# Emission of oxides of nitrogen ($NO_x$) and ammonia from the earth's surface[1]

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ABSTRACT

The natural emissions of oxides of nitrogen (odd nitrogen) and ammonia from the earth's surface in the northern hemisphere are estimated to have upper limits of $3 \times 10^{13}$ g(N) year$^{-1}$ and $13 \times 10^{13}$ g(N) year$^{-1}$ respectively based on considerations of boundary layer resistance. This estimate indicates that anthropogenic emissions are a major component of the nitrate cycle in the northern hemisphere.

## 1. Introduction

In this paper an estimate is made of the upper limit of the natural emission from the earth's surface of oxides of nitrogen and ammonia. Such estimates are needed to provide constraints in numerical models of atmospheric chemical processes and to evaluate the effect of anthropogenic sources on the various natural cycles of trace substances and thus the effect of these sources on either the biosphere or the climate. This analysis is confined to the northern hemisphere where the necessary measurements are available. The slow exchange rate between the two hemispheres in the troposphere, approximately 1 year (Newell et al., 1969) compared with the residence time of these species in the troposphere gives some justification for the separation.

## 2. Natural gaseous emissions from the earth's surface

The upper limit of the rate of natural emission from the earth's surface is estimated from measurements of the mixing ratio of the gas in "background" surface air and the bulk vertical eddy diffusivity of the planetary boundary layer. The transfer mechanism for natural emissions from the earth's surface to the free atmosphere also applies to anthropogenic emissions. However, the latter occur in very limited areas and are characterised by concentrations orders of magnitude higher than natural or "background" levels in the surface air. For the following calculations the two can be separated.

Considering the mixing ratio difference $\Delta\psi$ between the level $Z_S$ at which the mixing ratio $\psi_S$ is measured in surface air ($Z_S$ is usually 1 m) and some upper level $Z_T$ at the top of the boundary layer or in the free troposphere, the difference is $\Delta\psi = \psi_S - \psi_T$. This can be written as $\Delta\psi = f\psi_S$ where $f$ is some positive fraction or unity and the limiting case is $\Delta\psi = \psi_S$. Using $\Delta\psi = f\psi_S$ in the flux gradient equation

$$F = \varrho \bar{K} \Delta\psi / \Delta Z \qquad (1)$$

where $\varrho$ is the air density and $\bar{K}$ the bulk climatological average eddy diffusivity over the height interval $\Delta Z$, one can obtain a limit of $F$, the vertical flux of the gas. The upper limit of the flux is also the upper limit of the natural emission from the surface.

Six calculations are made of the natural emission for each substance. Two fractions for the mixing ratio difference and three estimates of the bulk eddy diffusivity are used. Two of the latter are for error estimates. The level $Z_T$ is set at 2 km and the selection of this will be discussed later.

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Table 1. *Gas mixing ratios in the surface air*
Units: $10^{-9}$ V/V

| | Continental | | Oceanic |
|---|---|---|---|
| | Temperate | Tropical | |
| $NO + NO_2$ | 4 | 1 | — |
| $NH_3$ | 7 | 18 | 4 |
| Area $10^{14}$ m$^2$ | 0.8 | 0.15 | 1.4 |

The mixing ratio difference $\Delta\psi$ will be set to 50% and 90% of the surface mixing ratio value, $\psi_S$. This sets the tropospheric mixing ratio values at a factor of two and an order of magnitude respectively below the surface values. Such decreases, if real, are very important boundary conditions for models of tropospheric chemistry.

The "background" values of mixing ratio of oxides of nitrogen and ammonia in the surface air are taken from Georgii (1963), Junge (1963), Hamilton et al. (1968), Pate et al. (1970*a*, *b*) and Breeding et al. (1973), see Table 1. The ammonia emissions are calculated for continental and ocean areas and the oxides of nitrogen emissions are calculated for continental areas only. There is no likely mechanism for producing NO or $NO_2$ in seawater. Georgii (1963) presented results showing for air passing over rainwater and distilled water that the $NO_2$ in the air is absorbed into the water, converted to nitrite then nitrate and irreversibly lost to the air. This process can be expected to take place at the ocean–air interface. The NO and $NO_2$ found over the oceans is probably advected from continental areas, and so no emission is calculated for oceanic areas.

The tropical area is defined as 0° to 15° N and the temperate area as 15° to 70° N. It is assumed that there is no deposition or emission north of 70° N (Robinson & Robbins, 1970). The bulk eddy diffusivity is calculated from an eddy diffusivity profile by integration of the flux profile equation. This profile has a linear form with a change of slope at 100 m. The long term climatological average eddy diffusivity values at various levels are 1 m: $10^3$ cm$^2$ s$^{-1}$; 100 m: $10^5$ cm$^2$ s$^{-1}$ and 2 km: $2 \times 10^5$ cm$^2$ s$^{-1}$. For error estimates the eddy diffusivity profiles take the following forms. The lower limit is where the eddy diffusivity is constant at $10^5$ cm$^2$ s$^{-1}$ from 100 m to 2 km. The upper limit is where the eddy diffusivity has a constant value of $2 \times 10^5$ cm$^2$ s$^{-1}$ from the surface to 2 km. The climatological average values of eddy diffusivity are consistent with average values observed for small scale mixing in the lower part of the planetary boundary layer (R. H. Clarke, private communication) and with those deduced from radioactivity studies in the free atmosphere for mixing on all scales (Bolin, 1965).

