BIOLOGICALLY PRODUCED VOLATILE COMPOUNDS:
N\textsubscript{2}O EMISSIONS FROM SOILS

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SUMMARY:

The objective of this research program was to study introus-oxide (N$_2$O) dynamics at the soil-atmosphere interface and their effects on the global N$_2$O budget.

A trend for increased tropospheric N$_2$O concentration has been established by careful studies over the last decade. The increase, at a rate of 0.2-0.4% per year amounts to net annual addition of 2.8-5.6.10$^6$ tons of N$_2$O-N to the atmosphere. The rate of increase is of the same order of magnitude as that observed for CO$_2$ in the atmosphere in the last 30 years, and may have important effects on the atmospheric chemical cycles, the thermal balance of the Earth, and biospheric processes. The net nitrogen loss in the form of N$_2$O from the earth surface amounts to 5-10% of the world's annual industrial nitrogen fixation for production of nitrogen fertilizers and although it is clear today that denitrification of N-fertilizers is not the sole source of this added atmospheric N$_2$O- the cycled N$_2$O-nitrogen is a non-negligible component of the biospheric nitrogen cycles.

During the past year of activity, analytical work has been conducted on systems that measure N$_2$O emission from soils. A detailed review of the literature related to N$_2$O cycles, emission from various ecosystems and possible effects on the atmosphere and biosphere has been conducted. An analysis of global cycles and the global budget of N$_2$O has been prepared and published (Banin et al., copy attached).
GLOBAL N2O CYCLES —
TERRESTRIAL EMISSIONS,
ATMOSPHERIC ACCUMULATION
AND BIOSPHERIC EFFECTS

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ABSTRACT
Tropospheric nitrous oxide concentration has increased by 0.2 - 0.4% per year over the period 1975 to 1982, amounting to net addition to the atmosphere of 2.8 - 5.6 Tg N2O-N per year. This perturbation, if continued into the future, will affect stratospheric chemical cycles, and the thermal balance of the Earth. In turn it will have direct and indirect global effects on the biosphere. Though the budget and cycles of N2O on Earth are not yet fully resolved, accumulating information and recent modelling efforts enable a more complete evaluation and better definition of gaps in our knowledge.

INTRODUCTION
Nitrous oxide (N2O) is a trace atmospheric component whose concentration is believed to be increasing in recent years as a result of anthropogenic effects. Thus it joins a group of trace gases including CO2, CO and CH4 whose atmospheric concentration are increasing, presumably due to human activities (/1/). Studies in the mid-1970's suggested rapid, almost catastrophic, increases in the atmospheric fluxes of N2O due to denitrification of fertilizer nitrogen, and combustion /2,3/. However, world wide systematic monitoring of atmospheric N2O from 1975 to 1978 by Singh et al. /4/ did not show a statistically significant increase in atmospheric N2O concentration. But more recently, data compiled for the period 1975 to 1982 have shown that N2O concentration did indeed increase by 0.2% - 0.4% per year /5,6/. Major increase in atmospheric N2O will measurably affect stratospheric chemical cycles and the thermal balance of the Earth, and the resulting perturbations may have growing effects on the biosphere. Besides its role in atmospheric chemistry, N2O is an important intermediate in biospheric nitrogen conversions and in the global nitrogen cycle.

In the following we will review in brief some of the recent findings on the budget and cycles of nitrous oxide on Earth. Sources and sinks for N2O on the land, in the ocean, and in the atmosphere will be estimated using recent information, and the possible climatic and biospheric effects of the increase in atmospheric N2O will be briefly assessed. Though these interactions are not yet fully resolved, the accumulating information and insight will lead to a more complete evaluation and a better definition of the gaps in our knowledge of N2O dynamics on Earth.

NITROUS OXIDE IN THE ATMOSPHERE
Concentration and distribution. The distribution of nitrous oxide in both the troposphere and stratosphere has been studied by several investigators. Singh et al. /4/ reported mixing fractions very close to 310 ppbv with no discernable latitudinal variation. An atmospheric N2O lifetime greater than 20 years was inferred from the data.

Schmeltekopf et al. /7/ and Vedder et al. /8/, have found that measured N2O mixing fractions at stratosphere altitudes, (i.e., height > 15 km) decreased more rapidly at high latitudes than in the tropics. This variation probably stems from both chemical and transport causes. At altitudes near the tropo-
pause, the observed mixing fraction appears to converge to that measured by Singh et al. /4/.

