Present and future Nitrogen cycle


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Outline

- The nitrogen cycle
  - Main nitrogen forms
  - Main pools: terrestrial, atmospheric and oceanic
  - The processes leading to reduced nitrogen
    - Fixation, denitrification, nitrification, ...
  - Anthropogenic perturbations:
    - Fertilizer production, combustion

- The impacts of reduced nitrogen
  - Impacts on human health and the environment
  - The importance of considering the scale
  - How to reduce the impacts?

- Predicting future changes in the N cycle
  - Evolution of the sources in the future
  - How will the global N budget change through the 21st Century?

- Measuring the changes
ORIGIN OF N ON EARTH

Solar system formation

- Solar winds
- Ice
- NH₃

N₂ (99.97%)
Nᵣ (0.03%)

Bacterial fixation

3.9 10⁹ Tg N

Nᵣ: Reactive N

Harries et al. 2015

Fowler et al. 2015

Marty 2012
The reservoirs are not in chemical equilibrium and 99.97% resides in the atmosphere in a relatively inert form.

- $\text{N}_2$: 99.97% ($3.9 \times 10^9 \text{Tg N}$)
- Fixed N ($\text{Nr}$): 0.03% ($1.4 \times 10^6 \text{Tg N}$)
THE NITROGEN POOLS

N₂
99.97% (3.9 x 10⁹ Tg N)

Terrestrial

280 Tg-N

- Dead Soil
- Organic Matter
- Plant N
- microbes
- NH₄⁺
- NO₃⁻

Buried

- Forests
- Soils
- Peatlands
- Aquifers

Buried
The processes in the Nitrogen cycle

- Terrestrial, oceanic and atmospheric nitrogen natural cycling
- Anthropogenic perturbation of the cycle
NITROGEN FORMS

Sources + Natural

Manure

Fertilizer industry

Combustion

Nitrogen

$\text{N}_2$

Transformations

Nitrate

Ammonia

Nitric acid

Nitrogen oxide

Nitrous oxide

Ammonium-Nitrate

$\text{NH}_2\text{NO}_3$

$\text{NO}_3$
THE TERRESTRIAL « NATURAL » NITROGEN CYCLE

Butterbach-Bahl et al. 2011

Le cycle de l'azote
The oceanic « natural » nitrogen cycle

PON: particulate organic nitrogen
DON: dissolved organic nitrogen

Both originate from bacteria in large proportions

Yamaguchi and McCarthy 2018.
THE ROLE OF BACTERIA

\[ \text{N}_\text{r} \quad \text{N}_2 \]

\[ \text{NH}_4^+ \quad \text{NO}_3^- \]

Ammonium

Nitrate

Nitrifying Bacteria
- Converts ammonia to nitrates.

Denitrifying Bacteria
- Reduces nitrates to molecular nitrogen.

Cellier et al. 2013

Voss & Montoya, 2009

Vertical gradient

Voss & Montoya, 2009

Increasing water depth
The fixation process

- Nitrogenase enzyme
- (i) reduction of Fe protein by electron carriers (ferredoxins and flavodoxins);
- (ii) transfer of single electrons from Fe protein to MoFe protein in a MgATP (adenosine triphosphate);
- (iii) electron transfer to the substrate at the active site within the MoFe protein.

\[
N_2 + 8H^+ + 8e^- + 16MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i
\]
THE ABIOTIC SOURCES

Small but not well known and difficult to distinguish biotic and abiotic

Other « natural » sources of Nr to the atmosphere

- Lightning
- Volcanoes
- Fires

Nitrogen oxides ($\text{NO}_x$) and ammonia ($\text{NH}_3$) emissions.
The atmospheric «natural» nitrogen cycle

**Lightning**

**Plasma dissociation and ionisation**

\[
\begin{align*}
\text{e}^- + \text{O}_2 & \rightarrow \text{O}^+ + 2\text{e}^- \\
\text{e}^- + \text{O}_2 & \rightarrow \text{O}^+ + \text{O} + 2\text{e}^- \\
\text{e}^- + \text{N}_2 & \rightarrow \text{N}_2^+ + 2\text{e}^- \\
\text{e}^- + \text{N}_2 & \rightarrow \text{N}^+ + \text{N} + 2\text{e}^- \\
\text{O}^+ + \text{N}_2 & \rightarrow \text{NO}^+ + \text{N} \\
\text{N}^+ + \text{O}_2 & \rightarrow \text{NO}^+ + \text{O} \\
\text{O}_2^+ + \text{NO} & \rightarrow \text{NO}^+ + \text{O}_2
\end{align*}
\]

