Present and future Nitrogen cycle

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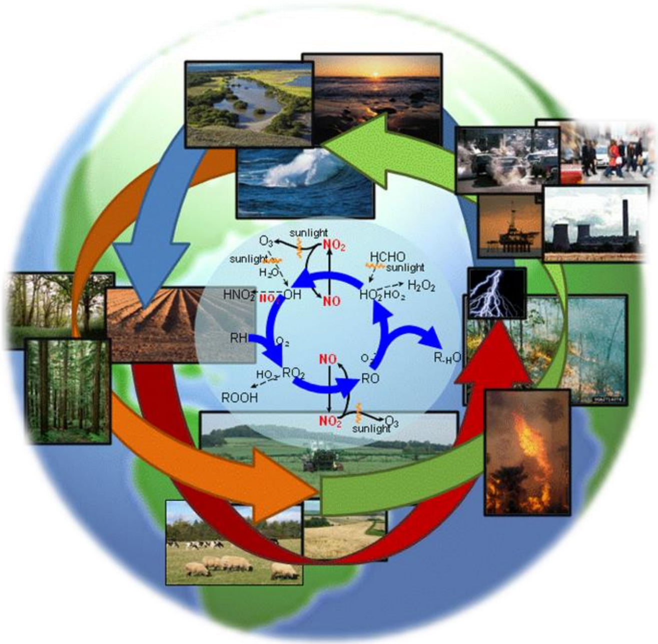

Google: "Loubet INRA"

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Master CLUES 23 November 2018

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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

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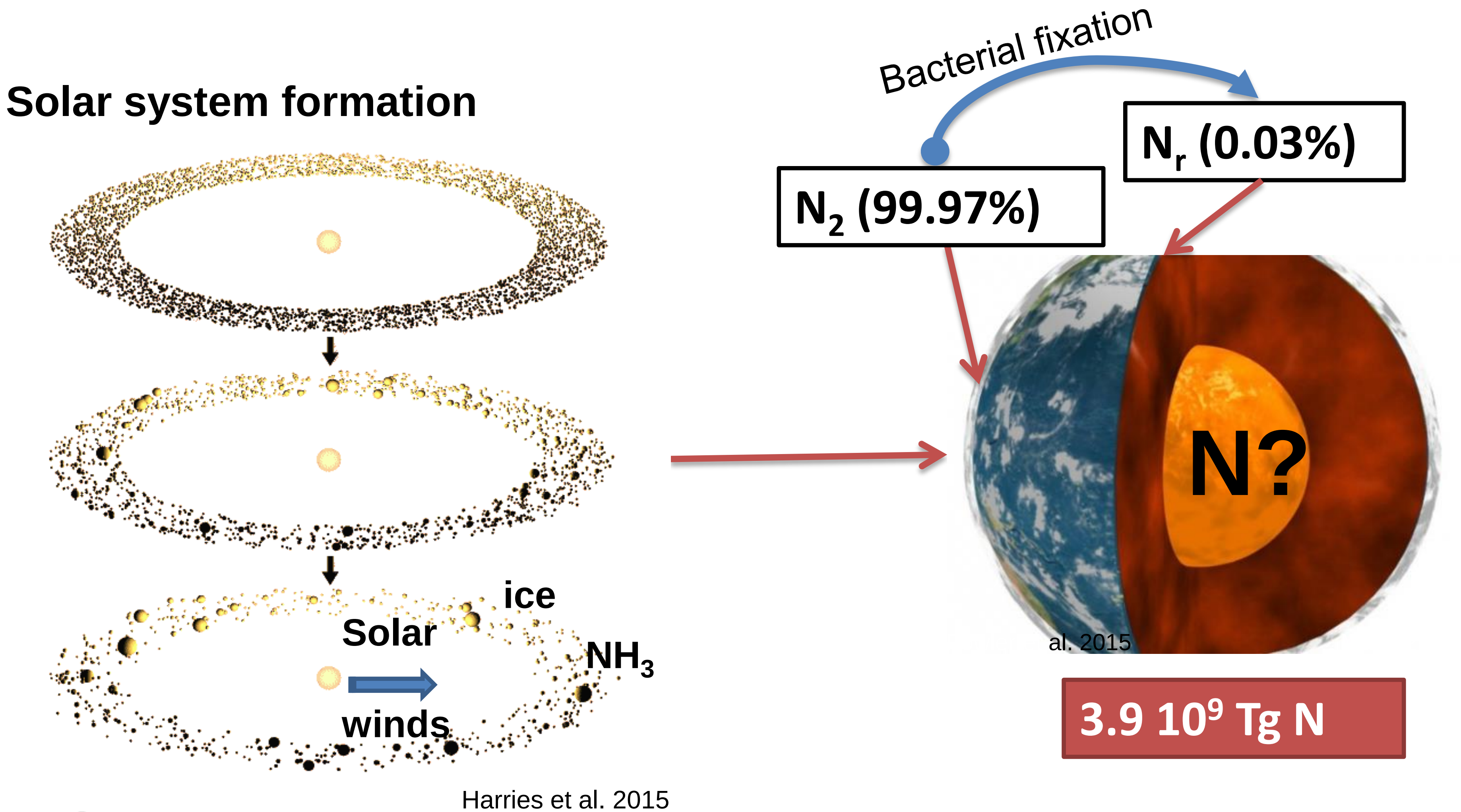
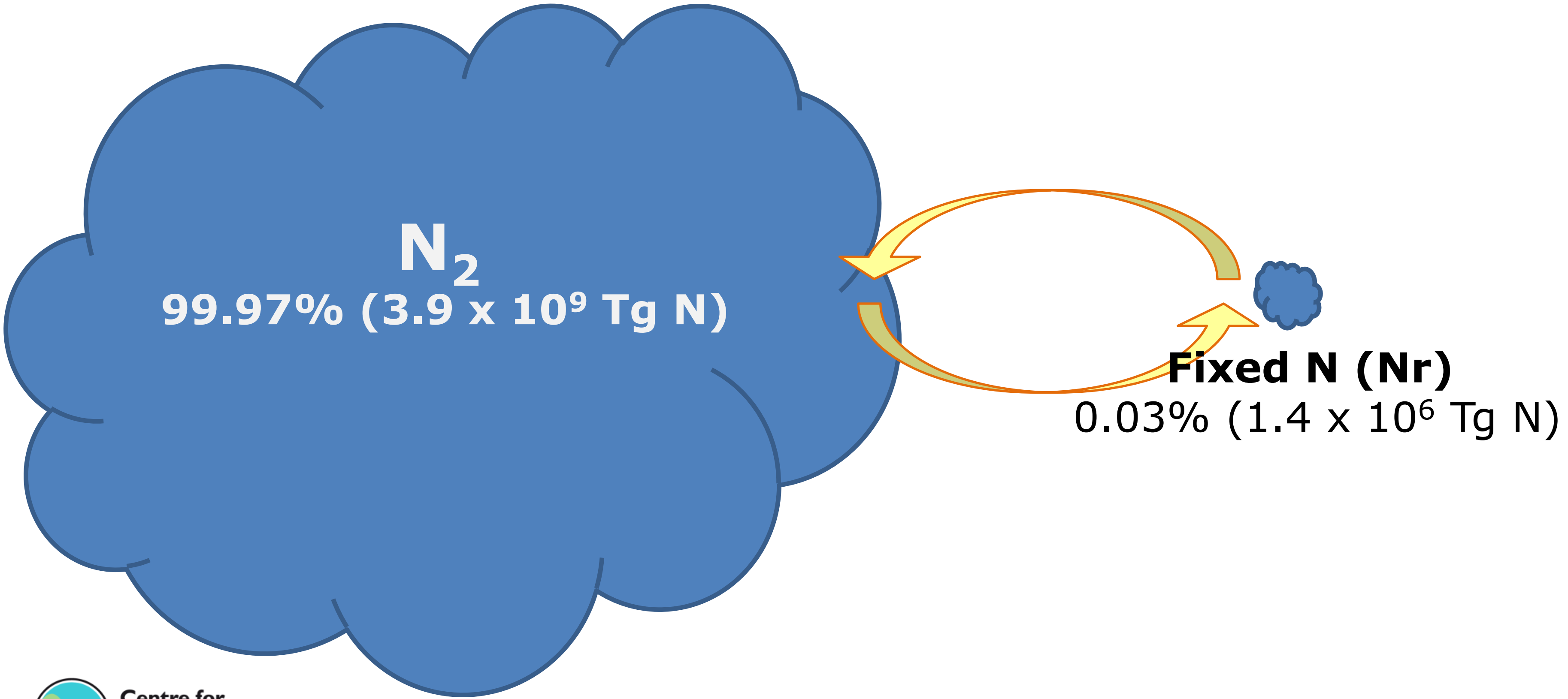
ORIGIN OF N ON EARTH



N_r: Reactive N

THE NITROGEN POOLS

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



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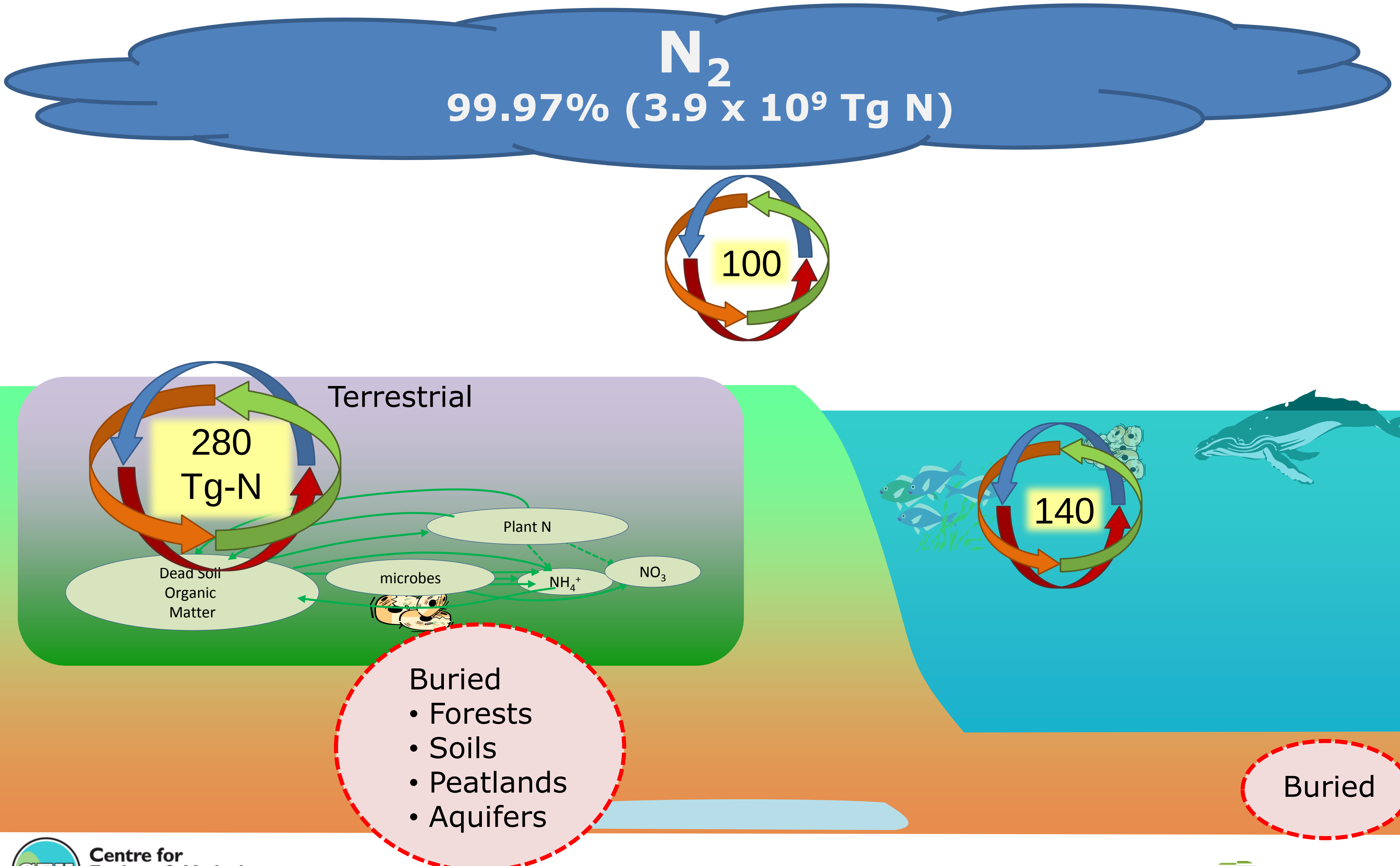
THE NITROGEN POOLS



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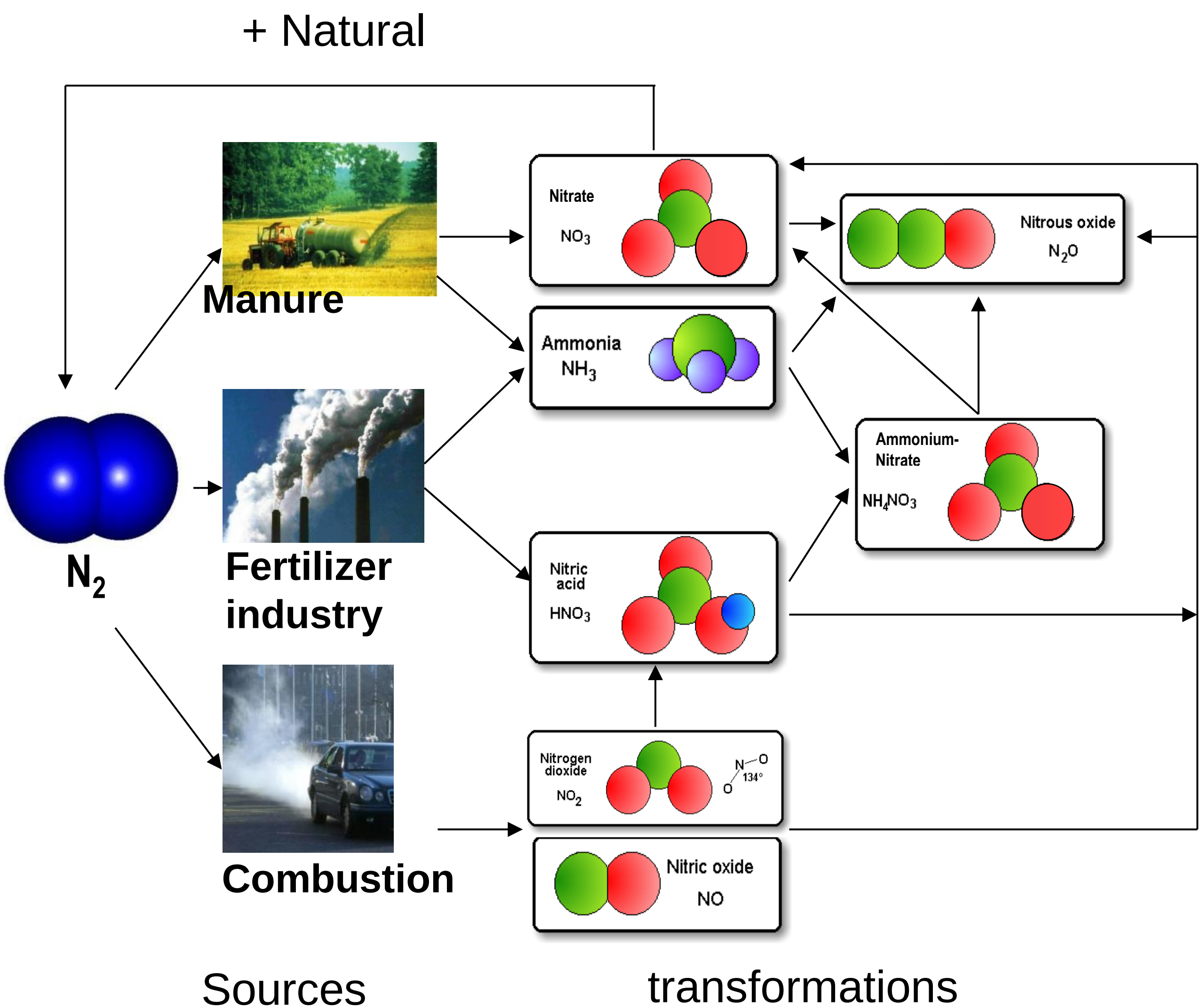
The processes in the Nitrogen cycle

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

NITROGEN FORMS



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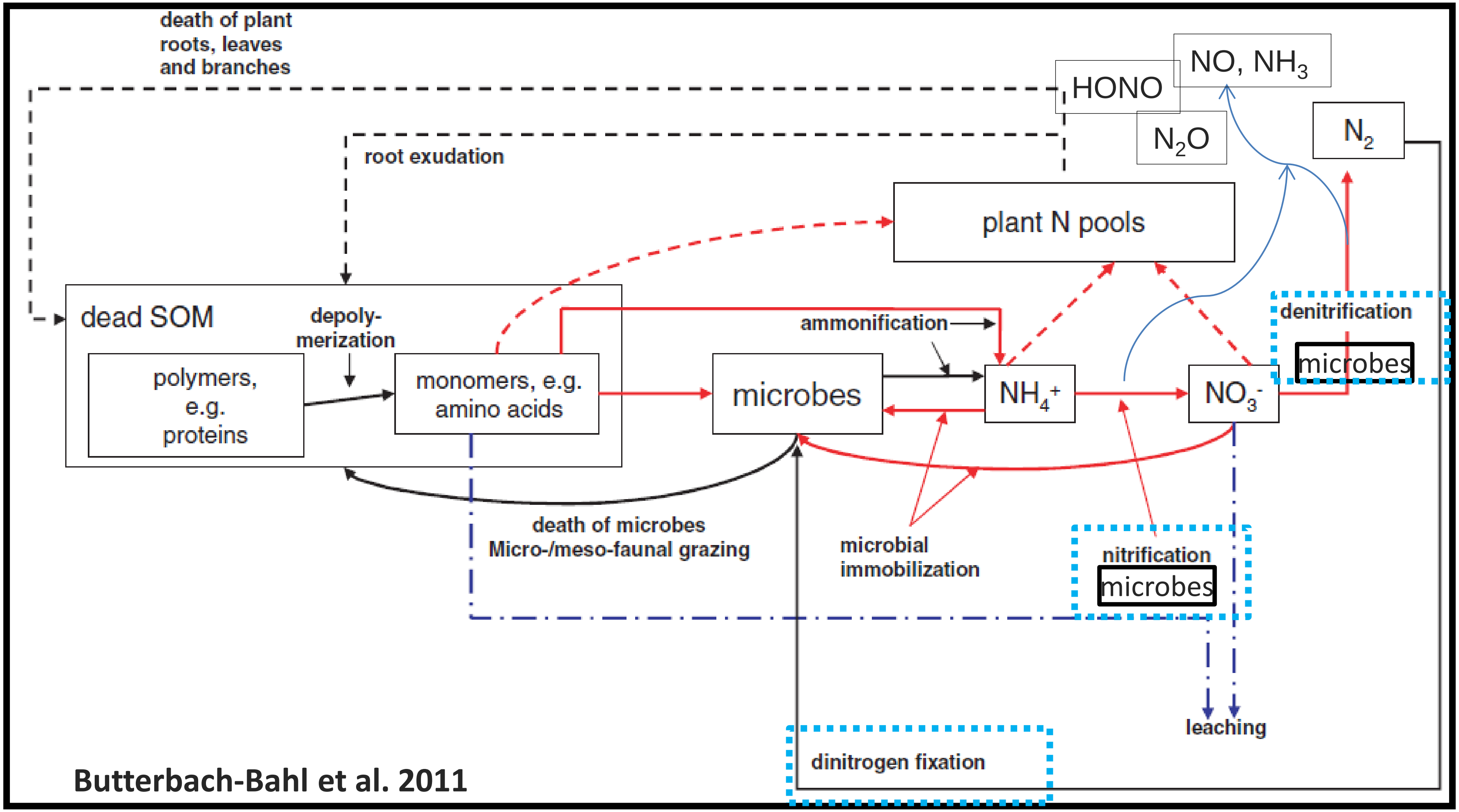
THE TERRESTRIAL « NATURAL » NITROGEN CYCLE



Butterbach-Bahl et al. 2011

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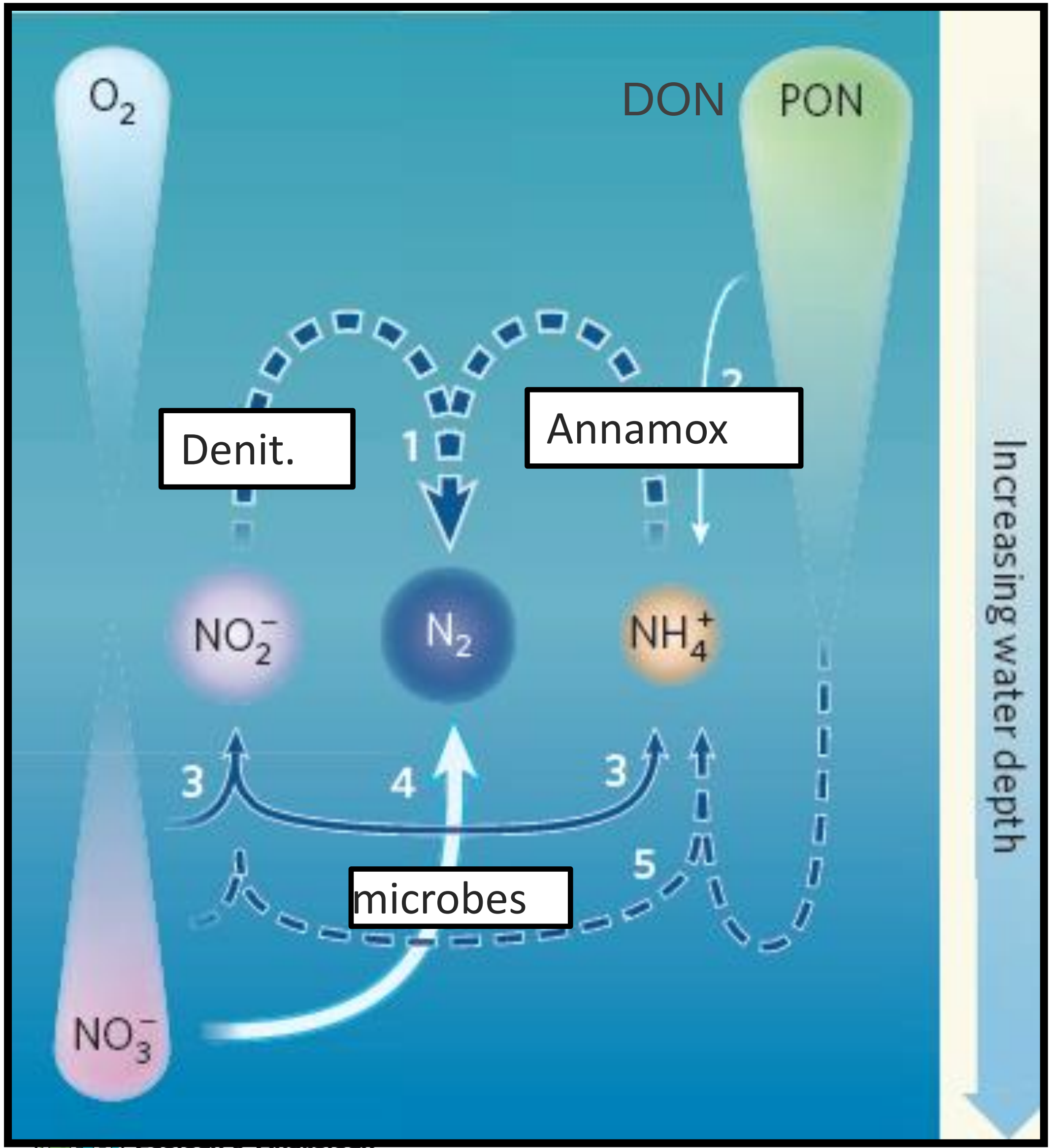
The oceanic « natural » nitrogen cycle



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Voss & Montoya, 2009

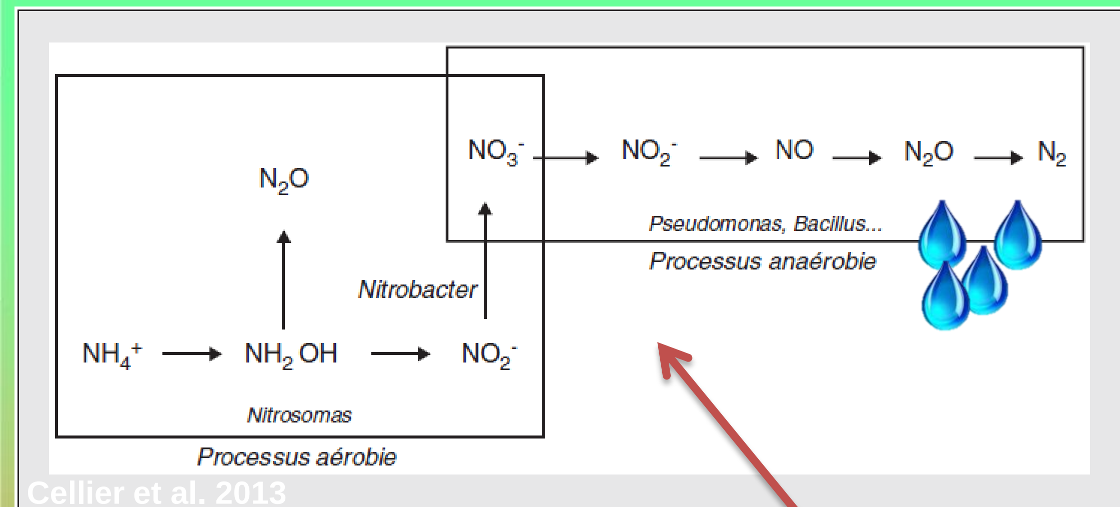
PON : particulate organic nitrogen
DON : dissolved organic nitrogen

Both originate from bacteria
in large proportions

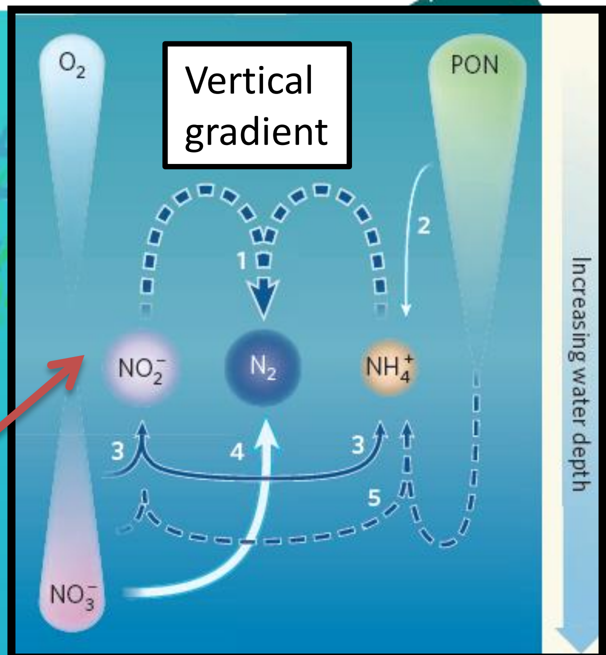
Yamaguchi and McCarthy 2018.