Atmospheric processes. Although the major sources of nitrous oxide are non-atmospheric, minor amounts are produced directly within the atmosphere. Lightning is the best understood of these processes and produces several thousand tonnes per year as a result of shock-induced reactions /9/, a minor source compared with the Earth surface reactions. Excited-species chemistry have been recently suggested as possible atmospheric source /10,11/, perhaps contributing up to 20 Tg N$_2$O-N yr$^{-1}$/11/.

There are no known significant processes for the destruction of nitrous oxide in the troposphere. Indeed, the only reaction for removing N$_2$O in the lower atmosphere is

\[ \text{N}_2\text{O} + \text{O}(^{1}\text{D}) \rightarrow 2\text{NO} \]

(1)

Because of the very small tropospheric abundance of O$(^{1}\text{D})$, the lifetime of N$_2$O is of the order of 10$^4$ years. In the stratosphere the direct photolysis of N$_2$O becomes the dominant sink with reaction (1) contributing about 20% of the total loss rate. The estimated lifetime of N$_2$O against the loss processes is of the order of 100-200 years /5,6/, and current estimates put the loss rate at 6 to 11 Tg N$_2$O-N yr$^{-1}$/12/.

Effect on ozone. The catalytic destruction of stratospheric ozone by nitrogen oxides (NO and NO$_2$) formed from N$_2$O decomposition (reaction 1) was first proposed by Crutzen /13/ as a possible mechanism for maintaining the ozone mixing fraction at its observed levels.

![Ozone decrease vs. N$_2$O increase](Fig. 1. Ozone decrease vs. N$_2$O increase.)
We employed two photochemical models which simulate both transport and atmospheric chemistry to assess the impact of increased N\textsubscript{2}O on stratospheric ozone. Figure 1 shows computed globally averaged ozone column decreases corresponding to atmospheric N\textsubscript{2}O increases of 10\%, 30\%, 60\%, and 100\%, using the one-dimensional stratospheric photochemical model of Turco and Whitten /14/. The results are consistent with those obtained with our two-dimensional model /15/ for a doubling of troposphere N\textsubscript{2}O. An average decrease of about 1.5\% in ozone column per 10\% increase in N\textsubscript{2}O is predicted.

Effect on climate. Nitrous oxide is an absorber of infrared radiation emitted by the earth, with strong bands at 7.78, 8.56, and 17.0 \textmu m. It is thus capable of contributing to the "greenhouse effect" in which part of the earth's infrared radiation is trapped in the troposphere rather than escaping to space. Wang et al., /16/ and Donner and Ramanathan /17/ have studied such effects with the aid of radiative-convective models. They estimated that a surface warming of 0.3 to 0.4° K may be likely for a doubling of N\textsubscript{2}O. More recently a WMO expert group report /18/, estimated that the combined effects of doubling N\textsubscript{2}O concentration, doubling methane and increasing chlorofluorocarbons (CFC's) from 0 to 1 ppb, will lead to a warming of the surface of the Earth by a total of 0.9° K. The same group estimated that doubling CO\textsubscript{2} concentration will cause a 2° K warming.

Biological effects. It is well-known that ultraviolet radiation of wavelengths in the range 290-310 nm (UV-B) is biologically active. Hence, atmospheric change which increase the UV-B intensity of solar radiation reaching the earth's surface, is expected to affect both plant and animal species. Studies of over 100 plant species and varieties /19,20/, show that about 1/5 are sensitive to UV-B increases, another 1/5 are rather tolerant of increases in UV-B (up to a factor of 4), and the remainder are intermediate. Probably the most widely publicized effect of UV-B radiation is the production of skin cancer in humans. The association between UV-B and non-fatal skin cancer is fairly well understood, with a 1% decrease in ozone leading to a 1% increase in the disease /21/. On the other hand, the relation of UV-B to the fatal melanoma is not well-understood; it appears to be dependent upon the rate of UV-B exposure rather than on the total exposure alone.

NITROUS OXIDE PROCESSES ON THE EARTH SURFACE

Nitrous Oxide production on land and in the oceans results mainly from biologically mediated nitrogen conversions. These include natural biospheric processes which are an integral part of the nitrogen cycles, and anthropogenically-enhanced activities, such as nitrogen-fertilization and waste-water treatment. Non-biological production was observed in nature by chemically driven nitrate and nitrite reduction ("chemodenitrification"). In addition, non-biological anthropogenic sources including combustion, synthesis in high voltage power lines coronas, and biomass burning, also release N\textsubscript{2}O to the atmosphere.

