The role of atmospheric ammonia in biogeochemical nitrogen circulation

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Reduced Nitrogen in Ecology and the Environment
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Outline

0. What Biogeochemistry does mean?
1. Historical remarks and first studies
2. Chemical remarks on ammonia
3. Origin and evolution of nitrogen and ammonia
4. Early studies on nitrogen and ammonia cycling
5. Interactions in biogeochemical circulation
6. Changes in biogeochemical circulation
7. Conclusions
Biogeochemistry ≠ Biochemistry + Geochemistry

= Chemistry of the Biosphere-Atmosphere Interaction

Biosphere = Sphere where Life is existing
(= Pedosphere + Hydrosphere + parts of Litho- and Atmosphere

Biochemistry = Chemistry of Organisms
(= Biology + Chemistry)

Geochemistry = Chemistry of the (solid) Earth
(= Geology + Chemistry)
Definition of a biogeochemical cycle

(from internet)

The transformation and transport of substances within and among the atmosphere, biosphere, hydrosphere, and lithosphere via biological, geological, and chemical processes that are often cyclical in nature.

The exchange of chemicals between living and nonliving reservoirs in the Earth System.

The transformation and transport of substances within and among the atmosphere, biosphere, hydrosphere, and lithosphere via biological, geological, and chemical processes that are often cyclical in nature.
1. Historical remarks and first studies
What means ammonia? Where the name is coming from?

In Greek:
αμμος = sand
αμμωνια = landscape in ancient Lybia (Ammon Temple, close to Egypt)

Its name is derived from deposits of camel manure near the Ammon temple in Egypt, from which *Sal Ammoniacum* has been produced.

*Amon* or *Ammon* (Egyptian, “hidden”), ancient Egyptian deity, originally a local Theban god of reproductive forces, represented as a ram. Later Amon was identified with the sun god Ra of Heliopolis, and was known as Amon-Ra, “the father of the gods, the fashioner of men, the creator of cattle, the lord of all being.” As a universal god he became the god of the Egyptian nation and the empire. Amon was worshiped in the ancient Greek colonies of Cyrene, where he was identified with Zeus, and in Rome, where he was associated with Jupiter.
Ammonium (άμμωνίαχόν after Dioscorides, c. 40-90 AD) was already known in ancient time: Hammoniacus Sal by Plinius (Gaius Plinius Secundus, c. 23-79 AD). However, in ancient time this salt mainly was rock salt (NaCl) and there are no signs that NH$_3$/NH$_4^+$ was known as pure substance. Pliny (Plinius) wrote Naturalis historia, the first encyclopaedia.

Djabir (Geber), the legend arabian scholar, expressed first NH$_4$Cl (called sal ammoniacum in Latin translations later) being a 4$^{th}$ „spirit“ beside mercury, sulphur and arsenium sulphide (zarnach).

Abu Musa Dschabir ibn Hayyan (arabian: ابو موسى جابر بن حيان), in Latin: Geber (about 721-815), „father of chemistry“ carried out first alchemistic experiments.
Albertus Magnus (1200-1280) called it sal-ammoniac
Johann Rudolph Glauber (1604-1679) called it sal armoniacum
Basilius Valentinus (15th century) called it Salarmoniac and showed that ammonia (NH₃) could be obtained by the reaction of alkalis on sal-ammoniac.

The German term Salmiak is a condensed version (sal-ammoniac) and first introduced end of 17th century.
Historical remarks on ammonia

Ammonia (NH₃)

was first studied from sal-amoniac in 13th century by Raymund Lull (c.1232-1315) and produced from putrefied urine (he called it spiritus animalis).

The alchemists called the lost substance while burning / heating salts volatile alkali (alcalicum volatile). They found it from treatise of urine, blood and animal rests.

Basilius called it spiritus salis urinae. Later it was called Alcali volatilis salis armoniaci. Bergman (1782) abbreviated it to Ammoniacum.

Pure gaseous ammonia was first isolated by Priestley (1774: Experiments and Observations on different Kinds of Air) and was termed by him alkaline air.

