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 Greak:
αμμος = sand
αμμωνία = 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 encyclopodia.

Plinius elder

Djabir (**Geber**), the legend arabian scholar, expressed first NH_4Cl (called sal ammoniacum in Latin translations later) being a 4th „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 (NH_3) could be obtained by the reaction of alkalis on sal-ammoniac.

Alchemistic characteristics

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

Historical remarks on ammonia

Ammonia (NH_3)

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).

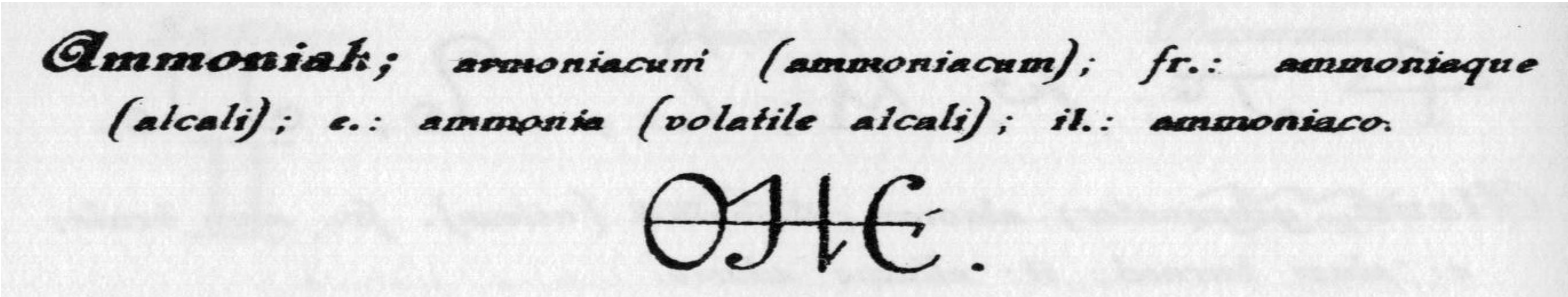
The alchemists called the lost substance while burning / heating salts volatile alkali (alcalicum volatile). They found it from treatise of urine, blood and animal rests.

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 (NH_3).

Different archaic names of ammonia



Ammoniak; armoniacum (ammoniacum); fr.: ammoniaque (alcali); e.: ammonia (volatile alcali); it.: ammoniaco.

German	English	Latin
alkalische Luft urinöse Luft flüchtig-alkalische Luft laugensalzige Luft	alkaline air volatile alkali spirit of hartshorn	spiritus salis urinae aer alcalicus mephitis urinosa gas alcalicum volatile gas ammonium

Milestones in discovering N in atmospheric air

1772	Cavendish privately told Priestley about his experiments with "mephistic air" (nitrogen); thus it seems likely that already knew before Rutherford "inflammable air" (N_2); 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)
1772	Hales was the first who analysed dew and rain, noted that "the air is full of acid and sulphurous particles"
1774	Nitrogen in rainwater (as nitrate NO_3^-) was first found by the German chemist Marggraf from Berlin in and soon later confirmed by the Swedish chemist Bergmann
1777	Scheele and Lavoisier recognized that air consists from two gases (O_2 and N_2)
1786	Scheele found ammonia in air by observing that on the cork from the bottle containing hydrochloric acid a precipitation originated, identified as salt ammonia (NH_4Cl)
1785/88	Cavendish and Priestley found formation of nitric acid (NO_y) in air by electric dicharges
1804	de Saussure stated that ammmonia gas is always in air
1825	first dedection of ammonium in rainwater by Brandes (1826/27 by Liebig)
1840	Liebig stated that ammonia is the most important N source for plants
1848	Begin of systematic rain water studies (first in Wiesbaden by Fresenius, later by Barral, Bineau, Boussinggault, Pierre, Smith,…)
1856	first Boussinggault stated that the evaporation of ammonia from the sea plays a role in its natural global budget

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 doupt 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

group / periode	1	2	3	4	5	6	7	8
1							**H**	
2				**C**	**N**	**O**	F	
3	Na	Mg	Al	Si	P	**S**	Cl	
4	K	Ca						

Essential elements for life
(in abundance order):

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

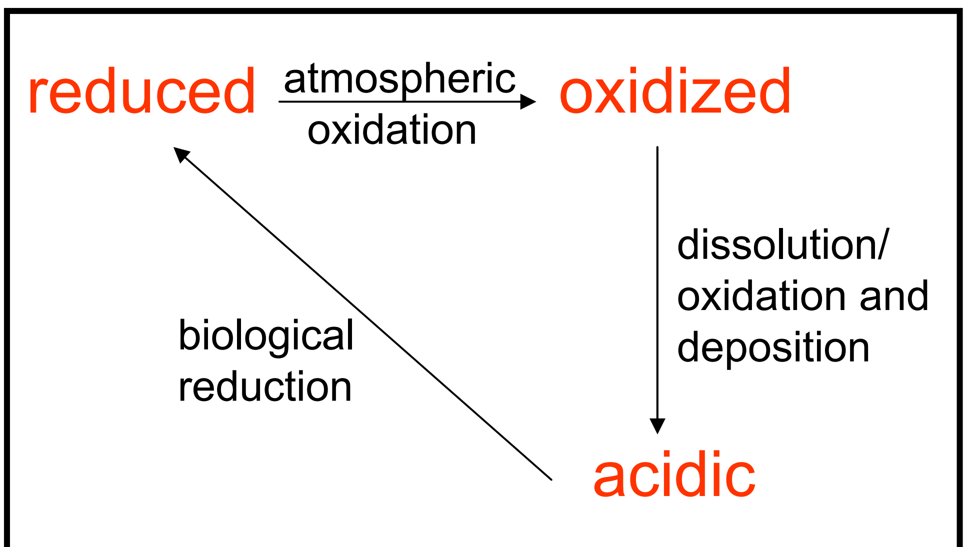
(blue: volatile, i.e. gaseous via the atmosphere
brown: non-volatile, i.e. only solid from soil)

Most important compounds:

gas	liquid	dissolved	solid
H_2O	H_2O	$H^+ + OH^-$	H_2O
CH_4	-	-	$C_yH_bO_cN_dS_e$ (biomass) PM
CO_2	-	$H^+ + HCO_3^-$	
NH_3	-	$OH^+ + NH_4^+$	
NO_y	-	$H^+ + NO_3^-$	
red. S	-	$H^+ + SO_4^{2-}$	

