UC Irvine

UC Irvine Previously Published Works

Title

ATMOSPHERIC N₂O: MEASUREMENTS TO DETERMINE ITS SOURCES, SINKS, AND VARIATIONS.

Permalink

<https://escholarship.org/uc/item/1sk4t8gj>

Journal

J Geophys Res, 83(C6)

ISSN

0148-0227

Authors

Cicerone, RJ
Shetter, JD
Kelly, TJ
[et al.](#)

Publication Date

1978

DOI

10.1029/JC083iC06p03042

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Atmospheric N₂O: Measurements to Determine Its Sources, Sinks, and Variations

R. J. CICERONE, J. D. SHETTER, D. H. STEDMAN, T. J. KELLY, AND S. C. LIU

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

Measurements of atmospheric N₂O concentrations in and around Ann Arbor, Michigan, between August 1976 and September 1977 yielded 329.5 ppb (parts per billion) (mole fraction in whole air samples) as the average with a standard deviation of 3.3 ppb. No seasonal or overall trend is discernible. Small, marginally significant diurnal variations of N₂O concentrations in the lowest 0.5 m of atmosphere can be seen in our data. Gas collectors applied to soils near our laboratory provided evidence that soils can consume atmospheric N₂O under some conditions. Soils were seen to be N₂O sources more often than sinks. Stronger source activity was evident in compost piles. Exhaust samples taken from several conventional vehicles showed less than ambient N₂O concentrations, while catalytic converter equipped autos produce N₂O. Samples of steaming volcanic vent air from Hawaii indicate that volcanoes are probably a source of atmospheric N₂O, although emissions at the Sulphur Bank contain much less than ambient values of N₂O. All measurements were made by electron capture-gas chromatography; techniques and equipment are described.

1. INTRODUCTION

Nitrous oxide (N₂O) is one of the more interesting gases in the earth's atmosphere. It is prominent in the aeronomy of the stratosphere through chemical reaction (R1b),

which is thought to be the dominant source of stratospheric nitrogen oxides [Crutzen, 1971], even though only a few percent of atmospheric N₂O undergoes (R1b). It is also involved in the cycles of nutrient nitrogen in soils and water bodies as a product of denitrification and other nitrate-reducing processes (see the review by Payne [1973]); nitrous oxide from these origins can escape to the atmosphere. Thus gaseous N₂O can serve as an indicator of microbiological activity. Indeed, there is 10¹⁸ more N₂O in the atmosphere than would exist in an abiological thermodynamic equilibrium atmosphere [Lovelock and Margulis, 1974]. Also, the fact that N₂O is produced in certain combustion processes [Pierotti and Rasmussen, 1976; Weiss and Craig, 1976] makes it a potential tracer of combustion plumes. On a larger scale, the vertical and latitudinal profiles of N₂O can serve as estimators of global circulation patterns and rates [Schmelttekopf et al., 1977]. Also, if N₂O levels ever undergo large increases, there could be a significant trapping of outgoing planetary radiation [Wang et al., 1976].

Because of (R1b) and subsequent chemical reactions of NO and NO₂ that catalytically destroy O₃ in the middle and high stratosphere, there is a basis for concern over any biospheric activities that might alter global N₂O levels. In particular, there is growing interest in the question of how much effect man's increased nitrogen fixation and combustion rates will have on atmospheric N₂O [Crutzen, 1974, 1976; McElroy et al., 1976; Liu et al., 1976; Sze and Rice, 1976; Weiss and Craig, 1976; McElroy, 1977]. These papers and recent reviews by Hahn and Junge [1977], McElroy et al. [1977], and Liu et al. [1977] have examined what is known about release rates of N₂O, its atmospheric chemistry, and possible oceanic sources and sinks. It is generally agreed that microbial denitrification is an important and possibly dominant source of atmospheric N₂O, that the only known sink is photolysis by ultraviolet

light in the stratosphere [Bates and Hays, 1967; Johnston and Selwyn, 1975; Stedman et al., 1976], and that this sink may consume only a fraction of all the N₂O released at ground level. Recent studies by Blackmer and Bremner [1976] imply that some soils under certain conditions can remove N₂O from the atmosphere at a rate as yet undetermined.

Similarly, without accurate knowledge of annual N₂O source and sink rates there is no consensus about the atmospheric residence time of N₂O. An independent method to estimate residence times of atmospheric gases due to Junge [1974] has been applied to N₂O statistics; an approximate 5-year residence time was inferred by Junge. While the idea of the Junge approach is elegant, the actual result for N₂O is not necessarily valid, for at least two reasons. (1) If the uniform source, uniform sink assumption is not true, i.e., if the measurements are taken in the proximity of local sources or sinks, the variability of the data will be relatively larger than it would be if local effects were negligible [Hahn, 1975]. This is no small problem in the case of N₂O because we are not yet sure of which source is dominant or even of the number and location of its extant sources. (2) Also, it must be true that the observed variance σ_o^2 must equal the sum of the actual variance σ^2 and the variance σ_A^2 introduced by the analytical technique and instruments used in the measurements: $\sigma_o^2 = \sigma^2 + \sigma_A^2$. The fact that very recent N₂O measurements by electron capture-gas chromatography (EC-GC) are more precise than those available before 1975 has been discussed by Pierotti and Rasmussen [1977] along with the accompanying conclusion, from reapplication of Junge's [1974] reasoning, that the atmospheric residence time of N₂O may be considerably longer than 25 years.

Thus there are major gaps in our understanding of N₂O in the natural atmosphere. With such a lack of knowledge of the sources, sinks, and residence time of atmospheric N₂O it is not possible to evaluate closely the atmospheric effects of increased fertilizer usage or even the effects of N₂O added in well-known amounts from other human activities such as combustion.