THE ROLE OF BACTERIA

N_r N_2



N_r N_2



Voss & Montoya, 2009

Ammonium

N_r → NH_4^+

N_r → NO_3^-

Nitrate

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.

$$N_2 + 8H^+ + 8e^- + 16MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i$$

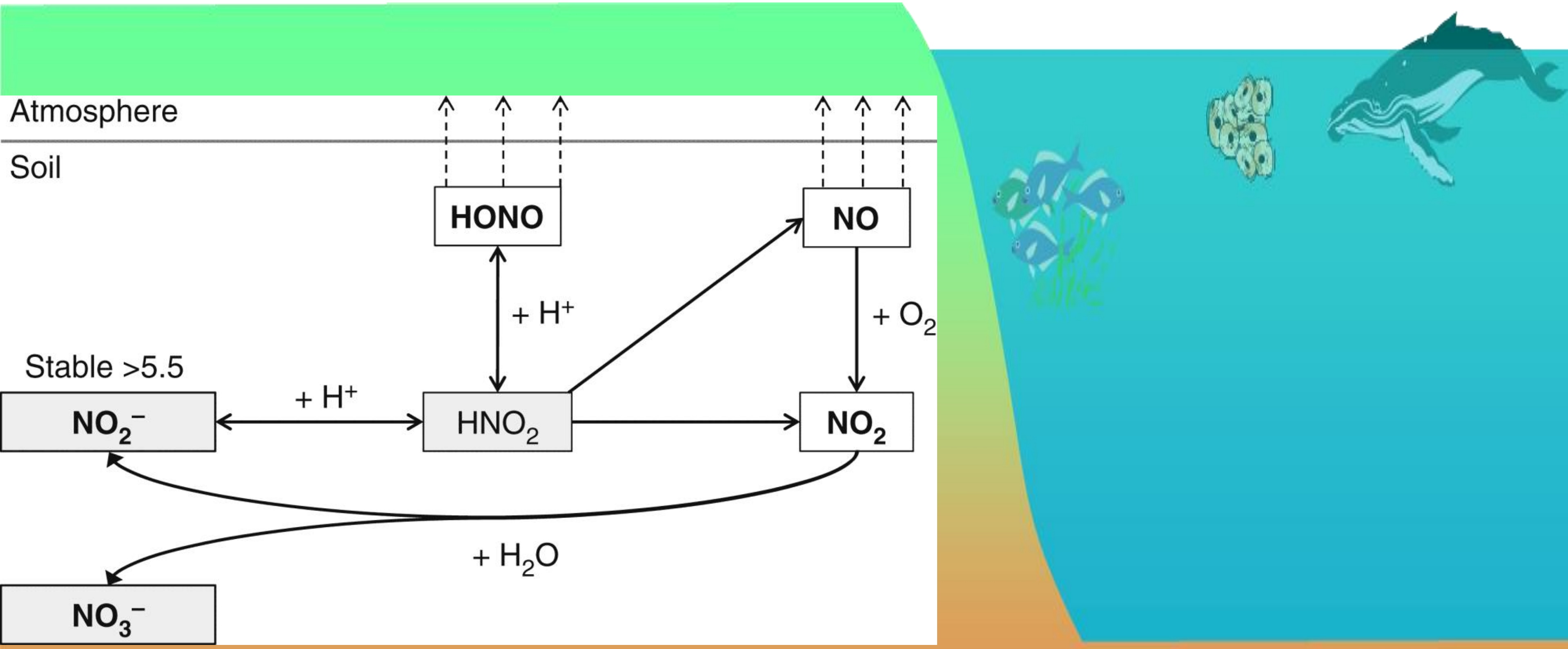
Chem. Rev. 1996, *96*, 2965–2982 2965

Structural Basis of Biological Nitrogen Fixation

James B. Howard* and Douglas C. Rees*

THE ABIOTIC SOURCES

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



Heil, J., Vereecken, H., and Bruggemann, N.: A review of chemical reactions of nitrification intermediates and their role in nitrogen cycling and nitrogen trace gas formation in soil, European Journal of Soil Science, 67, 23-39, 2016.

Other « natural » sources of Nr to the atmosphere

Lightning

NO_x

Volcanoes

NH_3

Fires

NO_x

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The atmospheric « natural » nitrogen cycle

Lightning

NO_x

Fires

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Plasma dissociation and ionisation

$$e^- + O_2 \rightarrow O_2^+ + 2e^-$$

$$e^- + O_2 \rightarrow O^+ + O + 2e^-$$

$$e^- + N_2 \rightarrow N_2^+ + 2e^-$$

$$e^- + N_2 \rightarrow N^+ + N + 2e^-$$

$$O^+ + N_2 \rightarrow NO^+ + N$$

$$N^+ + O_2 \rightarrow NO^+ + O$$

$$O_2^+ + NO \rightarrow NO^+ + O_2$$

Thermal production of NOx

At T°C > 1600°C:

Dissociation of N_2 in N and O_2 in O

$N_2 + O \rightarrow NO + N$

$N + O_2 \rightarrow NO + O$

$N + OH \rightarrow NO + H$

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The processes in the Nitrogen cycle

- Anthropogenic perturbations

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Which anthropogenic changes ?

Crop production

Meat production

Production D’énergie

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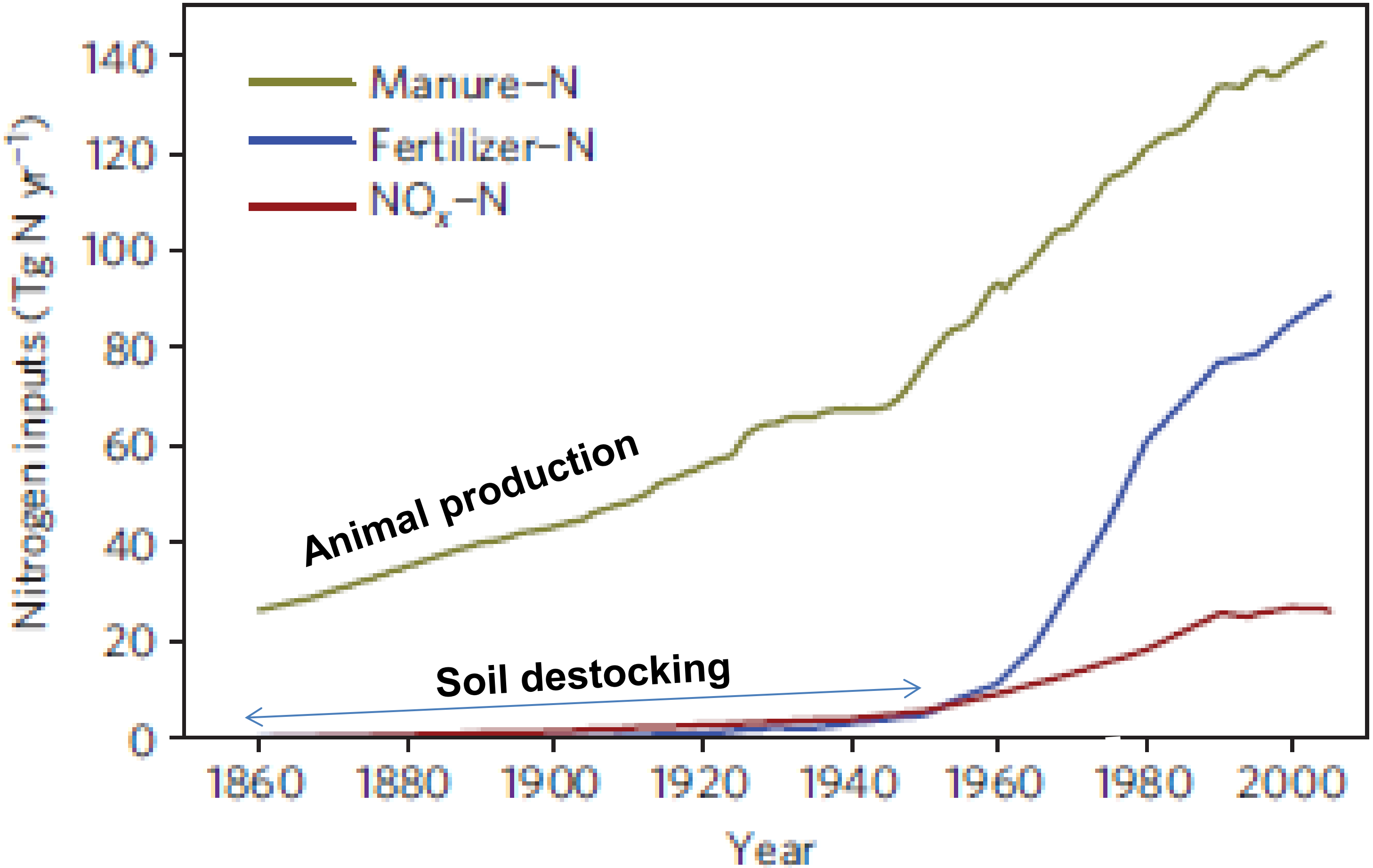
Which anthropogenic changes ?

Increase due to food production and energy consumption



Davidson 2014

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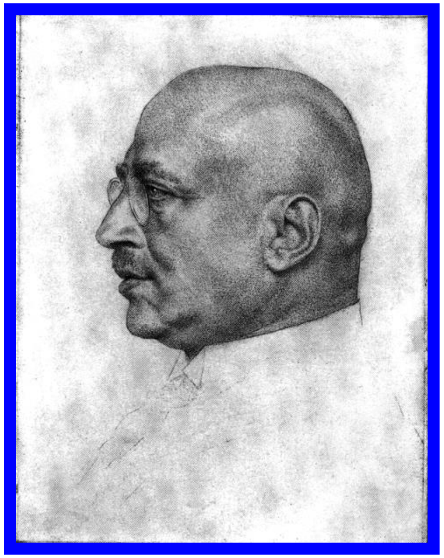
Industrial production of Nr



Fritz Haber (1868-1934)

Started working on NH_3, 1904
Firts patent, 1908
Firts 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 "

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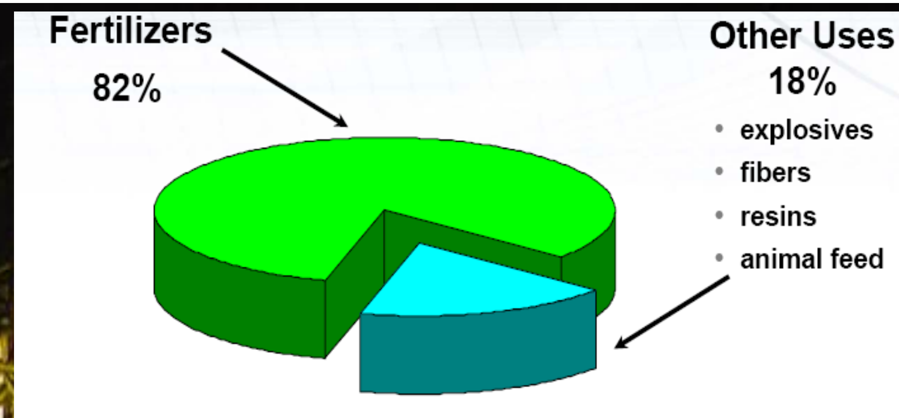
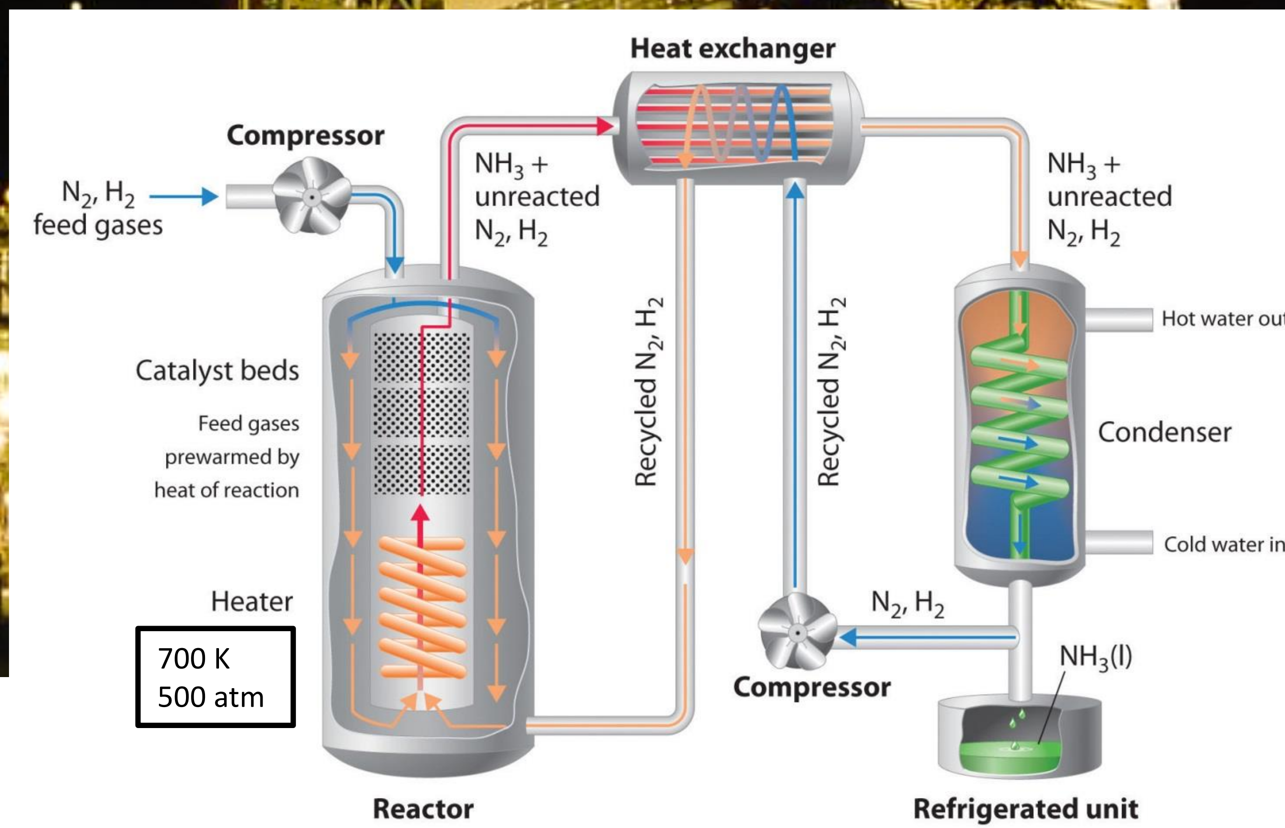
Industrial production of NH_3





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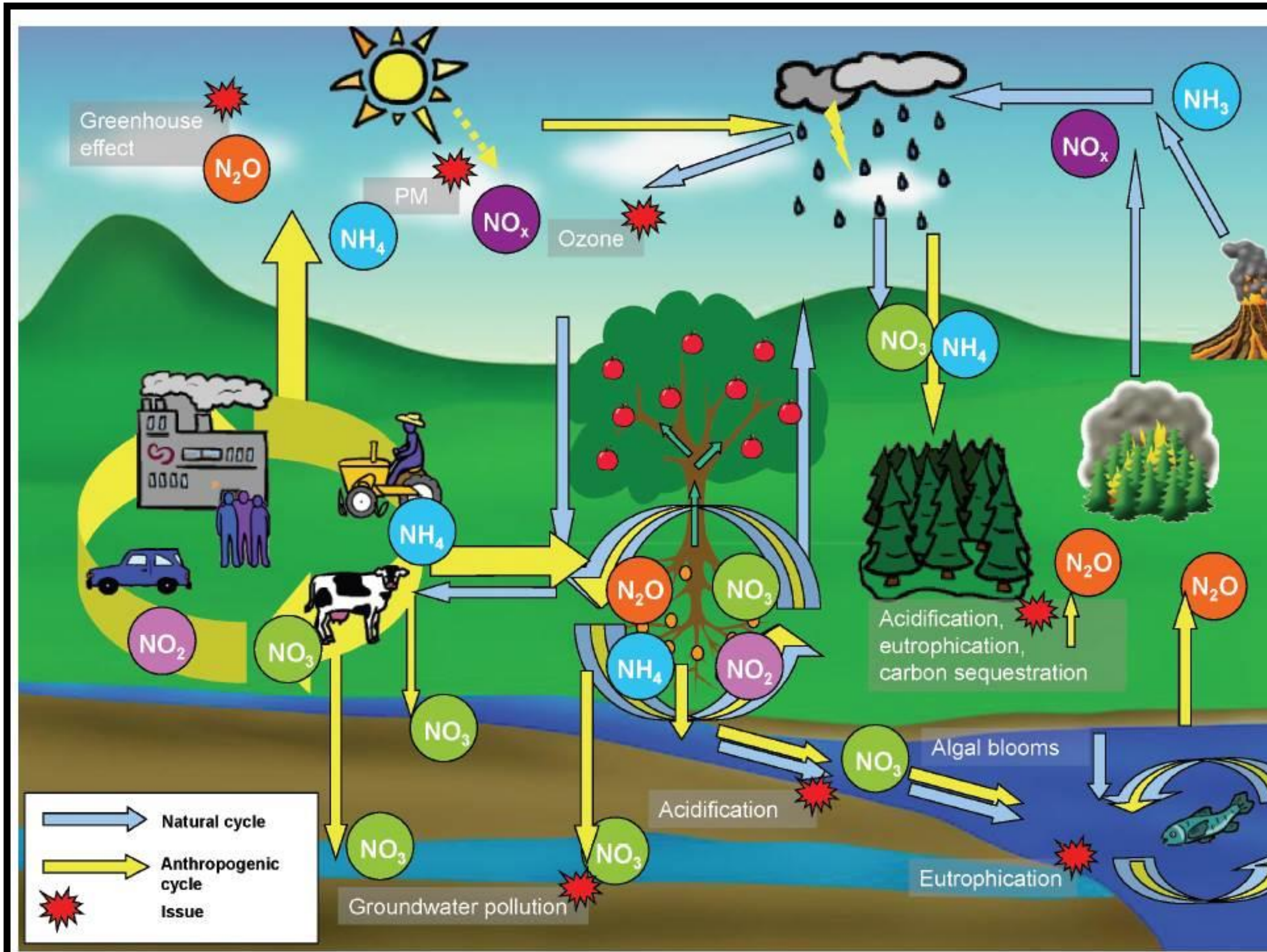
The anthropogenically perturbed nitrogen cycle



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Anne-Christine LeGall, ENA, 2011

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The processes in the Nitrogen cycle

- Quantifying the fluxes

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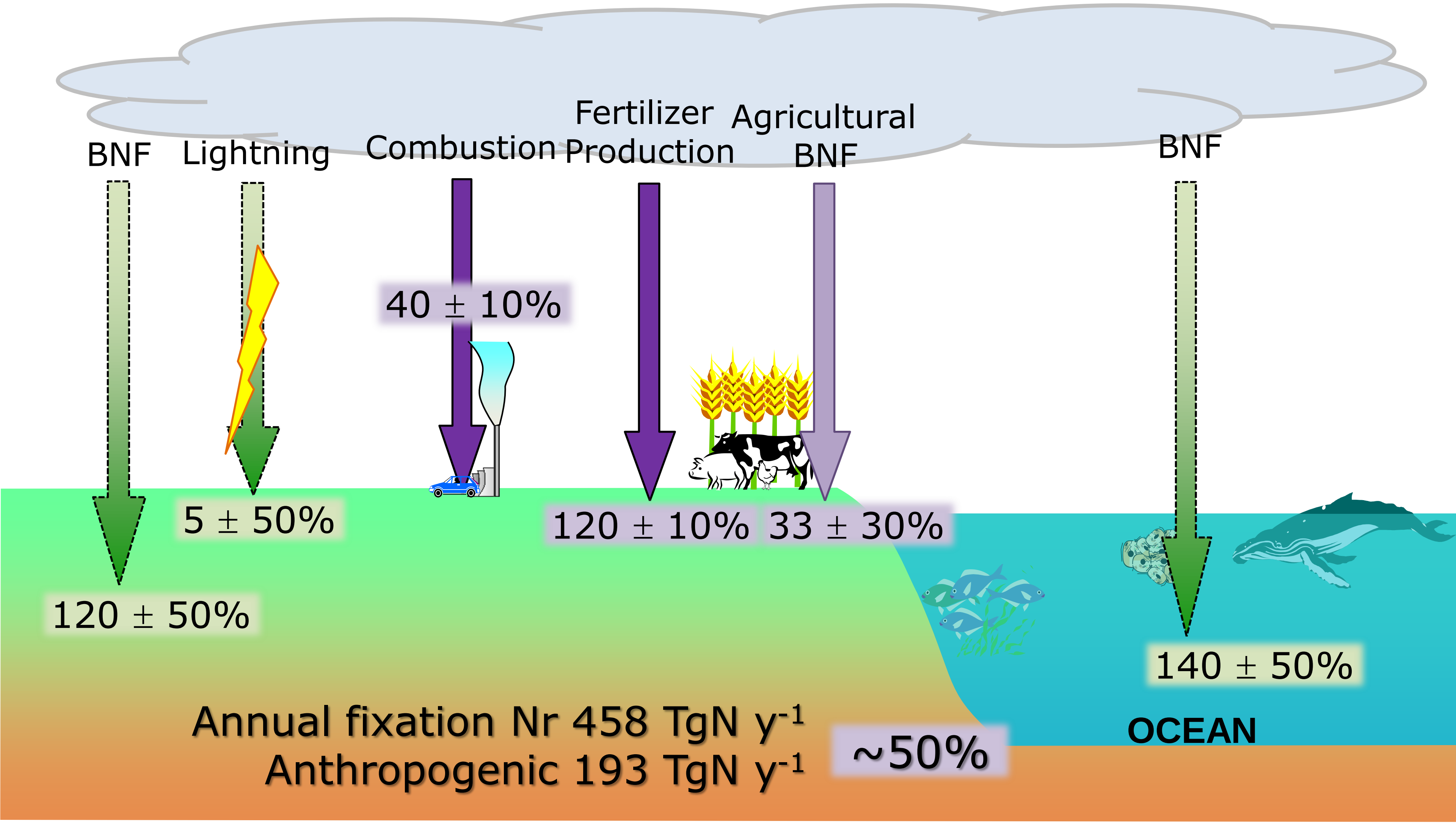
MAIN FLUXES : NITROGEN FIXATION $N_2 \rightarrow$ TO N_R (Tg-N)