group / periode	4	5	6
2	CH_4	NH_3	OH_2
3		PH_3	SH_2

group / periode	4	5	6
2	CO_x	NO_y	OO_x
3		x = 1, 2 y = 1, 2, 3 z = 2, 3	SO_z

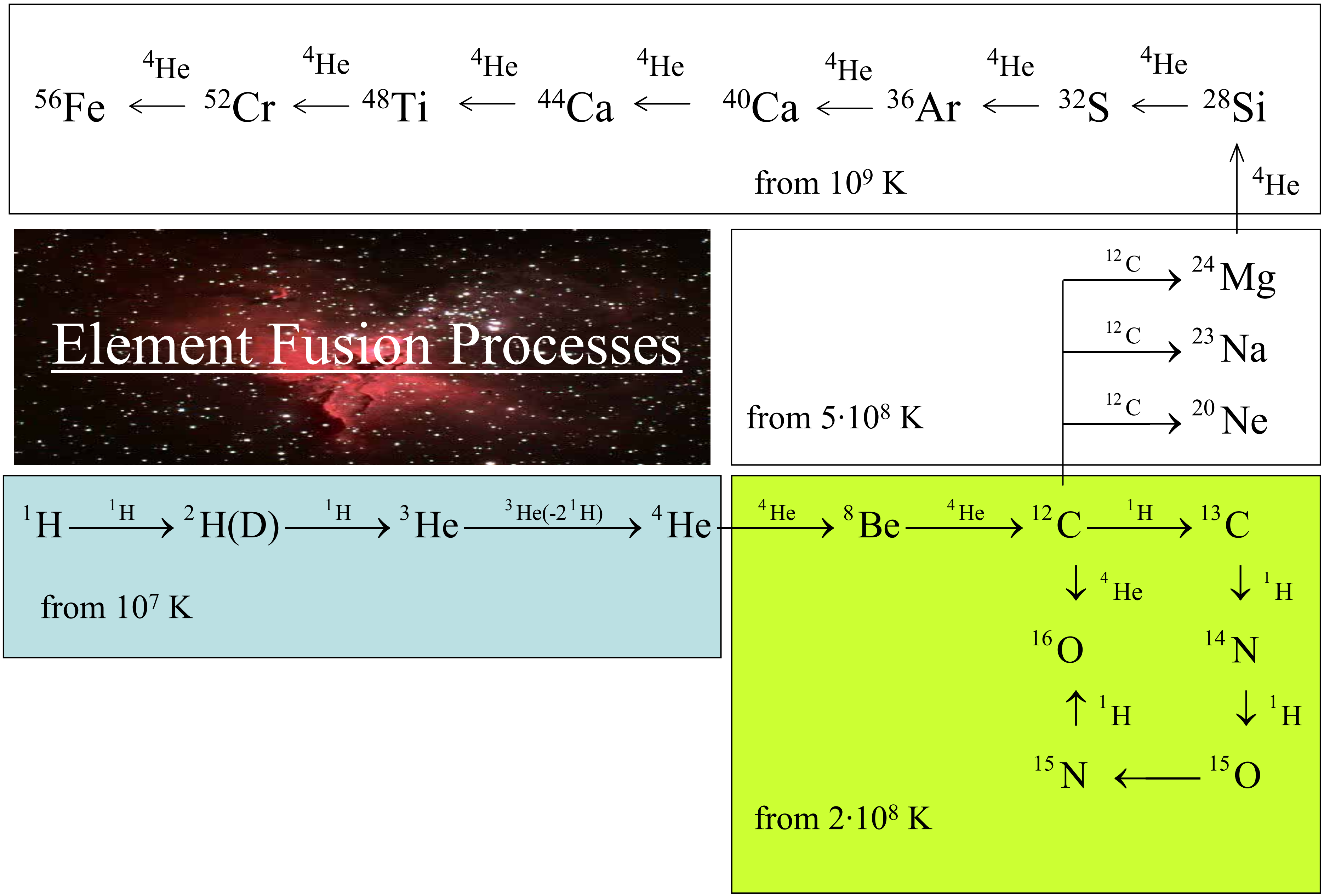


group / periode	4	5	6
2	H_2CO_3	HNO_3	H_2O_2
3		H_3PO_4	H_2SO_4

The role of hydrogen and oxygen

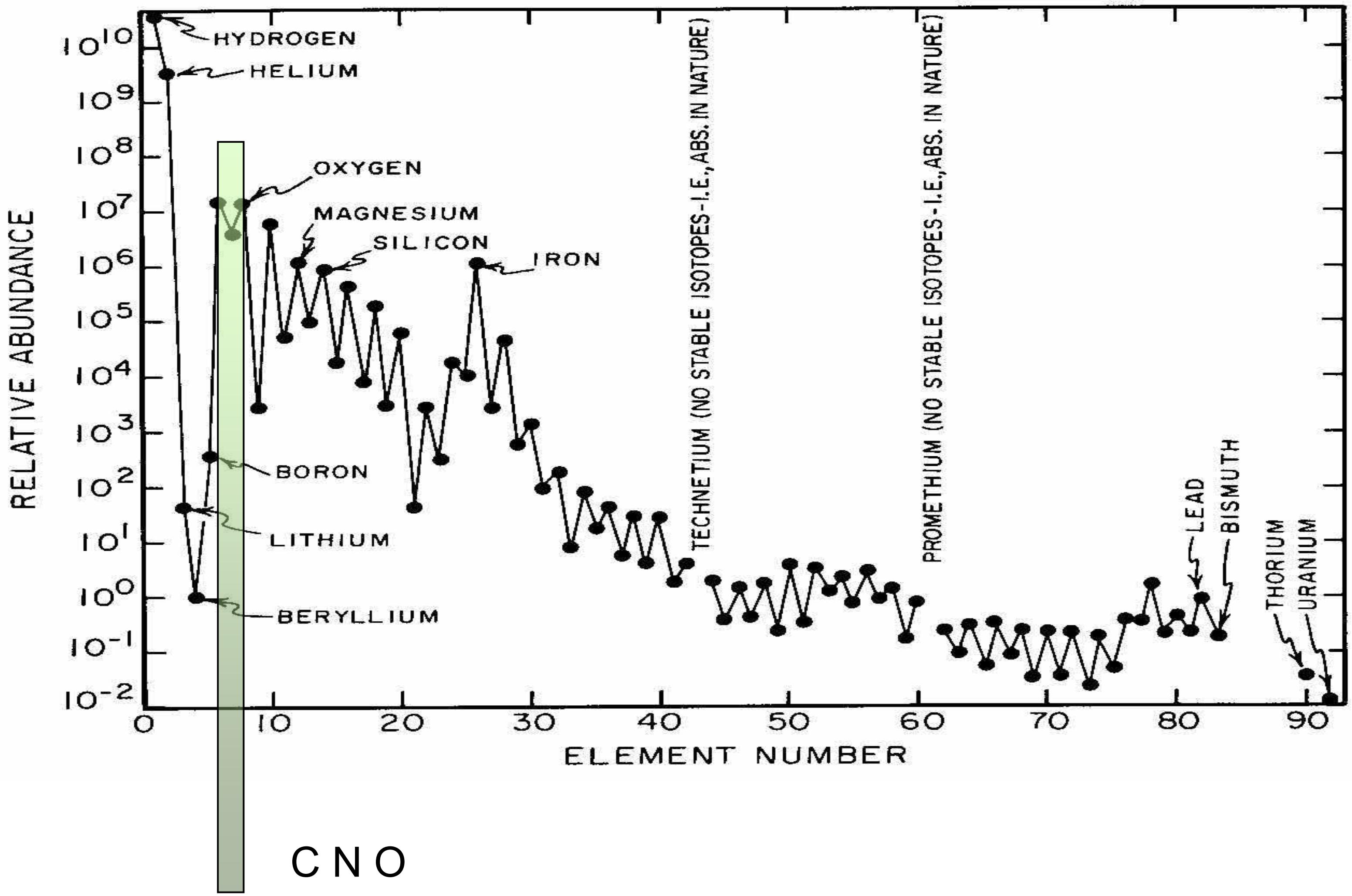
3.