The N₂O measurements reported here address the questions just mentioned. Specifically, we have performed some exploratory studies to try to identify sources of atmospheric N₂O and to begin to estimate the strengths of these sources. We have searched for N₂O emissions in several nitrogen-rich environments; automobile exhaust, air from cattle feedlots, compost

TABLE 1. Gas Chromatographic Instrumentation and Conditions Used in GC-EC Measurements of N₂O

Configuration	Gas Chromatograph	Column	L, m	T _c , °C	Detector		T _D , °C	Carrier Gas	Flow, ml/min	Backflushing?
					Foil	Radiation, mCi				
A	Perkin Elmer 3920	Porapak Q	3	50	⁶³ Ni	10	350	UHP N ₂	20	yes
B	Perkin Elmer 3920	Porasil B	3	50	⁶³ Ni	10	350	95% Ar, 5% CH ₄	30	yes
C*	Carle 111 (rebuilt)	Molesieve 5A	1.6	250	⁶³ Ni	2	250	95% Ar, 5% CH ₄	3	no
		Porapak Q	0.1	33						

Sample loops are filled to atmospheric pressure; sample loop volumes are 1 ml in most studies, but 5-ml loops are used occasionally. UHP is ultrahigh purity.

*Two-column (Molesieve 5A and Porapak Q) tandem system.

piles, fertilized soils, and natural soils and volcanoes. Results of these source identification studies are presented in section 3. In the course of our soil gas emission studies we have also found some evidence of N₂O consumption by soils. In less exploratory work we have regularly measured N₂O ambient concentrations at several locations around Ann Arbor, Michigan, and we report here the results of 1 year of monitoring. We have also sought evidence of diurnal variations of N₂O near ground level. We are paying attention both to absolute values and calibrations and to relative variations of N₂O. Results are presented in section 3 and discussed in section 4. Our instruments and methods are described in section 2.

2. INSTRUMENTATION AND TECHNIQUES

In this section we describe the instrumentation and methods that we have used to gather and analyze air samples for N₂O. The basic principles and methods of gas chromatographic separation and electron capture detection of N₂O have been discussed by *Wentworth and Freeman* [1973] and by *Rasmussen et al.* [1976]. Table 1 lists the chromatographic equipment and conditions that we have employed. As is mentioned later, in March 1977 we adopted the Porapak Q column and the conditions listed in the first row of Table 1; this led to significantly better precision than had been achieved earlier with Porasil. One reason for this improvement is that CO₂ and N₂O are better separated by Porapak Q than by Porasil B, at least for the conditions listed. Figure 1 shows a typical chromatogram of rural Ann Arbor air (~325 ppb (parts per billion) N₂O; ~330 ppm (parts per million) CO₂) with chromatographic configuration A (see Table 1). The CO₂ peak, negative in this case, is well separated from the N₂O; there is a flat base line (almost 30 s) between the peaks. Configuration C, two columns in series suggested by R. F. Weiss, separates CO₂ and N₂O even better. When volcanic air samples were analyzed (see section 3), the high CO₂ concentrations (≈1%) made it necessary to

lower the column temperature to 40°C for configuration A. Although it is not completely germane to the goal of the present paper, the sign of the CO₂ response in EC-GC systems appears to be determined capriciously, and we note that further investigations are needed. We find a positive CO₂ peak with configuration C, and P. D. Goldan (private communication, 1977) finds a negative peak with one GC-EC system and a positive peak with another system with the same carrier gas. Also, *Lovelock* [1974] reported that system sensitivity to N₂O was enhanced by CO₂ in the mixture. Detector geometry and surface condition, carrier gas impurities, and ion-molecule reactions in the system [see *Parkes*, 1972] all may be involved, and chromatographic interferences are possible.

Absolute calibration of the GC-EC system was performed by diluting pure N₂O with pretested zero-grade air; commercial calibration mixtures were avoided. Two distinct and independent dilution methods were devised. One is a multi-staged feedback flowing dilution system; the other uses an N₂O permeation tube which injects a small calibrated flow of pure N₂O into a much larger (measured) diluent flow stream. The permeation tube flow is not measured gravimetrically as is common elsewhere [e.g., *Dietz et al.*, 1974] but is measured instead by scanning pressure in a microvolume differential pressure transducer. Both the feedback flow and the permeation tube dilution systems can be used easily between about 50 ppb and 20 ppm (concentrations by volume) of N₂O or 1000 times smaller concentrations of CF₂Cl₂. The permeation tube dilution system easily generated 100–1000 ppb N₂O and 100 ppt (parts per trillion) to 2 ppb CF₂Cl₂. These flow dilution systems were used to prepare flows with known concentrations of N₂O, and the GC-EC response to each concentration was measured. Figure 2 shows one such set of results. Between the various N₂O flows, chromatograms of the standard tank to be calibrated were obtained. In this way a calibration curve was constructed, and a secondary standard (described below) was calibrated. By generating a calibration

Fig. 1. Typical chromatogram (electron capture detector response versus time) of ambient air with chromatographic configuration A of Table 1. The N₂O peak appears at 3.33 min. The negative peak preceding N₂O is due to CO₂.

Fig. 2. Results of a feedback flow system calibration study: GC-EC response versus N₂O concentration provided by diluting pure N₂O. One standard deviation of the data at each point equals the radius of that point. Each internal transfer standard (STD) is calibrated by repeatedly performing scans like this one.

curve and mapping out the system behavior over a range of concentrations, e.g., 0–600 ppb, one tests the system for linearity and demonstrates that there are no spurious, nonzero signals at zero N₂O concentration. The radii of the data points in Figure 2 represent actual standard deviations of each data set. High-precision work like this obviously requires a stable, sensitive GC-EC, pure carrier gas (and carrier stream purifiers), and great care. Occasionally, calibration runs did not yield data points to fit a line as well as is shown in Figure 2 or with a zero intercept. To date, we have gathered seven high-quality calibration curves like Figure 2, four with the feedback flow and three with the (independent) permeation tube flow dilution system. The agreement between the concentrations assigned to the standard tank under study in these seven calibrations can be measured by the statistics of seven independent trials. Their mean value was 383 ppb, and 1 standard deviation was 10 ppb. Thus we believe that our absolute N₂O values are known to $\pm 5.2\%$ with 95% confidence. In addition to these absolute calibration studies we have traded two samples each with P. D. Goldan (National Oceanic and Atmospheric Administration (NOAA)) and J. Krasnec and L. Heidt (National Center for Atmospheric Research (NCAR)). We found our values to be 1% higher than NCAR's and almost 2% higher than NOAA's. More extensive intercalibration studies are underway because of the great desirability of directly inter-comparing data from many laboratories, some of which disagree by as much as 15% (see the discussion by Pierotti and Rasmussen [1977]).