The production of N\textsubscript{2}O by biological nitrogen transformations has been observed during denitrification, nitrate reduction, and nitrification. These processes involve many groups of microorganisms, and N\textsubscript{2}O, in most cases, is an intermediate in a series of sequential oxidation-reduction nitrogen transformations. Both the oxidative conversion (nitrification) of ammonia nitrogen to nitrate (\text{NH}_3 \rightarrow \text{NO}_3^-) and the reductive conversion (denitrification) of nitrate to dinitrogen (\text{NO}_3^- \rightarrow \text{N}_2), have been shown to involve N\textsubscript{2}O as an intermediate in which the valency of N is +1. As an intermediate gaseous product, N\textsubscript{2}O may "leak" to the atmosphere before being consumed and further converted. The multitude of pathways by which N\textsubscript{2}O can be produced in nature, complicates the causal relationships between emission and environmental conditions, resulting in conflicting views with regard to N\textsubscript{2}O production mechanisms, emission rates and environmental affects /22,23/.

OCEANS

Nitrous oxide concentration in the water column and N\textsubscript{2}O emissions from the ocean have been measured and analyzed rather intensively since the early 1970's /24-32/. Interestingly, estimates of the ocean's contribution to the global N\textsubscript{2}O budget have been continuously decreasing over this period (Table 1).

Early works by Junge and Hahn /24/ and Hahn /25/, reported N\textsubscript{2}O concentrations ranging up to 230\% of saturation in the mixed layer of the north and
tropical Atlantic. The ocean was then identified as a major source of N\textsubscript{2}O, emitting to the atmosphere about 135 Tg N\textsubscript{2}O yr\textsuperscript{-1} (86 Tg N\textsubscript{2}O-N yr\textsuperscript{-1}), mostly due to denitrification /25/. However, a series of later studies showed lower or zero supersaturation of the mixed ocean layer, and undersaturation of deep ocean waters /26-29/. Localized emission may occur in upwelling areas /29-31/ and localized absorption may take place where anoxic conditions prevail /32/. Both of these, however, are believed to be unimportant on the global scale /5,11/. The more recent works suggested that most of the N\textsubscript{2}O released from the ocean is produced by nitrification rather than denitrification /27,28,30,32/. Although at present there is still considerable debate regarding the prevailing mechanisms of N\textsubscript{2}O production in the ocean /22/, it is believed now that the ocean is either a small source of 1-2 Tg N\textsubscript{2}O-N yr\textsuperscript{-1} /33/ or neither a source nor a sink for N\textsubscript{2}O on the global scale /11/.

**TABLE 1** Estimates of Global N\textsubscript{2}O Fluxes from (into) the Oceans

<table>
<thead>
<tr>
<th>Year of Publication</th>
<th>Reference</th>
<th>Suggested mechanism</th>
<th>Net Global Flux Tg N\textsubscript{2}O-N yr\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1974</td>
<td>Hahn /25/</td>
<td>Denitrification</td>
<td>86</td>
</tr>
<tr>
<td>1976</td>
<td>McElroy et al. /34/</td>
<td>Nitrification</td>
<td>-40</td>
</tr>
<tr>
<td>1977</td>
<td>Hahn &amp; Junge /35/</td>
<td>Denitrification</td>
<td>45</td>
</tr>
<tr>
<td>1978</td>
<td>Elkins et al. /30/</td>
<td>Mostly nitrification</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>1978</td>
<td>Weiss /29/</td>
<td>--</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>1979</td>
<td>Cohen &amp; Gordon /28/</td>
<td>Mostly nitrification</td>
<td>4-10</td>
</tr>
<tr>
<td>1979</td>
<td>Singh et al. /4/</td>
<td>Denitrification</td>
<td>13-19</td>
</tr>
<tr>
<td>1980</td>
<td>Pierotti &amp; Rasmussen /31/</td>
<td>Denitrification</td>
<td>48</td>
</tr>
<tr>
<td>1981</td>
<td>Hahn /36/</td>
<td>Denitrification</td>
<td>29 (8-76)</td>
</tr>
<tr>
<td>1982</td>
<td>Soderlund &amp; Rosswall /32/</td>
<td>Denitrification</td>
<td>20-80</td>
</tr>
<tr>
<td>1983</td>
<td>Crutzen /33/</td>
<td>--</td>
<td>1-2</td>
</tr>
<tr>
<td>1983</td>
<td>Kahlil &amp; Rasmussen /6/</td>
<td>--</td>
<td>6</td>
</tr>
<tr>
<td>1983</td>
<td>Stedman &amp; Shetter /11/</td>
<td>--</td>
<td>0</td>
</tr>
</tbody>
</table>