Origin and evolution of nitrogen and ammonia

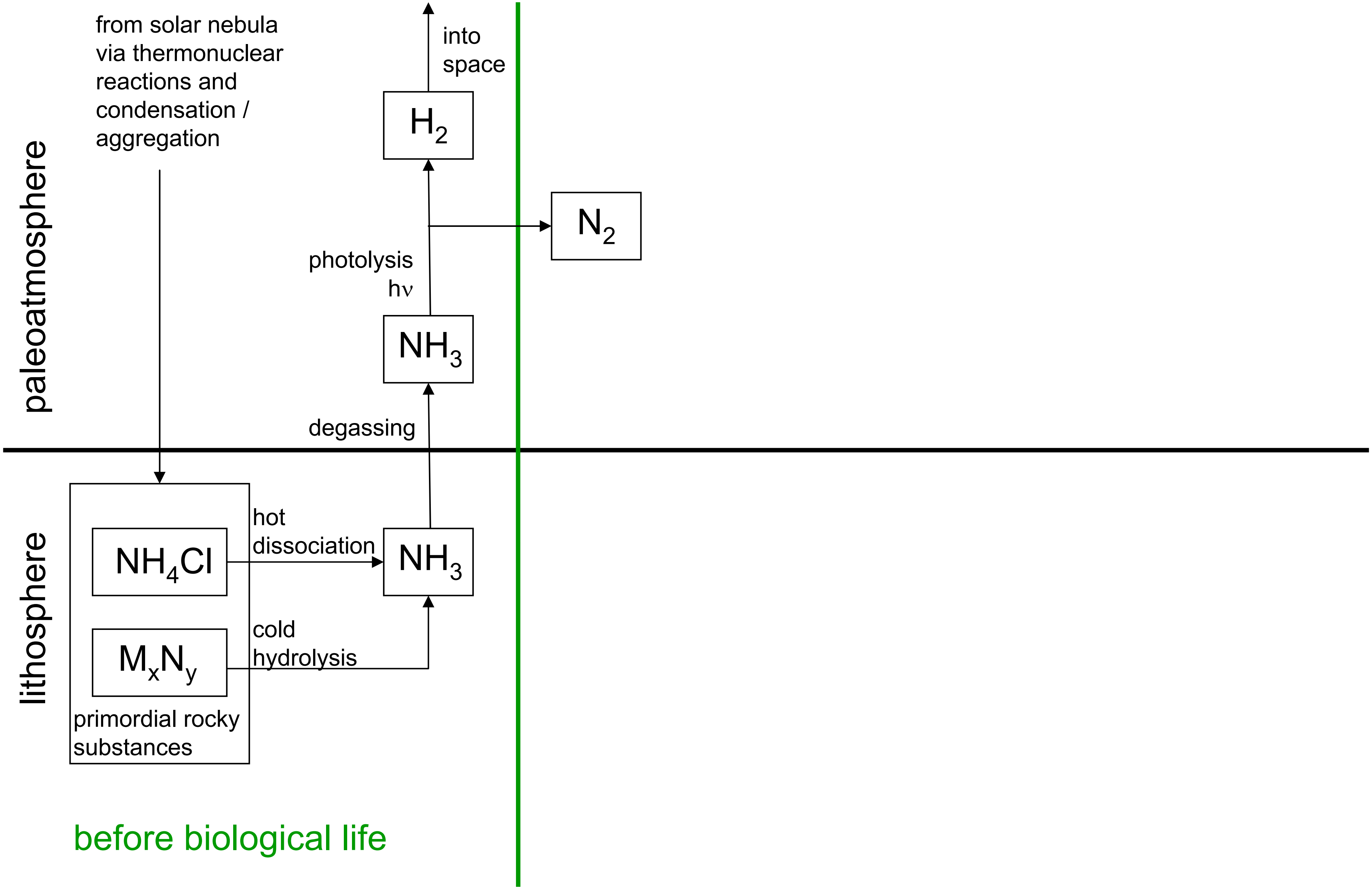


Element Fusion Processes
$^{56}Fe \xleftarrow{^{4}He} {}^{52}Cr \xleftarrow{^{4}He} {}^{48}Ti \xleftarrow{^{4}He} {}^{44}Ca \xleftarrow{^{4}He} {}^{40}Ca \xleftarrow{^{4}He} {}^{36}Ar \xleftarrow{^{4}He} {}^{32}S \xleftarrow{^{4}He} {}^{28}Si$
^{4}He
from 10^9 K
^{12}C → ^{24}Mg
^{12}C → ^{23}Na
^{12}C → ^{20}Ne
from $5 \cdot 10^8$ K
$^{1}H \xrightarrow{^{1}H} {}^{2}H(D) \xrightarrow{^{1}H} {}^{3}He \xrightarrow{^{3}He(-2\,^{1}H)} {}^{4}He$
from 10^7 K
$^{4}He \xrightarrow{^{4}He} {}^{8}Be \xrightarrow{^{4}He} {}^{12}C \xrightarrow{^{1}H} {}^{13}C$
^{4}He
^{16}O
^{1}H
^{14}N
^{1}H
^{1}H
^{15}N
^{15}O
from $2 \cdot 10^8$ K

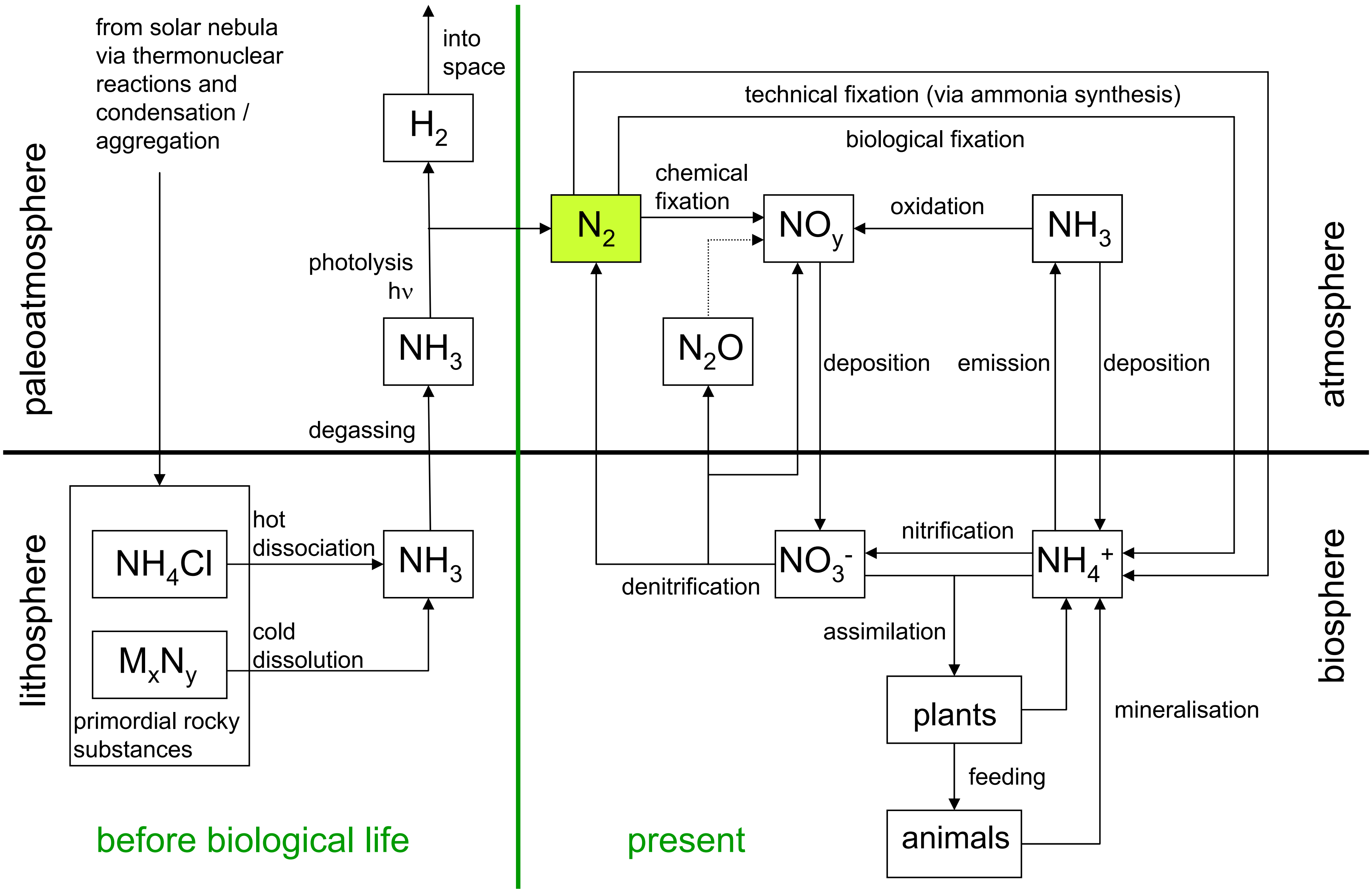
Abundance of elements in space



Evolution of the nitrogen circulation (1)



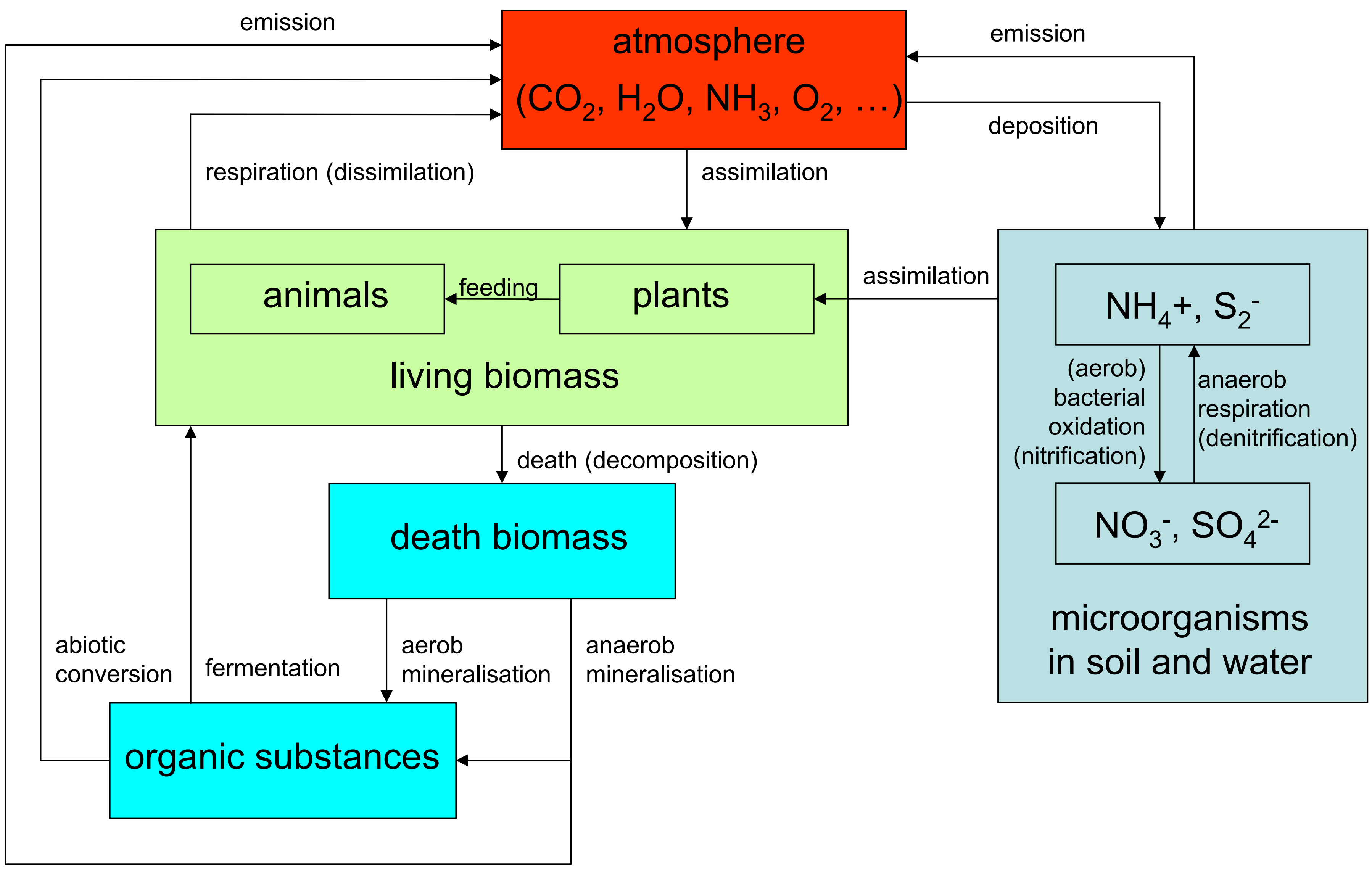
Evolution of the nitrogen circulation (2)



before biological life

present

The biogeochemical cycling



4.

