



Instituto Venezolano de Investigaciones Científicas



Atmospheric Nitrogen deposition

Tibisay Pérez

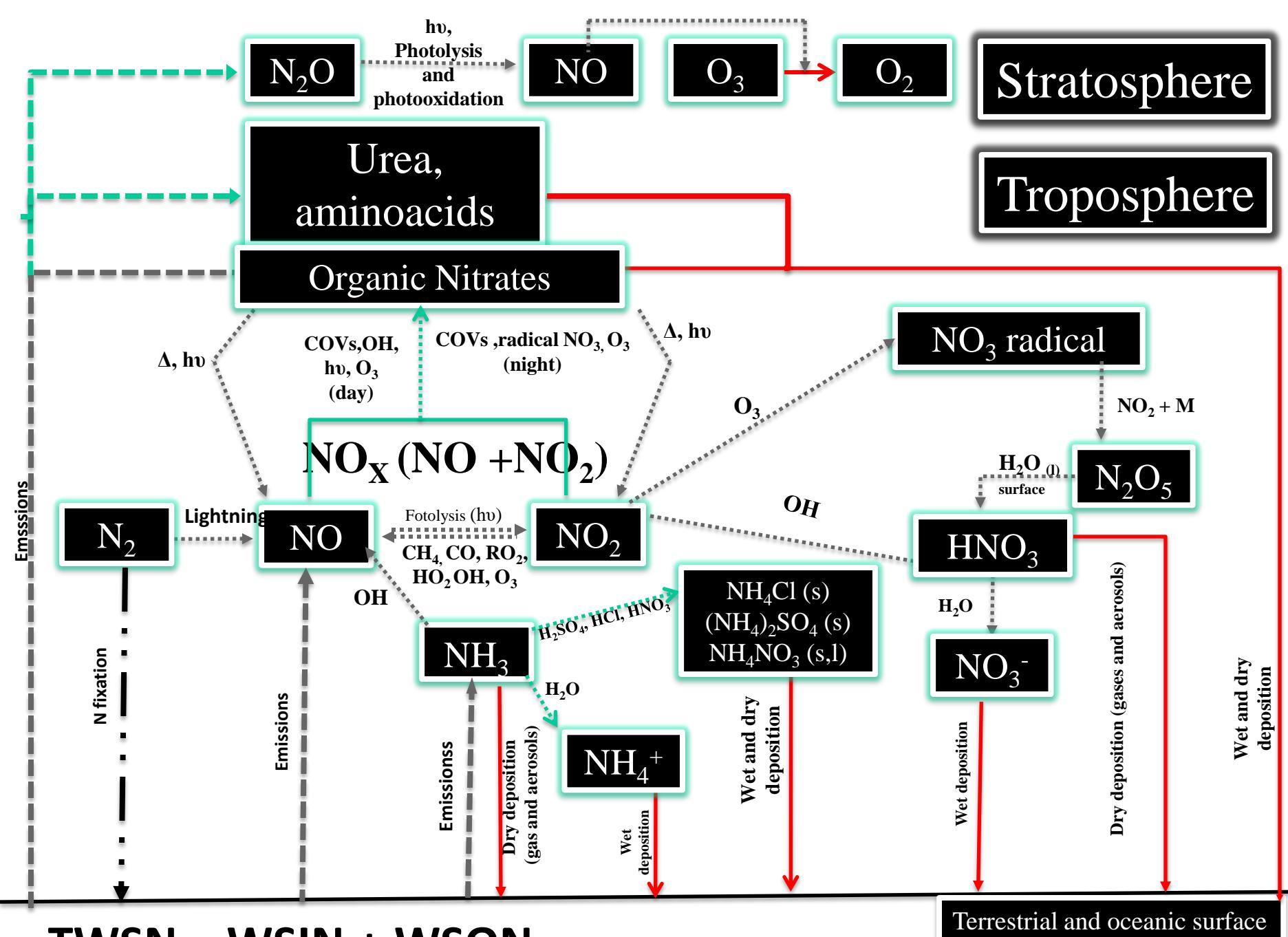
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August 6th, 2016.



School of Advanced Science on nitrogen cycling, environmental sustainability and climate change. 31 July – 10 August 2016, São Pedro, SP – Brazil.



$$\text{TWSN} = \text{WSIN} + \text{WSON}$$

Terrestrial and oceanic surface

(Slide borrowed from Rafael Rasse's PhD thesis defense, Atkinson, 2000; Finlayson-Pitts and Pitts, 2000; Atkinson and Arey, 2003; Seinfeld and Pandis, 2006)

Why N₂O is so relevant after Montreal Protocol?