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BNF – Biological Nitrogen Fixation

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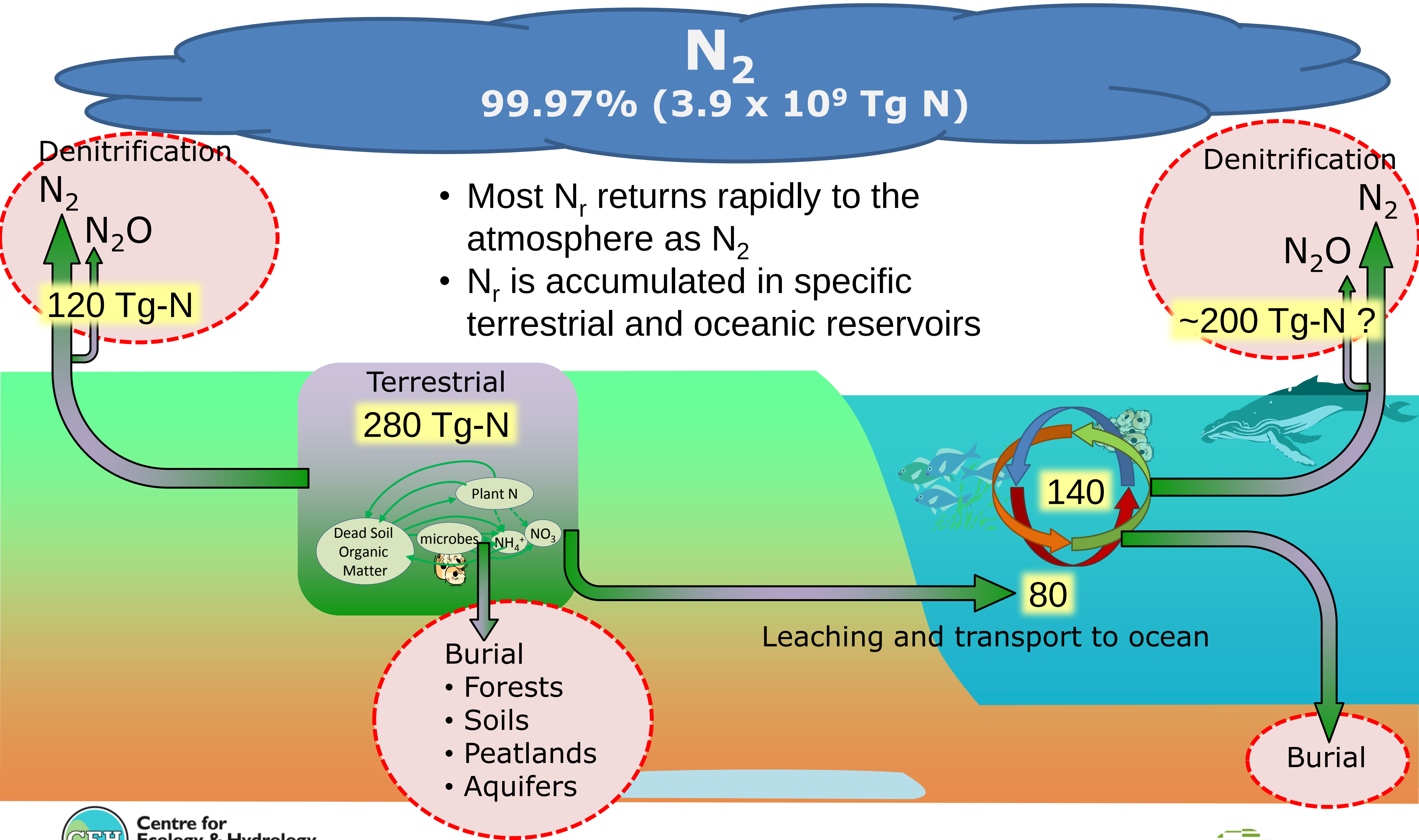
MAIN FLUXES : DENITRIFICATION



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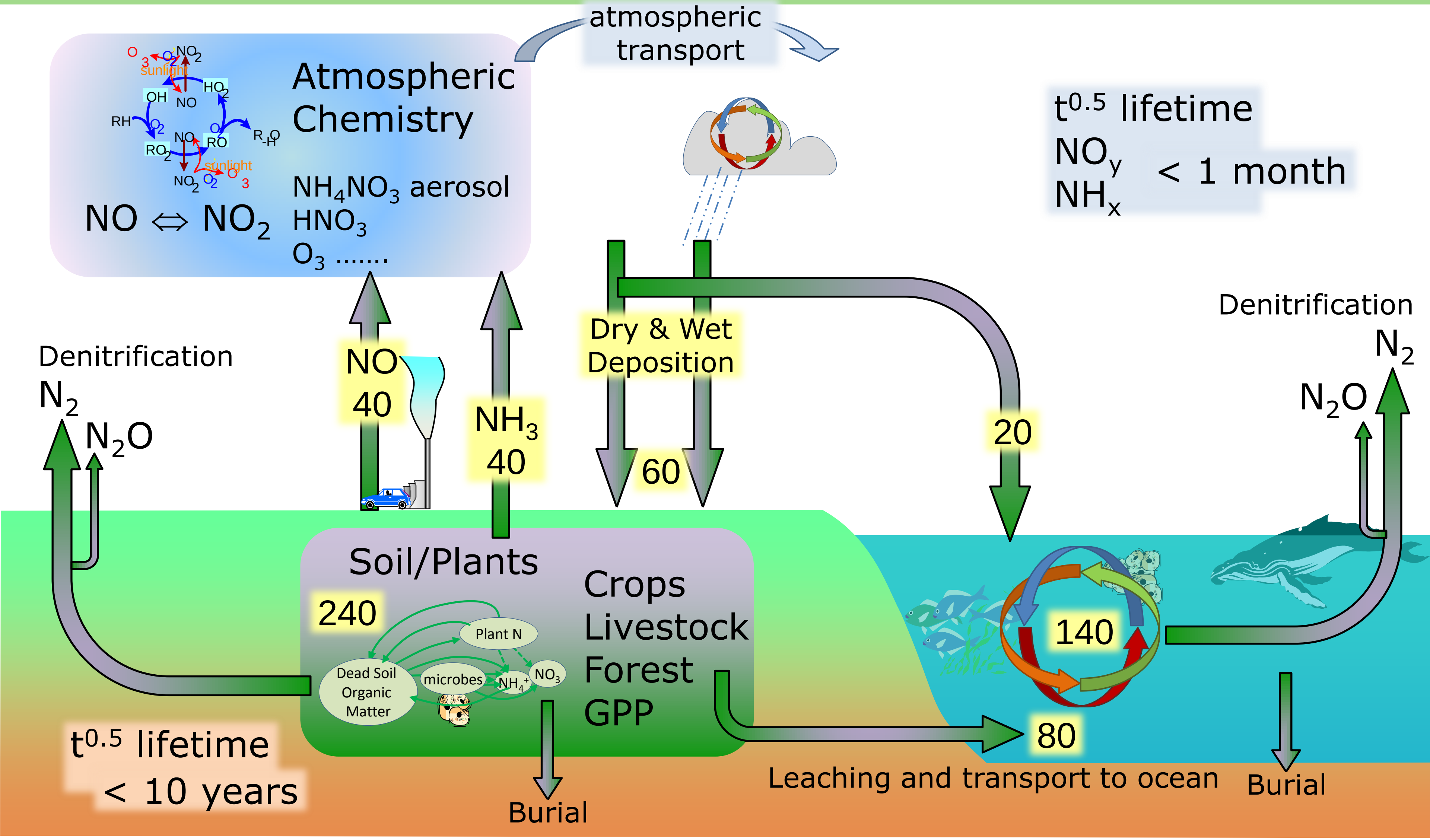
NITROGEN PROCESSING (CYCLING)



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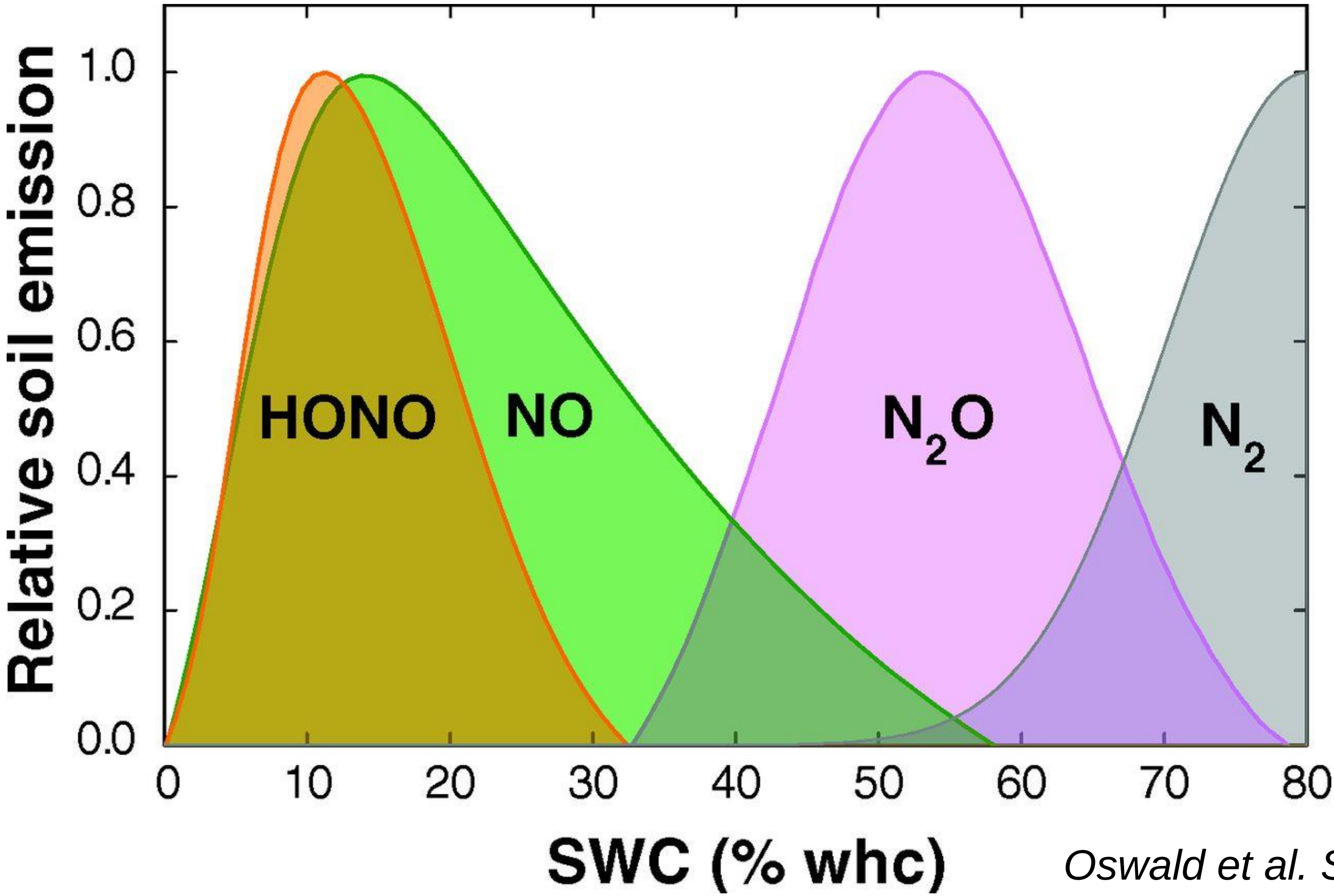
NITROGEN PROCESSING: EMISSIONS FROM SOILS



Oswald et al. Science ***2013***

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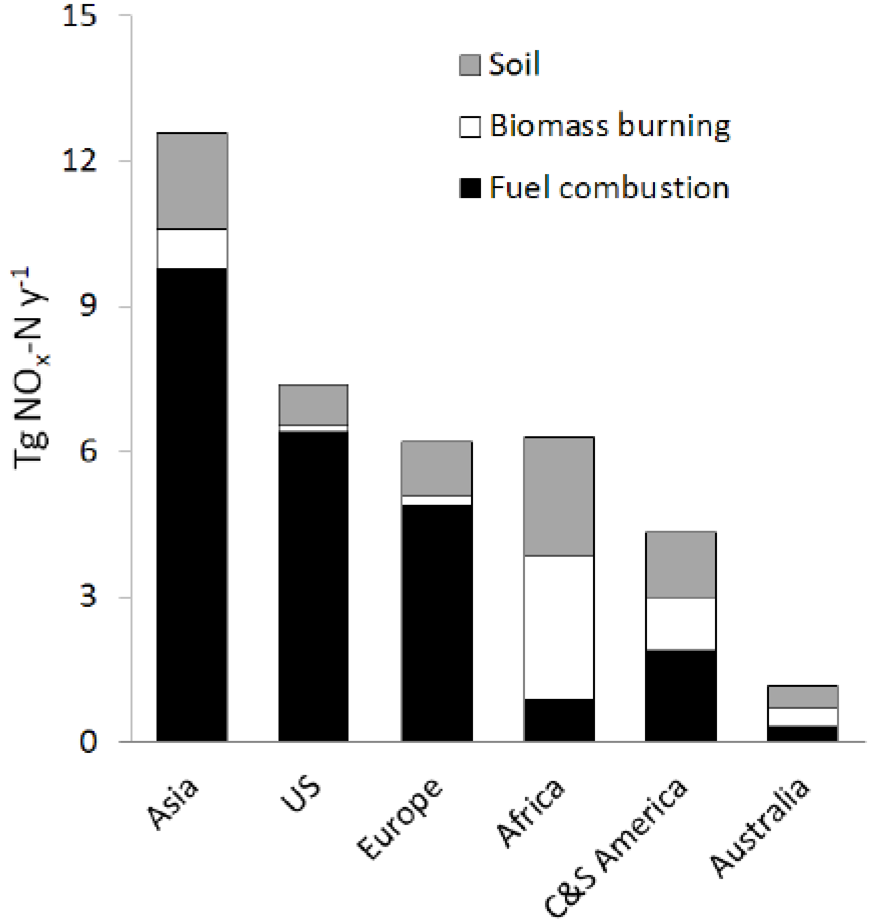
B-NO emissions source variable



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

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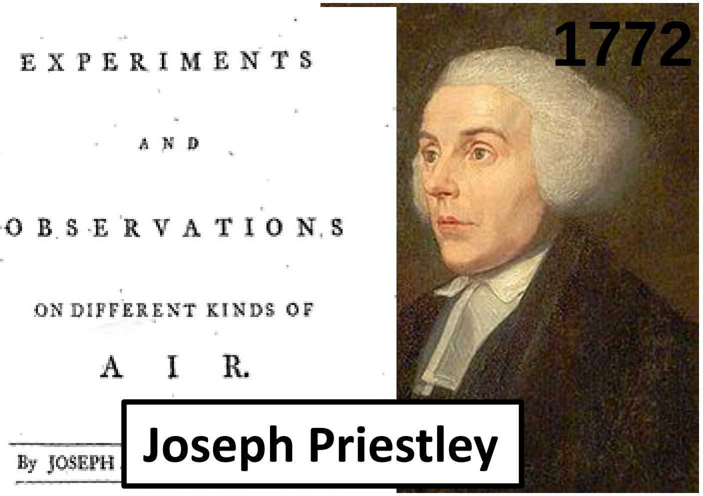
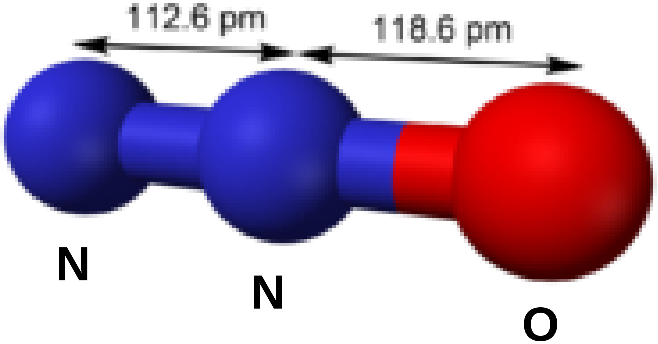
LAUGHING GAS: N2O

Discovered

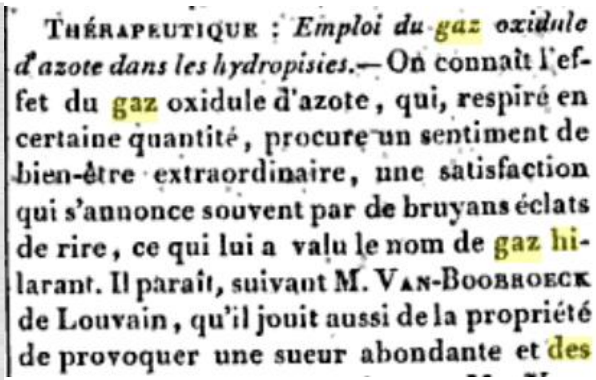


N_2O



Laughing gas

Anesthesic during the XIXth



THÉRAPEUTIQUE : *Emploi du gaz oxidule d'azote dans les hydropisies.*— On connaît l'effet du gaz oxidule d'azote, qui, respiré en certaine quantité, procure un sentiment de bien-être extraordinaire, une satisfaction qui s'annonce souvent par de bruyans éclats de rire, ce qui lui a valu le nom de gaz hilarant. Il paraît, suivant M. VAN-BOOBROECK de Louvain, qu'il jouit aussi de la propriété de provoquer une sueur abondante et des

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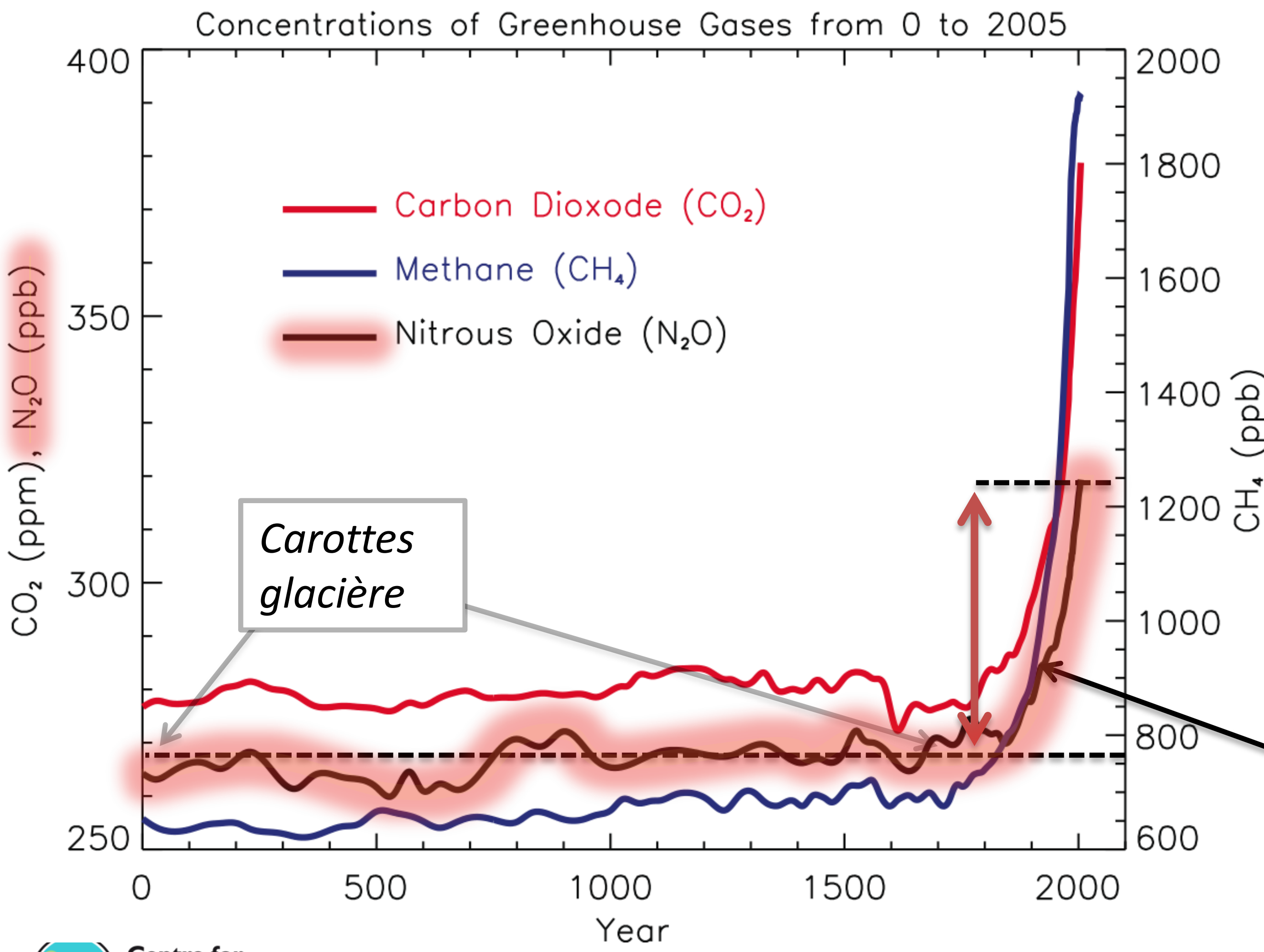
THE THIRD GREENHOUSE GAZ



James Lovelock (1958)

Chromatography With electron capture

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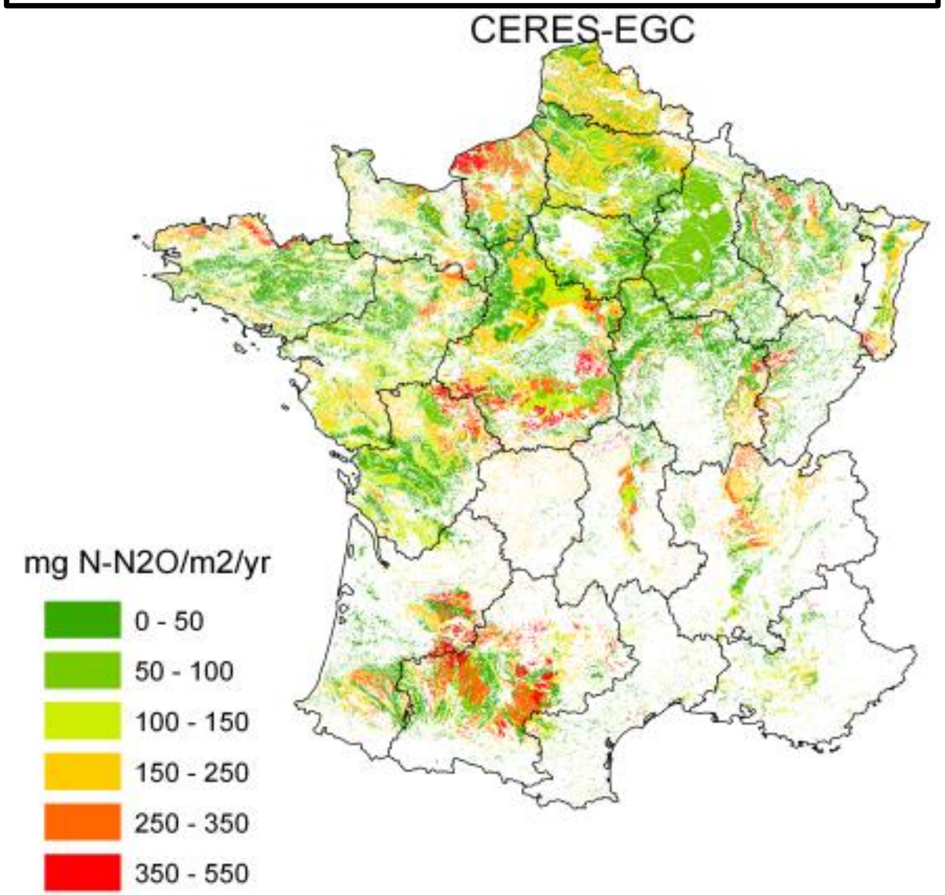
IPCC, 2007

