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

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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) 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),

\[ O(D) + N₂O → N₂ + O₂ \]  (R1a)

\[ O(\text{D}) + N₂O → NO + NO \]  (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 10^8 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 [Schmeltekopf 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 Brenner [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 σ₂ must equal the sum of the actual variance σ² and the variance σₐ² introduced by the analytical technique and instruments used in the measurements: σ₂ = σ² + σₐ². 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 reappliation 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 N\textsubscript{2}O

| Configuration | Gas Chromatograph | Column | L, m | T, °C | Foil | Radiation, mCi | T\textsubscript{sp}, °C | Carrier Gas | Flow, ml/min | Backflushing? |
|---------------|-------------------|--------|------|-------|------|---------------|----------------|-------------|--------------|--------------|
| A             | Perkin Elmer 3920 | Porapak Q | 3    | 50    | Ni   | 10            | 350            | UHP N\textsubscript{2}O | 20           | yes          |
| B             | Perkin Elmer 3920 | Porasil B | 3    | 50    | Ni   | 10            | 350            | 95% Ar, 5% CH\textsubscript{4} | 30           | yes          |
| C*            | Carle 111 (rebuilt) | Molesieve 5A | 1.6  | 250   | Ni   | 2             | 250            | 95% Ar, 5% CH\textsubscript{4} | 3            | no           |

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 N\textsubscript{2}O consumption by soils. In less exploratory work we have regularly measured N\textsubscript{2}O 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 N\textsubscript{2}O near ground level. We are paying attention both to absolute values and calibrations and to relative variations of N\textsubscript{2}O. 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 N\textsubscript{2}O. The basic principles and methods of gas chromatographic separation and electron capture detection of N\textsubscript{2}O 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 CO\textsubscript{2} and N\textsubscript{2}O 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) N\textsubscript{2}O; ∼330 ppm (parts per million) CO\textsubscript{2}) with chromatographic configuration A (see Table 1). The CO\textsubscript{2} peak, negative in this case, is well separated from the N\textsubscript{2}O; there is a flat baseline (almost 30 s) between the peaks. Configuration C, two columns in series suggested by R. F. Weiss, separates CO\textsubscript{2} and N\textsubscript{2}O even better. When volcanic air samples were analyzed (see section 3), the high CO\textsubscript{2} 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 CO\textsubscript{2} response in EC-GC systems appears to be determined capriciously, and we note that further investigations are needed. We find a positive CO\textsubscript{2} peak with configuration C, and P. D. Golden (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 N\textsubscript{2}O was enhanced by CO\textsubscript{2} 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 N\textsubscript{2}O 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 N\textsubscript{2}O permeation tube which injects a small calibrated flow of pure N\textsubscript{2}O 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 N\textsubscript{2}O or 1000 times smaller concentrations of CF\textsubscript{3}Cl. The permeation tube dilution system easily generated 100-1000 ppb N\textsubscript{2}O and 100 ppt (parts per trillion) to 2 ppb CF\textsubscript{3}Cl. These flow dilution systems were used to prepare flows with known concentrations of N\textsubscript{2}O, and the GC-EC response to each concentration was measured. Figure 2 shows one such set of results. Between the various N\textsubscript{2}O 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
3. N\textsubscript{2}O OBSERVATIONS

a. Exploratory Studies: N\textsubscript{2}O Sources and Sinks

In this section we report N\textsubscript{2}O measurements designed to identify sources and sinks of N\textsubscript{2}O. 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 N\textsubscript{2}O sources and sinks should not be underestimated, given the need to optimize N\textsubscript{2}O monitoring sites and to evaluate assumptions of uniform sources and uniform sinks in Junge's [1974] approach to interpreting N\textsubscript{2}O variability.