The N₂O reference standard mixtures mentioned above are stored in pressurized cylinders and occasionally checked by absolute calibration. One standard was prepared by introducing N₂O into an evacuated commercial (~50 l) gas cylinder that had previously contained ultrahigh-purity He. The tank was then pressurized to 1500 psi (10⁷ Pa) with zero-grade air. During the process we also arranged to obtain near-ambient amounts of CO₂, CF₂Cl₂, and CFCl₃. A second in-

ternal reference standard tank was prepared similarly in a 1-l electropolished stainless steel cylinder at 1000 psi (6.9×10^6 Pa). These two internal standards were prepared 6 months apart, and since the preparation of the second one, they have been measured in ratio for 5 months with no detectable change. Thus we believe that our reference standards have been stable so far but also that longer storage times will require continued checking and possibly more elaborate preparations. The ability of our rather rapid calibration techniques described above (and more fully by Stedman *et al.* [1977]) to perform frequent tests is advantageous in such work.

Our sample flasks are made from no. 316 stainless steel and are extruded with a center weld. Nupro bellows-seal stainless valves with stainless seats are used through $\frac{1}{8}$ -in. (1-cm) stainless tubing, and the flask volume is 2.7 l. The flasks were first electropolished and then rinsed with distilled water followed by absolute ethanol. The tubing and valves were then welded in place, and the assembly was attached to a high-vacuum system ($\sim 10^{-9}$ torr) and baked at 400°C. After cooling and backfilling with O₂ it was rebaked at 200°C in an attempt to place a uniform oxide coating on the interior. Finally, the flask was vacuum-baked at 350°C. Schmeltekopf *et al.* [1976] have pointed out that this type of procedure actually may activate surfaces to chlorocarbons, but our sample flasks have shown themselves to be stable for N₂O, CF₂Cl₂, and CFCl₃ for tropospheric sampling, at least after their initial usage. Repeated exposure to tropospheric air, especially H₂O, probably vitiates many problems which arise in stratospheric sampling. Also, our sampling procedure, to pressurize the flasks to about 35 psi (2.4×10^6 Pa) with a stainless steel bellows pump, further increases the ratio of surface-active molecules to surface sites. Before the flask is filled with pressurized sample, the flask is evacuated to 10 μ on a cryopump.

Actual data analysis consists of measuring the GC-EC response to a sample and then the response to our secondary (or transfer) standards, which are calibrated as described above. The GC sample loop is filled to the prevailing atmospheric pressure after being thoroughly flushed with each sample to be injected. Day-to-day variations in atmospheric pressure are of no concern because of this ratio method. In practice, GC response to our secondary standard is measured before and after each sample is analyzed.

Both peak height and peak area analyses have been performed on the data. As is shown later, our ambient N₂O data improved in precision in mid-March 1977, at which time we adopted an electronic peak integrator (HP 3380A) and a Porapak Q column. Clearly higher precision is possible by using electronic digital integration than by measuring peaks from a chart record.

3. N₂O OBSERVATIONS

a. Exploratory Studies:

N₂O Sources and Sinks

In this section we report N₂O measurements designed to identify sources and sinks of N₂O. In several cases we are able to deduce semiquantitative source strengths; in other instances, only qualitative (but definite) identifications are possible. The usefulness of simply identifying N₂O sources and sinks should not be underestimated, given the need to optimize N₂O monitoring sites and to evaluate assumptions of uniform sources and uniform sinks in Junge's [1974] approach to interpreting N₂O variability.

Combustion processes are a source of atmospheric N₂O

TABLE 2. N₂O Concentrations in Automobile Exhaust

Source of Sample	N ₂ O Concentration	Remarks
Detroit-Canada Tunnel	341 ppb	Air from exhaust ducts.
New passenger car with diesel engine	about 350 ppb	Previously used exhaust bags led to less than ideal results; several spurious peaks cluttered the chromatograms.
New vehicle with 350-in. ³ (5.7-l) engine, oxidation catalytic converter, and EGR	6–10 ppm	Congested highway simulation.
New vehicle with 225-in. ³ (3.7-l) engine and monolith oxidation catalytic converter	5–12 ppm	EPA 'highway' and 'sulfate' cycles.
New vehicle with 350-in. ³ (5.7-l) engine, oxidation catalytic converter, and EGR	8–16 ppm	Cold start.
	4–6 ppm	Hot, transient LA-4 test.
	7–15 ppm	Hot start.
New vehicle with 1.6-l, four-cylinder engine, oxidation catalytic converter, and EGR	9–14 ppm	Cold start.
	4–6 ppm	Hot, transient LA-4 test.
	8–12 ppm	Hot start.
Used vehicle, 1971 model, six cylinders, no catalytic converter	<300 ppb	Car was idling.
Used vehicle, 1961 model, V-8, no catalytic converter	220 ppb	LA-4 test average.

All samples from the new vehicles were gathered from simulation tests on properly maintained test vehicles.

[Pierotti and Rasmussen, 1976; Weiss and Craig, 1976]. Following Pierotti and Rasmussen [1976], we have detected N₂O in automobile exhaust. Our results in Table 2 show even more N₂O in the exhaust of catalytic converter equipped vehicles than Pierotti and Rasmussen [1976] reported. Because of the proximity and cooperation of the U.S. Environmental Protection Agency (EPA) Auto Emissions Laboratory in Ann Arbor we were able to test three distinct catalyst engines and a new diesel vehicle under a variety of driving conditions (see Table 2). From the EPA test facility we obtained Tedlar bags fitted with Nupro valves filled with diluted ($\times 15$) exhaust and control bags of background air. Each bag was analyzed within hours; stability tests of N₂O in the bags assured us that tests after 24 hours were still acceptable. Similarly, we found that conventional exhaust systems, a 1971 model and a 1961 model, emit air with a small N₂O deficit. In a related study we found 341 ppb N₂O in the air ducts that move air from the Detroit-Canada Tunnel (two lanes, 1.5 km) during moderate traffic. Similarly, we sampled air from busy city streets in stagnant air summer conditions and in a concrete parking structure in Ann Arbor. In several samples we found 330–350 ppb; on one occasion (a main street at 5:00 P.M. Friday) we found about 8 ppm N₂O, almost pure catalyst exhaust. Two points should be noted. First, the range of N₂O concentrations in the undiluted exhaust of catalyst-equipped vehicles as shown in Table 2 is far lower than the possible upper limits demonstrated by Otto and Shelef [1972]. Second, while it is difficult to convert these data into total U.S. or global N₂O annual emissions because (1) not all vehicles are catalyst equipped (the trend is up) and (2) it is likely that under road wear the exhaust systems will deviate from initial conditions, our extrapolations indicate that only 10⁶ metric tons of N as N₂O would be emitted annually from all U.S. car traffic. Finally, we note that tests of the 'three-way' catalyst might be interesting because it attempts to reduce NO_x emission further than catalysts tested here and it might become widely adopted in the future.