Scheele (1777) found (Abhandlungen über Luft und Feuer) that ammonia contains nitrogen. Berthollet (1785) determined the constitution (NH₃).
### Different archaic names of ammonia

<table>
<thead>
<tr>
<th>German</th>
<th>English</th>
<th>Latin</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkalische Luft</td>
<td>alkaline air</td>
<td>spiritus salis urinae</td>
</tr>
<tr>
<td>urinöse Luft</td>
<td>volatile alkali</td>
<td>aer alcalicus</td>
</tr>
<tr>
<td>flüchtig-alkalische Luft</td>
<td>spirit of hartshorn</td>
<td>mephitis urinosa</td>
</tr>
<tr>
<td>laugensalzige Luft</td>
<td></td>
<td>gas alcalicum volatile</td>
</tr>
<tr>
<td></td>
<td></td>
<td>gas ammonium</td>
</tr>
</tbody>
</table>
### Milestones in discovering N in atmospheric air

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1772</td>
<td>Cavendish privately told Priestley about his experiments with “mephistic air” (nitrogen); thus it seems likely that already knew before Rutherford “inflammable air” (N₂); Rutherford made experiments where he removed oxygen from air by burning substances (i.e., charcoal) and afterwards carbon dioxide by absorption with lime; the rest (nitrogen) he denoted as “phlogisted air” (Cavendish published his results first in 1783)</td>
</tr>
<tr>
<td>1772</td>
<td>Hales was the first who analysed dew and rain, noted that &quot;the air is full of acid and sulphurous particles&quot;</td>
</tr>
<tr>
<td>1774</td>
<td>Nitrogen in rainwater (as nitrate NO₃⁻) was first found by the German chemist Marggraf from Berlin in and soon later confirmed by the Swedish chemist Bergmann</td>
</tr>
<tr>
<td>1777</td>
<td>Scheele and Lavoisier recognized that air consists from two gases (O₂ and N₂)</td>
</tr>
<tr>
<td>1786</td>
<td>Scheele found ammonia in air by observing that on the cork from the bottle containing hydrochloric acid a precipitation originated, identified as salt ammonia (NH₄Cl)</td>
</tr>
<tr>
<td>1785/88</td>
<td>Cavendish and Priestley found formation of nitric acid (NO₃⁻) in air by electric discharges</td>
</tr>
<tr>
<td>1804</td>
<td>de Saussure stated that ammonia gas is always in air</td>
</tr>
<tr>
<td>1825</td>
<td>first deduction of ammonium in rainwater by Brandes (1826/27 by Liebig)</td>
</tr>
<tr>
<td>1840</td>
<td>Liebig stated that ammonia is the most important N source for plants</td>
</tr>
<tr>
<td>1848</td>
<td>Begin of systematic rain water studies (first in Wiesbaden by Fresenius, later by Barral, Bineau, Boussinggault, Pierre, Smith,...)</td>
</tr>
<tr>
<td>1856</td>
<td>first Boussinggault stated that the evaporation of ammonia from the sea plays a role in its natural global budget</td>
</tr>
</tbody>
</table>
NICOLAS THEODORE DE SAUSSURE (1767-1845), eldest son of Horace Benedict de Saussure (1740-1799), the great botanist, at Geneva.

Stated that there is no doubt on the presence of ammonia vapour in the atmosphere when considering that cake alum (aluminium sulphate) on free air converts into ammonia alum.

Recherches chimiques sur la végétation (Paris, 1804), p. 209

"This work laid the foundations of a new science, phytochemistry. Saussure examined the chief active components of plants, their synthesis, and their decomposition. He specified the relationships between vegetation and the environment and here, too, did pioneering work in what became the fields of pedology and ecology"
2. Chemical remarks on ammonia
Essential elements for life (in abundance order):

**O, C, H, N, Ca, K, Si, Mg, S, Al, P, ...**

(brown: non-volatile, i.e. only solid from soil)

(blue: volatile, i.e. gaseous via the atmosphere)

<table>
<thead>
<tr>
<th>gas</th>
<th>liquid</th>
<th>dissolved</th>
<th>solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$^+$ + OH$^-$</td>
<td>H$_2$O</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-</td>
<td>H$^+$ + HCO$_3^-$</td>
<td>-</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-</td>
<td>OH$^+$ + NH$_4^+$</td>
<td>-</td>
</tr>
<tr>
<td>NO$_y$</td>
<td>-</td>
<td>H$^+$ + NO$_3^-$</td>
<td>-</td>
</tr>
<tr>
<td>red. S</td>
<td>-</td>
<td>H$^+$ + SO$_4^{2-}$</td>
<td>-</td>
</tr>
</tbody>
</table>