Combustion processes are a source of atmospheric N\textsubscript{2}O...
[Pierotti and Rasmussen, 1976; Weiss and Craig, 1976]. Following Pierotti and Rasmussen [1976], we have detected N\textsubscript{2}O in automobile exhaust. Our results in Table 2 show even more N\textsubscript{2}O 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 fitting over Nupro valves filled with undiluted (\times 15) exhaust and control bags of background air. Each bag was analyzed within hours; stability tests of N\textsubscript{2}O 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 N\textsubscript{2}O deficit. In a related study we found 341 ppb N\textsubscript{2}O 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 N\textsubscript{2}O, almost pure catalyst exhaust. Two points should be noted. First, the range of N\textsubscript{2}O 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 N\textsubscript{2}O 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 10\textsuperscript{8} metric tons of N as N\textsubscript{2}O 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\textsubscript{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 N\textsubscript{2}O 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 N\textsubscript{2}O 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 then analyzed. These syringes proved, through storage tests with zero-grade air and with N\textsubscript{2}O-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 N\textsubscript{2}O. 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 N\textsubscript{2}O was observed by additional sampling at sunrise and sunset; diurnal activity for N\textsubscript{2}O 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 N\textsubscript{2}O was observed by additional sampling at sunrise and sunset; diurnal activity for N\textsubscript{2}O was included in the sample. CO\textsubscript{2} concentrations labeled E were estimated from GC-EC peak height; those labeled MS were determined by mass spectroscopy.

### Table 2. \(\text{N}_2\text{O}\) Concentrations in Automobile Exhaust

| Source of Sample                  | \(\text{N}_2\text{O}\) Concentration | Remarks                                      |
|----------------------------------|------------------------------------|---------------------------------------------|
| Detroit-Canada Tunnel            | 341 ppb about 350 ppb              | Air from exhaust ducts.                    |
| New passenger car with diesel engine |                                    | Previously used exhaust bags led to less ideal results; several spurious peaks cluttered the chromatograms. |
| New vehicle with 350-in.\(^*\) (5.7-1) engine, oxidation catalytic converter, and EGR | 6-10 ppm                             | Congested highway simulation.            |
| New vehicle with 225-in.\(^*\) (3.7-1) engine and monolith oxidation catalytic converter | 5-12 ppm                             | EPA 'highway' and 'sulfate' cycles.   |
| New vehicle with 350-in.\(^*\) (5.7-1) engine, oxidation catalytic converter, and EGR | 8-16 ppm                             | Cold start.                              |
| New vehicle with 1.6-l, four-cylinder engine, oxidation catalytic converter, and EGR | 9-14 ppm                             | Hot, transient LA-4 test.               |
| Used vehicle, 1971 model, six cylinders, no catalytic converter | 8-12 ppm                             | Hot start.                              |
| Used vehicle, 1961 model, V-8, no catalytic converter | 220 ppb                             | Car was idling.                         |

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

### Table 3. \(\text{N}_2\text{O}\) Concentrations in Samples Taken From Volcanic Steam Vents on Island of Hawaii in June 1977

| Location of Vent | \(\text{CO}_2\), ppm | \(\text{N}_2\text{O}\), ppb |
|------------------|----------------------|---------------------------|
| Cinder cone near Ilewa | 500 (E)              | 459                       |
| 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. \(\text{CO}_2\) concentrations labeled E were estimated from GC-EC peak height; those labeled MS were determined by mass spectroscopy.
chromatographic peak; see Figure 1) were observed to be much larger and more regular. In most cases, CO$_2$ 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, N$_2$O 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. CO$_2$ 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 N$_2$O 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; CO$_2$ 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 cm$^2$) covered area was in contact below the surface with a quasi-infinite earth. Also, because our experiments show the ability of soils to consume N$_2$O from air containing only normal (329 ppb) N$_2$O concentrations, they supplement the much more elegant and controlled experiments of Blackmer and Bremner [1976]. These authors, while the first to show that compost piles containing vegetation and mixed animal manure. There we found more rapid increases of N$_2$O, usually 1000 ppb/h, if the collector was over a firm, crustled 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 N$_2$O source activity have been performed. First, as was noted above, new or punctured compost piles emit N$_2$O 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 N$_2$O 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 N$_2$O, 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 N$_2$O over ambient (327 ppb) levels appeared in the air gathered near Hilo, indicating an N$_2$O source. A smaller excess was seen at Puhimau. At the Sulphur Bank we saw a very small N$_2$O 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 N$_2$O 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, N$_2$O in the volcanic samples was identified by its retention time on chromatographic columns of configurations A, B, and C of Table 1.

The CO$_2$ concentrations in Table 3 represent the mole fraction of CO$_2$ in the pressurized sample analyzed at room temperature. Appreciable amounts of H$_2$O present as steam in the volcanic vent condensed in our sample flasks. Thus, for example, the 54% CO$_2$ in the Sulphur Bank samples is an overestimate of the CO$_2$ concentration in the venting gas, because almost all the water vapor present during sample gathering was condensed during analysis.