In another group of exploratory studies we have attempted to test the source/sink capacity of soils by measuring the N₂O inside glass funnels placed (inverted) over test areas. The funnels are right circular cones with syringe guides mounted in

rubber stoppers in elongated glass necks; their dimensions are as follows: radius, 12 cm; height, 20 cm; and volume, about 4 l. Each inverted funnel was placed so that the funnel rim was in a groove in the soil; moderately good seals were obtained in this way. We have measured N₂O in these funnel gas collectors on about 60 days during August, September, October, and November 1976 and May, June, July, August, and September 1977. Samples were taken immediately after placing each funnel and at 9:00 A.M. and 4:30 P.M. local time for 2 or more days afterward. Each sample was drawn through the mounted syringe guide into a 30-ml polyethylene syringe with a butyl rubber stopper and was then analyzed. These syringes proved, through storage tests with zero-grade air and with N₂O-rich mixtures, to give results reliable to about 5% if samples were stored for less than 24 hours.

We have found indications of both soil source and soil sink activity for N₂O. In gases collected from funnels placed over a well-maintained grassy lawn outside our laboratory we have measured concentrations as high as 7 times ambient, about 2 ppm. Generally, after placing the funnels an increase in N₂O concentration occurred. After 2 or 3 days it reached 700–1000 ppb, where it would stay for the duration of the experiment (3–15 days). Irregular, small diurnal variations were occasionally observed by additional sampling at sunrise and sunset; diurnal variations in CO₂ concentrations (measured from the CO₂

TABLE 3. N₂O Concentrations in Samples Taken From Volcanic Steam Vents on Island of Hawaii in June 1977

Location of Vent	CO ₂ , ppm	N ₂ O, ppb
Cinder cone near Iilewa	500 (E)	450
Sulphur Bank	540,000 (MS)	118
Off Crater Rim Road	13,600 (MS)	332
Puhimau	4,400 (MS)	341
1974 eruption site near Halemaumau	16,000 (MS)	329

Samples were drawn from open vents, so some ambient, non-volcanic air was included in the sample. CO₂ concentrations labeled E were estimated from GC-EC peak height; those labeled MS were determined by mass spectroscopy.

Fig. 3. N₂O concentration (mole fraction of N₂O in whole air sample) measured in and around Ann Arbor, Michigan, from August 1976 to September 1977. Standard deviations of repeated analysis of each sample are shown as vertical bars $\pm 1\sigma$ above and below points.

chromatographic peak; see Figure 1) were observed to be much larger and more regular. In most cases, CO₂ would attain a peak in the early morning hours and return to normal levels by late afternoon. Perhaps the most interesting behavior was noted on 3 days in May, 8 days in June, and 3 days in July 1977. On these days, N₂O was noted to decrease in the funnels from its initial value (327 ppb) to about 150 ppb in funnels placed in very wet, mostly sun-shaded grassy areas. This behavior was repeatable; removing and cleaning the funnels and placing them in new spots led to identical results in four separate experiments between mid-May and mid-July 1977. CO₂ was seen to peak in early morning and to decrease to ambient values by midafternoon each day. These tests were conducted with two or three funnel collectors side by side. The redundancy in our design and the marked contrast to simultaneous test results from drier, sunnier test spots only 25 m away lead us to suggest that soils can consume atmospheric N₂O as well as produce it. From these exploratory studies it appears that season, soil moisture, temperature, and many other factors can regulate this possible sink activity. Clearly, our experiments altered the local environment in and under our funnel collectors; CO₂ concentrations rose and fell, and the glass served as a heat greenhouse. On the positive side, however, we did not perturb the subsurface temperature, and our small (625 cm²) covered area was in contact below the surface with a quasi-infinite earth. Also, because our experiments show the ability of soils to consume N₂O from air containing only normal (329 ppb) N₂O concentrations, they supplement the much more elegant and controlled experiments of *Blackmer and Bremner* [1976]. These authors, while the first to show that soils can consume N₂O, employed initial N₂O concentrations in the 10⁻¹ range. Similar funnel collection studies in an oak forest with natural ground cover (mostly leaves) have not yet shown any sink activity.

We have also used our funnel collection device at organic compost piles containing vegetation and mixed animal manure. There we found more rapid increases of N₂O, usually 1000 ppb/h, if the collector was over a firm, crusted spot. On new compost or on older piles where we intentionally punctured the surface we measured even more rapid increases: up to 20 ppm in 1 hour with little further increase.

A few more exploratory measurements that have provided

indications of N₂O source activity have been performed. First, as was noted above, new or punctured compost piles emit N₂O more rapidly than those with a well-formed crust. When we gathered an air sample from the air a few centimeters away from a new, loose organic compost pile in an open field, we found an N₂O concentration of 3.6 ppm. Similarly, about 50 cm from a crusted dung heap we found 345 ppb, a significantly higher amount than the 327 ppb 25 m away.