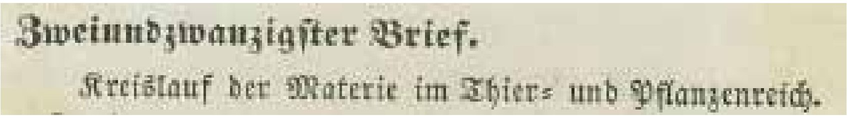
Early studies on nitrogen and ammonia cycling

κύκλος (Greek)= cycle (circulation) = Kreis (Kreislauf, Zyklus)

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 kwowledge 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:


Zweiundzwanzigster Brief.

Kreislauf der Materie im Thier- und Pflanzenreich.

Milestones in biosphere – atmosphere - interaction

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).

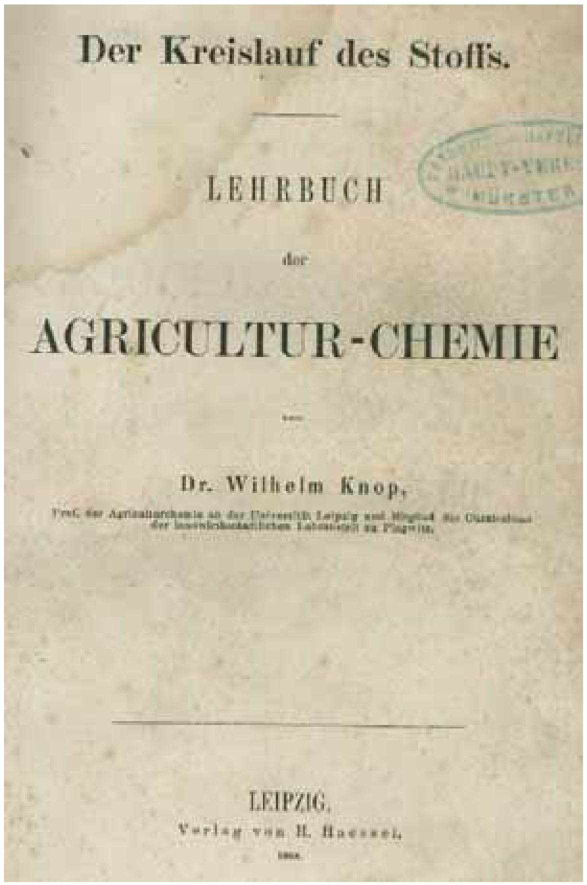
Liebig stated (1843) that plants receive all nitrogen from the atmosphere and that ammonia is the most important species. Because of the low amount of ammonia in rain, nitrogen must be taken up from the atmosphere in other forms.

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 cycle of matter.
Textbook of
Agricultural Chemistry

(1868)


Der Kreislauf des Stoffs.

LEHRBUCH

der

AGRICULTUR-CHEMIE

von

Dr. Wilhelm Knop,

LEIPZIG.
Verlag von H. Haessel.

The Nitrogen Cycle
and its
Role for the Rural Economy.

(1878)


Der Kreislauf des Stickstoffs

und seine

Bedeutung für die Landwirthschaft.

Von

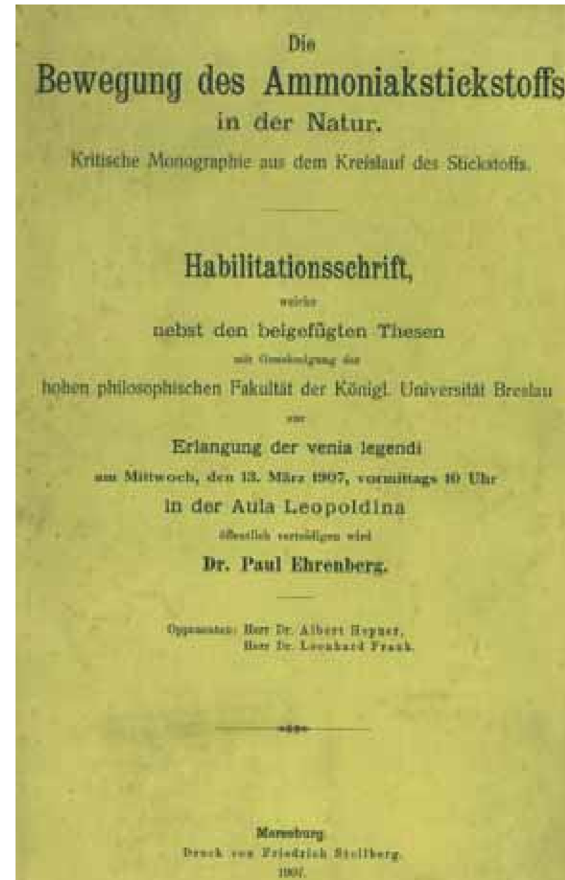
Dr. J. König,

Vorsteher der Landw. Versuchsstation Münster.

Münster, 1878.
Druck und Verlag der Theissing'schen Buchhandlung.

The
Flow of Ammonia-Nitrogen
through Nature.
Critical monography on the Nitrogen cycle.

(1907)


Die
Bewegung des Ammoniakstickstoffs
in der Natur.
Kritische Monographie aus dem Kreislauf des Stickstoffs.

Habilitationsschrift,
welche
nebst den beigefügten Thesen
mit Genehmigung der
hohen philosophischen Fakultät der Königl. Universität Breslau
zur
Erlangung der venia legendi
am Mittwoch, den 13. März 1907, vormittags 10 Uhr
in der Aula Leopoldina
öffentlich verteidigen wird
Dr. Paul Ehrenberg.

Opponenten: Herr Dr. Albert Hepner,
Herr Dr. Leonhard Frank.

Merseburg
Druck von Friedrich Stollberg.
1907.

Early German books on nitrogen cycling (all in relation to rural economy)

XXXIV. *The Distribution of Ammonia.*

By R. ANGUS SMITH, F.R.S. &c.

Read April 30th, 1878.

IF organic matter is everywhere, the presence of ammonia is everywhere possible; and if that matter is decomposing, ammonia is everywhere. That is the general statement which this paper illustrates. It is now many years since it

Contained in Memoirs of the Manchester Literary and Philosophical Society, 3 Series, Volume 6, pages 267-278

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 stucks to every thing, Smith wrote (1878). See Table:

Milligrammes of Ammonia per cubic metre of Air.

Prince's Road	·086
Open yard during rain	·119 and ·102
Front of laboratory	·167 ordinary.
Office	·167
Front and back during fog	·476
Close-shut-up room	·413
Closet outside	·800 to ·900
Densest part of fog	1·25

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!

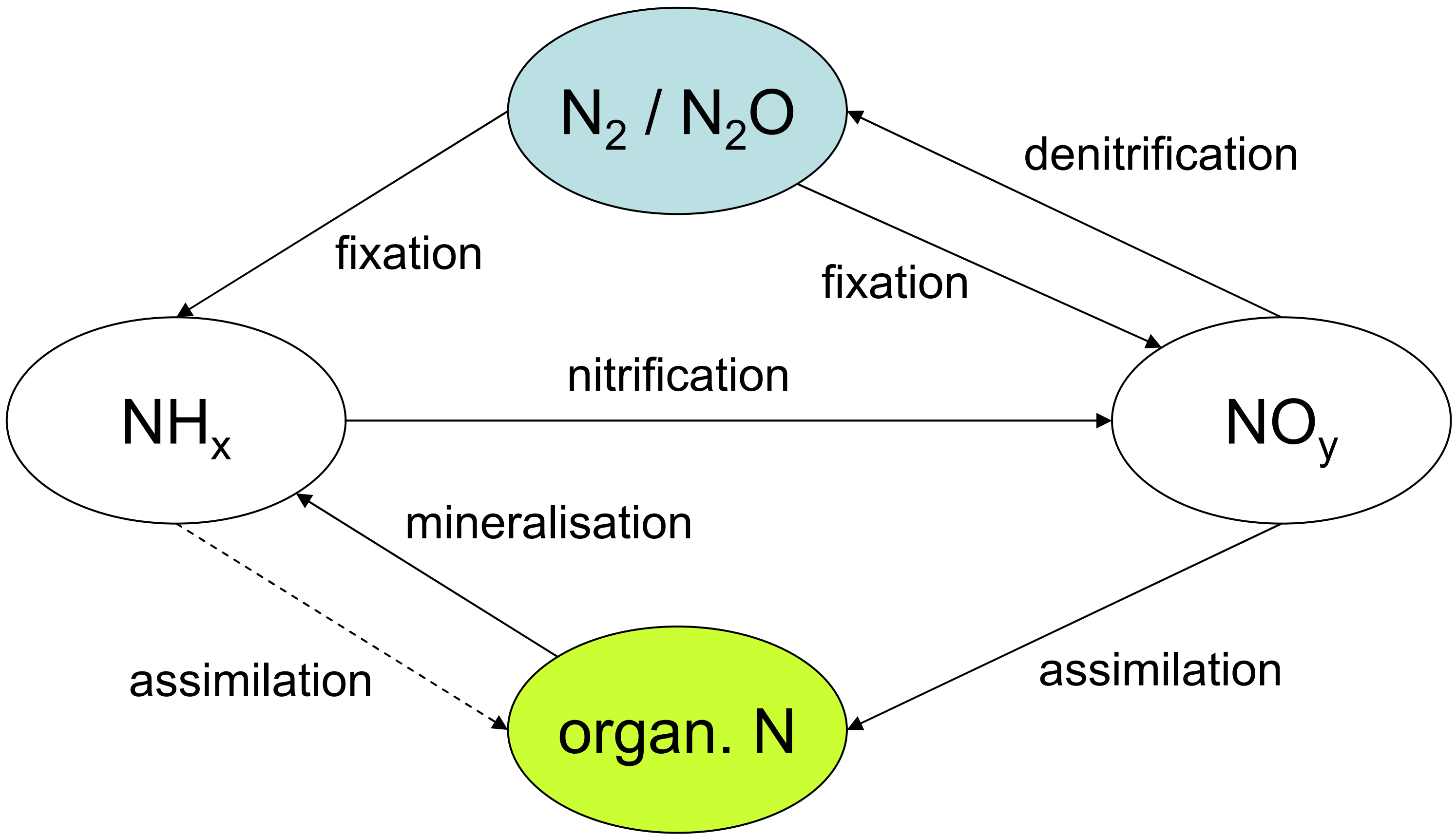
Present concentrations amount 0.001-0.020 $mg \cdot m^{-3}$,
i.e. on average 2 orders of magnitude less!