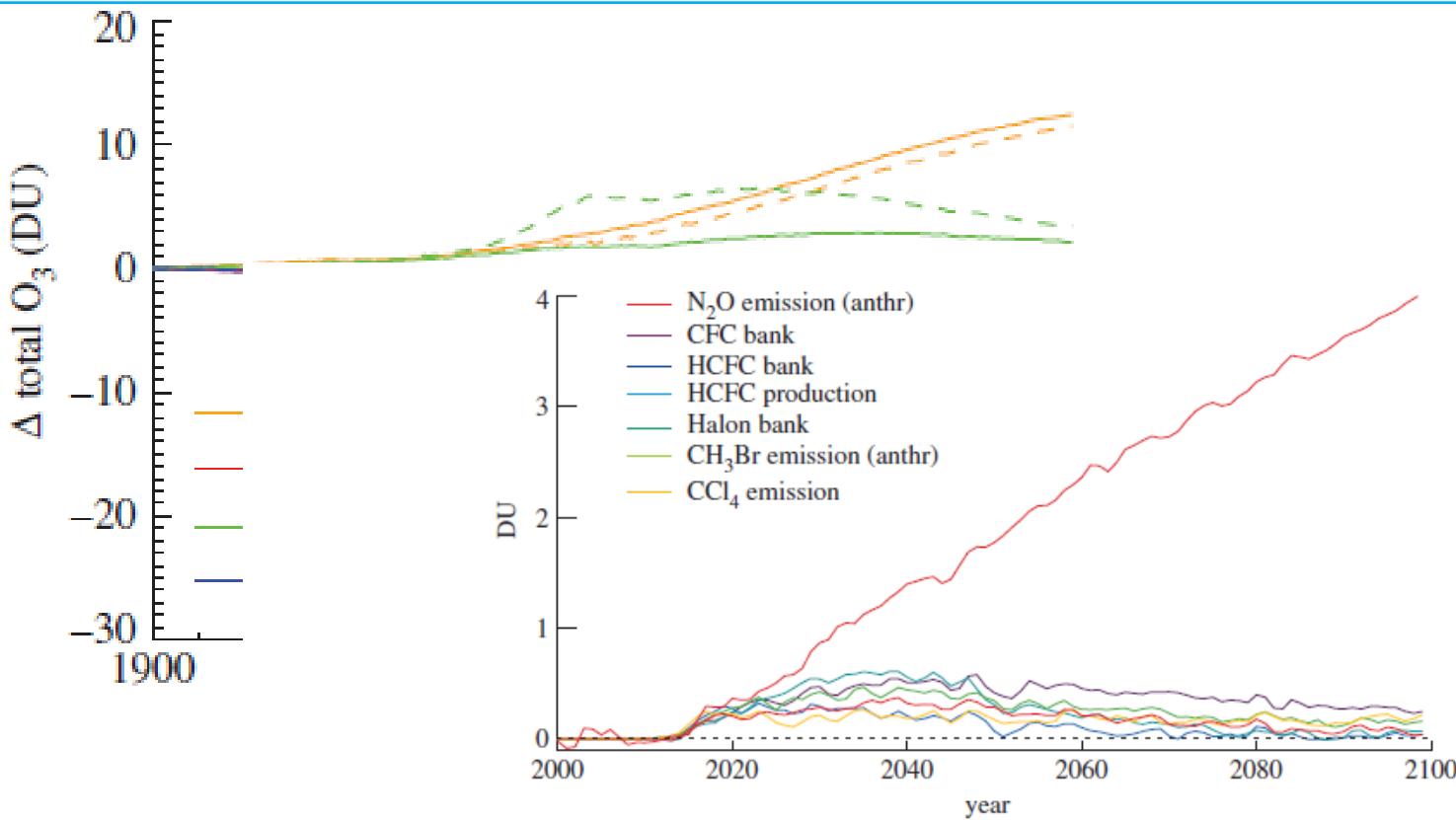