DES VARIATIONS RÉGIONALES FORTES

Emissions de N_2O des cultures



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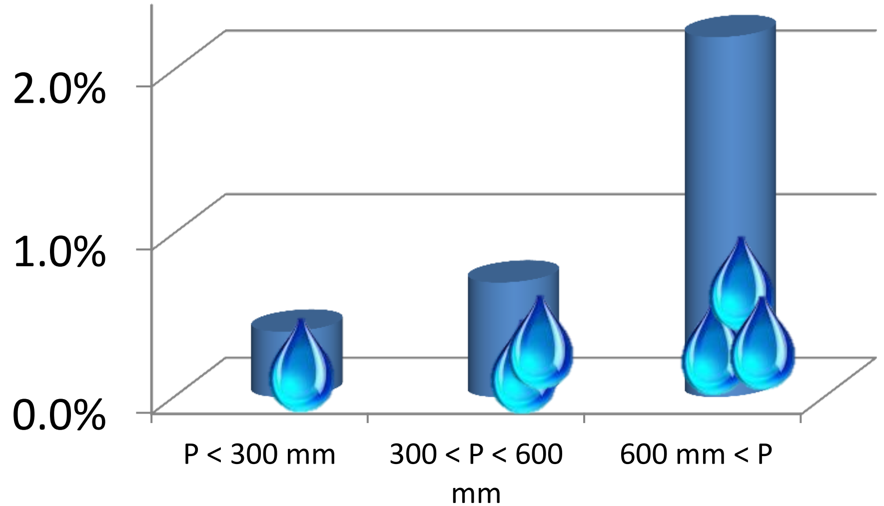
Les émissions sont plus élevées dans
- Les zones à forts apports d'azote
- Les sols humides



Pourcentage de N_2O émis par rapport
À la quantité d'azote apportée

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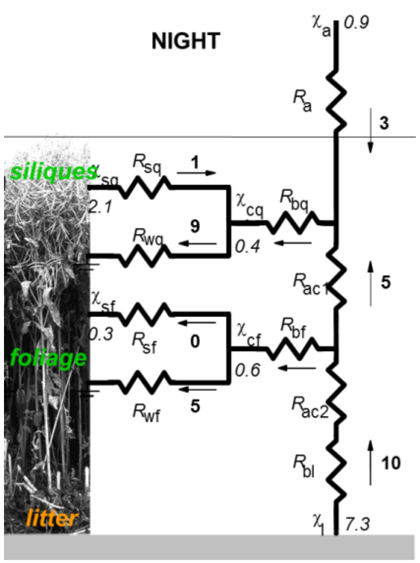
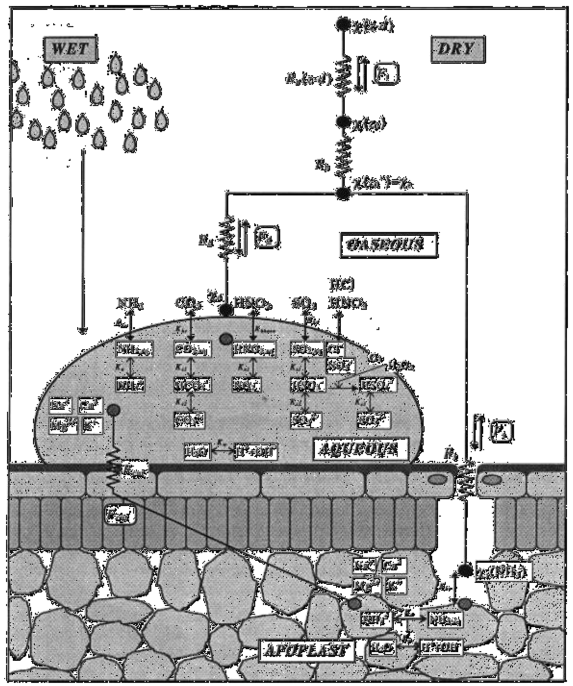
NITROGEN PROCESSING: DEPOSITION

Turbulent transfer

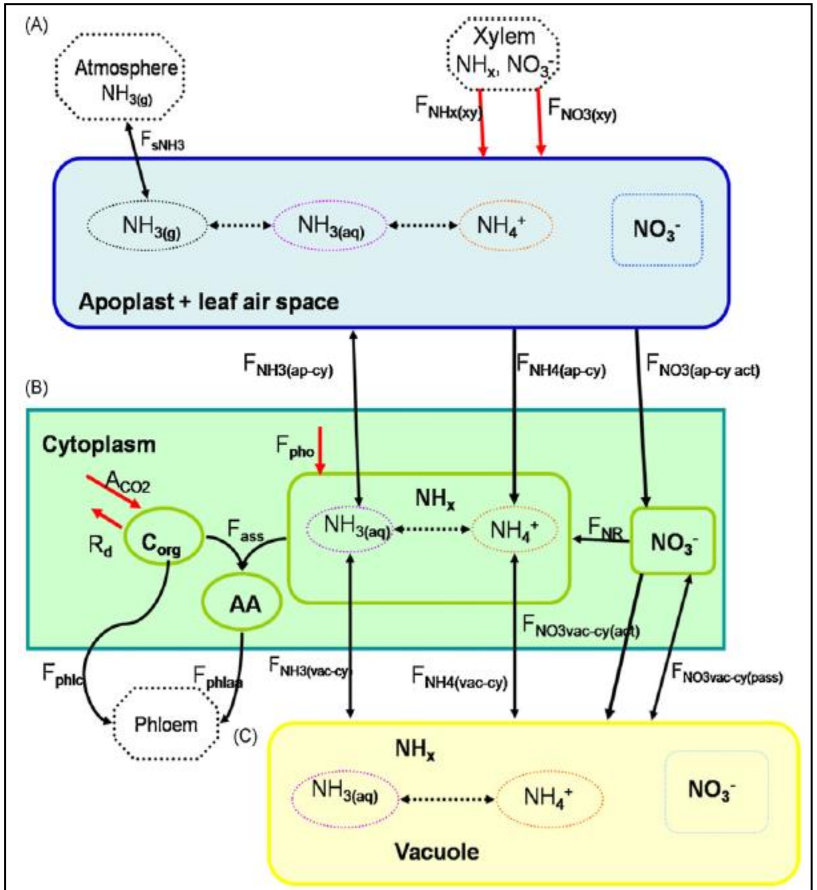


Surface exchange



Flechard et al. (1999)

Biological control



Massad et al. (2010)

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The impacts of Nr

- Health and environmental impacts

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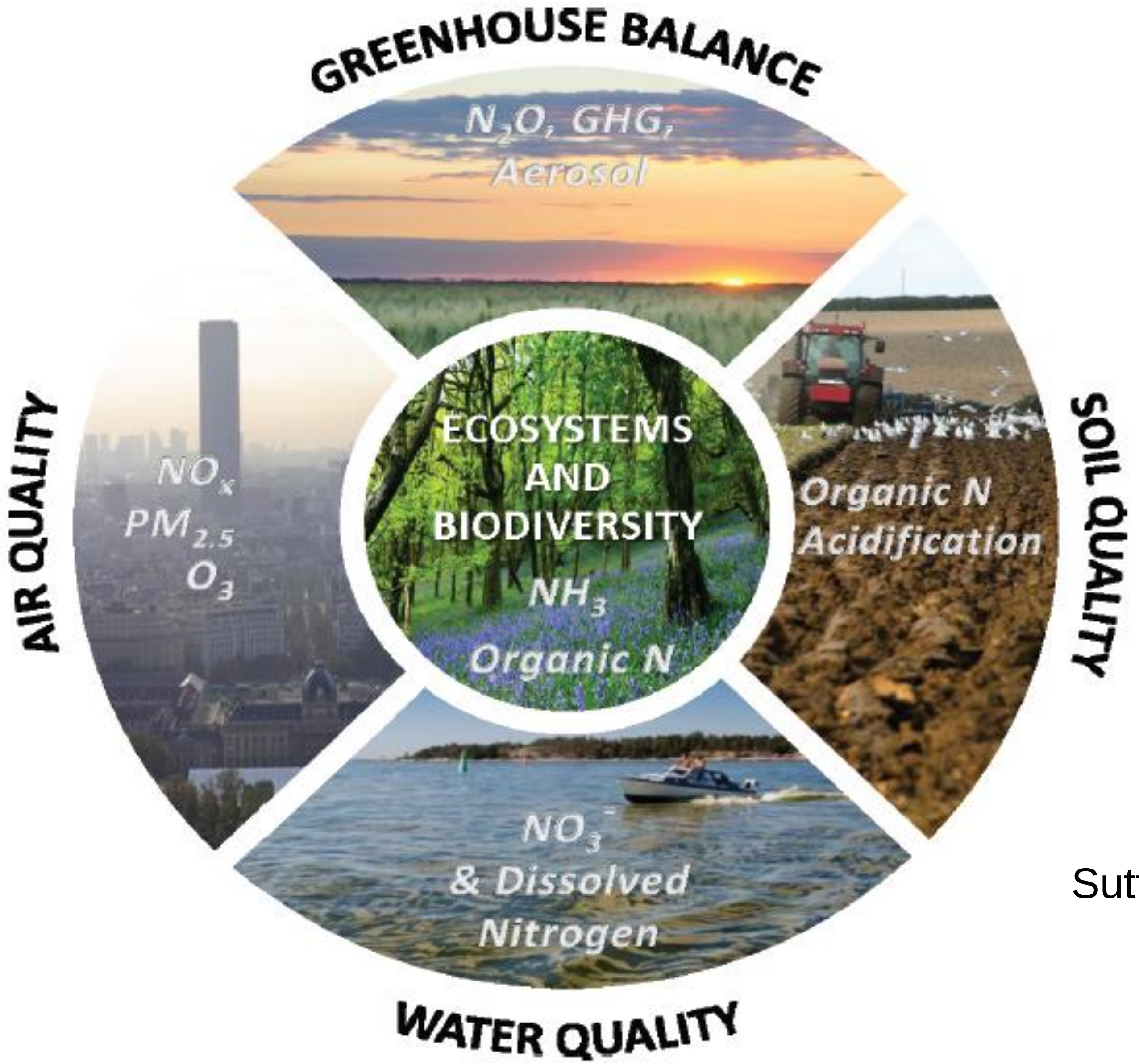
THE 5 KEY THREATS OF NITROGEN



Sutton et al. 2011

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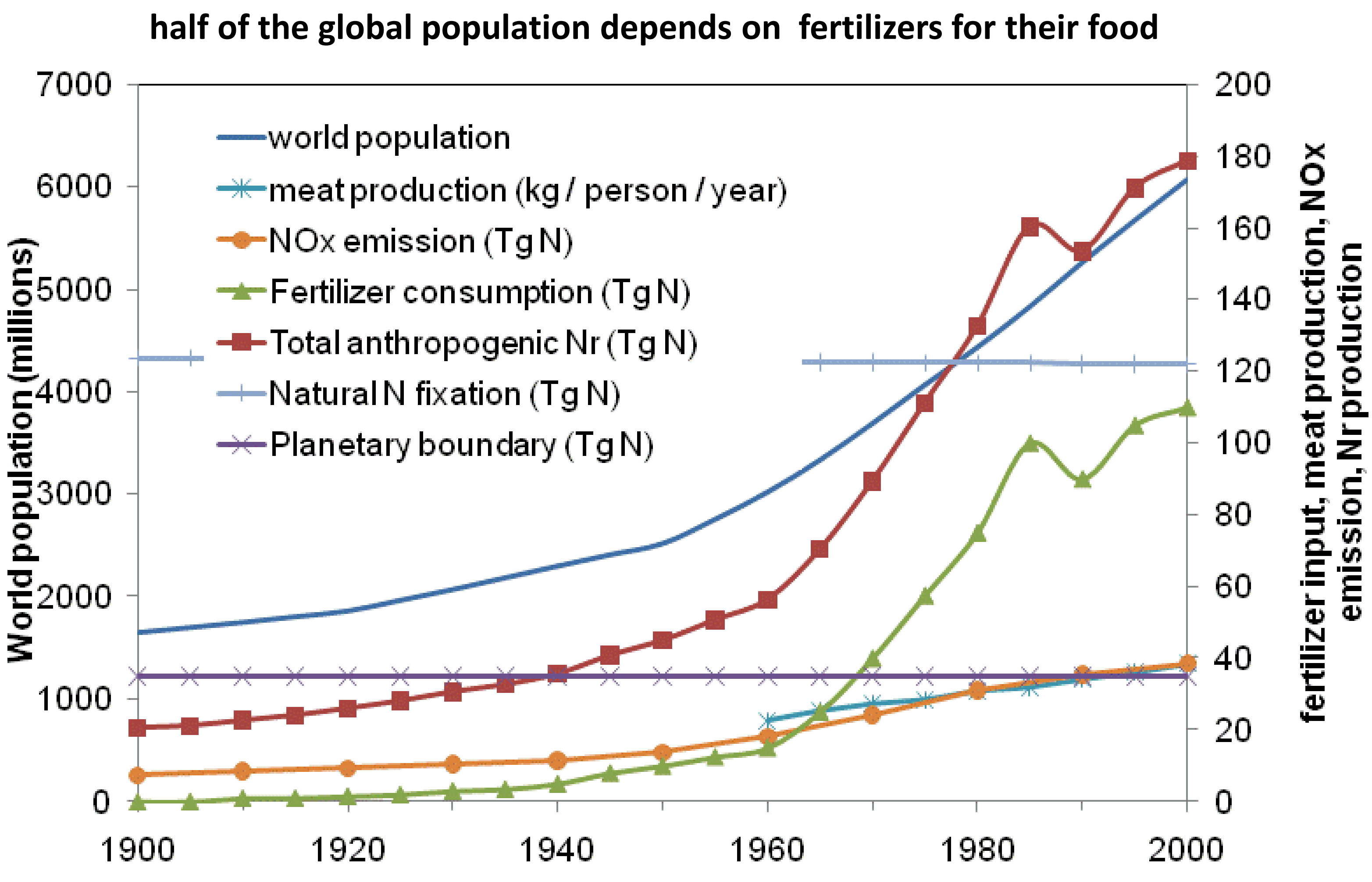
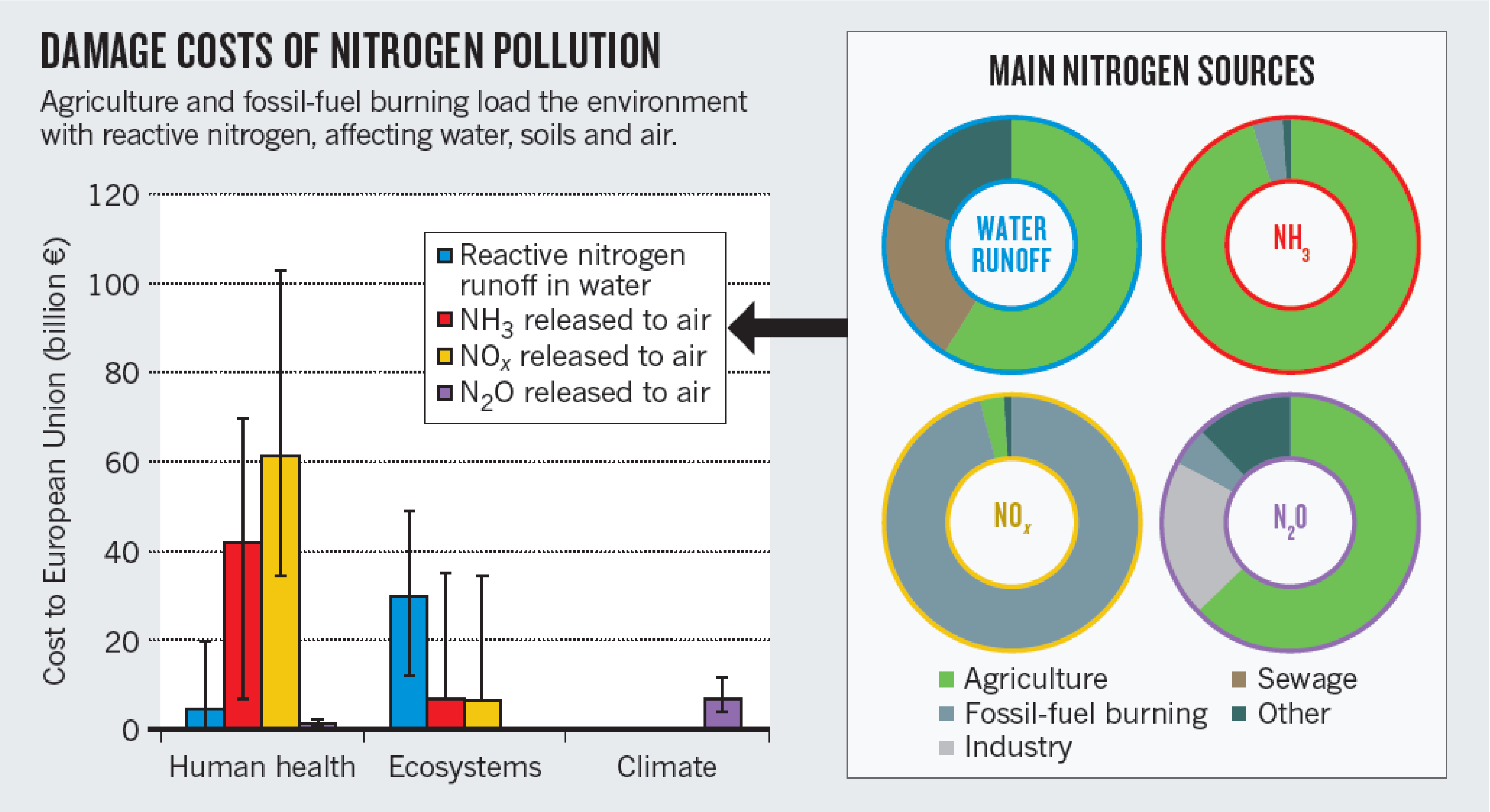
Nr for food and from energy between 1900 - 2000



“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)

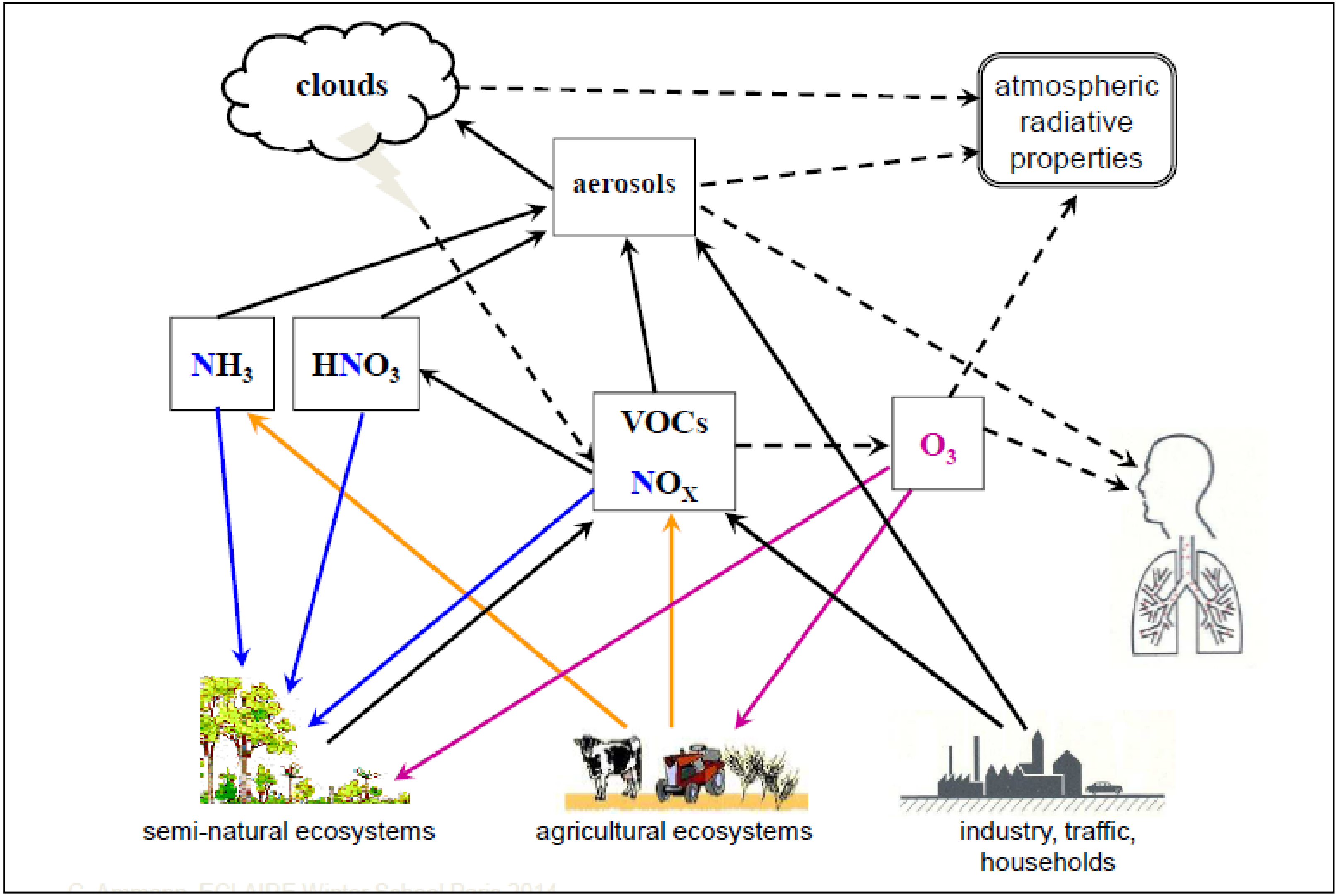
NITROGEN DAMAGE COSTS & SOURCES



EU Damage cost: 70 - 320 billion € / year

Nature 14 April 2011

IMPACT ON HUMAN HEALTH



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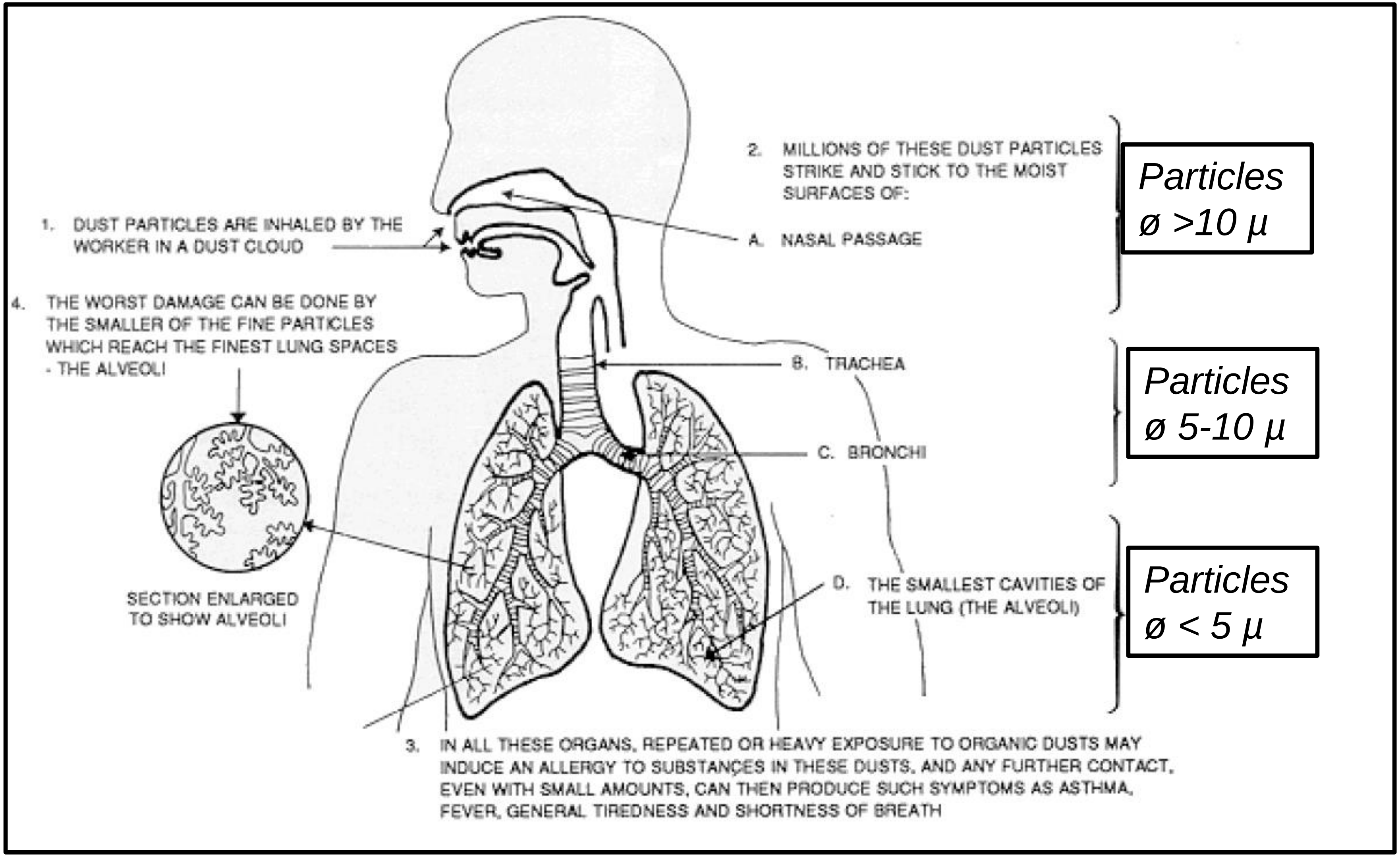
IMPACT ON HUMAN HEALTH