Conclusions from early air studies:

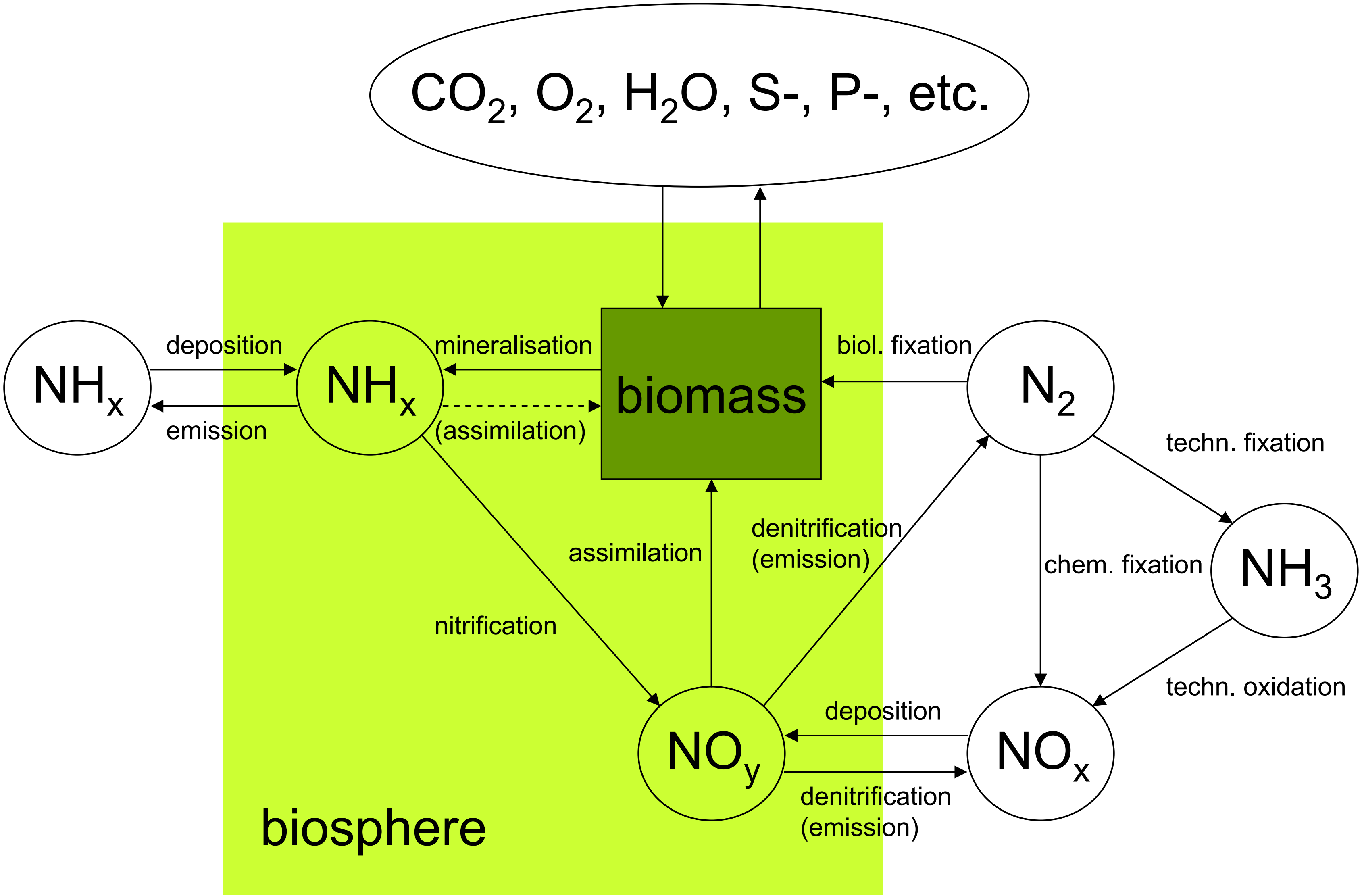
- One can conclude that in air ammonium carbonate and nitrate where dominant particulate species, which are washout out quantitatively by rain.
- It was found that fog contains large amounts of these species.
- It was considered that wet deposition and soil uptake (dry deposition) contributes significantly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

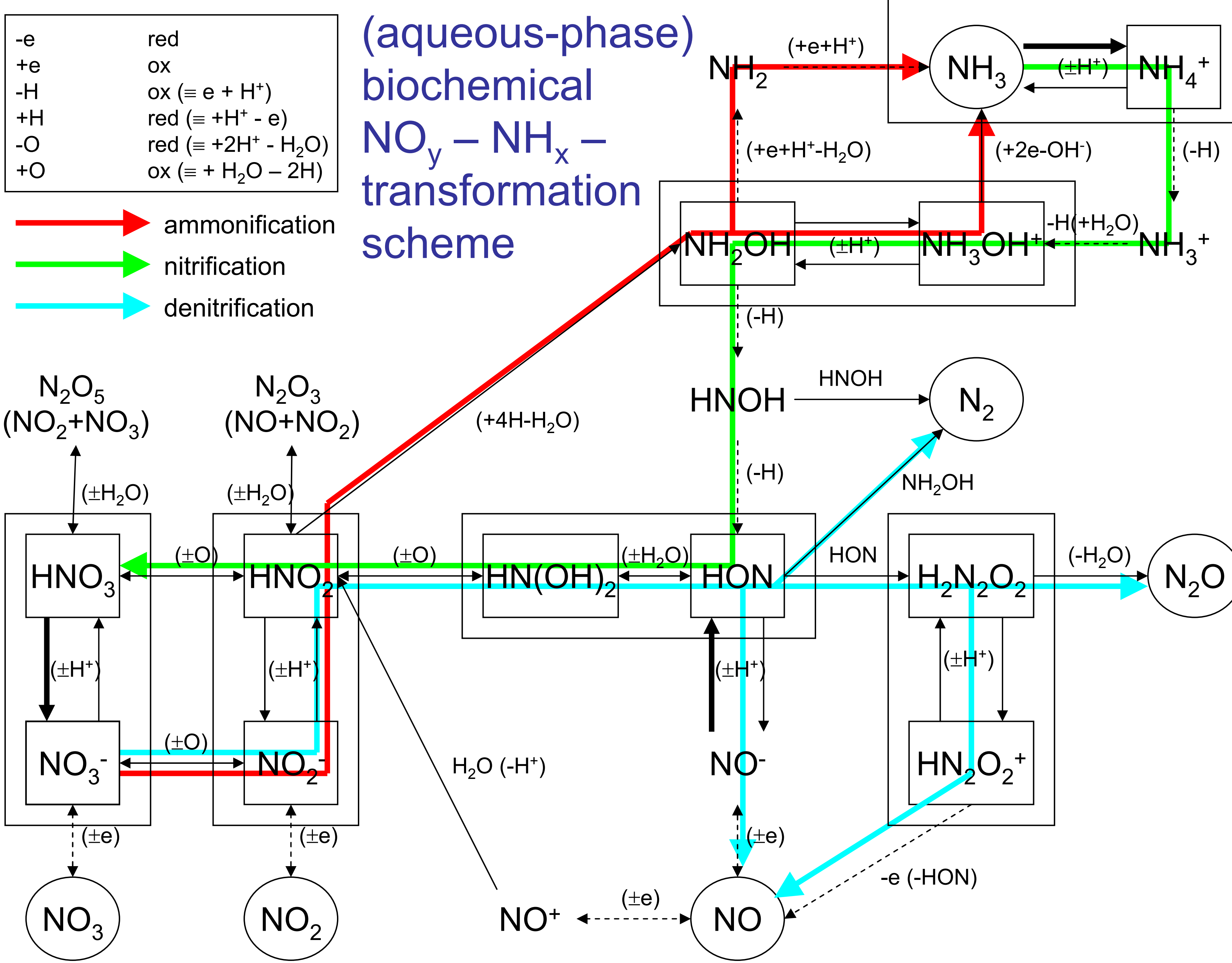
5.
Interactions in biogeochemical circulation