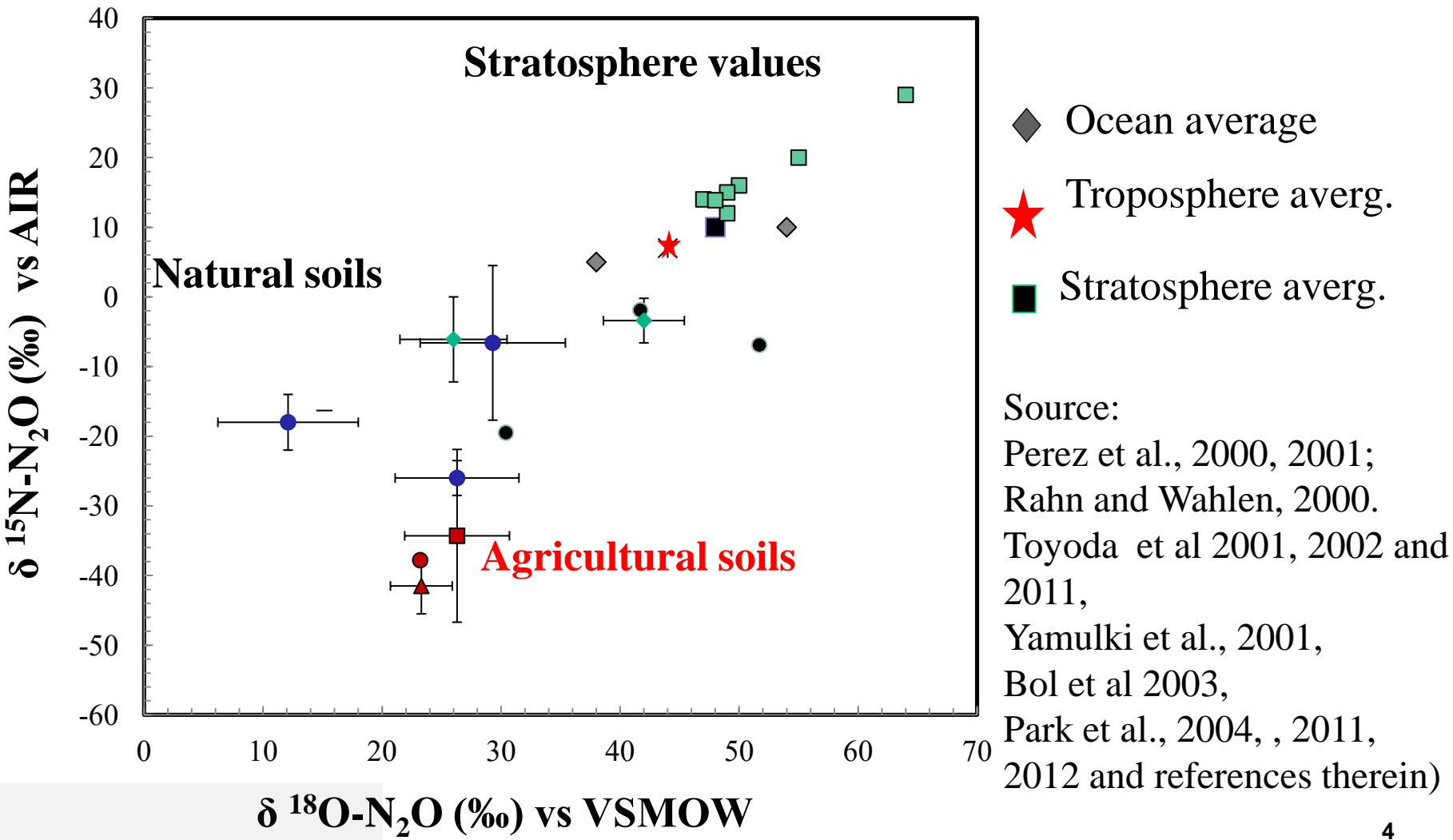