**LAND**

N\textsubscript{2}O emission from the land results from natural, mostly biological processes in soils, from soil processes enhanced by anthropogenic intervention and from purely anthropogenic processes. Our knowledge of this array of processes has improved considerably over the last decade, but is still far from complete. A major finding that complicates the picture is that N\textsubscript{2}O emissions on land have large spatial and temporal variability, thus requiring detailed, continuous and long-term monitoring in order to be quantitatively characterized.

**Soil Processes**

The annual rate of emission of N\textsubscript{2}O from soils into the atmosphere varies within wide limits as shown in Table 2, where variation spanning over two to three orders of magnitude is observed /38-47/. Daily, or hourly, fluxes may vary within even wider limits. A recent review /48/, showed that the rate of emission varies considerably with season, soil texture, soil temperature, soil moisture content, soil redox potential, soil-organic matter content, nitrogen application rates, fertilizer composition, vegetation type and its density, and agrotechnical and cultivational regimes. Technical problems and methodological differences were found also to cause differences between the findings of various research groups.
Table 2 Measured Ranges of N\textsubscript{2}O Emission Rates from Soil to the Atmosphere

\textbf{KG N\textsubscript{2}O-N HA\textsuperscript{-1}·YR\textsuperscript{-1}}

\begin{tabular}{|l|c|}
\hline
\textbf{NATIVE SOILS} & \\
\hline
FOREST SOILS & \\
TROPICAL FOREST & 0-13 \textit{KELLER et al. (1983) (BRAZIL)} \\
TEMPERATE FOREST & 0.4-39 \textit{ROBERTSON & TIDJE (1984) (MICHIGAN) (NON-DISTURBED CORES)} \\
BOREAL FOREST & 0-1.3 \textit{KELLER et al. (1983) (NEW HAMPSHIRE)} \\
GRASSLAND & \\
PRAIRIE & 0.1-4.2 \textit{MOSIER et al. (1981) (COLORADO)} \\
\hline
\textbf{CULTIVATED SOILS} & \\
FIELD-MINERAL SOILS & \\
NONFERTILIZED, NON-CULTIVATED SOILS; & 0.5-1.5 \textit{DUXBURY et al. (1982)} \\
INTERMEDIATELY FERTILIZED, SEMI-INTENSIVE CROPS & 3-4 \textit{RYDEN (1981). (PERENNIAL GRASS)} \\
& 1-2 \textit{ROLSTON et al. (1982), (PERENNIAL GRASS)} \\
& 2-3 \textit{HUTCHINSON & MOSIER (1979) (CORN)} \\
HEAVILY FERTILIZED, HEAVILY IRRIGATED & 6-40 \textit{RYDEN et al. (1979) (VEGETABLES)} \\
FIELD-ORGANIC SOILS & \\
ORGANIC SOILS, CULTIVATED & 50-150 \textit{DUXBURY et al. (1982)} \\
MICROPLOTS & \\
MINERAL, WATERLOGGED SOILS & 3-23 \textit{LENSI & CHALAMET (1982) EXTRAPOLATED FROM SHORT TERM (21 h) EXPERIMENTS TO A PER-YEAR RATE} \\
\hline
\end{tabular}

Natural soils. In the mid 1970’s it was believed that a major source of N\textsubscript{2}O emissions on land would be from N-fertilized fields /23/, but more recently Duxbury et al. /41/ have suggested that forest-soils and other non-cultivated lands still are, due to their much larger areal extent, the major source on Earth; however, only a few measurements of N\textsubscript{2}O emissions from natural soils have been reported. Keller et al. /38/ have recently measured relatively high rates of emission from the soil in a Brazilian tropical forest site. Robertson and Tiedje /39/ reported high rates of N\textsubscript{2}O emissions (using incubated, nondisturbed core samples), from soils sampled in hardwood and coniferous stands in a Michigan temperate forest. The rates were higher than those measured in many cultivated fields (Table 2), and there is a need for corroborating them by \textit{in situ} measurements in forest soils. Only a few rate measurements were conducted in native woodlands, savanna and grasslands, and the rates of emission were in the range of 0.1-5 g N\textsubscript{2}O-N ha\textsuperscript{-1} day\textsuperscript{-1} /40, 49/.