Finally, we attempted to detect N$_2$O in small electrostatic discharges. No N$_2$O 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 N$_2$O Concentrations and Variations

Since August 1976 we have been measuring N$_2$O 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 N$_2$O 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 N$_2$O values, the concentrations of CF$_2$Cl$_2$ and/or CFCl$_3$ 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               | N₂O, ppb | 1σ, ppb | Comments          |
|------------|--------------------|----------|---------|-------------------|
| Sept. 30   | North Lake         | 332.1    | 2.7     |                   |
| Sept. 30   | Radrick Farms      | 332.1    | 1.2     |                   |
| Sept. 8    | North Lake         | 329.5    | 1.5     |                   |
| Aug. 31    | outside SPRL       | 325.7    | 1.7     |                   |
| Aug. 30    | outside SPRL       | 330.2    | 2.0     |                   |
| Aug. 29    | outside SPRL       | 325.1    | 1.8     |                   |
| Aug. 17    | North Lake         | 326.2    | 1.6     |                   |
| Aug. 16    | Radrick Farms      | 330.4    | 1.4     |                   |
| July 29    | North Lake         | 327.2    | 3.1     |                   |
| July 29    | Radrick Farms      | 325.6    | 5.1     |                   |
| July 14    | North Lake         | 330.7    | 1.8     | no fluorocarbon analysis |
| July 14    | Radrick Farms      | 329.5    | 3.4     | CFCl₃ elevated    |
| July 2     | Radrick 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    | Radrick Farms      | 339.2    | 1.3     | CFCl₃ 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     | Radrick Farms      | 328.7    | 0.6     |                   |
| May 18     | North Lake         | 329.6    | 1.6     |                   |
| May 18     | Radrick Farms      | 326.6    | 2.8     |                   |
| May 13     | Radrick Farms      | 330.3    | 1.0     |                   |
| May 12     | North Lake         | 331.9    | 1.2     |                   |
| May 6      | North Lake         | 329.3    | 1.8     |                   |
| May 6      | Radrick Farms      | 329.5    | 1.0     |                   |
| April 26   | North Lake         | 333.2    | 3.0     | two flasks        |
| April 26   | Radrick Farms      | 333.0    | 1.4     |                   |
| April 21   | Radrick Farms      | 345.0    | only one analysis | CFCl₃ elevated |
| April 13   | North Lake         | 331.3    | 0.4     |                   |
| April 12   | North Lake         | 332.4    | only one analysis |              |
| April 8    | Radrick Farms      | 327.1    | only one analysis |              |
| March 29   | North Lake         | 326.5    | 0.4     |                   |
| March 29   | Radrick Farms      | 329.0    | only one analysis |              |
| March 21   | North Lake         | 329.4    | 5.4     |                   |
| March 18   | Radrick Farms      | 325.7    | 0.4     |                   |
| March 11   | North Lake         | 340.8    | 5.5     | CFCl₂, CFCl₃ elevated |
| March 3    | North Lake         | 340.0    | 0.6     | CFCl₂, CFCl₃ elevated |
| Feb. 28    | North Lake         | 328.6    | 6.0     |                   |
| Feb. 28    | Radrick Farms      | 337.0    | only one analysis | CFCl₂, CFCl₃ normal |
| Feb. 14    | North Lake         | 329.0    | only one analysis |              |
| Feb. 14    | Radrick Farms      | 327.8    | only one analysis |              |
| Jan. 20    | North Lake         | 330.3    | 4.0     |                   |
| Jan. 20    | Radrick Farms      | 340.5    | only one analysis | CFCl₂, CFCl₃ normal |
| Jan. 20    | outside SPRL       | 327.1    | only one analysis |              |
| Jan. 4     | North Lake         | 333.8    | 6.2     |                   |
| 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 | 320.0 | 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;
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 H\(_2\)O 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 N\(_2\)O concentrations were reported as the ratio of (N\(_2\)O density)/(air density − (H\(_2\)O density)). Also, it is worth noting that the high values of N\(_2\)O seen on March 3 and March 11 (accompanied by high CF\(_2\)Cl\(_2\) and CFCl\(_3\)) 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 CF\(_2\)Cl\(_2\) and CFCl\(_3\) as tracers in each sample along with N\(_2\)O, it would also be useful to measure CO or another substance which, like N\(_2\)O, can result from combustion. Such a procedure would facilitate data interpretation; high N\(_2\)O 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 N\(_2\)O concentrations in the boundary layer, specifically in the 50 cm of air above the surface. After the 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 N\(_2\)O 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% H\(_2\)O vapor by volume; N\(_2\)O mole fractions (ppb) relative to air with this H\(_2\)O mole fraction are shown in Figures 4a and 4b. Thus any apparent variation in the mole fraction of N\(_2\)O in air in Figures 4a and 4b cannot be ascribed to the confounding effect of possible H\(_2\)O 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 N\(_2\)O concentrations, at least in the lowest 0.5 m of air that we measured; the variation is larger than the ±1σ statistical spread. During August 29–31 and September 1 there is no clear diurnal variation except possibly on August 31, when morning N\(_2\)O 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 N\(_2\)O 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 N\(_2\)O the purposes of which were (1) to observe possible variations in atmospheric N\(_2\)O and (2) to identify sources and sinks of atmospheric N\(_2\)O. 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 N\(_2\)O 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 CF\(_2\)Cl\(_2\), CFCl\(_3\), and CO. After discarding several samples that showed higher than average N\(_2\)O concentrations and significantly elevated CF\(_2\)Cl\(_2\) and/or CFCl\(_3\) concentrations the remaining data base gave a mean N\(_2\)O 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 N\(_2\)O 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 N\(_2\)O 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.
as researchers strive to observe $\text{N}_2\text{O}$ levels and trends over seasons and years. The possibility of a small diurnal variation of $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ 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 Brenner [1976], and that of Brice et al. [1977] it may be suggested that there is a great variety of $\text{N}_2\text{O}$ source and sink activity by soils that depends on soil type, moisture, season, $\text{NO}_3^-$ and $\text{NH}_4^+$ levels, vegetation type, etc. Thus it is likely that diurnal variations of $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$. In this regard, a distinction must be made between the variability of $\text{N}_2\text{O}$ in the troposphere at large and that in the lowest few meters.