Figure 7. The changes in global mean ozone owing to elimination of anthropogenic N₂O emissions after 2010 when compared with the effect of eliminating the emissions of the CFC banks, HCFC production and banks, the halon banks, anthropogenic methyl bromide and carbon tetrachloride. The elimination of anthropogenic N₂O emission has the largest potential for reducing ozone depletion in the future. Adapted from fig. 4 of Daniel *et al.* [28].

Natural ecosystems emitted N₂O that is enriched in ¹⁵N compared to fertilized soils



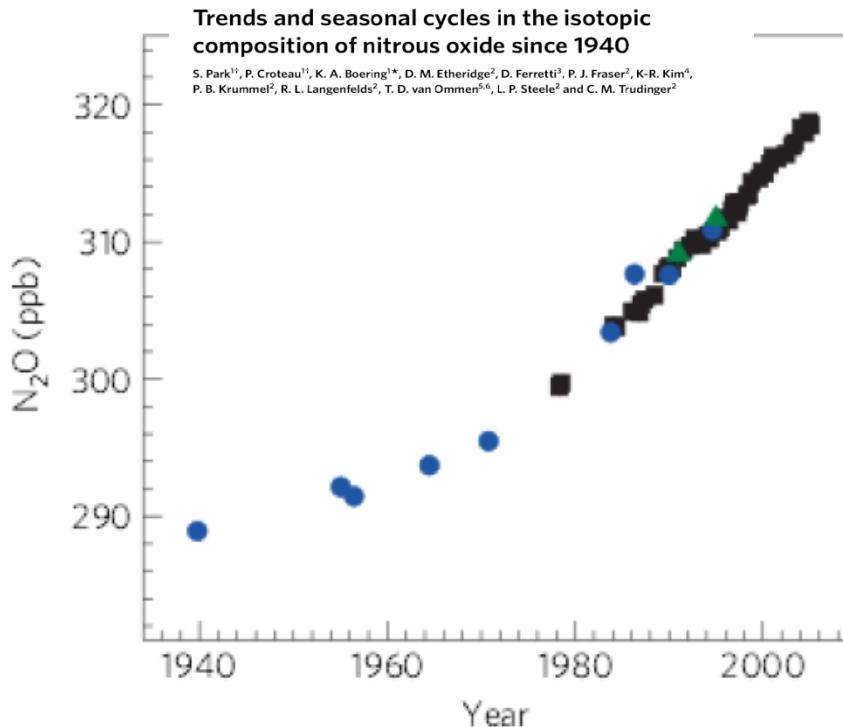
Tropospheric N₂O isotope trend inferred from archived air samples from Cape Grim