On the basis of the accumulating information for emissions of N\textsubscript{2}O from native and nonfertilized soils, (partly listed in Table 2), we have estimated the range of emissions from the various terrestrial ecosystems (Table 3; Banin et al., unpublished data to be discussed in detail elsewhere). Multiplying these emissions by the surface area of the various ecosystems /49/, we computed the ranges of individual ecosystem contributions and further obtained the total global emission from native lands (Table 3). On the basis of the present limited data, we estimate the terrestrial natural source to be in the range of 2.6 to 25.0 Tg N\textsubscript{2}O-N yr\textsuperscript{-1}. In a recently published N\textsubscript{2}O budget, Crutzen /33/ did not include any value for the contribution of native soils, while Stedman and Shetter /11/ suggested arbitrary source and sink terms of 38 and 50 Tg N\textsubscript{2}O-N yr\textsuperscript{-1}, respectively (net sink of 12 Tg N\textsubscript{2}O-N yr\textsuperscript{-1}).
Cultivated soils. Two major anthropogenic interventions in the nitrogen cycle in soils may increase $\text{N}_2\text{O}$ emissions: organic matter decay, and $\text{N}$ fertilization.

Cultivation causes rapid decrease of the organic matter content of native soils. Crutzen /33/ used estimated carbon release from cultivated soils to calculate emission of 1-3 Tg $\text{N}_2\text{O}$ N yr$^{-1}$ from this source. We have estimated (Table 3) global emissions of 0.75-2.25 Tg $\text{N}_2\text{O}$ N yr$^{-1}$ on the basis of area, and fluxes reported in the literature /41/; these values are still tentative.

### Table 3 Estimates of $\text{N}_2\text{O}$ Emissions from the World's Terrestrial Ecosystems

<table>
<thead>
<tr>
<th>MAJOR ECOSYSTEM TYPES</th>
<th>SURFACE AREA, km$^2$ x $10^6$</th>
<th>EMISSION, kg $\text{N}_2\text{O}$ N ha$^{-1}$ yr$^{-1}$</th>
<th>GLOBAL FLUX, Tg $\text{N}_2\text{O}$ N yr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FOREST</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TROPICAL RAIN</td>
<td>10.0</td>
<td>1-4</td>
<td>1.45-5.80</td>
</tr>
<tr>
<td>TROPICAL SEASONAL</td>
<td>4.5</td>
<td>0.5-10</td>
<td>0.30-6.00</td>
</tr>
<tr>
<td>TEMPERATE EVERGREEN</td>
<td>3.0</td>
<td>0.1-0.5</td>
<td>0.09-0.45</td>
</tr>
<tr>
<td>TEMPERATE DECIDUOUS</td>
<td>3.0</td>
<td>0.5-1.0</td>
<td>0.07-0.15</td>
</tr>
<tr>
<td>BOREAL</td>
<td>9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLANTATIONS</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>WOODLAND, GRASSLAND AND SAVANNA</strong></td>
<td>4.5</td>
<td>0.1-1.5</td>
<td>0.40-5.93</td>
</tr>
<tr>
<td>WOODLAND AND SHRUBLAND</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAVANNA</td>
<td>22.5</td>
<td>0.01-0.1</td>
<td>0.01-0.10</td>
</tr>
<tr>
<td>GRASSLAND</td>
<td>12.5</td>
<td>0.05-0.25</td>
<td>0.11-0.53</td>
</tr>
<tr>
<td><strong>TUNDRA</strong></td>
<td>9.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>DESERT AND SEMIDESERT (SCRUB)</strong></td>
<td>21.0</td>
<td>0.05-0.25</td>
<td>0.11-0.53</td>
</tr>
<tr>
<td><strong>EXTREME DESERT (PERMAFROST, ROCK, SAND)</strong></td>
<td>24.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>SWAMP AND MARSH</strong></td>
<td>2.0</td>
<td>1-5</td>
<td>0.20-1.00</td>
</tr>
<tr>
<td><strong>LAKE AND STREAM</strong></td>
<td>2.0</td>
<td>0.1-0.2</td>
<td>0.02-0.04</td>
</tr>
<tr>
<td><strong>CULTIVATED LAND</strong></td>
<td></td>
<td></td>
<td>2.65-25.00</td>
</tr>
<tr>
<td>MINERAL SOILS (Organic)</td>
<td>15.85</td>
<td>0.5-1.0</td>
<td>0.79-1.59</td>
</tr>
<tr>
<td>ORGANIC SOILS (Matter Decay)</td>
<td>0.15 (est.)</td>
<td>50-150</td>
<td>0.75-2.25</td>
</tr>
<tr>
<td><strong>HUMAN AREA AND OTHERS</strong></td>
<td>3.8</td>
<td></td>
<td>1.54-3.84</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>149.3</td>
<td></td>
<td>4.19-28.84</td>
</tr>
</tbody>
</table>