Scheme of basic nitrogen transformations

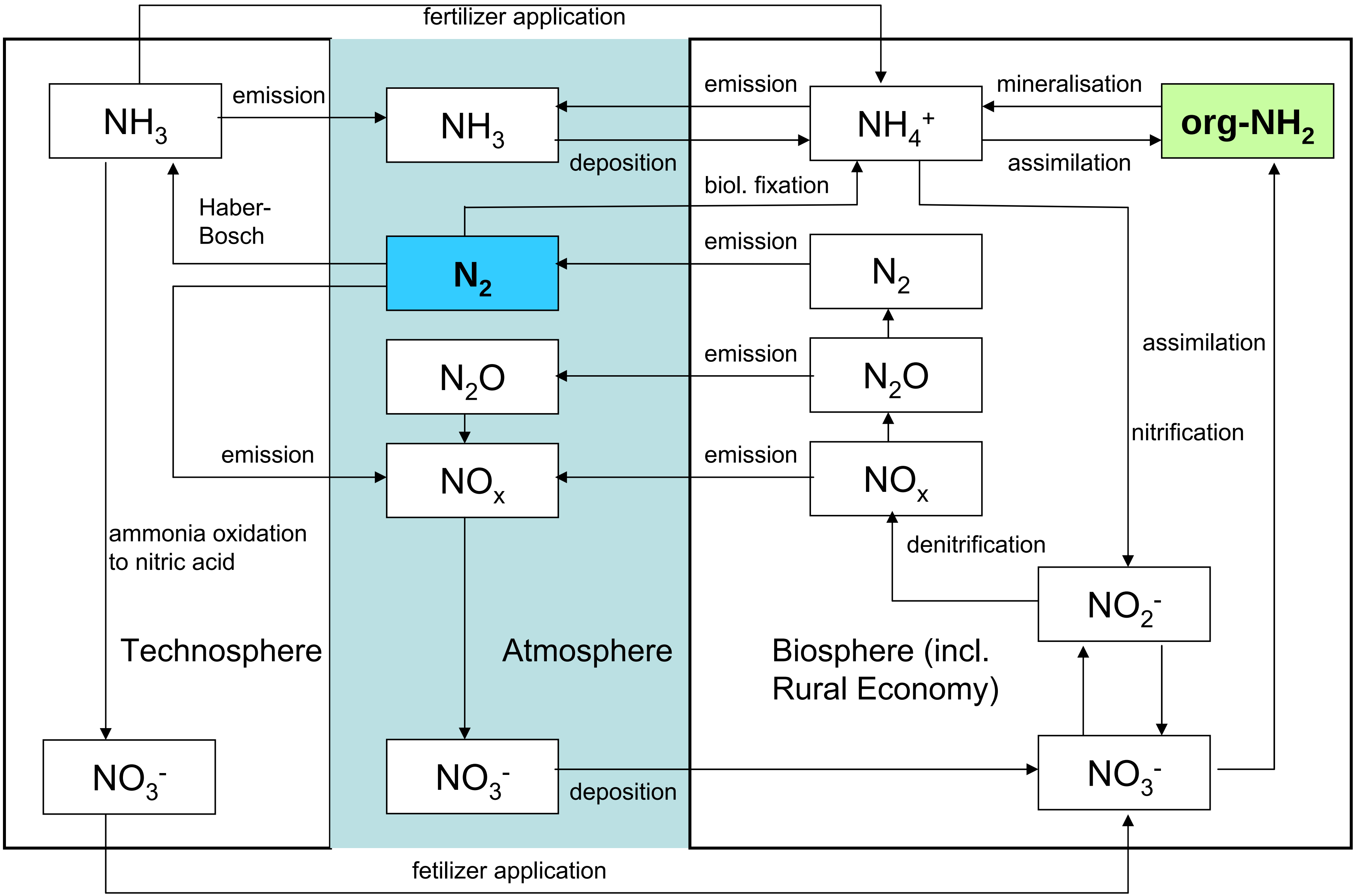


Simplified scheme (basic processes)

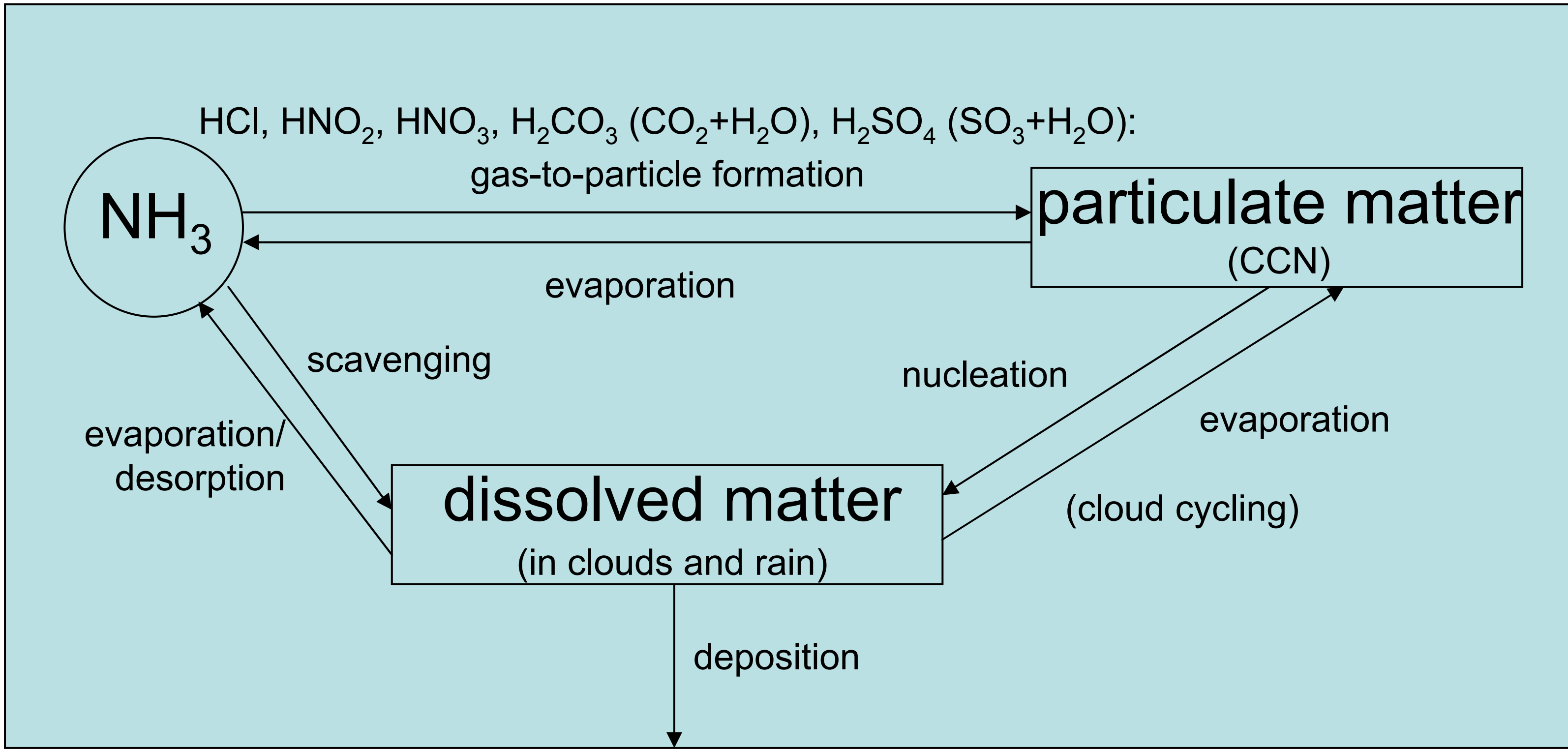



(aqueous-phase) biochemical NO_y – NH_x – transformation scheme
-e red
+e ox
-H ox (≡ e + H^+)
+H red (≡ +H^+ - e)
-O red (≡ +2H^+ - H_2O)
+O ox (≡ + H_2O – 2H)
ammonification
nitrification
denitrification
NH_2
(+e+H^+)
NH_3
($\pm H^+$)
NH_4^+
(+e+H^+-H_2O)
(+2e-OH^-)
(-H)
NH_2OH
($\pm H^+$)
NH_3OH^+
-H(+H_2O)
NH_3^+
(-H)
HNOH
HNOH
N_2
(+4H-H_2O)
(-H)
NH_2OH
N_2O_5
(NO_2+NO_3)
N_2O_3
(NO+NO_2)
($\pm H_2O$)
($\pm H_2O$)
($\pm$O)
($\pm$O)
($\pm H_2O$)
HON
(-H_2O)
HNO_3
HNO_2
$HN(OH)_2$
HON
$H_2N_2O_2$
N_2O
($\pm H^+$)
($\pm H^+$)
($\pm H^+$)
($\pm H^+$)
($\pm$O)
NO_3^-
NO_2^-
H_2O (-H^+)
NO^-
$HN_2O_2^+$
($\pm$e)
($\pm$e)
($\pm$e)
-e (-HON)
($\pm$e)
NO_3
NO_2
NO^+
NO

Man-made modified global nitrogen cycle



Atmospheric role of ammonia



- 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.