**PM**: C$_{y}$H$_{b}$O$_{c}$N$_{d}$S$_{e}$ (biomass)
The role of hydrogen and oxygen
3.

Origin and evolution of nitrogen and ammonia
Element Fusion Processes

\[
\begin{align*}
56\text{Fe} & \leftrightarrow 52\text{Cr} \leftrightarrow 48\text{Ti} \leftrightarrow 44\text{Ca} \leftrightarrow 40\text{Ca} \leftrightarrow 36\text{Ar} \leftrightarrow 32\text{S} \leftrightarrow 28\text{Si} \\
\text{from } 10^9 \text{ K}
\end{align*}
\]

\[
\begin{align*}
1^1\text{H} & \rightarrow 2^1\text{H(D)} \rightarrow 3^1\text{He} \rightarrow 3^2\text{He(-}2^1\text{H)} \rightarrow 4^1\text{He} \\
\text{from } 10^7 \text{ K}
\end{align*}
\]

\[
\begin{align*}
4^1\text{He} & \rightarrow 8^1\text{Be} \rightarrow 12^1\text{C} \rightarrow 13^1\text{C} \\
16^1\text{O} & \rightarrow 14^1\text{N} \\
15^1\text{N} & \rightarrow 15^1\text{O} \\
\text{from } 2 \cdot 10^8 \text{ K}
\end{align*}
\]
Abundance of elements in space
from solar nebula via thermonuclear reactions and condensation / aggregation

photolysis \( h^\nu \)

degassing

hot dissociation

cold hydrolysis

before biological life

Evolution of the nitrogen circulation (1)
Evolution of the nitrogen circulation (2)

from solar nebula via thermonuclear reactions and condensation / aggregation

hot dissociation

cold dissolution

photolysis hv

degassing

NH₄Cl

MₓNᵧ primordial rocky substances

NH₃

NH₄Cl

NH₃

into space

technical fixation (via ammonia synthesis)

N₂

N₂O

NO₃⁻

NH₄⁺

NH₃

NH₄⁺

NO₃⁻

N₂O

deposition emission deposition

chemical fixation

biological fixation

oxidation

denitrification

nitrification

assimilation

mineralisation

feeding

plants

animals

before biological life present
The biogeochemical cycling

- Atmosphere: \( \text{CO}_2, \text{H}_2\text{O}, \text{NH}_3, \text{O}_2, \ldots \)
- Assimilation
- Respiration (dissimilation)
- Fermentation
- Anaerobic mineralization
- Aerobic mineralization
- Microorganisms in soil and water
  - \( \text{NH}_4^+, \text{S}_2^- \)
  - \( \text{NO}_3^-, \text{SO}_4^{2-} \)
- Emission
- Deposition
- Feeding
- Abiotic conversion
- Death (decomposition)
- Living biomass
- Animals
- Plants
- Organic substances
The Greek philosophers already recognized the cycle of life, things and water (e.g. Aristoteles in his „Meteorologica“).

However, the „cycle of matter“ was not seen before knowledge of the chemical composition of the atmosphere, soils, plant and animals beginning of 19th century.

Likely Justus von Liebig in his „Chemische Briefe“ (1843) first mentioned the „cycle of matter“ in animality and plant kingdom“ in his 22th letter:
Heinrich Wilhelm Brandes, German physicist in Leipzig, known for the first synoptic weather map (1820), collected 1825 in Salzuffeln rain water and found the average quantity of foreign matter amounted 26 ppm(m); he qualitatively determined (beside organics, chlorine, sulphuric acid, soda, potasch, magnesia, carbonic acvid, lime and oxide of iron) ammonia salts.

In 1838, Jean Baptiste Boussingault conducted an elegant series of experiments and showed that legumes had higher nitrogen levels than cereals and, based on some crop rotation studies over 5 years, concluded that the atmosphere was the source of this nitrogen (it could have been particulate matter, nitrogen gas or ammonia - he did not specify which).