Estimates of the percentage of fertilizer-$\text{N}$ that is volatilized in the form of $\text{N}_2\text{O}$ have been considerably reduced, on the basis of field measurements, from the early estimates of up to 50% /34/. At present a value in the range of 0.1 to 2.5% may be taken as realistic /e.g., 42, 44-45, 50-53/. In extreme cases, particularly under conditions of concentrated nitrate fertilization in soils having high bacterial activity and which are under partial anaerobiosis, a much higher percentage of the applied fertilizer nitrogen is emitted as $\text{N}_2\text{O}$ /e.g., 53/. It is quite likely that because of the economical incentives involved, and on the basis of the continued study of nitrogen balances in cultivated soils, fertilization practices will be modified to minimize such losses. On the other hand, agricultural intensification, higher inputs of nitrogen fertilizers in existing and new arable lands and an increasing proportion of irrigated intensive agriculture in world production, may all cause higher yearly $\text{N}_2\text{O}$ emissions from fertilized soils in the future. Based on nitrogen fertilizer production of 57.2 Mt $\text{N}$ in 1979/1980 /54/, and the estimated range of values for the percentage emitted as $\text{N}_2\text{O}$ from the fertilizer (0.1-2.5%), a global flux of 0.06 to 1.43 Tg $\text{N}_2\text{O}$ N yr$^{-1}$ is calculated.
Soils as sinks for N\textsubscript{2}O. The consumption of N\textsubscript{2}O by soil biota is a potential sink for atmospheric N\textsubscript{2}O. In laboratory studies it was demonstrated that under reducing conditions, with no other available source of nitrogen, N\textsubscript{2}O was taken from the atmosphere into the soil and converted by enzymatic reactions. Systematic diurnal variation of N\textsubscript{2}O concentration in the air was brought as evidence for soils acting as a major sink for N\textsubscript{2}O by Brice et al. and supported by Cicerone et al. However, these measurements were taken for only a few days; in a year-long study under better-controlled conditions, Pierotti et al. have not found evidence for such diurnal variation. Uptake of N\textsubscript{2}O by soils in the field was observed by Ryden in a non-fertilized perennial ryegrass plot in England. On the other hand, a two year period of measurements of N\textsubscript{2}O emissions in agricultural fields by Duxbury et al., and various samplings in native soils by Mosier et al., have not shown N\textsubscript{2}O uptake. At present, our knowledge of the conditions at which field soils act as sinks for N\textsubscript{2}O, and the parameters affecting the influx when they do so, is too limited to evaluate their importance in the global budgets. More careful long-term measurements are needed to document and quantify this potentially important global sink.

Biomass Burning

Crutzen et al. estimated this source to be 8 Tg N\textsubscript{2}O-N yr\textsuperscript{-1}, an estimate that was used by Stedman and Shetter in their N\textsubscript{2}O budget. A revised lower figure, based on unpublished results, has been recently given by Crutzen (1983) as 1-2 Tg N\textsubscript{2}O-N yr\textsuperscript{-1}.

Purely Anthropogenic Sources

Combustion of fossil fuels. It was estimated that for the mid 1970's combustion processes produced between 1.6 and 2.2 N\textsubscript{2}O-N yr\textsuperscript{-1} and that this contribution is increasing by 3.5% per year.

Wastewater treatment. Modern wastewater treatments use bacterial nitrification-denitrification processes to reduce the level of dissolved nitrogen in the water. It was estimated that about 1-2 Tg N\textsubscript{2}O-N yr\textsuperscript{-1} is released from this source.

