# Molecular Nitrogen Fixation and Nitrogen Cycle in Nature

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## *Abstract*

The origin of nitrogen oxides in the atmosphere is discussed. Evidently only a small proportion of the nitrate- and nitrite-nitrogen found in the precipitation is formed through electric discharges from molecular nitrogen, photochemical nitrogen fixation being probably of greater importance. Formation of nitrate nitrogen through atmospheric oxidation of nitrous oxide ($N_2O$) evaporating from the soil is also considered likely.

Determination of nitrogen compounds at different altitudes is indispensable for gaining information of the $N_2$-fixation in the atmosphere and, in general, of the origin of nitrogen oxides and their decomposition. International co-operation is needed for this as well as for the quantitative determination of the nitrogen compounds removed from the soil by leaching and brought by waters into the seas.

In a recent issue of this journal ÅNGSTRÖM and HÖGBERG (1952) have dealt with the concentration of $NH_4$-N and $NO_3$-N in atmospheric precipitation and its dependence on the character of the air mass, in the light of the observations made in Sweden during recent years. At the request of Prof. Rossby I shall present in this paper some aspects of the nitrogen cycle which also may be of interest to meteorologists.

The atmosphere, with its 77,000 tons of molecular nitrogen per ha, is the nitrogen store of the earth, and the fixed nitrogen in the soil — also in good cultivated soil a few or at most some tens of tons per ha — originates chiefly from the nitrogen fixation by microorganisms (so-called biological nitrogen fixation). Without this process the earth would not have its present plant and animal kingdom. The most intensive nitrogen fixation takes place in the leguminous root nodules. A good lucerne or clover field fixes 150—400 kg $N_2$ per ha per summer. The amounts of nitrogen fixed by the action of free-living nitrogen-fixing microorganisms are much more modest varying perhaps from some kilograms to a few tens of kilograms per ha. $N_2$-fixation is not known to take place in soil independent of living cells. The share of industrial fertilizers in the nitrogen contained in the annual crops of the cultivated plants of the globe is only some two per cent. In regard to nitrogen fixation I refer to my recent lecture (VIRTANEN, 1952).

Nitrogen fixation can be expected in the atmosphere by electric discharges and photochemically. There is no reliable information as to how extensive is the $N_2$-fixation in the atmosphere. The studies have mostly been directed to the determination of nitrogenous compounds brought to the earth by precipitation. In this way, however, no elucidation can be obtained of the $N_2$-fixation in the atmosphere as will be seen from the following:

1. The precipitation contains more $NH_4$-N than $NO_3$-N. There is reason to assume that $NH_4$-N originates from the soil, for ammonia synthesis does not seem likely under atmos-

pheric conditions. Organic nitrogen which is found in the rain water originates from dust particles, insects and microorganisms in the air.

2. $NO_3$-N present in the rain water (and $NO_2$-N which also is found to some extent) can be formed by $N_2$-fixation. It must be assumed that some nitrogen oxides are derived from electric discharges connected with thunderstorms, a conclusion which follows from the knowledge of the conditions of $N_2$-oxidations. FINNELL and HOUGHTON (1932) have tried to estimate the increase in the nitrate nitrogen of rain effected by thunderstorms in Goodwell (Oklahoma), and HUTCHINSON (1944) has calculated on the basis of the values reported that at most 140—350 g $N_2$ is fixed per ha in temperate regions through electric discharges. Since the annual precipitation contains about one kilogram $NO_3$-N per ha, electric discharges would, on the average, have no great part in the production of this nitrate.

It is quite possible that most of the $N_2$-fixation in the atmosphere is photochemical. The conditions for this fixation exist probably in the ozonosphere, at altitudes of over 10 km, where both oxygen and nitrogen have great energy. Ozone oxidizes the nitrogen oxide formed to nitrogen pentoxide which has been spectroscopically found by ADEL and LAMPLAND (1938) in the ozonosphere, in amounts of about 1 mol. per 100 mol. ozone. The downward moving nitrogen pentoxide may be brought with rain to the earth's surface, the rising nitrogen pentoxide becomes exposed to a more and more energetic radiation which causes the molecules to decompose. The observations of ELVEY (1942) on the spectral bands of NO at altitudes of about 90—140 km is in accord with this.