To investigate the possibility that volcanoes can produce N₂O, we gathered air samples at five locations on the island of Hawaii; at each site, active steam venting was underway, but no molten lava was flowing or exposed. Table 3 displays the results. A substantial excess of N₂O over ambient (327 ppb) levels appeared in the air gathered near Iilewa, indicating an N₂O source. A smaller excess was seen at Puhimau. At the Sulphur Bank we saw a very small N₂O concentration, 118 ppb. At all sites, air was drawn from steaming vents through a 1-m stainless tube. Excessive heat bursts and wind gusts caused us to jerk the tube from the vents several times during sampling; thus ambient, nonvolcanic air was doubtlessly included in the samples. Near-ambient N₂O values from the Crater Rim Road vent and the 1974 eruption site vents could represent entrained ambient air. As is true of the other results reported in this section, N₂O in the volcanic samples was identified by its retention time on chromatographic columns of configurations A, B, and C of Table 1.

The CO₂ concentrations in Table 3 represent the mole fraction of CO₂ in the pressurized sample analyzed at room temperature. Appreciable amounts of H₂O present as steam in the volcanic vent condensed in our sample flasks. Thus, for example, the 54% CO₂ in the Sulphur Bank samples is an overestimate of the CO₂ concentration in the venting gas, because almost all the water vapor present during sample gathering was condensed during analysis.

Finally, we attempted to detect N₂O in small electrostatic discharges. No N₂O was seen in experiments conducted to measure the production rate of NO in such discharges (see the paper by *Chameides et al.* [1977] for experimental details).

b. Ambient N₂O Concentrations and Variations

Since August 1976 we have been measuring N₂O concentrations in air samples taken at several locations in and near Ann Arbor, Michigan. Results of these measurements are shown in Figure 3 and Table 4. The North Lake site is rural, located about 40 km northwest of Ann Arbor. North Lake is about 2 km in diameter, and about 35 houses surround it. Radrick Farms is a private golf course adjacent to a large botanical garden about 10 km east of Ann Arbor. Space Physics Research Laboratory (SPRL), our laboratory, is about 5 km northeast of central Ann Arbor. Most of the air samples were taken in pairs at North Lake and at Radrick Farms on the same day, approximately 2 weeks apart. Table 4 has 56 entries, all of which are shown in Figure 3 except for the December 26 and 31, 1976, and the June 18, 1977, points from Hawaii. The average concentration of N₂O from some 55 points of Table 4 (the December 26 Hawaii point is omitted) is 330.5 ppb; the standard deviation is 4.59 ppb. Five other data points can be excluded: March 3 and 11 from North Lake and April 21, June 10, and September 8 from Radrick Farms. In these samples, all of which gave elevated N₂O values, the concentrations of CF₂Cl₂ and/or CFCl₃ were measured to be at least 2 times normal background values. Thus either the air sample was taken from a polluted air parcel, or the sample flask itself was

TABLE 4. Concentration (Mole Fraction) of N₂O in Whole Air Samples Measured in and Near Ann Arbor, Michigan, August 1976 to September 1977

Date	Site	N ₂ O, ppb	1σ, ppb	Comments
<i>1977 Measurements</i>				
Sept. 30	North Lake	332.1	2.7	
Sept. 30	Radricks Farms	332.1	1.2	
Sept. 8	North Lake	329.5	1.5	
Sept. 8	Radricks Farms	338.2	1.5	CFCI ₃ elevated
Sept. 1	outside SPRL	325.7	1.7	
Aug. 31	outside SPRL	330.2	2.0	
Aug. 30	outside SPRL	325.1	1.8	
Aug. 29	outside SPRL	325.1	3.0	
Aug. 17	North Lake	326.2	1.6	
Aug. 16	Radricks Farms	330.4	1.4	
July 29	North Lake	327.2	3.1	
July 29	Radricks Farms	325.6	5.1	
July 14	North Lake	337.0	1.8	no fluorocarbon analysis
July 14	Radricks Farms	329.5	3.4	CFCI ₃ elevated
July 2	Radricks Farms	329.8	1.4	
July 1	North Lake	331.6	1.1	
June 18	Kailua-Kona, Hawaii	328.8	1.3	three flasks
June 12	North Lake	326.7	1.7	
June 10	Radricks Farms	339.2	1.3	CFCI ₃ elevated
May 27	outside SPRL	329.4	2.3	
May 26	outside SPRL	327.8	2.9	
May 25	outside SPRL	327.7	1.0	
May 24	North Lake	331.4	1.1	
May 24	Radricks Farms	328.7	0.6	
May 18	North Lake	329.6	1.6	
May 18	Radricks Farms	326.6	2.8	
May 13	Radricks Farms	330.3	1.0	
May 12	North Lake	331.9	1.2	
May 6	North Lake	329.3	1.8	
May 6	Radricks Farms	329.5	1.0	
April 26	North Lake	333.2	3.0	two flasks
April 26	Radricks Farms	333.0	1.4	
April 21	Radricks Farms	345.0	only one analysis	CFCI ₃ elevated
April 13	North Lake	331.3	0.4	
April 12	North Lake	332.4	only one analysis	
April 8	Radricks Farms	327.1	only one analysis	
March 29	North Lake	326.5	0.4	
March 29	Radricks Farms	329.0	only one analysis	
March 21	North Lake	329.4	5.4	
March 18	Radricks Farms	325.7	0.4	
March 11	North Lake	340.8	5.5	CF ₂ Cl ₂ , CFCI ₃ elevated
March 3	North Lake	340.0	0.6	CF ₂ Cl ₂ , CFCI ₃ elevated
Feb. 28	North Lake	328.6	6.0	
Feb. 28	Radricks Farms	337.0	only one analysis	CF ₂ Cl ₂ , CFCI ₃ normal
Feb. 14	North Lake	329.0	only one analysis	
Feb. 14	Radricks Farms	327.8	only one analysis	
Feb. 1	North Lake	330.3	4.0	
Feb. 1	Radricks Farms	340.5	only one analysis	CFCI ₃ , CF ₂ Cl ₂ normal
Jan. 20	outside SPRL	327.1	only one analysis	
Jan. 20	North Lake	329.0	7.1	
Jan. 20	Radricks Farms	321.0	11.0	
Jan. 4	North Lake	333.8	6.2	
<i>1976 Measurements</i>				
Dec. 31	Pahoa, Hawaii	327.5	3.0	
Dec. 26	Kailua-Kona, Hawaii	373.7	4.3	in harbor
Oct. 18 to Nov. 1	outside SPRL and North Lake	332.0	22.3	samples from 5 days
Aug. 11–25	outside SPRL	330.0	9.6	samples from 11 days