Possible natural sources of nitrate within the air include lightning and oxidation of nitrous oxide. Georgii (1963) gives evidence indicating there is no significant fixing of nitrogen by lightning. McConell (1973) computes the rate of oxidation of nitrous oxide to be $\sim 10^{11}$ g(N) per year and so compared with the natural emission $\sim 10^{13}$ g(N) per year it can be neglected in the lower atmosphere.

This analysis requires also that there be constant fluxes of these gases, i.e. no sinks, between the surface and $Z_T$. The known sinks for these gases are absorption on water droplets in the cloud layer and conversion in the gas phase by reaction with hydroxyl radicals (Crutzen, 1974). The upper level $Z_T$ is chosen to be the maximum thickness (giving the minimum estimate of the natural emission), that is consistent with negligible divergence of the vertical fluxes of these gases due to sink mechanisms. $Z_T$ is set at 2 km. This is below the average condensation level. The divergence of the vertical fluxes due to the hydroxyl reactions can be calculated from a simple analytical model. Using a global long term average hydroxyl concentration in the lower atmosphere of $5 \times 10^5$ mol cm$^{-3}$ (see Crutzen, 1974, for values in sunlit air), it appears that the following calculations underestimate the surface flux of oxides of nitrogen by less than 20% for the mean eddy diffusivity calculation and less than 10% for the upper limit calculation. This error for the fluxes of ammonia is in all cases less than 1%.

## 3. Comparison of various sources and sinks

The calculated natural emission rates, estimated anthropogenic source strength, deposition in rainwater, and a previous estimate of

Table 2. *Nitrate and ammonium sources and sinks in the Northern Hemisphere*

Units: $10^{12}$ g year$^{-1}$ (nitrogen)

| | $NO_3-N$ | $NH_4-N$ |
|---|---|---|
| *Sources* | | |
| Natural emission | | |
| Mixing ratio decrease | | |
| 50 % | $2\pm1$ | $7\pm3$ |
| 90 % | $3\pm2$ | $13\pm5$ |
| Previous estimate (half of global estimate, see text) | 11 | 43 |
| Anthropogenic emission | 1.5 | 0.4 |
| *Sinks* | | |
| Deposition in Rain | 2 | 3 |

natural emission rate (Robinson & Robbins, 1970) are presented in Table 2. Two points are evident from the table.

(1) The calculated natural emission rates are much smaller than previous estimates.

(2) The anthropogenic emission of oxides of nitrogen in the northern hemisphere is comparable in magnitude with the estimate of the upper limit of natural emission calculated here.

It should be noted that the anthropogenic emission rate is for 1965 (Robinson & Robbins, 1970). More than 90% of this emission takes place in the northern hemisphere. It can be seen from the fossil fuel consumption figures of Rotty (1973) and an estimate of oxides of nitrogen emission factors for combustion that the anthropogenic oxides of nitrogen emission rate increased by about 60% between 1960 and 1970 on the 1960 value. An equivalent or larger increase can be expected during the current decade.

The deposition of nitrate and ammonium in rainwater is based on the data of Junge (1958), Lodge et al. (1968), Angström & Hogberg (1952) and Petrenchuk & Selezneva (1970). These data are based on measurements during the last three decades. If the older data presented in Eriksson (1952) is used then a deposition rate approximately twice that in Table 2 is obtained. The data presented in Table 2 show that natural emissions are adequate to explain the deposition of nitrate and ammonium separately.

## 4. Conclusions

An estimate of the natural emission of oxides of nitrogen and ammonia from the earth's surface is presented. It appears that in the northern hemisphere the anthropogenic and natural emission of oxides of nitorgen are comparable in magnitude with the latter somewhat larger. Consequently nitrate aerosol and deposition probably have significantly increased during the last few decades due to increased fossil fuel consumption. Isotopic analysis of tropospheric nitrate possibly can resolve the actual contributions of man made and natural sources.

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## ЭМИССИЯ ОКИСЛОВ АЗОТА ($NO_x$) И АММИАКА ПОВЕРХНОСТЬЮ ЗЕМЛИ

Оценивается, что естественные эмиссии окислов азота и аммиака с земной поверхности в северном полушарии имеют верхние пределы, соответственно, в $3 \cdot 10^{13}$ *г* (N)/год и $13 \cdot 10^{13}$ *г* (N)/год, что получено путем рассмотрения сопротивления пограничного слоя. Эти оценки указывают, что антропогенные эмиссии в северном полушарии являются главными компонентами нитратного цикла.