There is, however, no certainty that all the $NO_3$-N in the precipitation is produced by $N_2$-fixation. On the contrary, it is very possible that a part of it is formed through oxidation of $NH_4$-N. Nitrous oxide $N_2O$, which evaporates from the soil and is liberally formed, in addition to $N_2$, in the decomposition of nitrate by bacteria (denitrification), also may be partly oxidized in the atmosphere to higher nitrogen oxides. ADEL (1939, 1951) was the first to find $N_2O$ in the atmosphere. According to him, $N_2O$ is decomposed

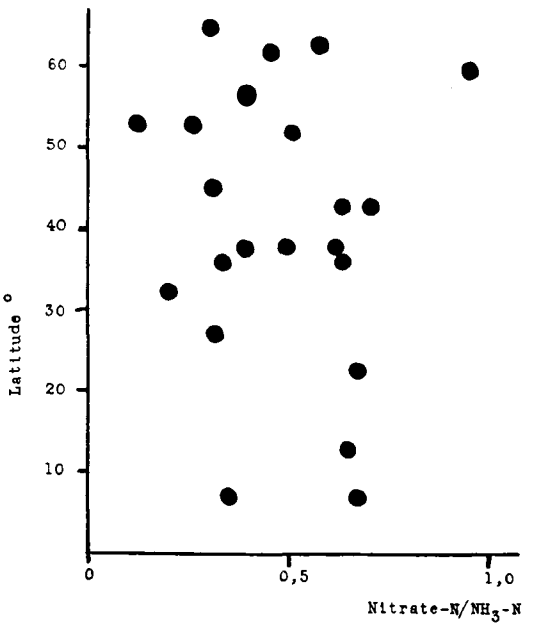


Fig. 1. Inter-relationship between nitrate-N and ammonium-N in precipitation at different latitudes.

photochemically to $N_2$, $O_2$, and NO by $\lambda <$ 2,000 A in the upper atmosphere. The latter product is further dissociated photochemically to $N_2$ and $O_2$. While NO is being brought to the lower atmosphere it may, however, be oxidized to $NO_2$ and even further to higher nitrogen oxides (author's opinion). Consequently, there is a possibility that a part of the $NO_3$-N found in the precipitation may originate from the $N_2O$ evaporated from the soil.

The amount of nitrogen compounds in the atmosphere is nowadays also very much affected by man. In industrial centres and densely populated districts as a whole, both nitrogen oxides (mainly $NO_2$) and ammonium nitrogen are brought to the atmosphere as products of burning solid and liquid fuels. This makes explicable the enormous amounts of $NO_3$-N and $NH_4$-N (12.3 kg and 15.9 kg per ha respectively) found by SCHARRER and FAST (1952) in the annual precipitation near Giessen in Germany. (In Iceland RUSSEL and RICHARDS (1919) found 0.912 kg. $NH_4$-N and 0.292 kg. $NO_3$-N in precipitation per ha; in East Bothnia, Finland, FINNBERG (1923) found 1.8 kg. $NH_4$-N, 0.825 kg. $NO_3$-N,

and 0.025 kg. $NO_2$-N in precipitation per ha). It must also be borne in mind that some $N_2$-fixation obviously also takes place in internal combustion engines and that with the increasing number of automobiles, tractors etc. nitrogen oxides may be brought to the atmosphere, although their amount is relatively insignificant.

ÅNGSTRÖM and HÖGBERG consider on the basis of the Swedish data, that the annual precipitation at Uppsala contains normally 1.90 kg. $NH_4$-N and 0.91 kg. $NO_3$-N per ha. Hence the ratio of $NO_3$-N to $NH_4$-N would be almost constant, about 0.5, which seems to suggest a common origin. However, such a ratio is not regularly found in the analyses of precipitation reported in the literature. Fig. 1 gives the inter-relationship of $NO_3$-N and $NO_4$-N in precipitation at different latitudes in the northern hemisphere computed from values found in the literature.

The personal opinion of the author is that the analyses of the precipitation do not give full information of the atmospheric nitrogen compounds, of their origin, and of the possible participation of nitrogen oxides in the chemical reactions in the atmosphere. It would be necessary to obtain quantitative data of the different nitrogen compounds in various layers of the atmosphere from the ground level to high altitudes. Such determinations would probably give a definite idea of the formation of nitrogen oxides from $N_2$ and of their decomposition at different altitudes, as well as of the nitrogen compounds evaporating from the earth's surface. The nitrogen cycle in nature would thus become more defined. This work is difficult in method, but as far as I can see there is no other way.

In order to get elucidation on the nitrogen status of the earth and changes therein, systematic analytical work would be needed for determination of the amounts of different nitrogen compounds which are annually brought by waters into the seas. Nitrogen analyses should be made at definite intervals in different parts of the world at the mouth of representative rivers, both large and small. In order to obtain a realiable picture of the quantitative side of the nitrogen cycle international cooperation is indispensable. If the nitrogen analyses of the riverwaters are accompanied by determinations of phosphate, potassium, and calcium (and possibly other elements), material will be obtained which will be of immense significance to the agriculture and forestry of the world, in other words, for the living possibilities of man.

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