Standard deviations of repeated analyses are also shown. See text for sample mean and standard deviation.

contaminated. In any case, the average N₂O concentration over the remaining 50 data points of Table 4 is 329.5 ppb with a standard deviation of 3.35 ppb. This standard deviation is similar to that reported by *Goldan et al.* [1978]; thus *Junge's* [1974] method to estimate the atmospheric residence time of N₂O from its measurement statistics yields the same value

when it is applied to our data as when it is applied to their selected highest-precision data, namely, about 14 years. It is clear that *Junge's* formula is approximate and that a portion of the observed variance is instrumental and not necessarily variance in actual N₂O concentrations. Indeed, it is clear from Table 4 and Figure 3 that our system precision has improved;

Fig. 4a. N₂O concentration (mole fraction of N₂O in air with 1.2% H₂O by volume) versus local time for May 25–27, 1977. Vertical bars represent 1 standard deviation above and below points; where bars are not shown, there was only one analysis.

the standard deviations of data points since February 1977 are smaller than those before that date. Low-precision measurements taken on several days during August 1976 were grouped together as one point, as was another set in late October and early November 1976 (see Table 4 and Figure 3).

Another source of data variance involves the variability of the H₂O partial pressure in ambient air [Goldan *et al.*, 1978]. It is likely that our standard deviation of 3.3 ppb would be smaller if our N₂O concentrations were reported as the ratio of (N₂O density)/[(air density) – (H₂O density)]. Also, it is worth noting that the high values of N₂O seen on March 3 and March 11 (accompanied by high CF₂Cl₂ and CFCl₃) appeared to be associated with air trajectories that had passed over a few houses with oil-burning heaters. Thus while it is advisable if not essential to measure CF₂Cl₂ and CFCl₃ as tracers in each sample along with N₂O, it would also be useful to measure CO or another substance which, like N₂O, can result from combustion. Such a procedure would facilitate data interpretation; high N₂O values could then be reasonably attributed to local sources or to sample contamination. Further discussion of the data in Table 4 and Figure 3 appears in section 4.

On several occasions in 1977 we searched for possible diurnal variations in N₂O concentrations in the boundary layer, specifically in the 50 cm of air above the surface. After the

Fig. 4b. Same as Figure 4a but for August 29 through September 1, 1977.

report by Brice *et al.* [1977] of substantial day/night differences in England we repeated the search. Specifically, we sampled air about 0.5 m above ground level every 6 hours over a 54-hour period on May 25–27, 1977, and again on August 29–31 and September 1 over a 74-hour period. All samples were gathered from inside an oak forest (about 300 × 100 m) near our laboratory. Figures 4a and 4b show the N₂O concentrations measured over these respective periods. Simultaneous measurements of air temperature and humidity allowed us to scale the actual measured values to air containing 1.2% H₂O vapor by volume; N₂O mole fractions (ppb) relative to air with this H₂O mole fraction are shown in Figures 4a and 4b. Thus any apparent variation in the mole fraction of N₂O in air in Figures 4a and 4b cannot be ascribed to the confounding effect of possible H₂O variations.

Standard deviations of individual data points are shown as vertical uncertainty bars. Where these bars are not shown, samples were analyzed only once. Thus there appears to be a diurnal variation in the May 25–27 N₂O concentrations, at least in the lowest 0.5 m of air that we measured; the variation is larger than the $\pm 1\sigma$ statistical spread. During August 29–31 and September 1 there is no clear diurnal variation except possibly on August 31, when morning N₂O concentrations were significantly higher than those of the previous and following evenings. Figure 5 shows a combination of all data points between the local hours of 0000–0600, 0600–1200, 1200–1800, and 1800–2400 for the late May and late August dates from the data of Figures 4a and 4b. There is a slight suggestion from these lumped data that the 1200–1800 hour time period sees significantly (at the 1σ level) lower N₂O concentrations than does the period 0000–0600 hours local time.

4. ADDITIONAL DISCUSSION AND CONCLUSION

In this paper we have reported results of measurements of N₂O the purposes of which were (1) to observe possible variations in atmospheric N₂O and (2) to identify sources and sinks of atmospheric N₂O. Air samples from two rural sites outside Ann Arbor, Michigan, and one in Ann Arbor that were gathered frequently between August 1976 and September 1977 show no discernible seasonal or overall trend in N₂O concentrations (see Figure 3 and Table 4). In the course of gathering these data we have improved our system precision; thus the most recent data are of higher quality. We have also seen the necessity of analyzing the samples for tracers of man-made pollution such as CF₂Cl₂, CFCl₃, and CO. After discarding several samples that showed higher than average N₂O concentrations and significantly elevated CF₂Cl₂ and/or CFCl₃ concentrations the remaining data base gave a mean N₂O concentration (mole fraction in whole air) of 329.5 ppb. One standard deviation of the data set was about 1% of the mean, or 3.35 ppb. Although it is not completely applicable or quantitative, Junge's [1974] method of estimating the atmospheric residence time τ of N₂O would yield 14 years as the lower limit for τ . One should regard the standard deviation of our measurements (or of any experimental measurement) as having a real component and a separate component due to instrument imprecision.

In our air sampling near Ann Arbor we have seen indications of elevated N₂O concentrations arising even in lightly polluted areas in winter, possibly due to oil-burning heating units on farms and in scattered houses. Similar perturbations are likely to be found near heavily traveled highways under calm wind conditions. Thus sampling sites must be chosen carefully to avoid repeated incidents of contamination

Fig. 5. The N₂O versus local time data of Figures 4a and 4b grouped and averaged into 0000–0600, 0600–1200, 1200–1800, and 1800–2400 hour intervals. Numbers in parentheses are the number of points in each interval. Vertical bars above and below each point are ± 1 standard deviation.

as researchers strive to observe N₂O levels and trends over seasons and years.