Corona production. N\textsubscript{2}O synthesis by corona processes in the atmosphere surrounding high voltage electrical transmission lines was estimated by Hill et al. to be 0.02-0.44 Tg N\textsubscript{2}O-N yr\textsuperscript{-1} for the U.S.A. in 1980. This may be another possibly important global anthropogenic source of atmospheric N\textsubscript{2}O.

THE GLOBAL N\textsubscript{2}O BUDGET

Recent measurements have shown that the intrinsic variability of the N\textsubscript{2}O mixing ratio in the atmosphere is smaller than was measured earlier; thus its atmospheric lifetime is quite likely longer than 100-150 years. Further, it established that atmospheric N\textsubscript{2}O concentration increases with time but that the rate of increase is just 0.2-0.4% per year. These two observations put a strict upper boundary on the N\textsubscript{2}O flux into the atmosphere, limiting it to only 9-17 Tg N\textsubscript{2}O-N yr\textsuperscript{-1}. This is still difficult to reconcile with reliable evidence of significant emissions from various sources on Earth, as reviewed and estimated in the preceding sections. A global N\textsubscript{2}O budget for the late 1970's is given in Table 4. The budget is based on available rate measurements and on conservative estimates of emissions from various natural ecosystems and anthropogenic sources. It shows an excess of documented sources by 0-51 Tg N\textsubscript{2}O-N yr\textsuperscript{-1} over documented sinks. We are forced to conclude that the global N\textsubscript{2}O budget is still unbalanced, on paper at least. Precise, long term measurements are needed on the earth-surface, particularly on land to define quantitatively the sources and sinks of N\textsubscript{2}O — an important atmospheric and biospheric gas.

ACKNOWLEDGEMENTS

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TABLE 4 The Global N$_2$O Budget (For the Late 1970's)

<table>
<thead>
<tr>
<th>SOURCES</th>
<th>Tg N$_2$O-N·yr$^{-1}$</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>• LAND</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NATURAL SOILS AND ECOSYSTEMS</td>
<td>2.6-25.0</td>
<td>(BANIN et al., 1984)</td>
</tr>
<tr>
<td>CULTIVATED SOILS</td>
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<td></td>
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<tr>
<td>FERTILIZER N-CONVERSIONS</td>
<td>0.1-1.5</td>
<td>(BANIN et al., 1984)</td>
</tr>
<tr>
<td>ORGANIC MATTER DECAY</td>
<td>1.5-3.8</td>
<td>(BANIN et al., 1984)</td>
</tr>
<tr>
<td>BIOMASS BURNING</td>
<td>1-2</td>
<td>(CRUTZEN, 1983)</td>
</tr>
<tr>
<td>FOSSIL FUEL BURNING</td>
<td>1-2</td>
<td>(CRUTZEN, 1983)</td>
</tr>
<tr>
<td>WASTE-WATER TREATMENT</td>
<td>1-2</td>
<td>(STEDMAN &amp; SHETTER, 1983)</td>
</tr>
<tr>
<td>• OCEANS (INCLUDING ESTUARIES)</td>
<td>7.36*</td>
<td></td>
</tr>
<tr>
<td>• ATMOSPHERE</td>
<td>1-10</td>
<td>(COHEN &amp; GORDON, 1978)</td>
</tr>
<tr>
<td>LIGHTNING</td>
<td>&lt;0.01</td>
<td>(HILL, 1984)</td>
</tr>
<tr>
<td>POWER LINE CORONA</td>
<td>0.02-0.5</td>
<td>(HILL, 1984)</td>
</tr>
<tr>
<td>EXCITED SPECIES CHEMISTRY</td>
<td>0-20 (?)</td>
<td>(STEDMAN &amp; SHETTER, 1983)</td>
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<tr>
<td>SINKS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STRatospheric PHOTOlytic Decomposition</td>
<td>6-11</td>
<td>(CRUTZEN &amp; SCHMAILZL, 1983)</td>
</tr>
<tr>
<td>ATMOSPHERIC ACCUMULATION</td>
<td>0.2-0.4% PER YEAR</td>
<td>2.8-5.6</td>
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<td>UNACCOUNTED FOR</td>
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<td></td>
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<tr>
<td>UNKNOWN SINK: TROPOSPHERE(?)</td>
<td>3-6</td>
<td>(KAHLIL &amp; RASMUSSEN, 1983)</td>
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<tr>
<td>BIOSPHERE(?) PEDOSPHERE(?)</td>
<td>0.51</td>
<td></td>
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</table>

*TOTALS ARE ROUNDED OFF.

REFERENCES