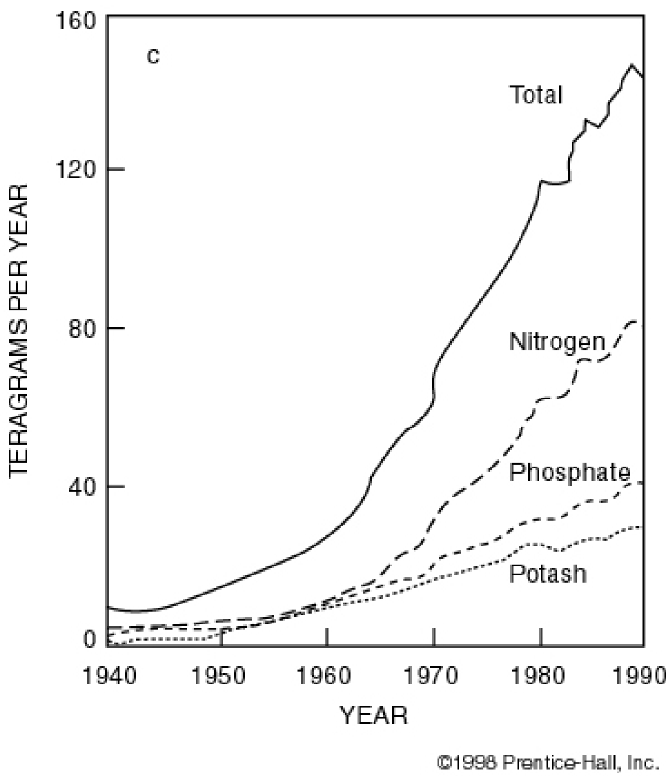
Changes in biogeochemical circulation

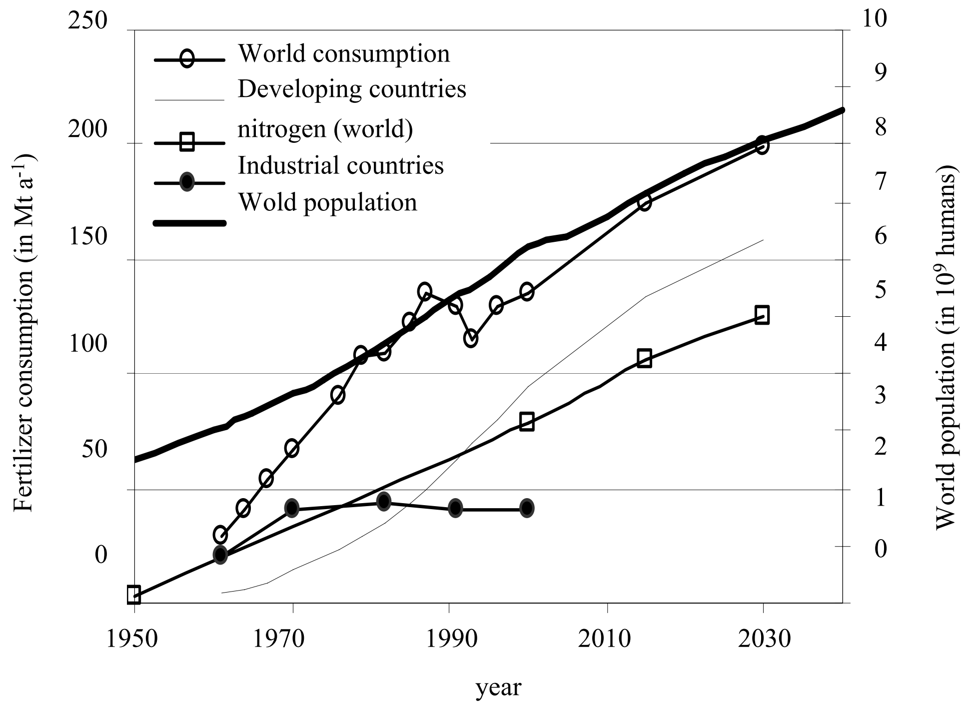
1890: 9

1990: 43

(man-made NH_3 emission Tg N yr^{-1} after Van Aardenne, 2001)

Evolution of world fertilizer use between 1940 and 2030



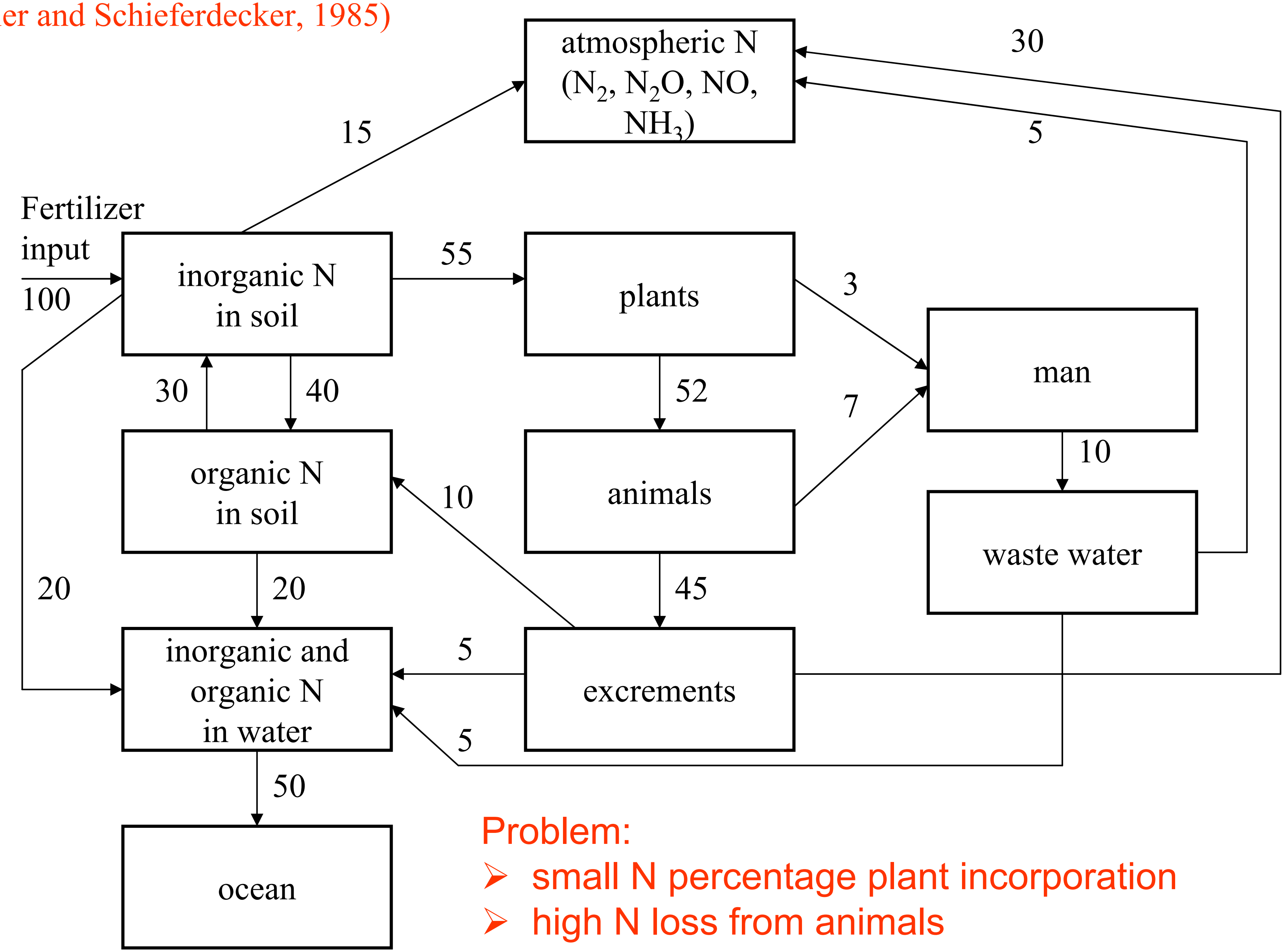


Möller (2003)

Brasseur, G. P., J. J. Orlando and G. S. Tyndall, eds. (1999) Atmospheric chemistry and global change. Oxford Univ. Press, New York