The possibility of a small diurnal variation of N₂O concentration in near-surface air cannot be ruled out by data that we gathered every 6 hours on May 25–27 and August 29 to September 1, 1977. Indeed, a variation significant at the 1σ level was observed in May 1977 and in the average for 6 days in May and August. Our slight elevations of N₂O in the earliest morning hours are in contrast to the much larger late afternoon and evening elevations seen in England by *Brice et al.* [1977] at 5-m heights. On the basis of our own work, that of *Blackmer and Bremner* [1976], and that of *Brice et al.* [1977] it may be suggested that there is a great variety of N₂O source and sink activity by soils that depends on soil type, moisture, season, NO₃⁻ and NH₄⁺ levels, vegetation type, etc. Thus it is likely that diurnal variations of N₂O near the earth's surface may vary in size and phase from place to place and with time. Studies should be undertaken to measure these variations; they are likely to be clues to intense soil activity with respect to N₂O. In this regard, a distinction must be made between the variability of N₂O in the troposphere at large and that in the lowest few meters.

By measuring N₂O in automobile exhaust we have confirmed and extended the work of *Pierotti and Rasmussen* [1976]. Table 2 shows that 5- to 10-ppm concentrations of N₂O are not unusual in the exhaust of vehicles equipped with catalytic converters. With these N₂O concentrations we extrapolate to only 10⁶ metric tons of N as N₂O as the yearly emissions of U.S. vehicles if all were equipped as our test vehicles and if they behaved as new vehicles. Possible adoption of the three-way catalyst (designed to reduce NO_x emission) could increase N₂O emissions well above our measured values toward the potential upper limits of *Otto and Shelef* [1972] that were discussed by *Weiss and Craig* [1976].

In exploratory studies of the emission of soils we found strong evidence of N₂O source activity. After covering about 500 cm² of grass-covered soil and forest floor with a gas collector as described in section 3 we observed increases in N₂O concentrations above the soil. Often, the N₂O increase would be about 300 ppb/d and cease after 2 days. On several occasions the concentration increased to 2 ppm, about 6 times

the ambient concentration, within 18 hours. On 8 days out of the 60, we observed apparent sink activity by grass-covered soil; N₂O in our glass collector decreased from its initial value (329 ppb) to 160 ppb within 12 hours and stayed at this low value until the experiment was terminated. This behavior was seen in May and August in wet, generally shaded grass and was quite repeatable, even though gas collectors only 25 m away over drier soil showed N₂O emissions.

On the basis of these studies and the work of *Blackmer and Bremner* [1976] it is reasonable to suggest that soils can consume N₂O from the atmosphere as well as release N₂O to the atmosphere. If so, the study of soil control of atmospheric N₂O will be even more complicated than was previously thought, and measurements of many variables will be needed simultaneously. Soil NO₃⁻, NH₄⁺, O₂, temperature, moisture, and type are among the most important.

Similar collectors mounted on compost piles always showed N₂O increases of about 1 ppm/h. By rupturing the crust of several compost piles we collected much larger emissions; 20 ppm of N₂O was measured within 1 hour, as was the case with fresh uncrusted compost. It is likely that denitrification occurs within the compost pile, where anerobic sites are plentiful, but that the crusted exterior impedes gaseous loss and allows more time for further reduction of gaseous N₂O to N₂.

Collection of gases from five steaming vents on the island of Hawaii revealed that some emissions were N₂O rich and one was N₂O poor with respect to the ambient air. On the basis of these few results we suspect that volcanic vents are a small source of atmospheric N₂O, but considering the rich variety of volcanic geometries, temperatures, and dynamic repertoires, there is clearly room for more study of them.

A further word about absolute calibration is needed. Despite our success with two independent methods for absolute calibration and our rather close agreement in several interlaboratory comparisons we must admit that further study is required, especially with detection techniques other than the electron capture detector. While it is an exquisitely sensitive detector, its physics are not well enough understood [e.g., *Siegel and McKeown*, 1976] to rule out all possible interferences. By achieving a very accurate absolute intercalibration ($\sim 1\%$) of various laboratories active in N₂O measurements the grouping of data from differing regions and future time periods will be made possible. Such direct intercomparisons of data from all active groups would lessen the difficulty in determining whether the natural sources (and sinks) of atmospheric N₂O amount to 200×10^6 metric tons/yr (7-year atmospheric residence time) or, say, 15×10^6 metric tons/yr (100-year residence time). Presently, this entire range is not incompatible with available data.

Finally, we would be remiss if we did not specifically note the need for research on water bodies, both oceanic and fresh. Pioneering investigations on N₂O in water bodies have been discussed in a critical review of atmospheric nitrous oxide by *Hahn and Junge* [1977]. Because of the many gaps in our understanding of atmospheric N₂O and of the nitrogen cycle in water bodies it is not at all clear whether the two are closely coupled; some attention should be directed to marine research on N₂O in polluted and unpolluted areas. Recent measurements by *Cicerone et al.* [1978] show that N₂O is produced in municipal sewage treatment and water treatment.

Acknowledgments. This research was supported by the Atmospheric Sciences Section of the National Science Foundation under NSF grants ATM 74-11478-A05 and ATM 77-22347. Special thanks are due G. R. Carignan, in whose laboratory these studies were

performed, for useful discussions and many North Lake air samples. We also appreciate the time and facilities provided us in our auto exhaust studies by the EPA Auto Emissions Laboratory in Ann Arbor, especially by T. Baines. G. Eaton of the U.S. Geological Survey provided guidance at the Hawaiian Volcanoes National Park, as did M. Ogata. Access to the Detroit-Canada Tunnel was permitted by the Detroit-Windsor Tunnel Corporation. We also thank P. D. Goldan, L. Heidt, J. Krasnec, R. A. Rasmussen, A. L. Schmeltekopf, J. B. Singh, and R. F. Weiss for helpful discussions and D. Yalvac for laboratory assistance.