Liebig stated (1843) that plants receive all nitrogen from the atmosphere and that ammonia is the most important species. Because of the low amount of ammonia in rain, nitrogen must be taken up from the atmosphere in other forms.

Reiset (1856) was the first who has shown based on experiments that nitrogen iy cycled through the biological world. He reported that decaying plant and animal materials pour out nitrogen into the atmosphere.

Schloesing and Muntz (1877) and Hellriegel and Wilfarth (1889) conducted many experiments in showing the biological nitrogen fixation.
The Nitrogen Cycle and its Role for the Rural Economy.

(1878)

Critical monography on the Nitrogen cycle.

(1907)

Early German books on nitrogen cycling (all in relation to rural economy)
Robert Angus Smith (1817-1884)

was a Scottish chemist, who investigated numerous environmental issues. He stayed from 1839 in Germany to study under Justus von Liebig, earning a Ph.D. in 1841. He became first chief inspector of the alkali industry under the United Kingdom's Alkali Works Act of 1863. He also studied the chemistry of the atmosphere, the results of which he published in his 1872 book, “Air and Rain, the Beginning of a chemical climatology”.

To me, he is being the first Atmospheric Chemist.
There was an analytical problem in 19th century because ammonia was everywhere and ammonia stuck to every thing, Smith wrote (1878). See Table:

<table>
<thead>
<tr>
<th>Milligrammes of Ammonia per cubic metre of Air.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prince’s Road ..................................</td>
</tr>
<tr>
<td>Open yard during rain ..........................</td>
</tr>
<tr>
<td>Front of laboratory ............................</td>
</tr>
<tr>
<td>Office .........................................</td>
</tr>
<tr>
<td>Front and back during fog ....................</td>
</tr>
<tr>
<td>Close-shut-up room .............................</td>
</tr>
<tr>
<td>Closet outside .................................</td>
</tr>
<tr>
<td>Densest part of fog ...........................</td>
</tr>
</tbody>
</table>

Concentration where much higher then present due to missing canalisation and huge ammonia evaporation in urban areas. Ammonia was considered as a key substance for decaying matter, and thus, of waste (organic) substances. Many works on ammonia did not consider the absorption onto samples and sampling devices resulting in overestimated data. However, the dominant trace gas in 19th century atmosphere was ammonia!

Present concentrations amount 0.001-0.020 mg·m⁻³, i.e. on average 2 orders of magnitude less!
Conclusions from early air studies:

- One can conclude that in air ammonium carbonate and nitrate were dominant particulate species, which are washout out quantitatively by rain.
- It was found that fog contains large amounts of these species.
- It was considered that wet deposition and soil uptake (dry deposition) contributes significantly to the plant nitrogen budget.
- Gaseous ammonia was an urban problem (much higher concentrations than nowadays).
- Rainwater concentrations similar to present ones: historical emission data underestimated?
5.
Interactions in biogeochemical circulation
Scheme of basic nitrogen transformations

- **NH<sub>x</sub>** → **N<sub>2</sub> / N<sub>2</sub>O** via **fixation**
- **N<sub>2</sub> / N<sub>2</sub>O** → **NO<sub>y</sub>** via **denitrification**
- **NH<sub>x</sub>** → **organ. N** via **assimilation**
- **NO<sub>y</sub>** → **organ. N** via **mineralisation**
- **organ. N** → **NH<sub>x</sub>** via **assimilation**
Simplified scheme (basic processes)

- CO₂, O₂, H₂O, S-, P-, etc.