Fate of applied nitrogen fertilizers

(Möller and Schieferdecker, 1985)



Problem:

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

Global NH_x Budget (in Tg N yr^{-1})

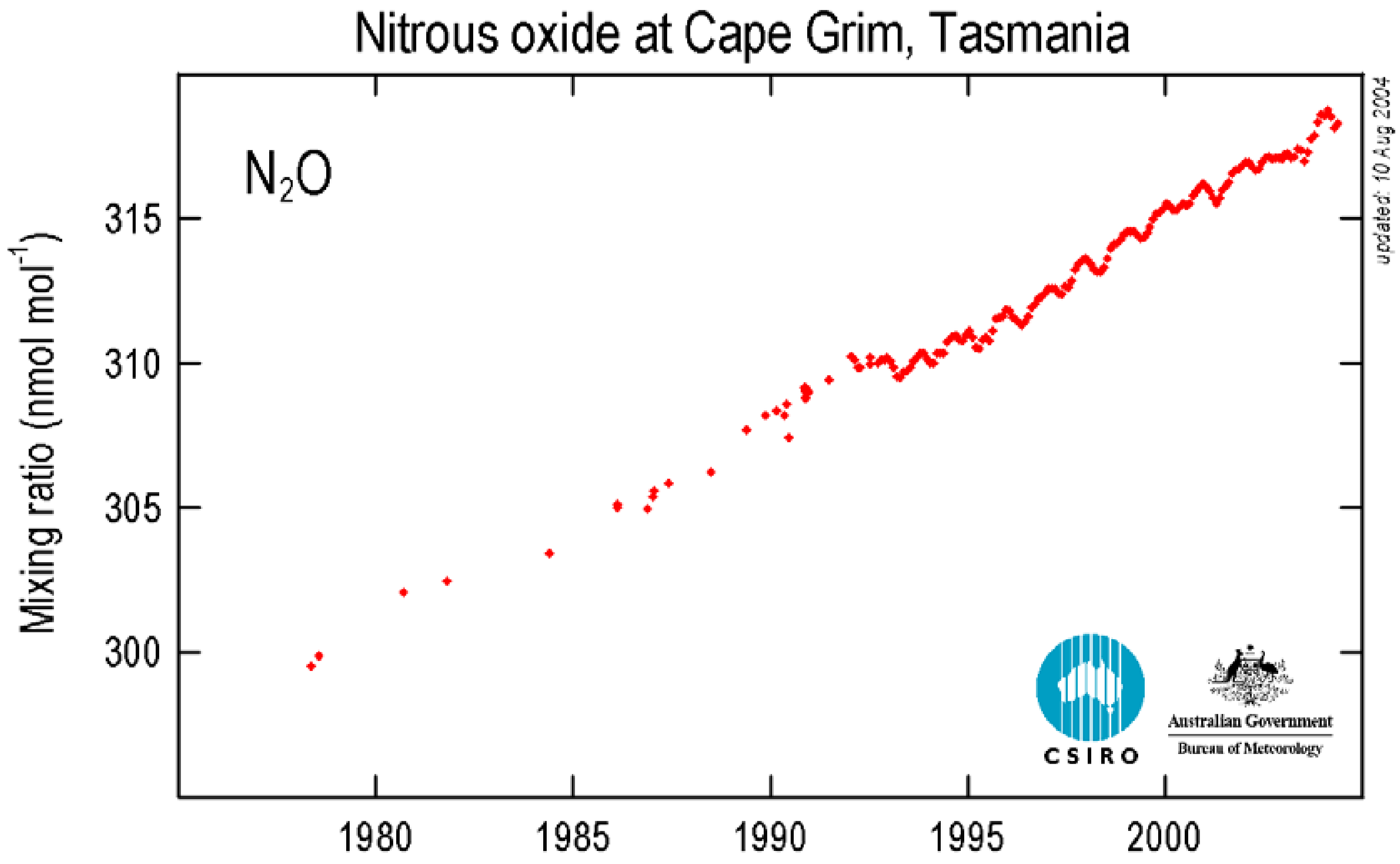
	natural emission		biomass burning	man-made emission	total emission	deposition
	terestrial	oceanic				
Söderlund and Svensson (1976)	2-6	-	-	24-47	30-50	72-153
Jaffe (1992)	-	-	-	-	122	112
Möller (1996)	8	15	-	30	53	55
Bouwman et a. (1997)	7.2	8.2	4.1	34.1	54	-
Schlesinger (1997)	-	13	-	52	-	56
Friedrich and Obermeier (2000)	3	10	7.2	-	-	-
Watts (2000)	4-8	10-15	5-7	20-40	50-60	-
Brasseur et al. (2003)	12	-	-	40	52	52

- : means no data given

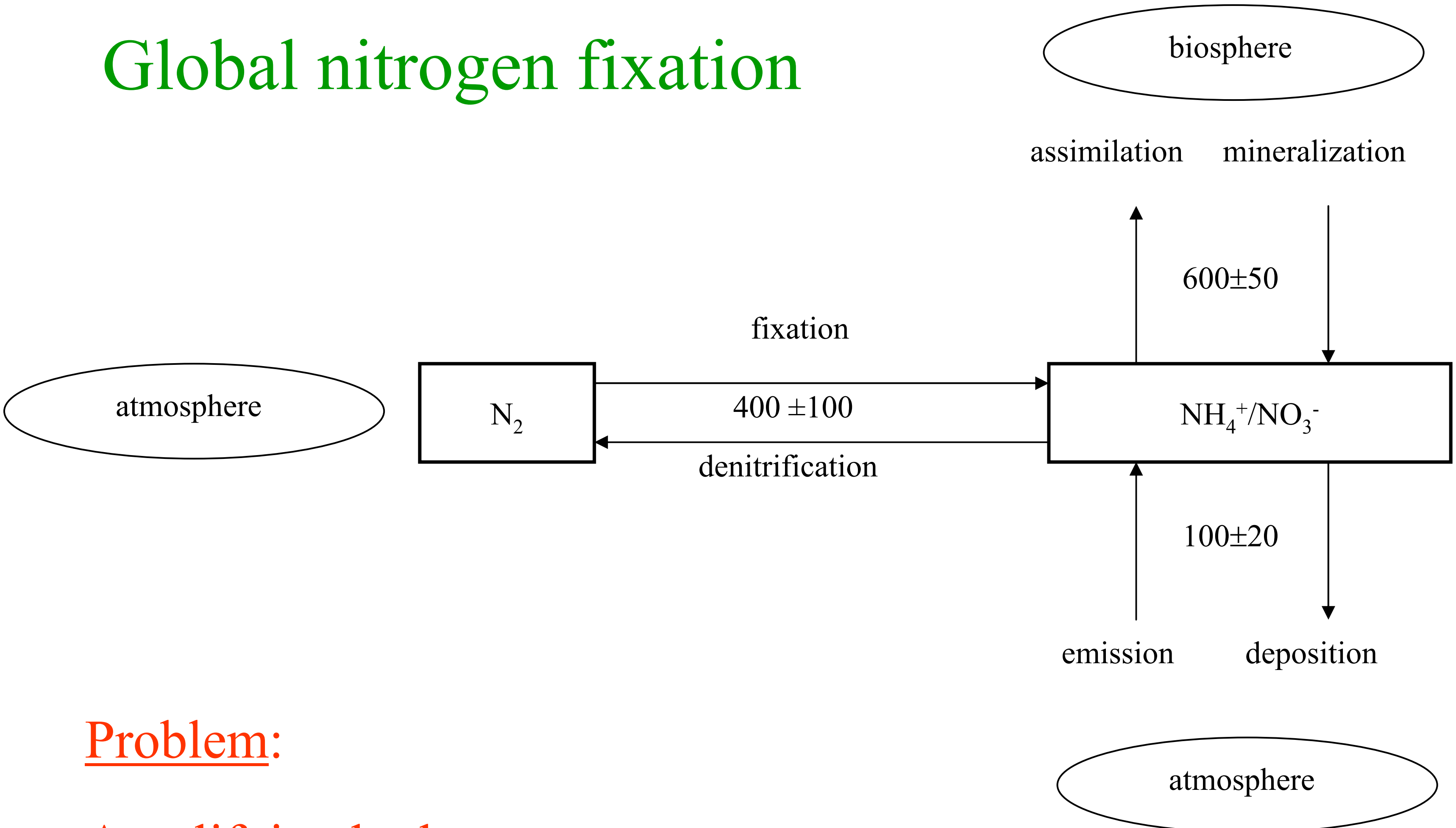
„best“ figures: man-made: 40±5
natural: 15-25

Problems:

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


Nitrous oxide at Cape Grim, Tasmania
N2O
Mixing ratio (nmol mol-1)
315
310
305
300
1980
1985
1990
1995
2000
updated: 10 Aug 2004
CSIRO
Australian Government
Bureau of Meteorology

Global nitrogen fixation



Problem:

Amplifying by humans:

- increase of fluxes among the spheres
- increase of soil and atmospheric NH_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 ($\rightarrow$ 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!