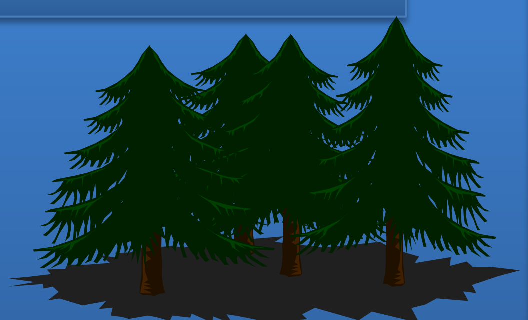
DES EFFETS COMPLEXES SUR L'ENVIRONNEMENT
EXEMPLE DE L'AMMONIAC

NH_3
NH_4^+

Formation d'aérosols

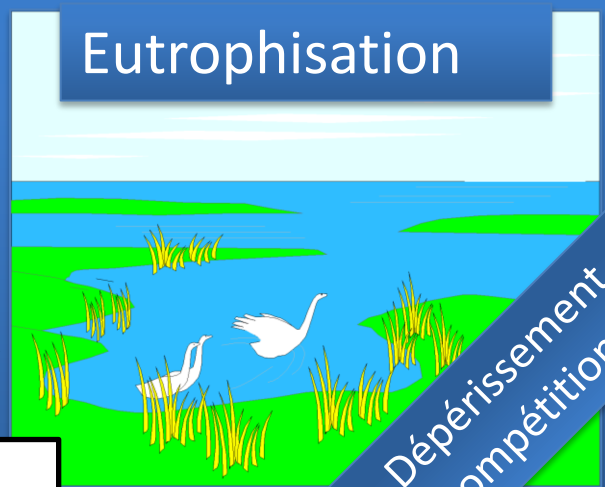
NH_4^+ NO_3^- SO_4^{--} Cl^-

Acidification



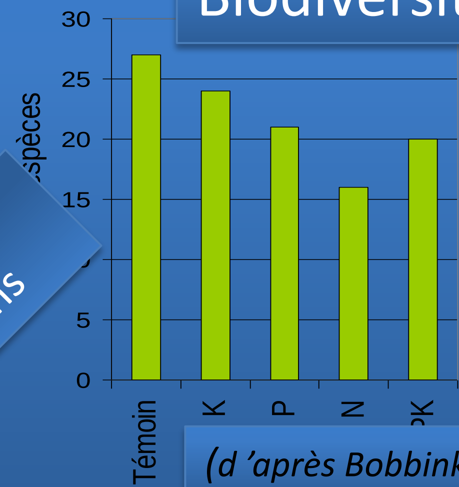
$NH_4^+ \rightarrow NO_3^- + 2H^+ + ...$

Eutrophisation



Dépérissement
compétitions

Biodiversité



Prairie

(d 'après Bobbink, 1991)

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PERTE DE BIODIVERSITÉ

Sous-bois des forêts suédoises

+15 kg N / ha / an

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ILLUSTRATION D'UN EFFET D'EUTROPHISATION

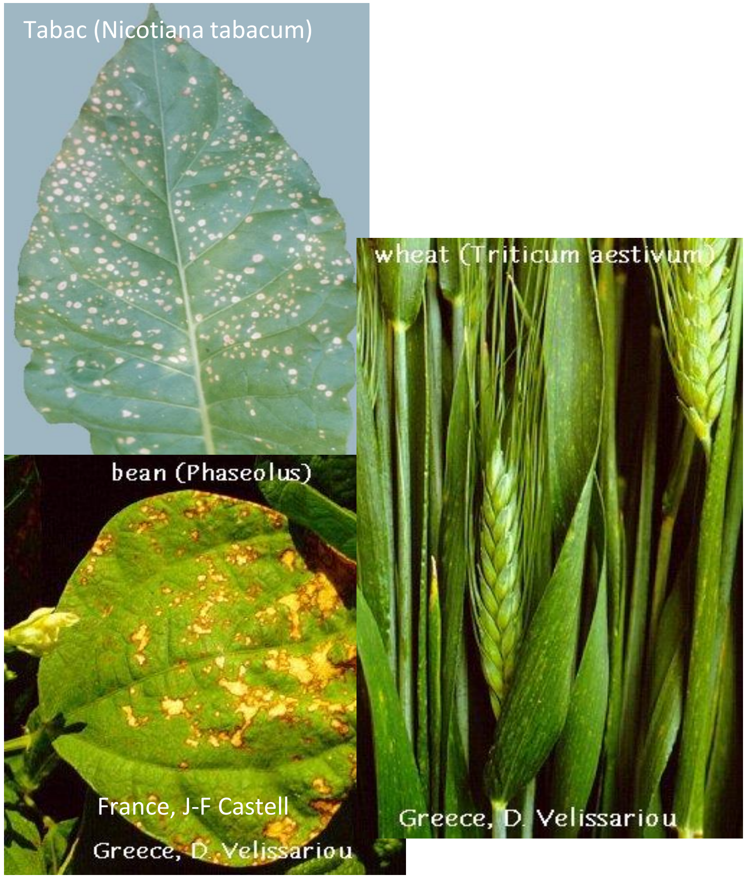
Gauche: lichen dans un environnement naturel

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

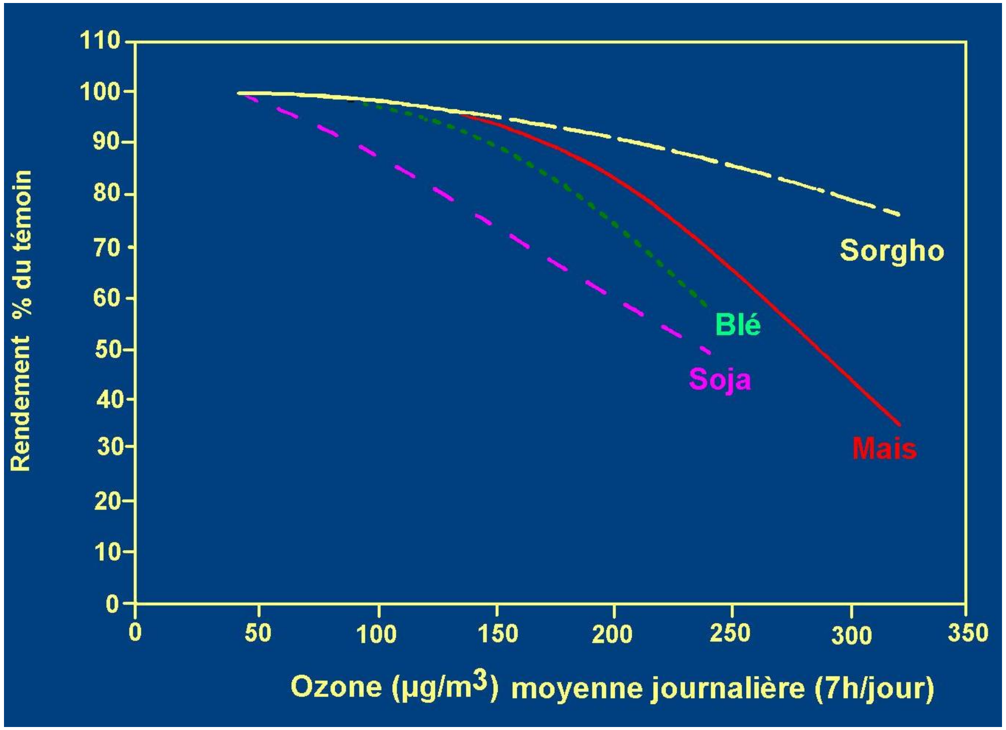
Excès d'azote en zone côtière sur la formation d'algues (*Phaeocystis globosa)* à l'origine de la formation de mousse gélatineuse

Ozone impacts on agriculture

Des dégâts foliaires :



Des impacts agronomiques :



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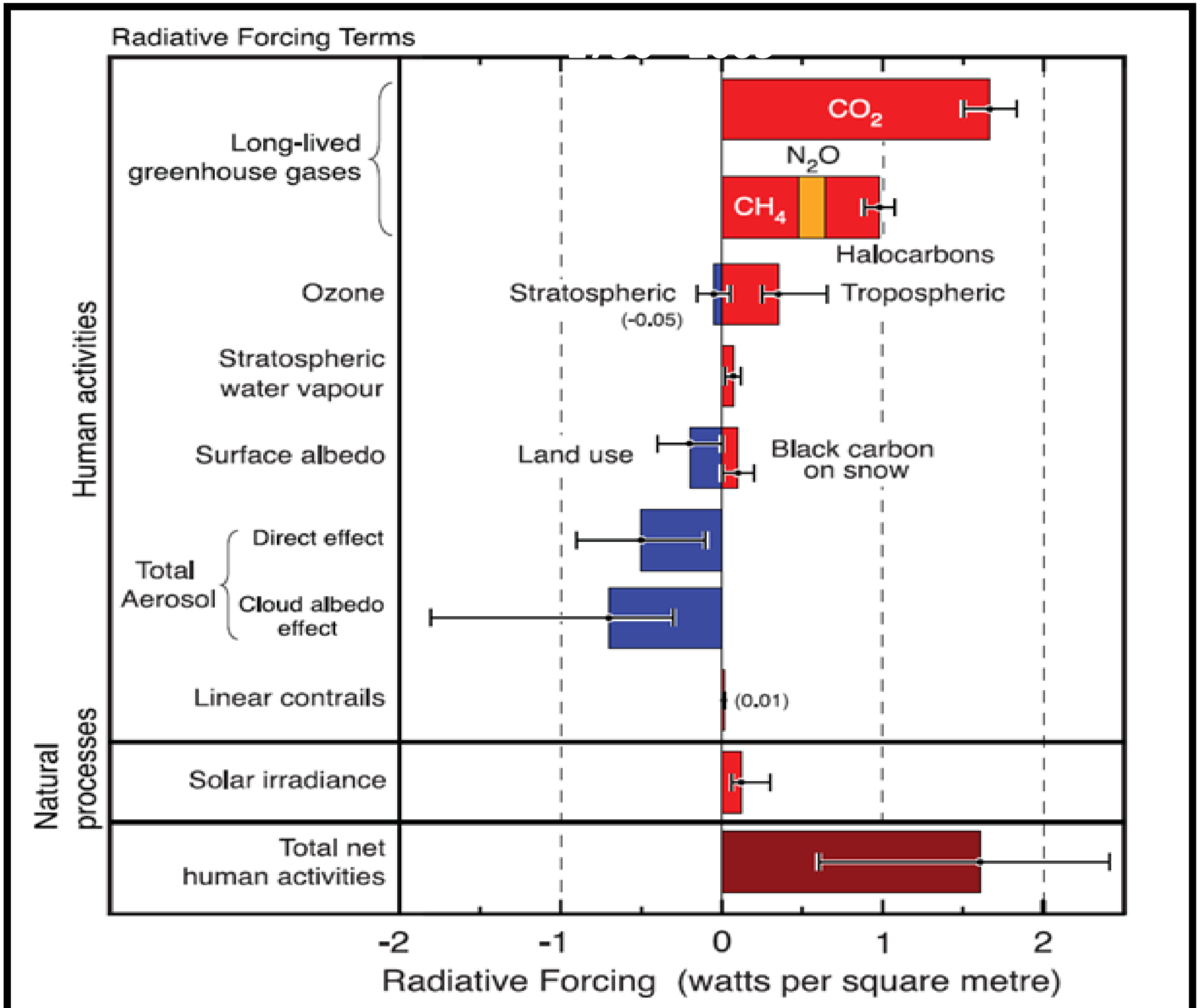
LE FORCAGE RADIATIF ET LE RÉCHAUFFEMENT GLOBAL



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Int. Panel. Clim. Ch.

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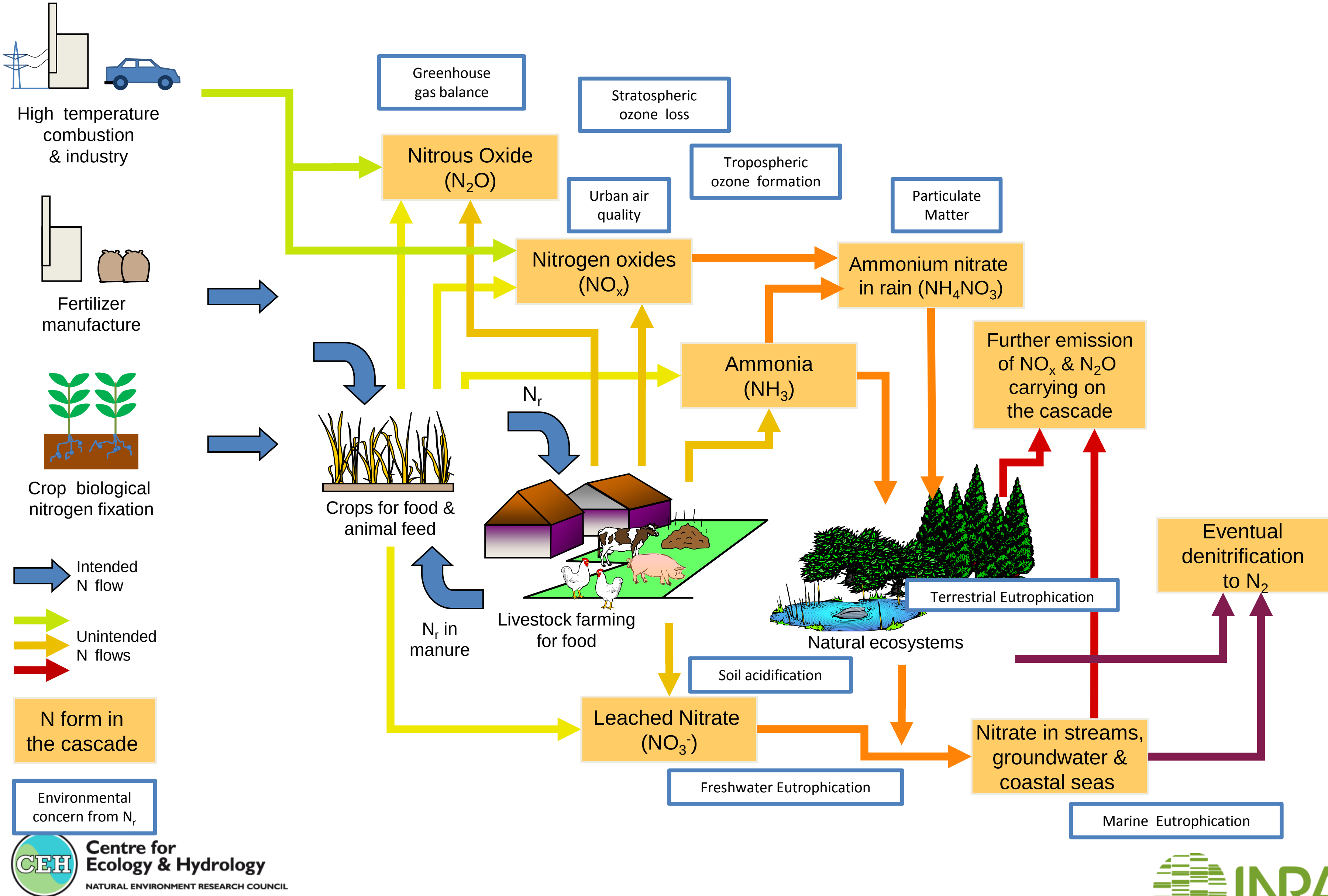
Simplified view of the Nitrogen Cascade



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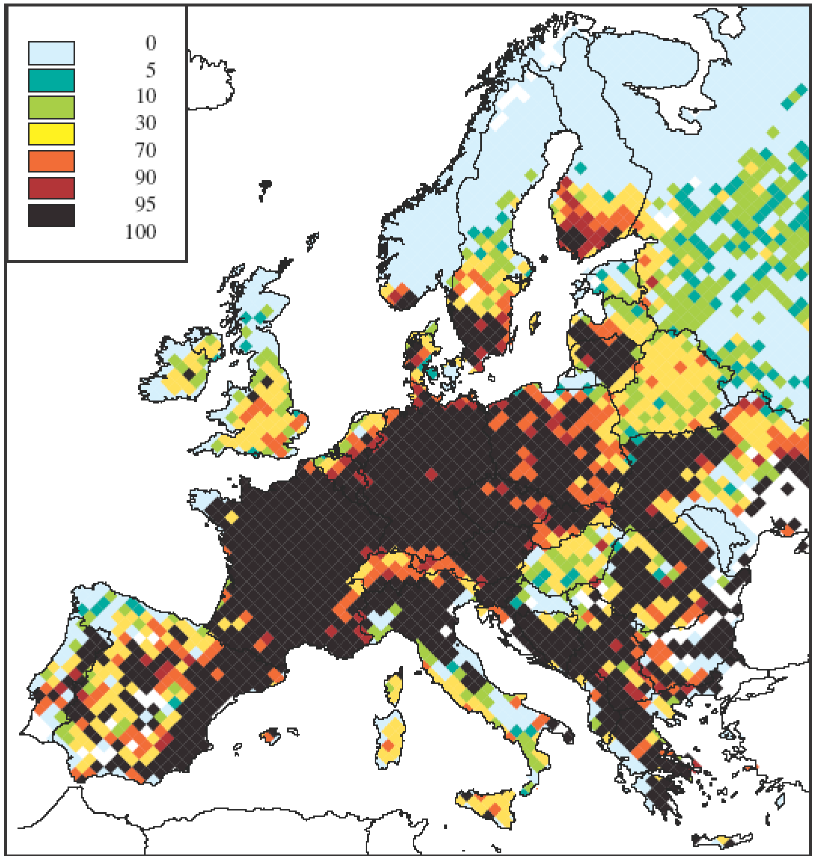
Sutton et al. (2011 European Nitrogen Assessment, ENA Ch 5)

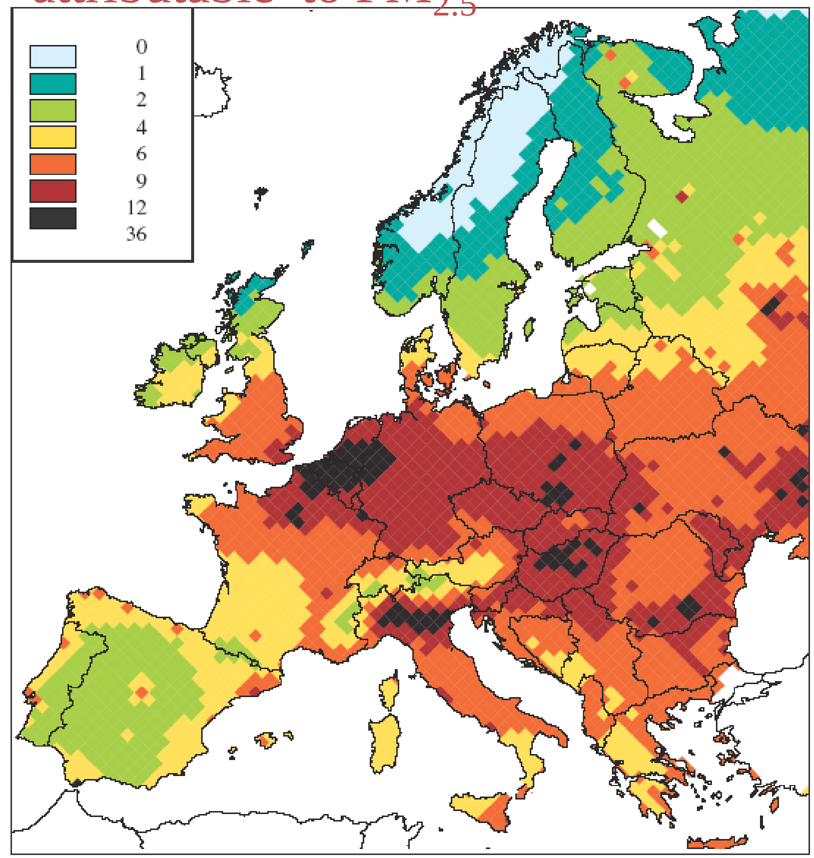
Predicted effects across Europe

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)