**Fires**

**Thermal production of NOx**

At T°C > 1600°C:

Dissociation of N\(_2\) in N and O\(_2\) in O

\[
\begin{align*}
\text{N}_2 + \text{O} & \rightarrow \text{NO} + \text{N} \\
\text{N} + \text{O}_2 & \rightarrow \text{NO} + \text{O} \\
\text{N} + \text{OH} & \rightarrow \text{NO} + \text{H}
\end{align*}
\]
The processes in the Nitrogen cycle

• Anthropogenic perturbations
Which anthropogenic changes?

- Crop production
- Meat production
- Production D'énergie
Which anthropogenic changes?

Increase due to food production and energy consumption

Davidson 2014
Industrial production of Nr

Fritz Haber (1868-1934)
- Started working on NH₃, 1904
- First patent, 1908
- First commercial test, 1909
- Nobel price in chemistry, 1918
  - "Ammonia synthesis"

Carl Bosch (1874-1940)
- Perfect Catalyser, 1910
- Large scale production, 1913
- Ammonia to nitrate transform, 1914
- Nobel price in chemistry, 1931
  - "High pressure production methods"
Industrial production of NH$_3$

- **Fertilizers**: 82%
- **Other Uses**: 18%
  - explosives
  - fibers
  - resins
  - animal feed

Diagram:
- **Compressor**
- **Catalyst beds**: Feed gases prewarmed by heat of reaction
- **Heater**: 700 K, 500 atm
- **Reactor**: NH$_3$ + unreacted N$_2$, H$_2$
- **Heat exchanger**: Recycled N$_2$, H$_2$
- **Condenser**: Hot water out, Cold water in
- **Refrigerated unit**: NH$_3$(l)
The anthropogenically perturbed nitrogen cycle

Anne-Christine LeGall, ENA, 2011
The processes in the Nitrogen cycle

• Quantifying the fluxes
MAIN FLUXES: NITROGEN FIXATION $\text{N}_2 \rightarrow \text{TO N}_\text{R} \text{ (Tg-N)}$

- **BNF (Biological Nitrogen Fixation)**
- **Lightning**
- **Combustion**
- **Fertilizer Production**
- **Agricultural BNF**
- **Ocean BNF**

**Annual fixation**
- $\text{Nr} \approx 458 \text{TgN yr}^{-1}$
- Anthropogenic $\approx 193 \text{TgN yr}^{-1}$
- $\approx 50\%$

BNF – Biological Nitrogen Fixation

INRA

Centre for Ecology & Hydrology
NATURAL ENVIRONMENT RESEARCH COUNCIL
MAIN FLUXES: DENITRIFICATION

N₂
99.97% (3.9 x 10⁹ Tg N)

- Most Nᵣ returns rapidly to the atmosphere as N₂
- Nᵣ is accumulated in specific terrestrial and oceanic reservoirs

Denitrification

N₂
N₂O
120 Tg-N

Terrestrial
280 Tg-N

Burial
- Forests
- Soils
- Peatlands
- Aquifers

Plant N
Dead Soil Organic Matter
microbes
NH₄⁺
NO₃⁻

Leaching and transport to ocean

Burial

~200 Tg-N?

Denitrification

N₂
N₂O
NITROGEN PROCESSING: EMISSIONS FROM SOILS

Oswald et al. Science 2013

The graph shows the relative soil emission of different gases (HONO, NO, N₂O, N₂) as a function of SWC (% whc) for soil nitrogen processing. The emissions peak at different SWC levels, indicating the importance of water content in soil for nitrogen processing emissions.
B-NO emissions source variable

Fowler et al. (2013). Jaeglé et al. (2005),
Laughing gas

Discovered

Joseph Priestley

1772

Laughing gas: \( \text{N}_2\text{O} \)

Anesthetic during the XIXth century
THE THIRD GREENHOUSE GAS

Concentrations of Greenhouse Gases from 0 to 2005

- Carbon Dioxide (CO₂)
- Methane (CH₄)
- Nitrous Oxide (N₂O)

Carottes glacière

James Lovelock (1958)
Chromatography With electron capture

IPCC, 2007
Les émissions sont plus élevées dans
- Les zones à forts apports d’azote
- Les sols humides