- NH₃
- NOₓ
- N₂
- NH₃
- NOₓ

**Processes:***
- **NH₃**
  - deposition
  - emission
  - biol. fixation
  - assimilation (emission)
  - nitrification

- **NOₓ**
  - deposition
  - denitrification (emission)

- **N₂**
  - techn. fixation
  - chem. fixation
  - techn. oxidation

- **biosphere**
(aqueous-phase) biochemical NO\(_y\) – NH\(_x\) – transformation scheme
Man-made modified global nitrogen cycle

- NO2
- NOx
- N2O
- N2
- NO3
- NH3
- NH4+
- org-NH2
- Haber-Bosch
- Technosphere
- Atmosphere
- Biosphere (incl. Rural Economy)
- ammonia oxidation to nitric acid
- fertilizer application
- deposition
- emission
- mineralisation
- assimilation
- denitrification
- nitrification
Atmospheric role of ammonia

- NH$_3$ particulate matter (CCN)
- HCl, HNO$_2$, HNO$_3$, H$_2$CO$_3$ (CO$_2$+H$_2$O), H$_2$SO$_4$ (SO$_3$+H$_2$O):
  - gas-to-particle formation
- evaporation
- evaporation/desorption
- scavenging
- nucleation
- evaporation (cloud cycling)
- deposition

- particle production: water cycle and climate
- N redistribution and (long-range) transportation
- buffering of acidity (fixing of gaseous acids)

Note: NH$_3$ oxidation by OH (into NO) is negligible
6. Changes in biogeochemical circulation

(1890: 9, 1990: 43) (man-made NH₃ emission Tg N yr⁻¹ after Van Aardenne, 2001)
Evolution of world fertilizer use between 1940 and 2030

Fate of applied nitrogen fertilizers
(Möller and Schieferdecker, 1985)

Problem:
- small N percentage plant incorporation
- high N loss from animals

Diagram:
- Fertilizer input (100)
  - Inorganic N in soil (30, 40, 55)
    - Organic N in soil (30, 10)
      - Inorganic and organic N in water (20)
        - Ocean (50)
    - Organic N in soil (20)
      - Inorganic and organic N in water (20)
        - Ocean (50)
  - Atmospheric N (N₂, N₂O, NO, NH₃) (15)
    - Plants (55)
      - Animals (7, 45)
        - Excrements (5)
        - Waste water (10)
      - Man (3, 52)
    - Waste water (30)


## Global NH\textsubscript{x} Budget (in Tg N yr\textsuperscript{-1})

<table>
<thead>
<tr>
<th></th>
<th>natural emission</th>
<th>biomass burning</th>
<th>man-made emission</th>
<th>total emission</th>
<th>deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>terrestrial</td>
<td>oceanic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Söderlund and Svensson (1976)</td>
<td>2-6</td>
<td>-</td>
<td>-</td>
<td>24-47</td>
<td>30-50</td>
</tr>
<tr>
<td>Jaffe (1992)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>122</td>
</tr>
<tr>
<td>Möller (1996)</td>
<td>8</td>
<td>15</td>
<td>-</td>
<td>30</td>
<td>53</td>
</tr>
<tr>
<td>Bouwman et al. (1997)</td>
<td>7.2</td>
<td>8.2</td>
<td>4.1</td>
<td>34.1</td>
<td>54</td>
</tr>
<tr>
<td>Schlesinger (1997)</td>
<td>-</td>
<td>13</td>
<td>-</td>
<td>52</td>
<td>-</td>
</tr>
<tr>
<td>Friedrich and Obermeier (2000)</td>
<td>3</td>
<td>10</td>
<td>7.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Watts (2000)</td>
<td>4-8</td>
<td>10-15</td>
<td>5-7</td>
<td>20-40</td>
<td>50-60</td>
</tr>
<tr>
<td>Brasseur et al. (2003)</td>
<td>12</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>52</td>
</tr>
</tbody>
</table>

- : means no data given

„best“ figures: man-made: 40±5
natural: 15-25

### Problems:

- oceanic emission most important natural source (?)
- biomass burning as source is man-made (!)
- Natural terrestrial emission still uncertain
Global nitrogen fixation

Problem:

Amplifying by humans:

- increase of fluxes among the spheres
- increase of soil and atmospheric NH\textsubscript{x} burden
Conclusions:
Role of NH$_3$ in biogeochemical circulation

- Intermediate in biological N recycling
- Redistribution of N via atmosphere
- Fixation of free H$^+$ in atmosphere (transformation of strong into weak acidity) - „buffering“
- Partnership with acids in gas-to-particle formation (→ CCN and climate)
- Carrier of acidity: release of strong acidity (free H$^+$) in soils (biochemically)
- Intermediate in technical N fixation

Note: NH$_x$ is (geo-)chemically almost inactive!