples at seven stations, both at 1m below the surface and 1m above lake bottom. N_2O saturation factors ranged from 1.02 to 1.45; the highest values were found nearest the Detroit and Maumee River mouths. By contrast, three samples from L. Michigan (1 km off eastern shore, 9-21-77, 0 to 14 m depths) gave 1.00, 1.02 and 0.98 values. A fourth sample from the nearby Grand River gave 1.70. Four samples from L. Huron (9-19-77, surface on northern and western shore) gave values of 1.16, 0.99, 0.98 and 1.00.

From the Huron River and Detroit River data it seems clear that a portion of man's N wastes are being converted into N_2O either in the treatment process (possibly through chlorination) or in the effluent stream or both. Also, the supersaturated river and lake surface waters clearly imply an N_2O flux to the atmosphere. To relate these supersaturations to fluxes we have begun to measure fluxes by observing the N_2O increase after 30 and 60 minutes in a glass collector (see previous section) suspended over test waters. Over Ford Lake on Nov. 8, an extremely calm day with mirror-like surface waters, we measured a linear N_2O increase in our collector that implied an N_2O flux of $7 \times 10^9 \text{cm}^{-2}\text{sec}^{-1}$ from 475% supersaturated surface water. On Oct. 7 we found a flux of $2.7 \times 10^{10} \text{cm}^{-2}\text{sec}^{-1}$ from the Huron River surface when the surface was fairly calm (small ripples) and was supersaturated by 710%. A constant flux of $10^{10} \text{cm}^{-2}\text{sec}^{-1}$ through a 5 km^2 surface would yield about 0.7 metric tons N as N_2O annually. Multiplying this result by the ratio of U.S. population using municipal sewage treatment to the population contributing to the Huron River, Ford Lake area we would extrapolate to a corresponding U.S. annual emission of 350 metric tons N. For $3 \times 10^{10} \text{cm}^{-2}\text{sec}^{-1}$ the extrapolation yields 1000 metric tons N/yr, or 10^{-4} x the U.S. N fertilizer consumption. Clearly, many more data are needed for different regions, seasons, etc. and the conclusion of this extrapolation could easily change. Experiments are being conducted for various surface conditions to establish a range of attainable fluxes, but it is already clear experimentally that some of the N_2O produced in water does escape into the air.

Conclusion

The extent to which the nitrogen wastes of man and animals are converted into atmospheric N_2O is an important question given the roles of atmospheric N_2O and the accelerating anthropogenic N fixation rates in combustion and fertilizer production. Our findings of N_2O supersaturations in municipal drinking water and in water bodies near sewage treatment plants establish that conversion of soluble fixed N into N_2O takes place in these waters and/or in the treatment processes. Our experiments suggest that chlorination causes much of the N_2O production.

To deduce the absolute, annual average N_2O flux and to relate it to the yearly N input will require a longer series of measurements. A combination of direct flux measurements such as those reported here and indirect flux deductions based on simple diffusion models of the water-air interface will be required. We intend to continue our efforts to determine the attainable range of fluxes over the domain of surface conditions and supersaturations of nearby water bodies by systematic, direct measurements. Extrapolation to global rates of N_2O release from fresh waters will be difficult because it appears from our data that the relatively smaller, more polluted water bodies (such as rivers

Table 2. N_2O Saturation Factors (see Table 1) for water samples from sites on the Detroit River (locations: see Figure 1), The Huron River (locations: see text), and Lake Erie (locations: at seven stations spanning the western basin).

Station No.	Detroit River (10-04-77) (Figure 1)	Huron River (11-04-77)	Lake Erie (9-19-77)
1	1.01	1.04	1m: 1.35
2	1.04	0.99	9m: 1.43
3	1.08	1.00	1m: 1.15
4	1.01	1.01	4m: 1.07
5	0.98	108.00	1m: 1.36
6	6.04	13.80	6m: 1.40
7	2.17	13.30	1m: 1.13
8	1.04	5.38	8m: 1.13
9	1.12	5.38	1m: 1.06
10	11.01	5.37	9m: 1.11
11	2.09	5.06	1m: 1.11
12	1.15	5.57	10m: 1.08
13	4.77	5.51	1m: 1.09
14	1.45		9m: 1.07
15	1.10		

that receive N wastes) might contribute a significant fraction of the total N_2O flux. In addition, it should be instructive to continue exploratory measurements to identify other N_2O sources and sinks in water bodies. For example, several lake sediment samples consumed ambient N_2O in laboratory tests and four wells we have tested showed dissolved N_2O to be 0.14 to 0.19 of the equilibrium concentration.