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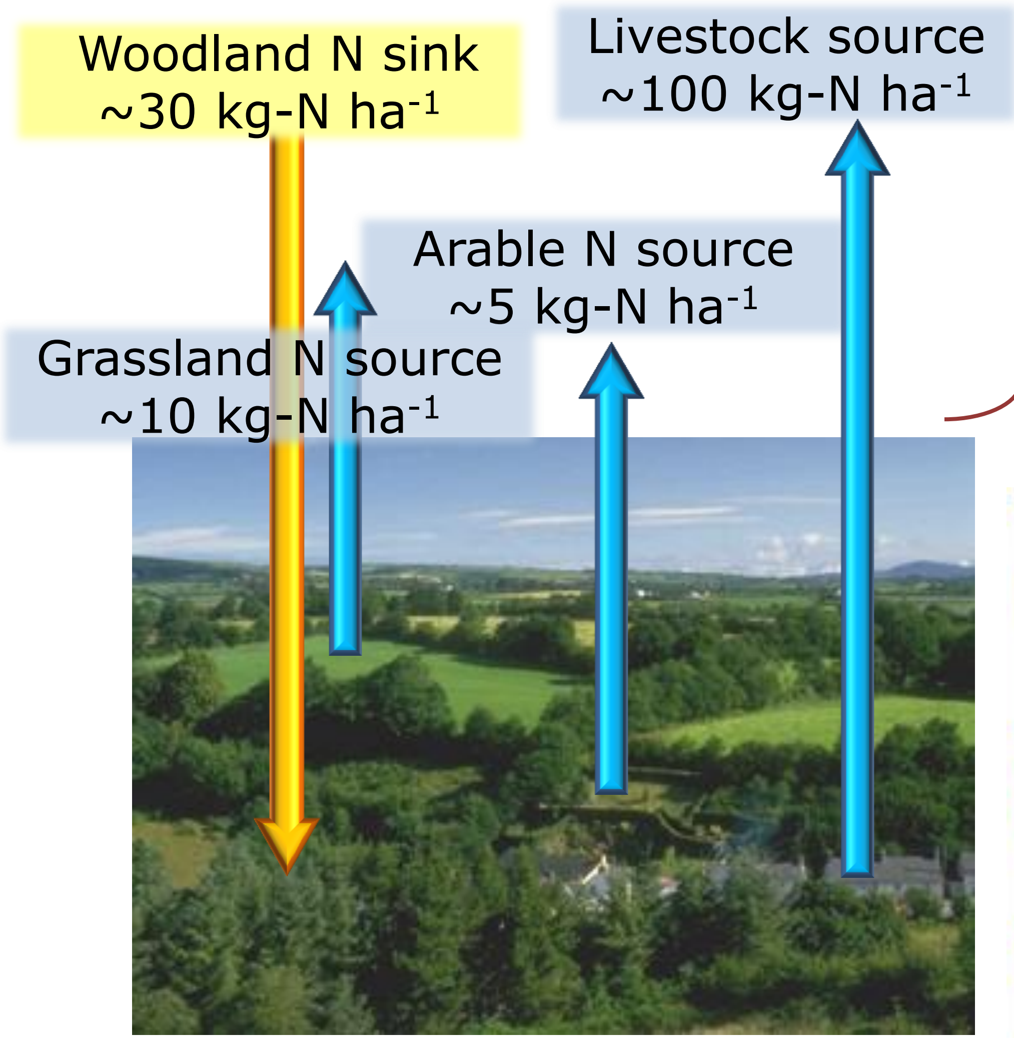
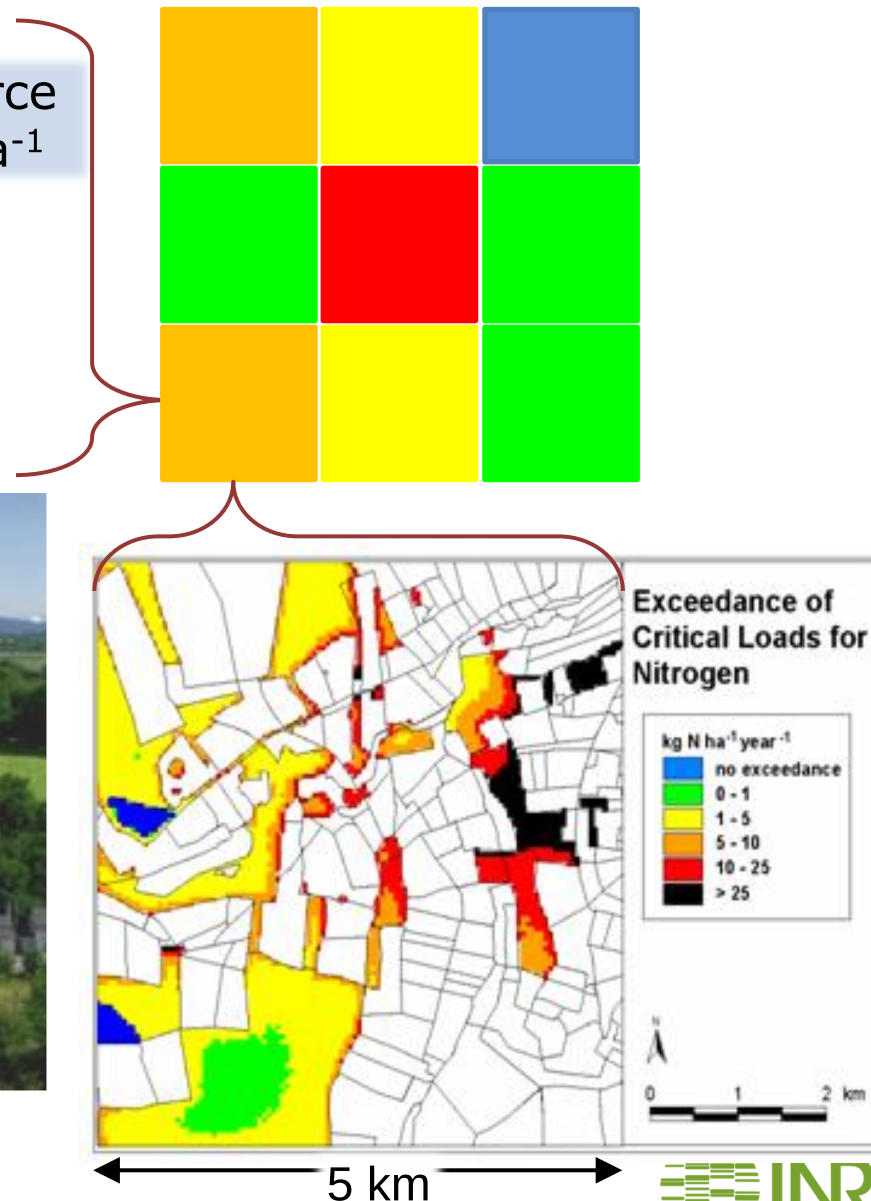
SCALE ISSUES

The spatial scale of assessment strongly influences outcomes

FLUXES AND EFFECTS IN THE FIELD OCCUR AT FINE SCALE





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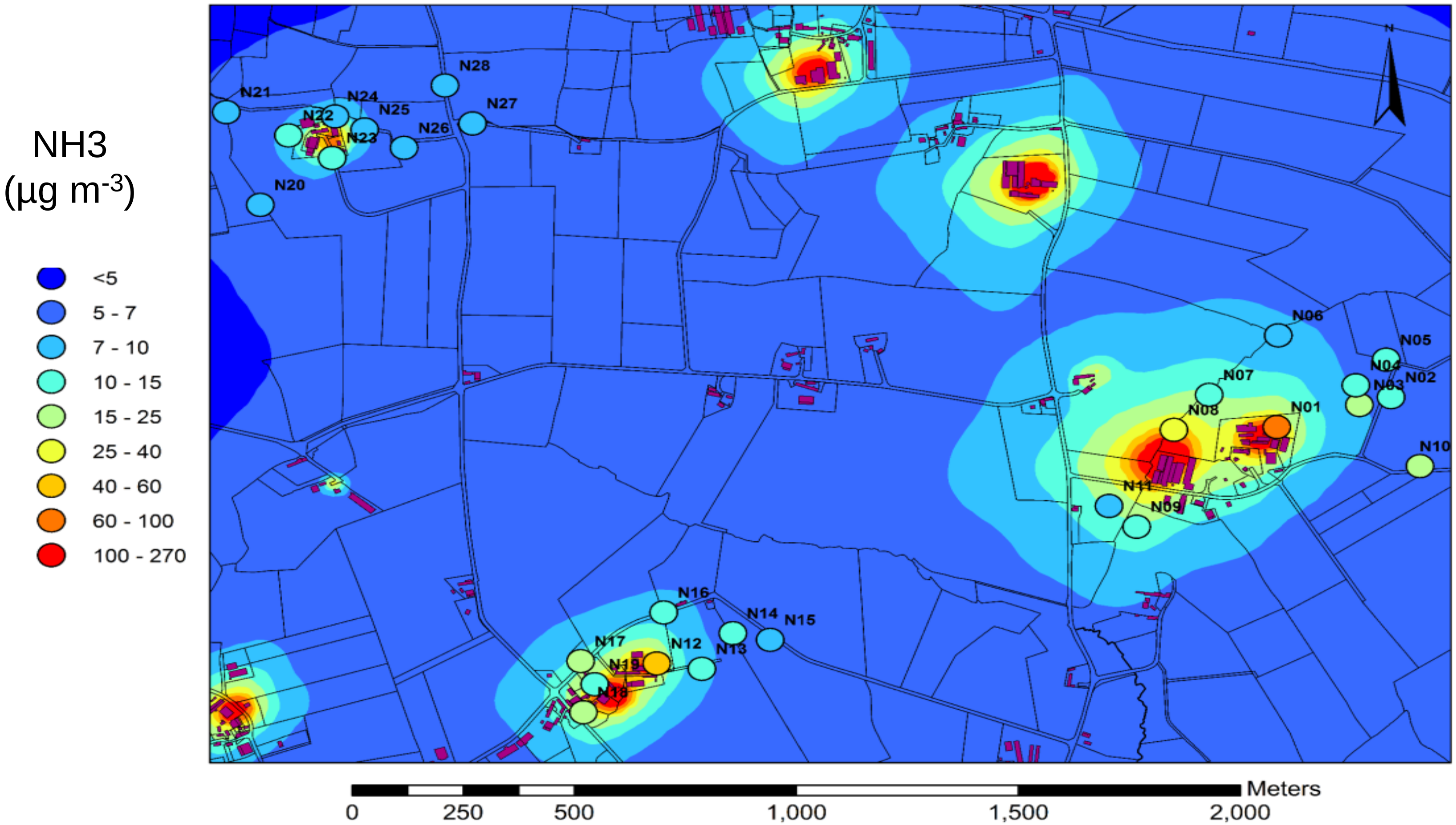
• Hot-spots needs changing of scales



(PhD Michael Bell, INRA Rennes)

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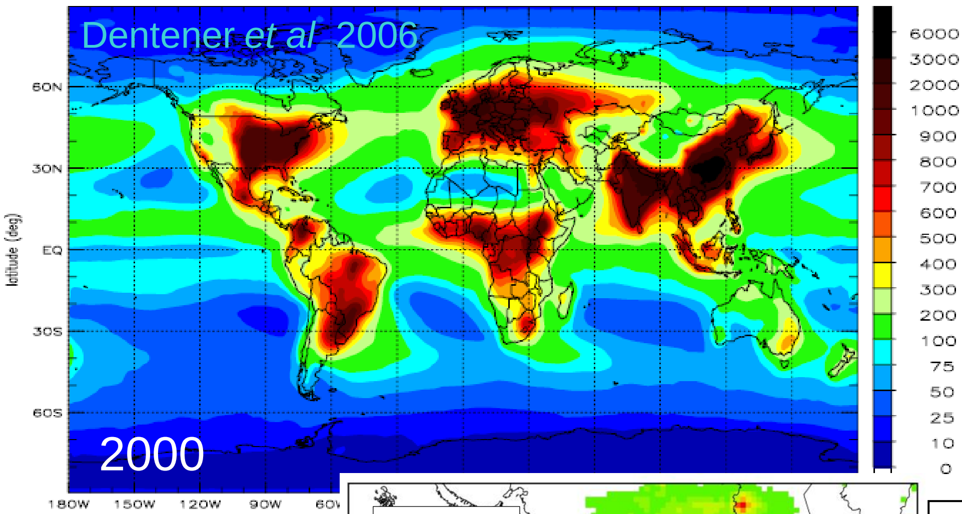
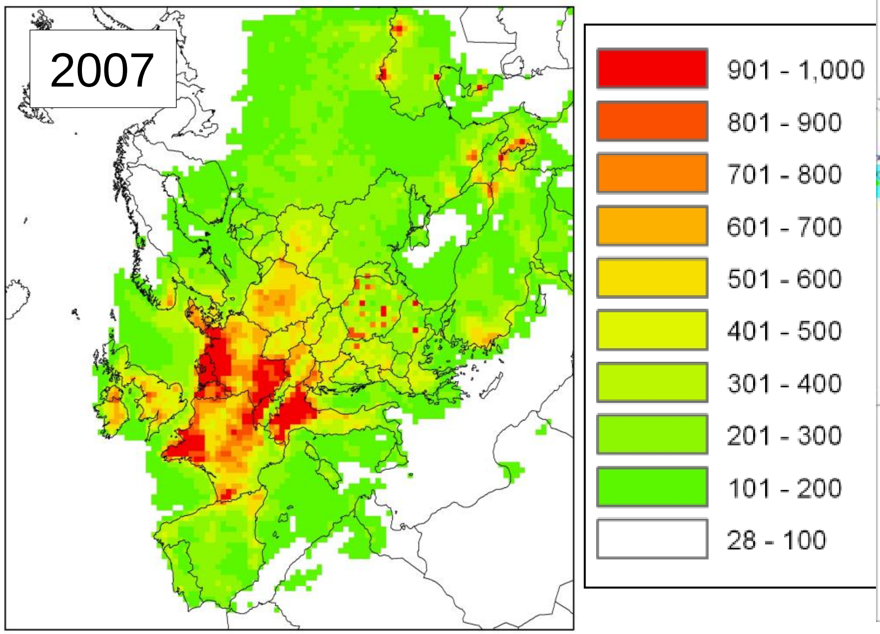
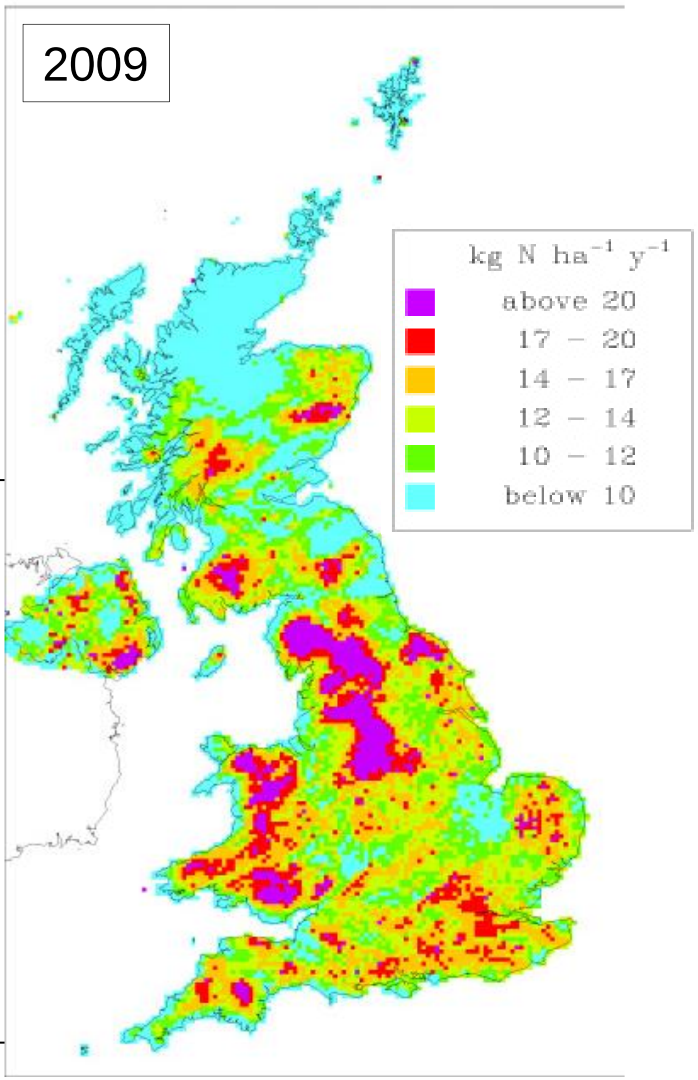
ATMOSPHERIC NITROGEN DEPOSITION: GLOBAL, REGIONAL, LOCAL (Nr mg-N m^{-2})







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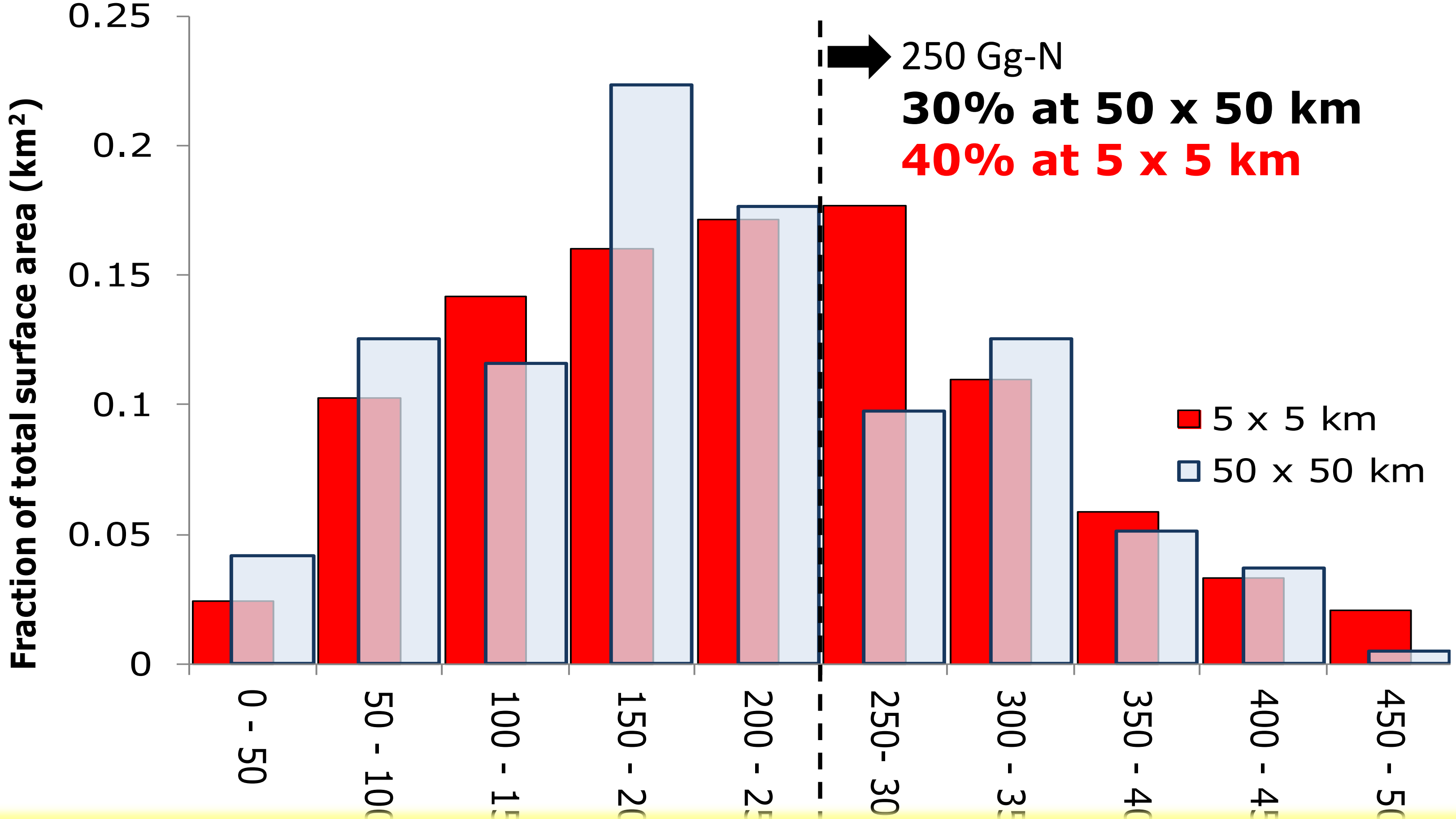
QUANTIFYING SPATIAL DISTRIBUTIONS



- 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

2000 TO 2100 TRENDS (WHAT IS THE FUTURE?)

Two important issues:

1. 'Best' estimates of projected emissions of NO_x ,NH_3, and N_2O
2. Influence of climate change on the N cycle (emissions).

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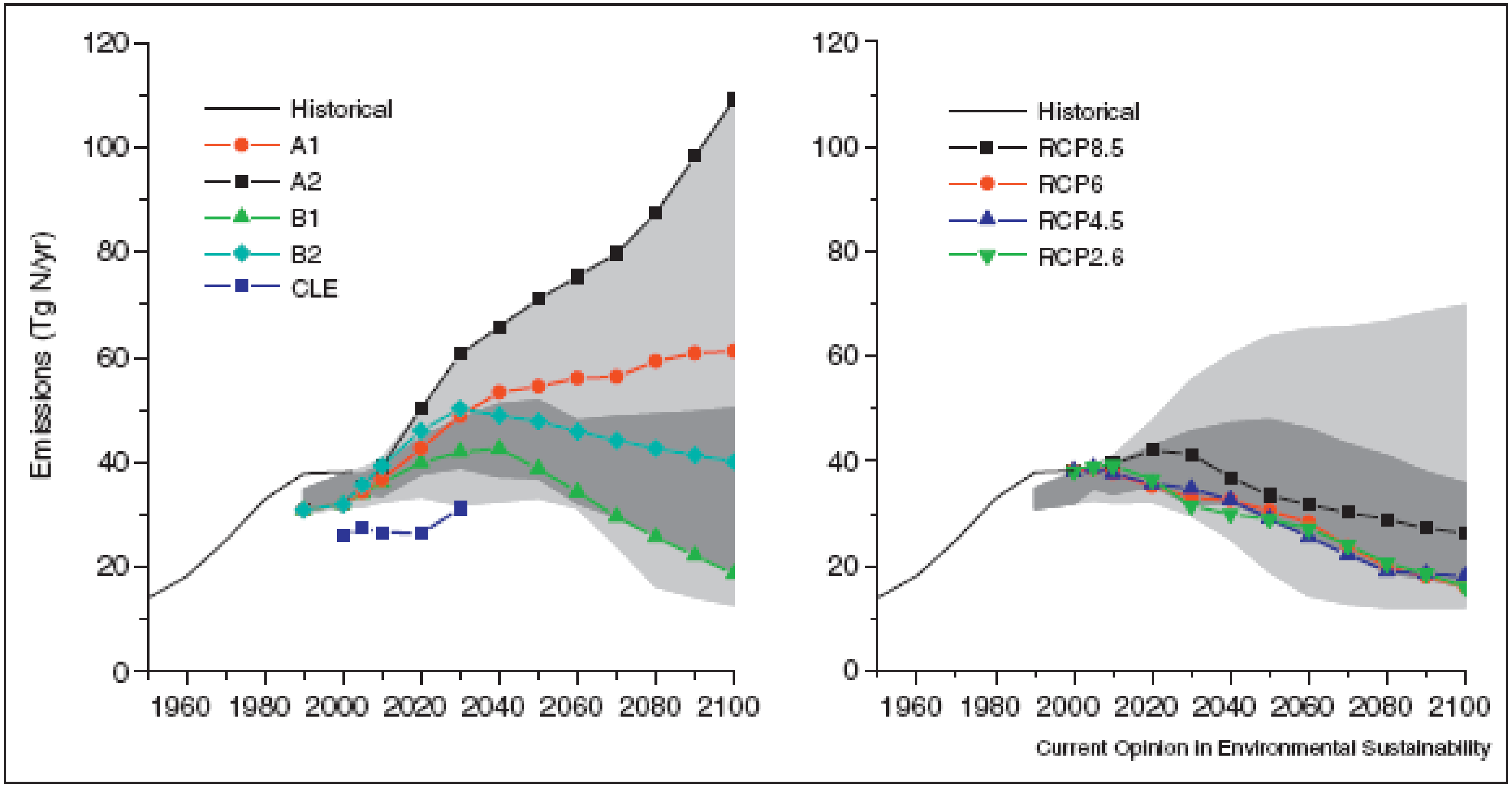
NO_x EMISSIONS (VAN VUUREN et al 2011)



Future NO_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].

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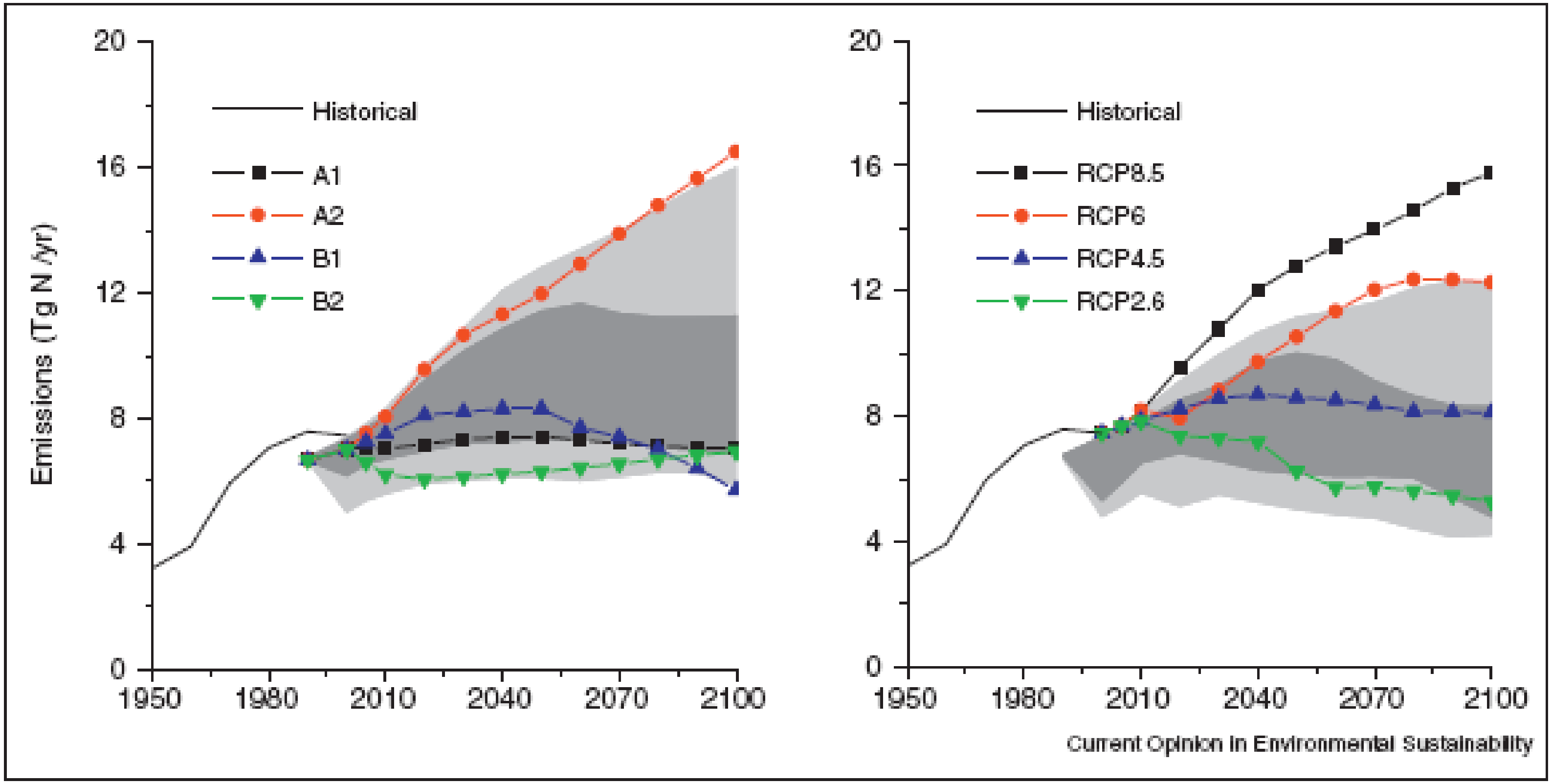
N_2O EMISSIONS 1950-2100 (VAN VUUREN et al 2011)



Future N_2O 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).