Pourcentage de $\text{N}_2\text{O}$ émis par rapport à la quantité d’azote apportée
NITROGEN PROCESSING: DEPOSITION

Turbulent transfer

Surface exchange

Flechard et al. (1999)

Biological control

Massad et al. (2010)
The impacts of Nr

- Health and environmental impacts
THE 5 KEY THREATS OF NITROGEN

Sutton et al. 2011
half of the global population depends on fertilizers for their food

“boundary for N, was based on the production of new reactive N (all N compounds except N2) by fixing N2 from the atmosphere by humans. It was simply set at 25% of its current value, or 35 Tg N yr1 without any further background for its basis” (de Vries et al. 2013)
NITROGEN DAMAGE COSTS & SOURCES

DAMAGE COSTS OF NITROGEN POLLUTION
Agriculture and fossil-fuel burning load the environment with reactive nitrogen, affecting water, soils and air.

EU Damage cost: 70 - 320 billion € / year
IMPACT ON HUMAN HEALTH

The diagram illustrates the impact of various atmospheric compounds on human health and ecosystems. Key components include:

- **NH₃** (Ammonia)
- **HNO₃** (Nitric Acid)
- **VOCs** (Volatile Organic Compounds)
- **NOₓ** (Nitrogen Oxides)
- **O₃** (Ozone)
- Clouds
- Aerosols

These components interact through pathways that affect:

- Semi-natural ecosystems
- Agricultural ecosystems
- Industry, traffic, households

The diagram highlights the radiative properties of aerosols and their role in atmospheric processes.
IMPACT ON HUMAN HEALTH

1. Dust particles are inhaled by the worker in a dust cloud.

2. Millions of these dust particles strike and stick to the moist surfaces of:
   - A. Nasal passage

4. The worst damage can be done by the smaller of the fine particles which reach the finest lung spaces - the alveoli.

3. In all these organs, repeated or heavy exposure to organic dusts may induce an allergy to substances in these dusts, and any further contact, even with small amounts, can then produce such symptoms as asthma, fever, general tiredness and shortness of breath.

Particles
- \( \varnothing > 10 \mu \)
- \( \varnothing 5 - 10 \mu \)
- \( \varnothing < 5 \mu \)
DES EFFETS COMPLEXES SUR L’ENVIRONNEMENT
EXEMPLE DE L’AMMONIAC

Formation d’aérosols

\[ \text{NH}_4^+ \rightarrow \text{NO}_3^- + 2\text{H}^+ + \ldots \]

Acidification

Eutrophisation

Biodiversité

(d’après Bobbink, 1991)
PERTE DE BIODIVERSITÉ

Sous-bois des forêts suédoises

+15 kg N / ha / an

Copyright A. Nordin

Copyright A. Nordin
**ILLUSTRATION D’UN EFFET D’EUTROPHISATION**

*Gauche:* lichen dans un environnement naturel

*Droite:* lichens remplacés par des algues sous l’effet de l’ammoniac

**Excès d’azote en zone côtière** sur la formation d’algues (*Phaeocystis globosa*) à l’origine de la formation de mousse gélatineuse
Ozone impacts on agriculture

Des dégâts foliaires :

Tabac (Nicotiana tabacum)

Des impacts agronomiques :

![Graph showing the impact of ozone on crops]

France, J-F Castell
Greece, D Velissariou

Ozone (μg/m³) moyenne journalière (7h/jour)
LE FORCAGE RADIATIF ET LE RÉCHAUFFEMENT GLOBAL

Simplified view of the Nitrogen Cascade

High temperature combustion & industry

Fertilizer manufacture

Crop biological nitrogen fixation

Intended N flow

Unintended N flows

N form in the cascade

Environmental concern from N

Nitrogen oxides (NOx)

Nitrous Oxide (N2O)

Ammonia (NH3)

Ammonium nitrate in rain (NH4NO3)

Further emission of NOx & N2O carrying on the cascade

Terrestrial Eutrophication

Natural ecosystems

Urban air quality

Tropospheric ozone formation

Particulate Matter

Stratospheric ozone loss

Greenhouse gas balance

Soil acidification

Freshwater Eutrophication

Nitrate in streams, groundwater & coastal seas

Marine Eutrophication

Sutton et al. (2011 European Nitrogen Assessment, ENA Ch 5)
Predicted effects across Europe

Critical load exceedance for N effects on ecosystems

% of ecosystems area with grid average N deposition > eutrophication (for 2000)