Acknowledgements. We thank H. Mieske and J. Amerman (Ann Arbor Water Treatment Plant), Chas. Herdendorf and J. Zapatowski (Center for Lake Erie Area Research, Ohio State University), N. Thomas and E. McCue (U.S. EPA Large Lake Research Station), D. Rea, G. Meadows, and D. Stedman (University of Michigan) for assistance in gathering samples and for useful discussions. Numerous intrepid colleagues in our laboratory gathered municipal water samples during travels. Supported by NSF Atmospheric Research Section and NASA Upper Atmosphere Research Program.

References

Bolin, B., and E. Arrhenius (eds.), Nitrogen - An essential life factor and a growing environmental hazard, AMBIO, 6, 96-105, 1977.

Cicerone, R., J. Shetter, D. Stedman, T. Kelly, and S. Liu, Atmospheric N_2O: Measurements to determine its sources, sinks and variations, J. Geophys. Res., 83, in press, 1978.

Crutzen, P. J., Ozone production rates in an oxygen-hydrogen-nitrogen atmosphere, J. Geophys. Res., 76, 7311-7327, 1971.

Crutzen, P., Upper limits on atmospheric ozone reductions following increased application of fixed nitrogen to the soil, Geophys. Res. Lett., 3, 169-172, 1976.

Crutzen, P. and D. Ehhalt, Effects of nitrogen fertilizers and combustion on the stratospheric ozone layer, AMBIO, 6, 112-117, 1977.

Goldan, P., Y. Bush, F. Fehsenfeld, D. Albritton, P. Crutzen, A. Schmeltekopf, and E. Ferguson, Tropospheric N_2O mixing ratio measurements, J. Geophys. Res., 83, in press, 1978.

Hahn, J., and C. Junge, Atmospheric nitrous oxide: A critical review, Z. Naturforsch, 32a, 190-214, 1977.

Liu, S., R. Cicerone, T. Donahue and W. Chameides, Limitation of fertilizer-induced ozone reduction by the long lifetime of the reservoir of fixed nitrogen, Geophys. Res. Lett., 3, 157-160, 1976.

Liu, S., R. Cicerone, T. Donahue and W. Chameides, Sources and sinks of atmospheric N_2O and the possible ozone reduction due to industrial fixed nitrogen fertilizers, TELLUS, 29, 251-263, 1977.

McElroy, M., J. Elkins, S. Wofsy and Y. Yung, Sources and sinks for atmospheric N_2O, Revs. Geophys. Space Phys., 14, 143-150, 1976.

McElroy, M., S. Wofsy and Y. Yung, The nitrogen cycle: Perturbations due to man and their impact on atmospheric N_2O and O_3, Phil. Trans. Roy Soc., 277B, 159-181, 1977.

Pierotti, D., and R. Rasmussen, Combustion as a source of nitrous oxide in the atmosphere, Geophys. Res. Lett., 2, 265-267, 1976.

Pierotti, D., and R. Rasmussen, The atmospheric distribution of nitrous oxide, J. Geophys. Res., 82, 5823-5832, 1977.

Sze, N., and H. Rice, Nitrogen cycle factors contributing to N_2O production from fertilizers, Geophys. Res. Lett., 3, 343-346, 1976.

Weiss, R. F., and H. Craig, Production of atmospheric N_2O by combustion, Geophys. Res. Lett., 3, 751-753, 1976.

Wilhelm, E., R. Battino and R. Wilcox, Low-pressure solubility of gases in liquid water, Chem. Revs., 77, 219-262, 1977.

Yung, Y., W. Wang and A. Lacis, Greenhouse effect due to atmospheric nitrous oxide, Geophys. Res. Lett., 3, 619-621, 1976.

(Received December 20, 1977;
accepted January 23, 1978.)