By measuring $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ are not unusual in the exhaust of vehicles equipped with catalytic converters. With these $\text{N}_2\text{O}$ concentrations we extrapolate to only 10⁴ metric tons of N as $\text{N}_2\text{O}$ 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 NOx emission) could increase $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ concentrations above the soil. Often, the $\text{N}_2\text{O}$ 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; $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ emissions.

On the basis of these studies and the work of Blackmer and Brenner [1976] it is reasonable to suggest that soils can consume $\text{N}_2\text{O}$ from the atmosphere as well as release $\text{N}_2\text{O}$ to the atmosphere. If so, the study of soil control of atmospheric $\text{N}_2\text{O}$ will be even more complicated than was previously thought, and measurements of many variables will be needed simultaneously. Soil $\text{NO}_3^-$, $\text{NH}_4^+$, $\text{O}_3$, temperature, moisture, and type are among the most important.

Similar collectors mounted on compost piles always showed $\text{N}_2\text{O}$ increases of about 1 ppm/h. By rupturing the crust of several compost piles we collected much larger emissions; 20 ppm of $\text{N}_2\text{O}$ was measured within 1 hour, as was the case with fresh uncruised compost. It is likely that denitrification occurs within the compost pile, where anaerobic sites are plentiful, but that the crusted exterior impedes gaseous loss and allows more time for further reduction of gaseous $\text{N}_2\text{O}$ to $\text{N}_2$.

Collection of gases from five steaming vents on the island of Hawaii revealed that some emissions were $\text{N}_2\text{O}$ rich and one was $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$, 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 inter-laboratory 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 inter-calibration (~1%) of various laboratories active in $\text{N}_2\text{O}$ measurements the grouping of data from differing regions and future time periods will be made possible. Such direct inter-comparisons of data from all active groups would lessen the difficulty in determining whether the natural sources (and sinks) of atmospheric $\text{N}_2\text{O}$ amount to $200 \times 10^6$ metric tons/yr (7-year atmospheric residence time) or, say, $15 \times 10^6$ 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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ 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 $\text{N}_2\text{O}$ in polluted and unpolluted areas. Recent measurements of Cicerone et al. [1978] show that $\text{N}_2\text{O}$ is produced in municipal sewage treatment and water treatment.

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