REFERENCES

- Bates, D. R., and P. B. Hays, Atmospheric nitrous oxide, *Planet. Space Sci.*, **15**, 189–197, 1967.
- Blackmer, A., and J. Bremner, Potential of soil as a sink for atmospheric nitrous oxide, *Geophys. Res. Lett.*, **3**, 739–742, 1976.
- Brice, K., A. Eggleton, and S. Penkett, An important ground surface sink for atmospheric nitrous oxide, *Nature*, **268**, 127–129, 1977.
- Chameides, W., D. Stedman, R. Dickerson, D. Rusch, and R. Cicerone, NO_x production in lightning, *J. Atmos. Sci.*, **34**, 143–149, 1977.
- Cicerone, R. J., J. D. Shetter, and S. C. Liu, Nitrous oxide in Michigan waters and in U.S. municipal waters, *Geophys. Res. Lett.*, **5**, 173–176, 1978.
- Crutzen, P. J., Ozone production rates in an oxygen-hydrogen-nitrogen atmosphere, *J. Geophys. Res.*, **76**, 7311–7327, 1971.
- Crutzen, P. J., Estimates of possible variations in total ozone due to natural causes and human activities, *Ambio*, **3**, 201–210, 1974.
- Crutzen, P. J., Upper limits on atmospheric ozone reductions following increased application of fixed nitrogen to the soil, *Geophys. Res. Lett.*, **3**, 169–172, 1976.
- Dietz, R., E. Cote, and J. Smith, New method for calibration of permeation wafer and diffusion devices, *Analyt. Chem.*, **46**, 315, 1974.
- Goldan, P., Y. Bush, F. Fehsenfeld, D. Albritton, P. Crutzen, A. Schmeltekopf, and E. Ferguson, Tropospheric N₂O mixing ratio measurements, *J. Geophys. Res.*, **83**, 935–939, 1978.
- Hahn, J., N₂O measurements in the northeast Atlantic Ocean, *Meteorol. Forschungsergeb., Reihe A*, **16**, 1–14, 1975.
- Hahn, J., and C. Junge, Atmospheric nitrous oxide: A critical review, *Z. Naturforsch. A*, **32**, 190–214, 1977.
- Johnston, H., and G. Selwyn, New cross section for the absorption of near ultraviolet radiation by nitrous oxide (N₂O), *Geophys. Res. Lett.*, **2**, 549–551, 1975.
- Junge, C., Residence time and variability of tropospheric trace gases, *Tellus*, **XXVI**, 477–478, 1974.
- 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 N₂O and the possible ozone reduction due to industrial fixed nitrogen fertilizers, *Tellus*, **29**, 251–263, 1977.
- Lovelock, J. E., The electron capture detector, *J. Chromatogr.*, **88**, 3–12, 1974.
- Lovelock, J. E., and L. Margulis, Atmospheric homeostasis by and for the biosphere: The Gaia hypothesis, *Tellus*, **26**, 1–9, 1974.
- McElroy, M. B., Chemical processes in the solar system: A kinetic perspective, *Phys. Chem., Ser. 2*, **9**, 1977.
- McElroy, M. B., J. Elkins, S. Wofsy, and Y. Yung, Sources and sinks of atmospheric N₂O, *Rev. Geophys. Space Phys.*, **14**, 143–150, 1976.
- McElroy, M. B., S. C. Wofsy, and Y. L. Yung, The nitrogen cycle: Perturbations due to man and their impact on atmospheric N₂O and O₃, *Phil. Trans. Roy. Soc. London, Ser. B*, **277**, 159–181, 1977.
- Otto, K., and M. Shelef, Studies of surface reactions of NO by isotope labeling, IV, The reaction between NO and NH₃ over copper surfaces at 150–200°, *J. Phys. Chem.*, **76**, 37–43, 1972.
- Parkes, D. A., Negative ion reactions in nitrous oxide + carbon dioxide mixtures, *J. Chem. Soc. Faraday Trans.*, **68**, 2121–2128, 1972.
- Payne, W. J., Reduction of nitrogenous oxides by microorganisms, *Bacteriol. Rev.*, **37**, 409–452, 1973.
- Pierotti, D., and R. Rasmussen, Combustion as a source of nitrous oxide in the atmosphere, *Geophys. Res. Lett.*, **3**, 265–267, 1976.
- Pierotti, D., and R. Rasmussen, The atmospheric distribution of nitrous oxide, *J. Geophys. Res.*, **82**, 5823–5832, 1977.
- Rasmussen, R., J. Krasnec, and D. Pierotti, N₂O analysis in the atmosphere via electron capture-gas chromatography, *Geophys. Res. Lett.*, **3**, 615–618, 1976.
- Schmeltekopf, A., P. Goldan, W. Harrop, T. Thompson, D. Albritton, M. McFarland, A. Sapp, and W. Henderson, Balloon-borne stratospheric grab-sampling system, *Rev. Sci. Instrum.*, **47**, 1479–1485, 1976.
- Schmeltekopf, A., D. Albritton, P. Crutzen, P. Goldan, W. Harrop, W. Henderson, J. McAfee, M. McFarland, H. Schiff, and T. Thompson, Stratospheric nitrous oxide altitude profiles at various latitudes, *J. Atmos. Sci.*, **34**, 729–736, 1977.
- Siegel, M. W., and M. C. McKeown, Ions and electrons in the electron capture detector: Quantitative identification by atmospheric pressure ionization mass spectrometry, *J. Chromatogr.*, **122**, 397–413, 1976.
- Stedman, D., R. Cicerone, W. Chameides, and R. Harvey, Absence of N₂O photolysis in the troposphere, *J. Geophys. Res.*, **81**, 2003–2004, 1976.
- Stedman, D., T. Kelly, R. Shetter, J. Shetter, and R. Cicerone, Feed-back flow and permeation systems for the calibration of very low gas concentration, submitted to *Analyt. Chem.*, 1977.
- Sze, N., and H. Rice, Nitrogen cycle factors contributing to N₂O production from fertilizers, *Geophys. Res. Lett.*, **3**, 343–346, 1976.
- Wang, W., Y. Yung, A. Lacis, T. Mo, and J. Hansen, Greenhouse effects due to man-made perturbations of trace gases, *Science*, **194**, 685–690, 1976.
- Weiss, R. F., and H. Craig, Production of atmospheric N₂O by combustion, *Geophys. Res. Lett.*, **3**, 751–753, 1976.
- Wentworth, W., and R. Freeman, Measurement of atmospheric nitrous oxide using an electron capture detector in conjunction with gas chromatography, *J. Chromatogr.*, **79**, 322–323, 1973.

(Received October 11, 1977;
revised January 16, 1978;
accepted January 23, 1978.)