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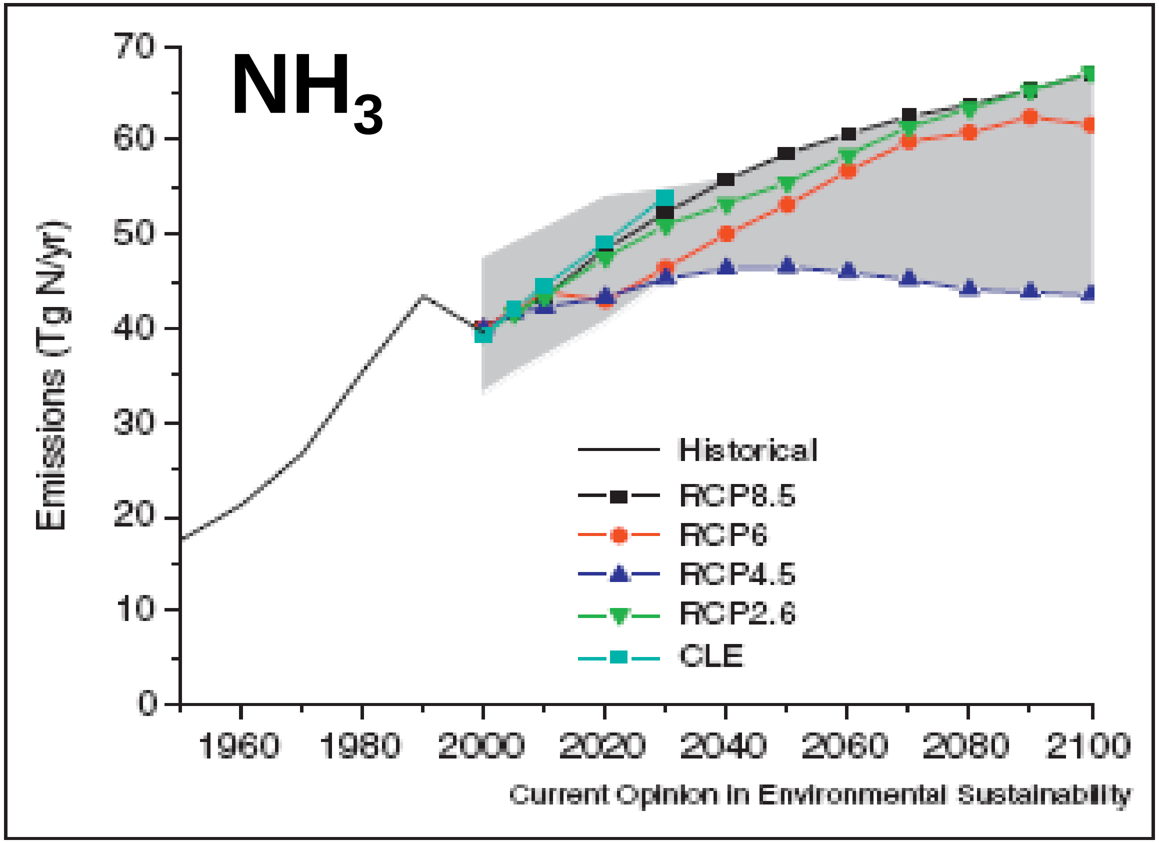
VAN VUUREN et al 2011



Future NH_3 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]).

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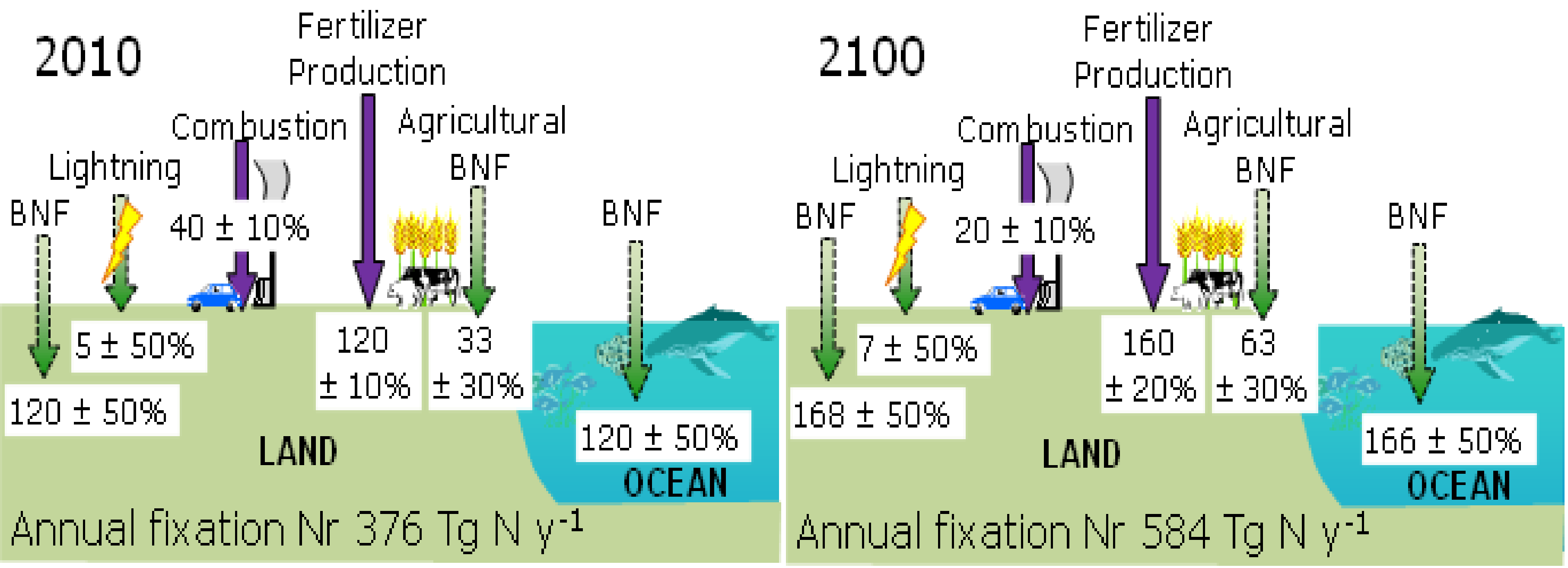
Change in annual fixation

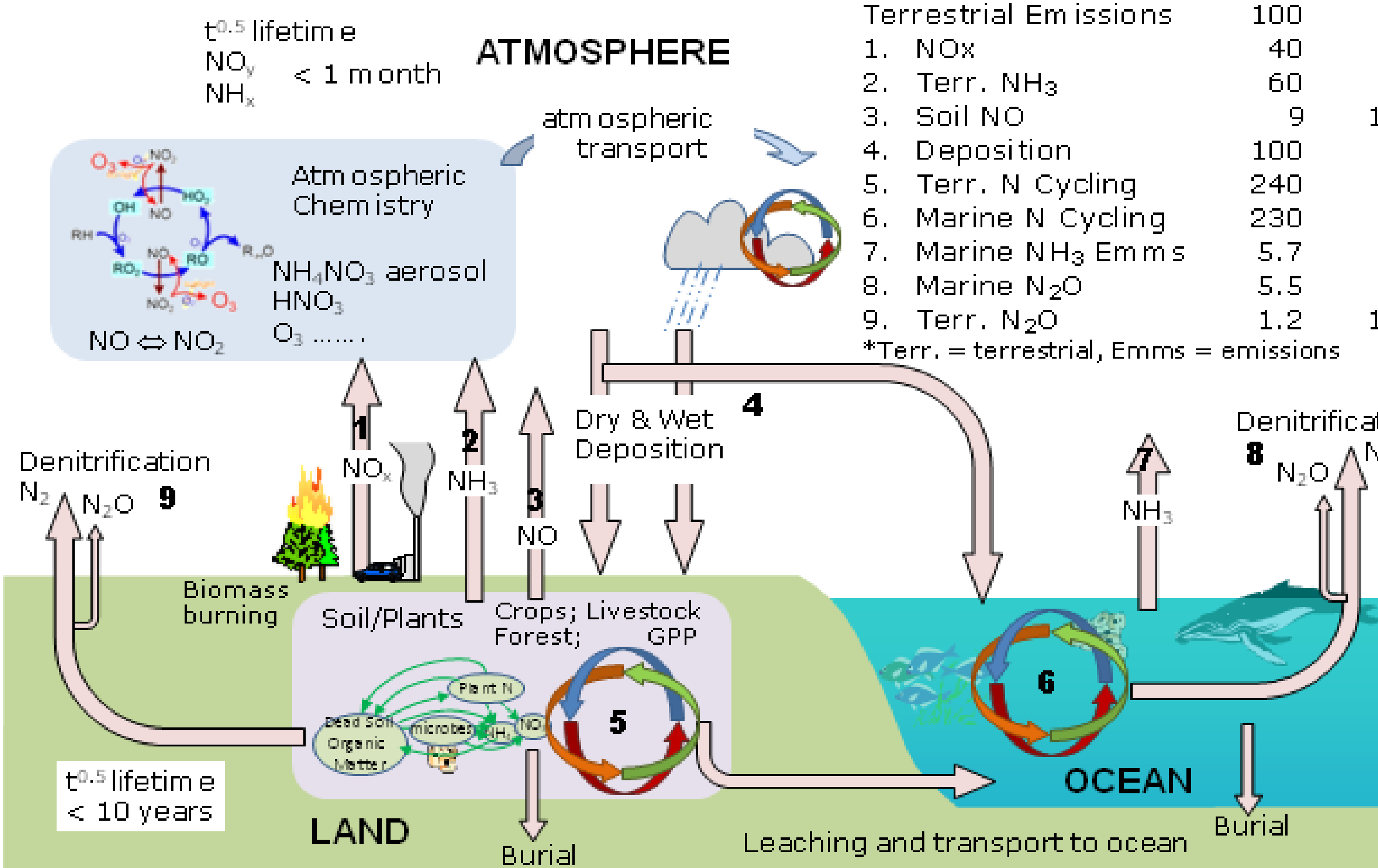


BNF – Biological Nitrogen Fixation

Changes in Land & Ocean Fluxes (Tg-N y^{-1})

	2010	2100
Terrestrial Emissions	100	165
1. NOx	40	30
2. Terr. NH_3	60	135
3. Soil NO	9	11.5
4. Deposition	100	120
5. Terr. N Cycling	240	328
6. Marine N Cycling	230	290
7. Marine NH_3 Emms	5.7	1.7
8. Marine N_2O	5.5	8
9. Terr. N_2O	1.2	14.4

*Terr. = terrestrial, Emms = emissions



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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)

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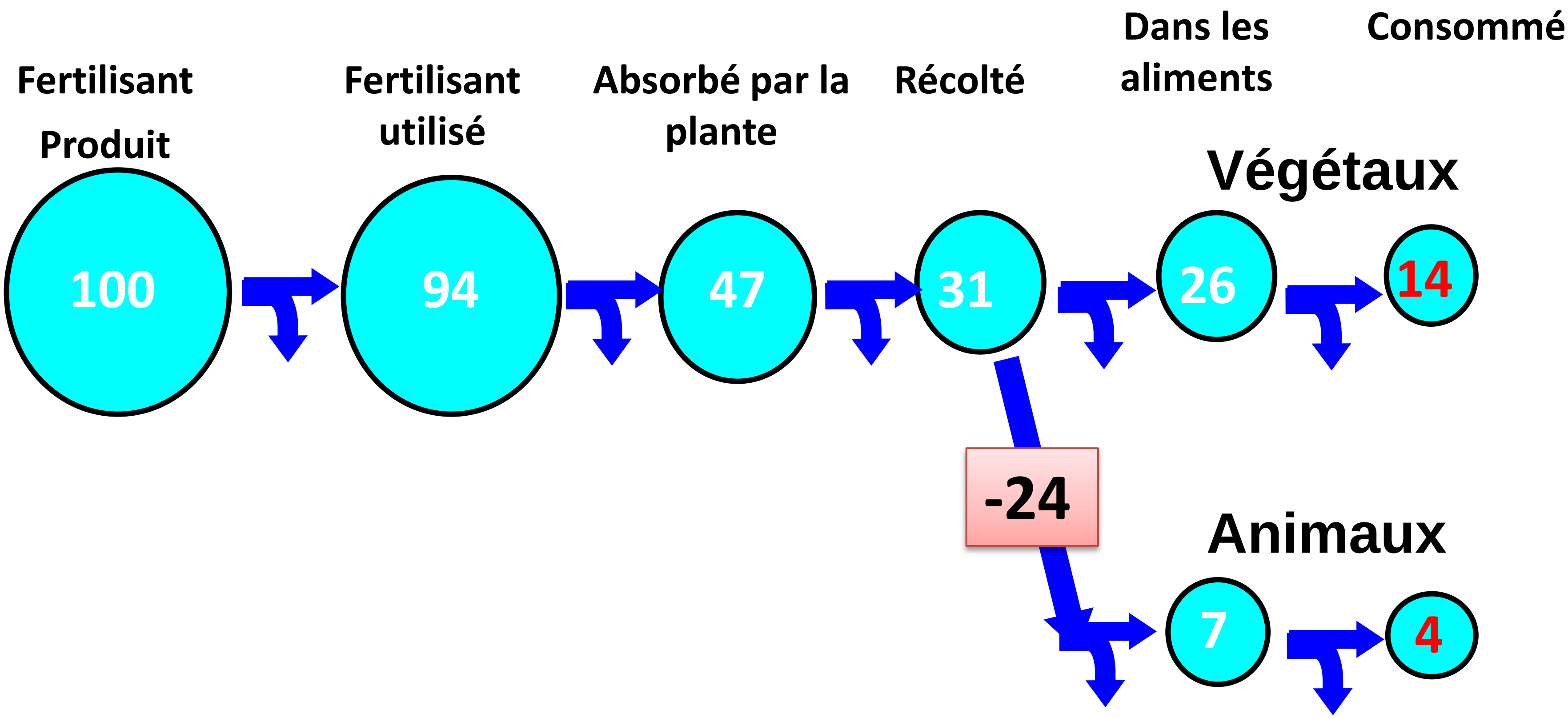
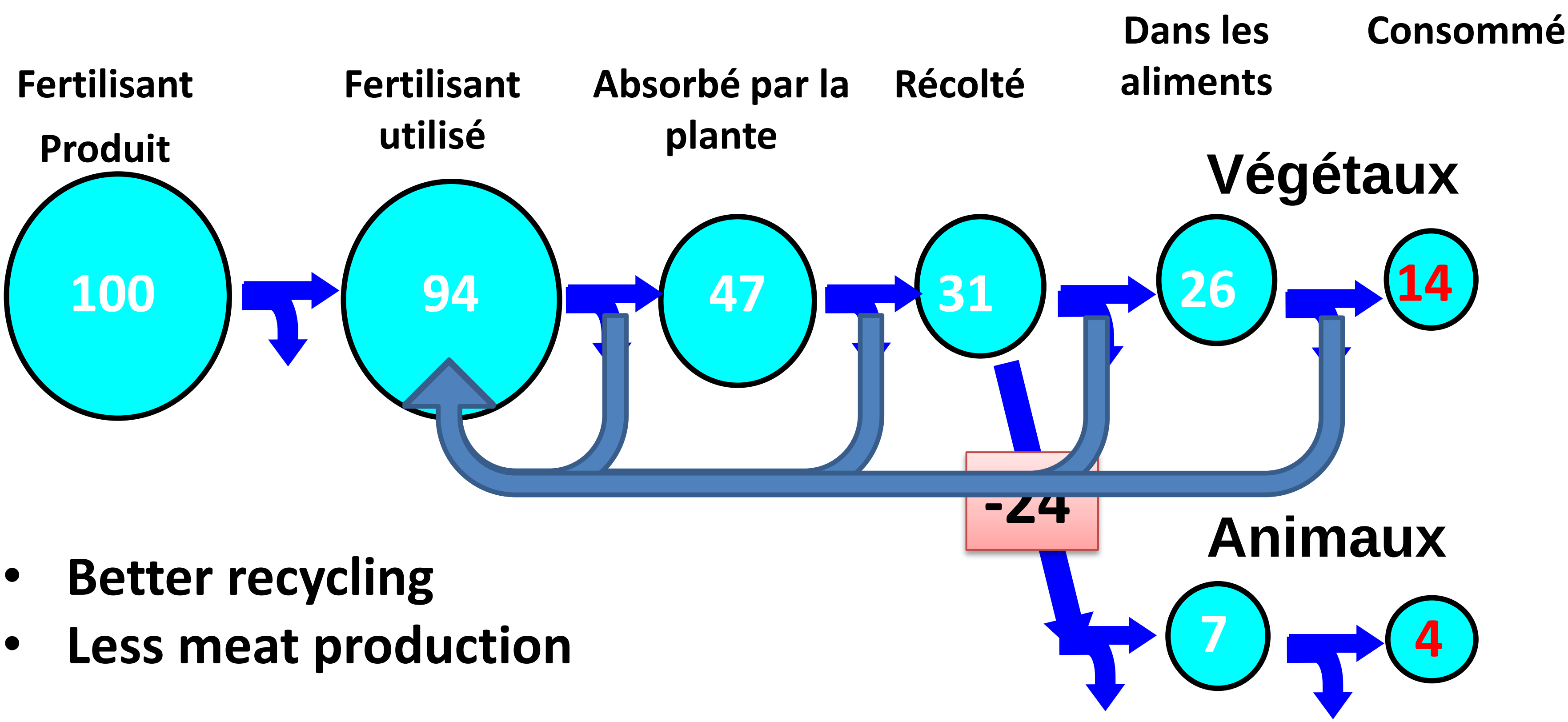
BETTER USE NITROGEN



Galloway JN and Cowling EB. 2002

BETTER USE NITROGEN



- **Better recycling**
- **Less meat production**

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Galloway JN and Cowling EB. 2002

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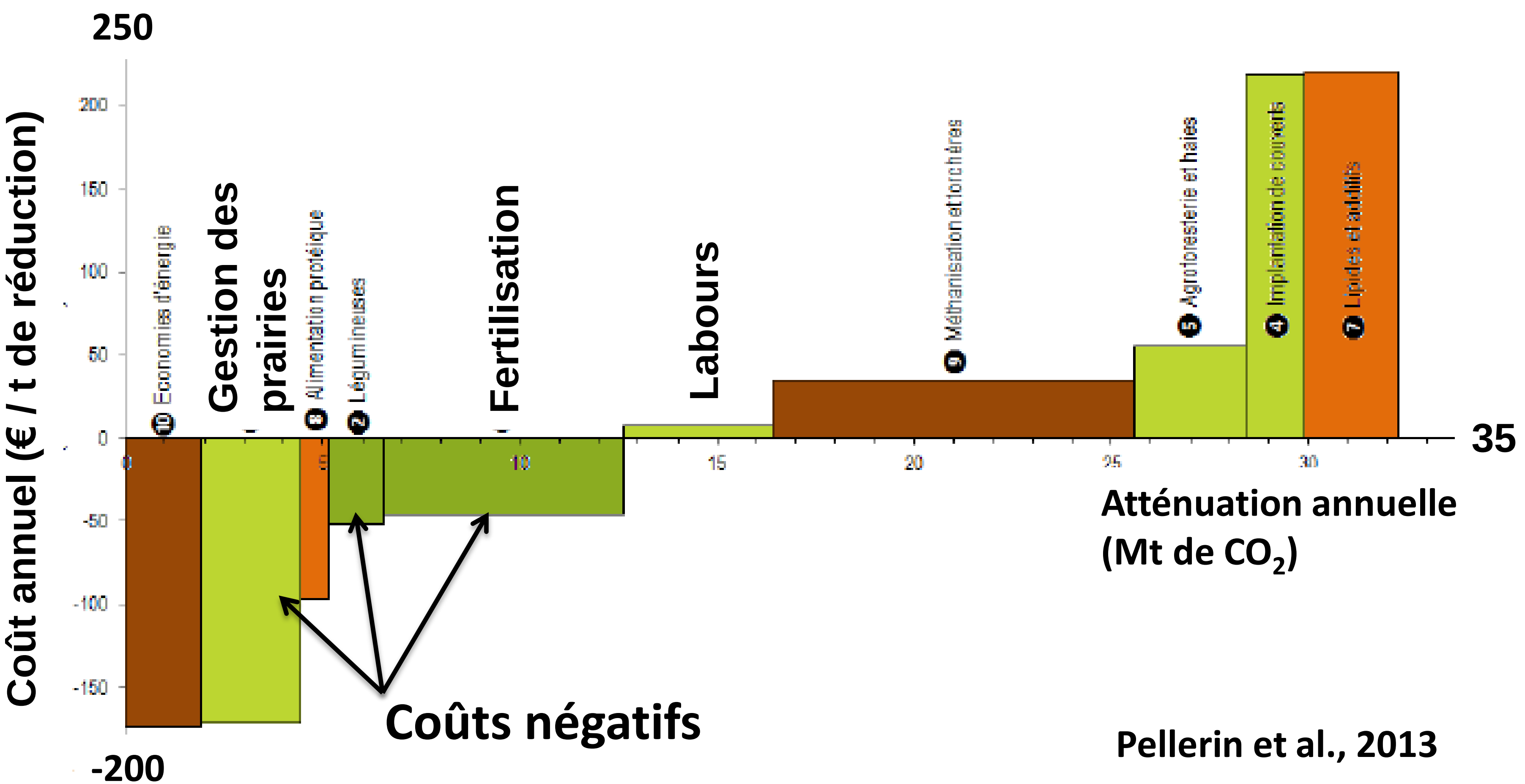
AT WHICH COSTS



Pellerin et al., 2013

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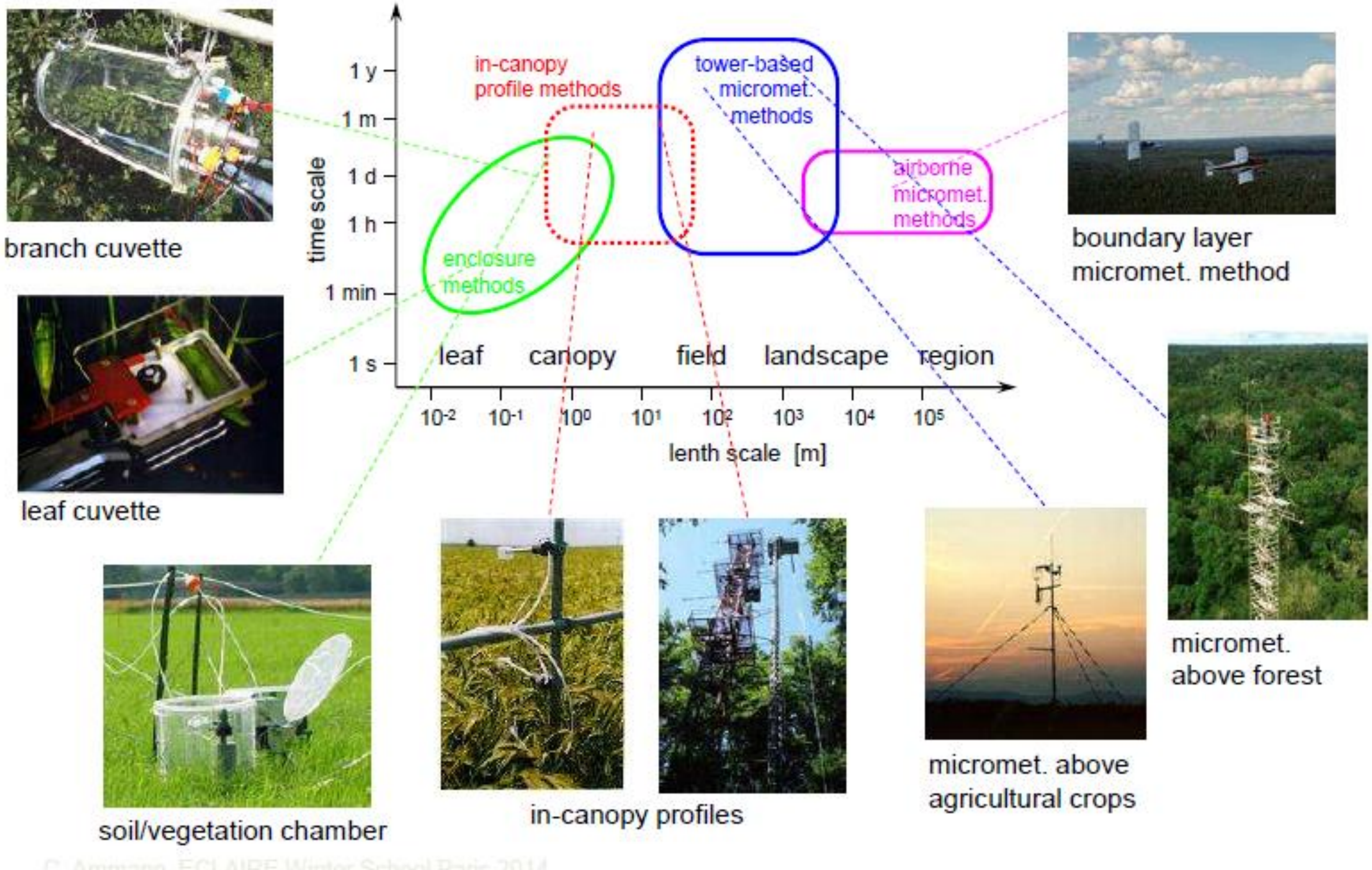
HOW TO MEASURE THE CHANGE