Loss in life expectancy attributable to PM$_{2.5}$

Loss in average life expectancy in months due to identified anthropogenic PM$_{2.5}$ (for 2000)
The spatial scale of assessment strongly influences outcomes.
FLUXES AND EFFECTS IN THE FIELD OCCUR AT FINE SCALE

Woodland N sink
~30 kg-N ha\(^{-1}\)

Livestock source
~100 kg-N ha\(^{-1}\)

Arable N source
~5 kg-N ha\(^{-1}\)

Grassland N source
~10 kg-N ha\(^{-1}\)

Exceedance of Critical Loads for Nitrogen

kg N ha\(^{-1}\) year\(^{-1}\)
no exceedance
0 - 1
1 - 5
5 - 10
10 - 25
> 25
• Hot-spots needs changing of scales

NH₃ (µg m⁻³)

(PhD Michael Bell, INRA Rennes)
QUANTIFYING SPATIAL DISTRIBUTIONS

- As the resolution increases, the magnitude of peak values increases and the exceedance of thresholds increases.
- With developments in understanding and increases in computing power, exceedances of thresholds increase.
Two important issues:

1. ‘Best’ estimates of projected emissions of $\text{NO}_x$, $\text{NH}_3$, and $\text{N}_2\text{O}$

2. Influence of climate change on the N cycle (emissions).
NO\textsubscript{x} EMISSIONS (VAN VUUREN et al 2011)

Future NO\textsubscript{x} emissions according to various scenarios (light grey area covers the 10–90th percentile; dark grey area the 25–75th percentile). The right hand panel only includes scenarios without climate policy (22 scenarios); the left hand panel includes the full set of scenarios (with and without climate policy) (40 scenarios). The graph also shows the scenarios of the IPCC-SRES set [37], the IIASA-CLE scenario (both sets do not include climate policy) [26] and the RCPs (including climate policy) [40].
Future N$_2$O emissions according to various scenarios (light grey area covers the 10–90th percentile; dark grey area the 25–75th percentile). The right hand panel only includes scenarios without climate policy; the left hand panel includes the full set of scenarios (with and without climate policy). In addition, the graph shows the scenarios of the IPCC-SRES set and the RCPs (including climate policy) (sources see Figure 1).
Future NH₃ emissions according to various scenarios (light grey area covers the 10–90th percentile; dark grey area the 25–75th percentile). Source: CLE [26] and RCP scenarios and the underlying baselines [40].
Change in annual fixation

**2010**
- Lightning: 5 ± 50%
- Combustion: 120 ± 10%
- Agricultural BNF: 33 ± 30%

**2100**
- Lightning: 7 ± 50%
- Combustion: 160 ± 20%
- Agricultural BNF: 63 ± 30%

**Annual fixation**
- **LAND**: 120 ± 50% (2010), 168 ± 50% (2100)
- **OCEAN**: 120 ± 50% (2010), 166 ± 50% (2100)

**BNF** – Biological Nitrogen Fixation
### Changes in Land & Ocean Fluxes (Tg-N y⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial Emissions</td>
<td>100</td>
<td>165</td>
</tr>
<tr>
<td>1. NOₓ</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>2. Terr. NH₃</td>
<td>60</td>
<td>135</td>
</tr>
<tr>
<td>3. Soil NO</td>
<td>9</td>
<td>11.5</td>
</tr>
<tr>
<td>4. Deposition</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>5. Terr. N Cycling</td>
<td>240</td>
<td>328</td>
</tr>
<tr>
<td>6. Marine N Cycling</td>
<td>230</td>
<td>290</td>
</tr>
<tr>
<td>7. Marine NH₃ Emms</td>
<td>5.7</td>
<td>1.7</td>
</tr>
<tr>
<td>8. Marine N₂O</td>
<td>5.5</td>
<td>8</td>
</tr>
<tr>
<td>9. Terr. N₂O</td>
<td>1.2</td>
<td>14.4</td>
</tr>
</tbody>
</table>

*Terr. = terrestrial, Emms = emissions

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**Centre for Ecology & Hydrology**

**Natural Environment Research Council**

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**Science & Impact**
HOW TO LIMIT THE IMPACTS
IMPACT ON ENVIRONMENT VS FOOD PRODUCTION

- Eased agricultural intensification
- 40% of the world population benefit from nitrogen fertilisation
- ... But most Nr is released to the environment