Time Scales and Spatial Scales



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Ammann, 2014

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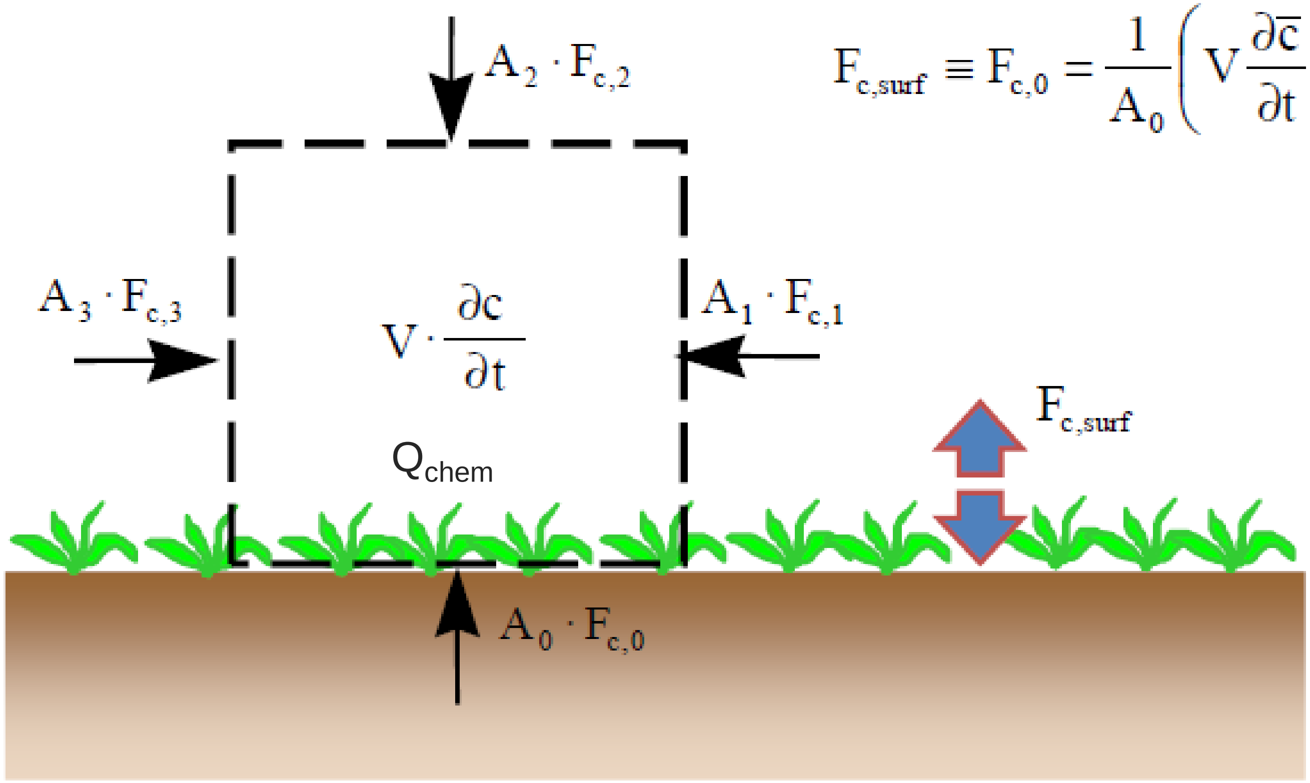
Measurements in the gaseous phase (atmosphere)

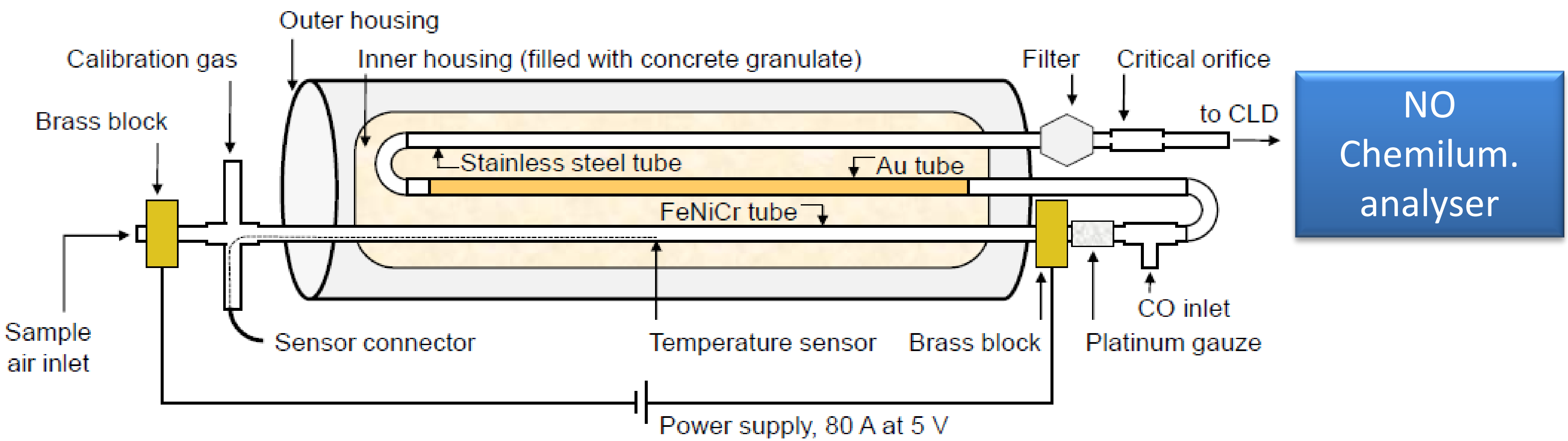
- general principle: mass balance for a (virtual) air volume: $V\frac{\partial \bar{c}}{\partial t} = \sum_{i=0}^{m} A_i \cdot F_{c,i} + Q_{chem}$

$$F_{c,surf} \equiv F_{c,0} = \frac{1}{A_0}\left(V\frac{\partial \bar{c}}{\partial t} - \sum_{i=1}^{m} A_i \cdot F_{c,i}\right) - Q_{chem}$$



Ammann, 2014

Total Nitrogen flux with converter and chemiluminescence



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

$$NH_4NO_3 \xrightarrow{\Delta T} NH_3 \uparrow + HNO_3 \uparrow$$

$$2\,HNO_3 \xrightarrow{\Delta T} 2\,NO_2 + H_2O + 1/2\,O_2$$

$$HONO \xrightarrow{\Delta T} NO + OH$$

$$4\,NH_3 + 5\,O_2 \xrightarrow{\Delta T, Pt} 4\,NO + 6\,H_2O$$

$$NO_2 + CO \xrightarrow{\Delta T, cat} NO + CO_2$$

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Marx et al. 2012

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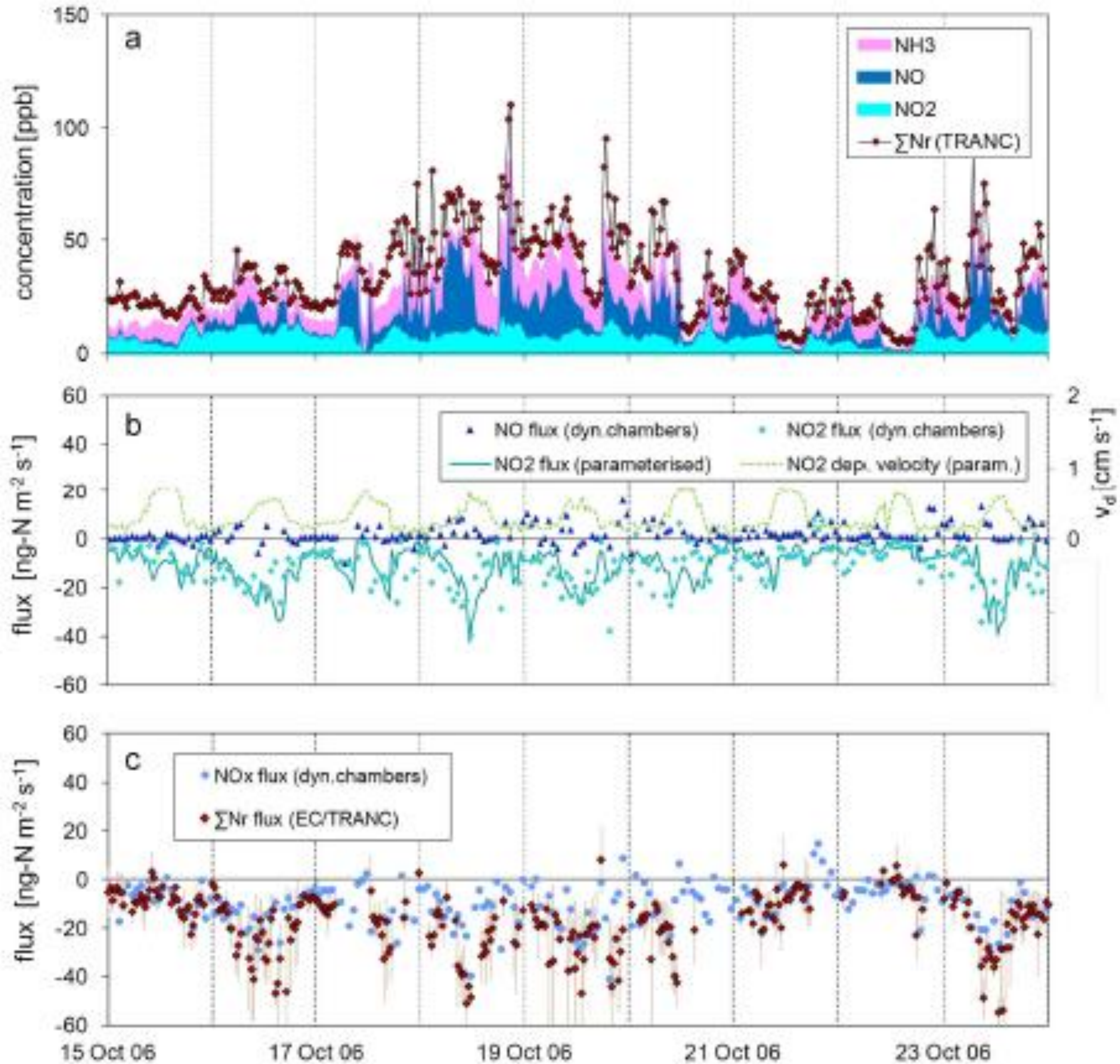
Total Nitrogen flux



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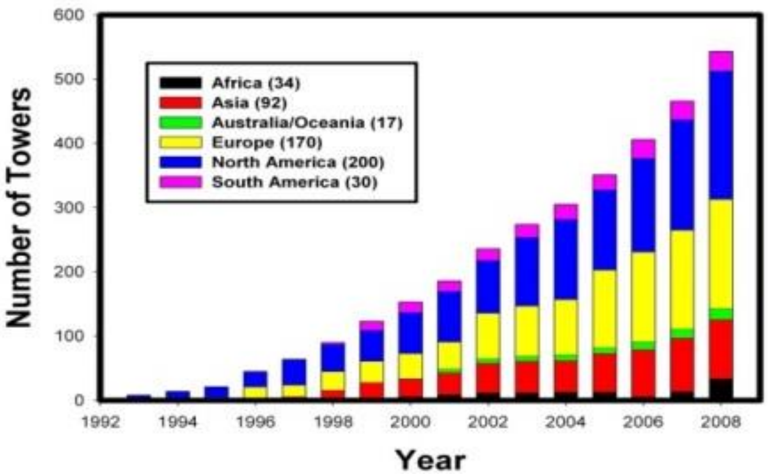
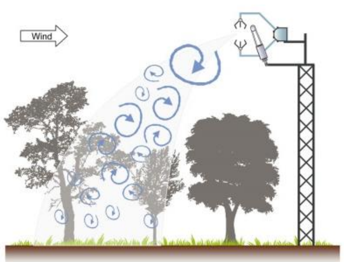
Worldwide sites for CO_2 -> to measure nitrogen !!

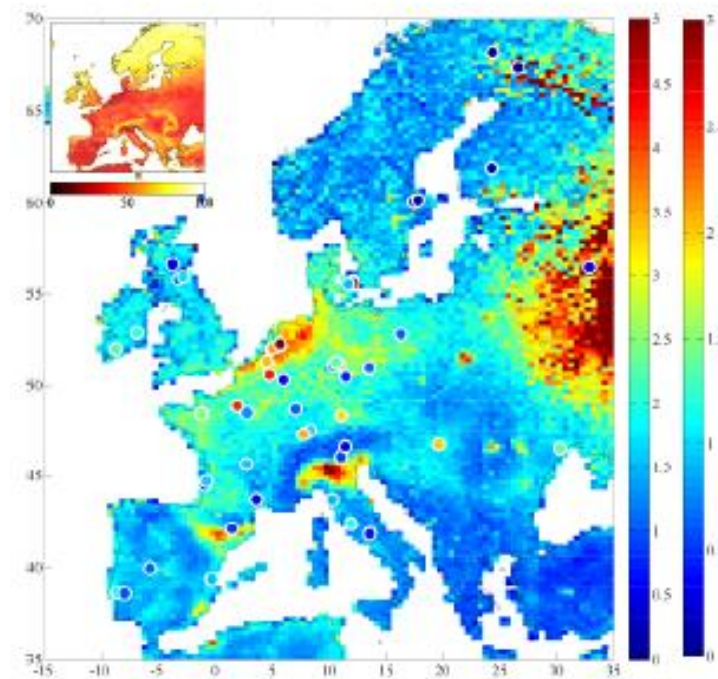
ICOS sites





TCON
GOSAT
OCO2
IASI

NH_3
(µg m-3)



Van Damme et al., A. Meas. Tech, 201

COMBLER LE FOSSÉ ENTRE OBSERVATIONS SATELLITE ET RÉSEAUX DE MESURE AU SOL

(FP7-ECLAIRE)

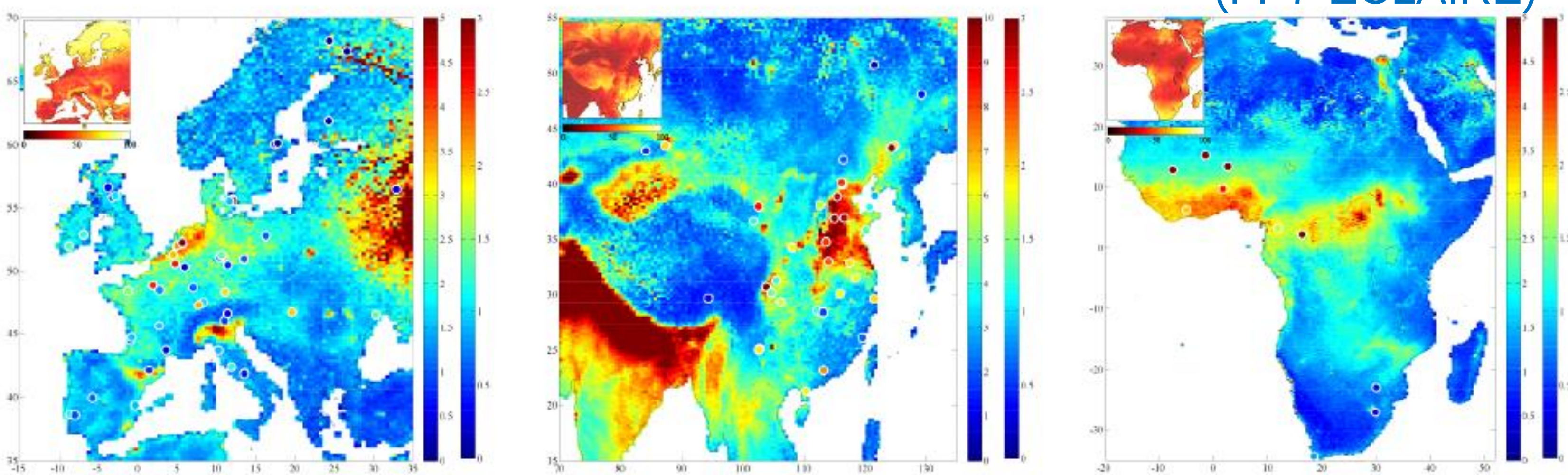


Figure 3. Top: ground-based quantities (left vertical color bar) from NEU ($\mu g\, m^{-3}$, left panel), NNDMN ($\mu g\, m^{-3}$, middle panel) and IDAF (ppbv, right panel) data sets plotted on top of the NH_3 satellite columns ($\times 10^{16}$ molec cm^{-2}, right vertical color bar) distribution gridded at 0.25° lat × 0.5° long, both averaged for the period covered by the data sets. Stations with less than two-thirds of measurement availability for

Towards validation of ammonia (NH_3) measurements from the IASI satellite

M. Van Damme[1,2], L. Clarisse[1], E. Dammers[2], X. Liu[3], J. B. Nowak[4,5,*], C. Clerbaux[1,6], C. R. Flechard[7], C. Galy-Lacaux[8], W. Xu[3], J. A. Neuman[4,5], Y. S. Tang[9], M. A. Sutton[9], J. W. Erisman[2,10], and P. F. Coheur[1]

Atmos. Meas. Tech., 8, 1575–1591, 2015
www.atmos-meas-tech.net/8/1575/2015/
doi:10.5194/amt-8-1575-2015

- Représentativité spatiale des mesures au sol pour le pixel satellite
- Profil vertical NH_3 dans la troposphère

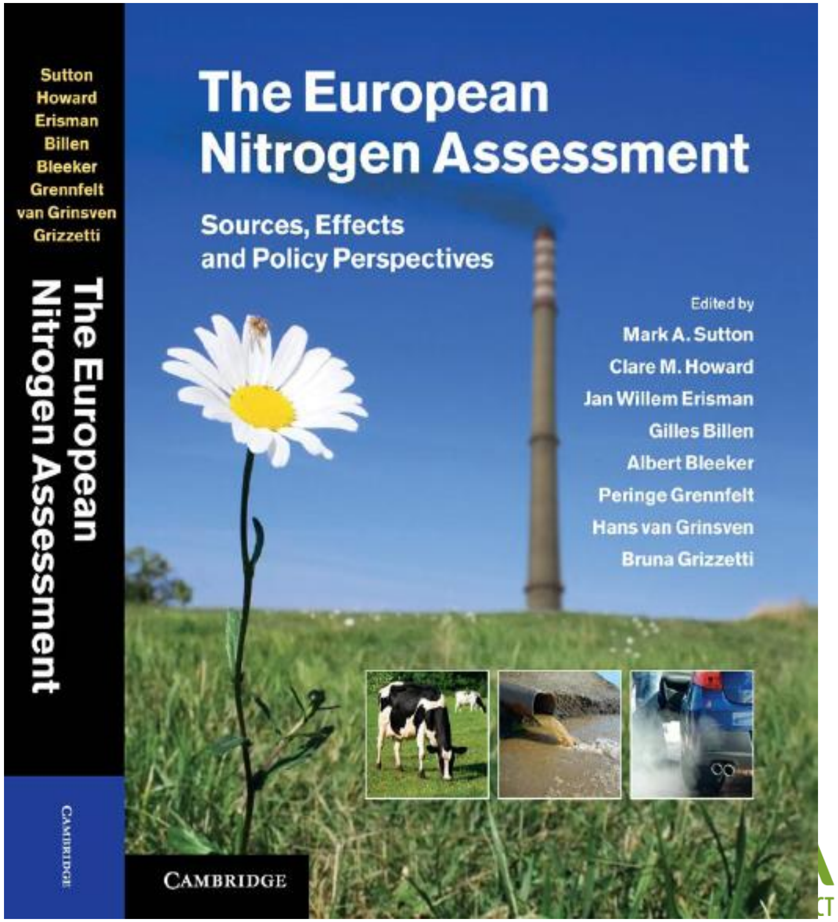
=> Assimilation dans les modèles de chimie de l'atmosphère

To read

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

(aller dans l'onglet Productions / Cours)

Google :
Loubet INRA ECOSYS



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TRAINING OR WORKING AT INRA

- CO_2, O_3, NH_3 and VOC flux measurements
- Modelling the ecosystem and its exchange with atmosphere
- Carbon an nitrogen cycling
- Atmospheric pollution

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

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To read

- **Effects of global change during the 21st century on the nitrogen cycle**
-
- David Fowler[1] , Claudia E Steadman[1,2] , David Stevenson2 , Mhairi Coyle[1] , Robert M Rees[3] , Ute M. Skiba[1] , Mark A. Sutton[1] J. Neil Cape[1] , Tony Dore[1] , Massimo Vieno[1,2] , David Simpson[4] , Sönke Zaehle[5] , Benjamin Stocker[6] , Matteo Rinaldi[7] , Christina Facchini[7] , CR Flechard[8] , Eiko Nemitz[1] , Marsailidh Twigg[1] , Jan Willem Erisman[9] and Jim Galloway
- Atmospheric Chemistry and Physics Discussion 2014

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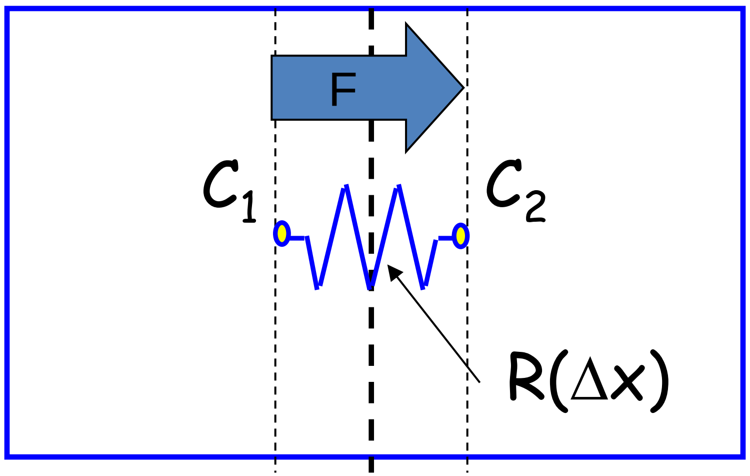
LE CONCEPT DE RÉSISTANCE DE TRANSFERT

Définition de la résistance au transfert diffusif

Hypothèse de flux constant



$R(\Delta x) = \Delta x / D$

Fick $$F_c = -K_c \frac{dC}{dZ}$$

Ohm $$F_c = \frac{c1 - c2}{r_a} = h_c (c1 - c2)$$

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

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Quelle hypothèse est nécessaire pour passer de Fick à Ohm?

LE CONCEPT DE RÉSISTANCE DE TRANSFERT

Définition de la résistance au transfert diffusif

$$F_c = \mathrm{cte}$$

$$F_c \cdot \int_{z1}^{z2} \frac{dz}{K_c} = -\int_{c1}^{c2} dc = c_1 - c_2$$

$$\mathrm{r_a} = \frac{1}{\mathrm{h_c}} = \int_{z1}^{z2} \frac{\mathrm{dz}}{\mathrm{K_c}}$$

$$F_c = \frac{c1 - c2}{r_a} = h_c(c1 - c2)$$