(Nitrogen use efficiency = NUE)
BETTER USE NITROGEN

Galloway JN and Cowling EB. 2002

Fertilisant Produit

100

Fertilisant utilisé

94

Absorbé par la plante

47

Récolté

31

Dans les aliments

26

Consommé

14

Végétaux

-24

Animaux

7

4
- Better recycling
- Less meat production

Galloway JN and Cowling EB. 2002
At which costs

Coûts négatifs

Pellerin et al., 2013
HOW TO MEASURE THE CHANGE
Measurements in the gaseous phase (atmosphere)

- general principle: mass balance for a (virtual) air volume: 
  \[ V \frac{\partial c}{\partial t} = \sum_{i=0}^{m} A_i \cdot F_{c,i} + Q_{chem} \]

\[ F_{c,surf} \equiv F_{c,0} = \frac{1}{A_0} \left( V \frac{\partial c}{\partial t} - \sum_{i=1}^{m} A_i \cdot F_{c,i} \right) - Q_{chem} \]
Total Nitrogen flux with converter and chemiluminescence

Sublimation and thermal conversion at 810 °C
Oxydation to NO on Au and Pt catalyser

\[
\begin{align*}
\text{NH}_4\text{NO}_3 & \xrightarrow{\Delta T} \text{NH}_3 \uparrow + \text{HNO}_3 \uparrow \\
2 \text{HNO}_3 & \xrightarrow{\Delta T} 2 \text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \\
\text{HONO} & \xrightarrow{\Delta T} \text{NO} + \text{OH} \\
4 \text{NH}_3 + 5 \text{O}_2 & \xrightarrow{\Delta T, \text{Pt}} 4 \text{NO} + 6 \text{H}_2\text{O} \\
\text{NO}_2 + \text{CO} & \xrightarrow{\Delta T, \text{cat}} \text{NO} + \text{CO}_2
\end{align*}
\]

Marx et al. 2012
Total Nitrogen flux

![Graphs showing nitrogen flux over time](image)
Worldwide sites for CO2 -> to measure nitrogen!!

ICOS sites

- TCON
- GOSAT
- OCO2
- IASI

NH3 (µg m⁻³)

Van Damme et al., A. Meas. Tech, 2015
Représentativité spatiale des mesures au sol pour le pixel satellite

Profil vertical NH₃ dans la troposphère

=> Assimilation dans les modèles de chimie de l’atmosphère
http://www6.versailles-grignon.inra.fr/ecosys
(aller dans l’onglet Productions / Cours)

Google :
Loubet INRA ECOSYS
TRAINING OR WORKING AT INRA

- CO2, O3, NH3 and VOC flux measurements
- Modelling the ecosystem and its exchange with atmosphere
- Carbon and nitrogen cycling
- Atmospheric pollution

http://www6.versailles-grignon.inra.fr/ecosys
To read

- Effects of global change during the 21st century on the nitrogen cycle

- David Fowler¹, Claudia E Steadman¹,², David Stevenson², Mhairi Coyle¹, Robert M Rees³, Ute M. Skiba¹, Mark A. Sutton¹, J. Neil Cape¹, Tony Dore¹, Massimo Vieno¹,², David Simpson⁴, Sönke Zaehle⁵, Benjamin Stocker⁶, Matteo Rinaldi⁷, Christina Facchini⁷, CR Flechard⁸, Eiko Nemitz¹, Marsailidh Twigg¹, Jan Willem Erisman⁹ and Jim Galloway

- Atmospheric Chemistry and Physics Discussion 2014
LE CONCEPT DE RÉSISTANCE DE TRANSFERT

Définition de la résistance au transfert diffusif

Hypothèse de flux constant

Fick
\[ F_c = -K_c \frac{dC}{dZ} \]

Ohm
\[ F_c = \frac{c_1 - c_2}{r_a} = h_c (c_1 - c_2) \]

ra, résistance aérodynamique s / m
hc, Coefficient d’échange m / s

Quelle hypothèse est nécessaire pour passer de Fick à Ohm?
Définition de la résistance au transfert diffusif

\[ F_c = \text{cte} \]

\[ F_c \int_{z_1}^{z_2} \frac{dz}{K_c} = - \int_{c_1}^{c_2} dc = c_1 - c_2 \]

\[ r_a = \frac{1}{h_c} = \int_{z_1}^{z_2} \frac{dz}{K_c} \]

\[ F_c = \frac{c_1 - c_2}{r_a} = h_c (c_1 - c_2) \]