nature
geoscience

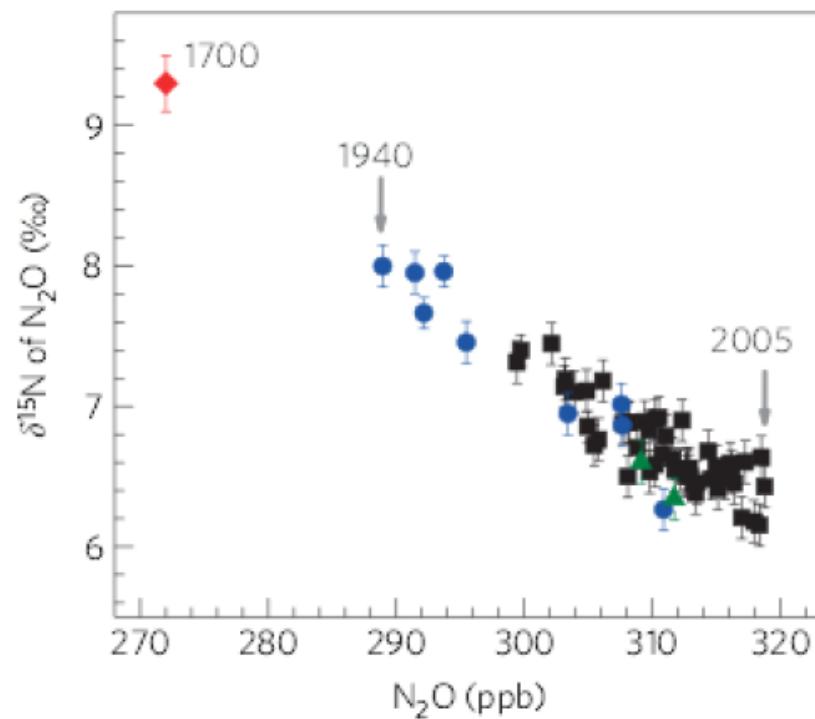
LETTERS

PUBLISHED ONLINE: 11 MARCH 2012 | DOI: 10.1038/NGEO1423

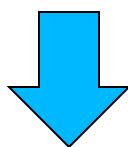
a



b



Decrease in δ¹⁵N
of 0.3 ‰/decade



Fertilizer use



Hot spots of N₂O found in permafrost peatlands

Peat Circles

Diameter 4 to 25 m
Areas 10 to 500 m²

**nature
geoscience** LETTERS
PUBLISHED ONLINE: 15 FEBRUARY 2009 DOI: 10.1038/ngeo2434

Cover $\sim 4\%$ the peat plateau

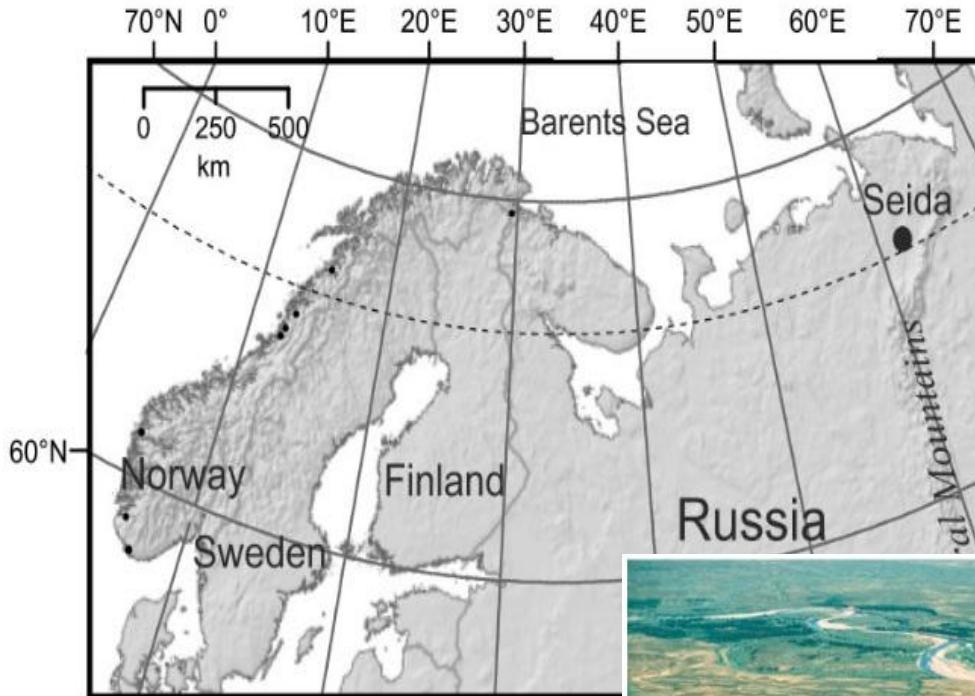
**Large N₂O emissions from Pyroturbation peatsoil 20% of Arctic and
in tundra**

Maija E. Repo¹, Sanna Susiluoto², Saara E. Lind¹, Simo Jokinen¹, Vladimir Elsakov³, Christina Biasi¹,
Tarmo Virtanen² and Pertti J. Martikainen^{1*}

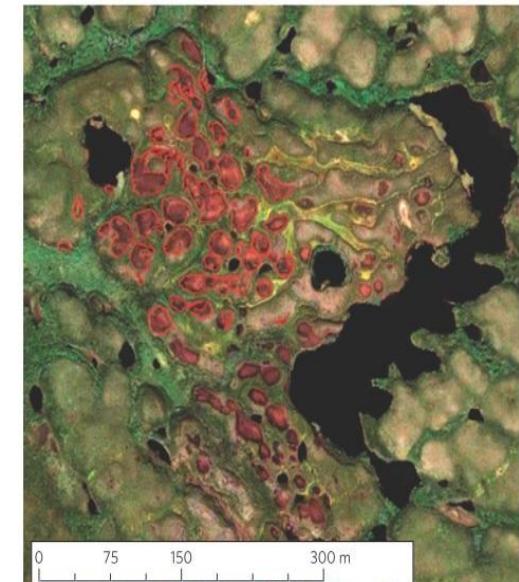


Would the enhanced emissions from tundra pit circles shift tropospheric N₂O isotopic composition?

Study Site



Discontinuous permafrost
Subarctic East European tundra
(62°57'E, 67°03'N)
Annual precip. ≈ 505 mm
Mean annual temp. ≈ -5.8 °C
Growing season: Mid Jun-August



Research Project DEFROST

Graduate student Jenie Gil



Impacts of a changing cryosphere-
Depicting ecosystem-climate feedbacks from permafrost, snow and ice

J. Gil¹, T. Perez, K. Boering, P.J. Martikainen, C.
Biasi

Academy of Finland, project CryoN 2010-2014
European Union 7th Framework Program under
project(DEFROST)-Nordic Centre of Excellence
Program

We wanted to know also which microbial/chemical processes contribute to the pit circle N_2O production

Bare peat soil profile



3 soil profile (PC1;PC2;PC3)

[N_2O]; [CO_2]
 $\delta^{15}\text{N}_2\text{O}$; $\delta^{18}\text{O}$; ^{15}N -SP
[NH_4^+]; [NO_3^-] and $\delta^{15}\text{N}$
Soil T; [O_2]; soil moisture

Bare peat soil surface (Static chamber)

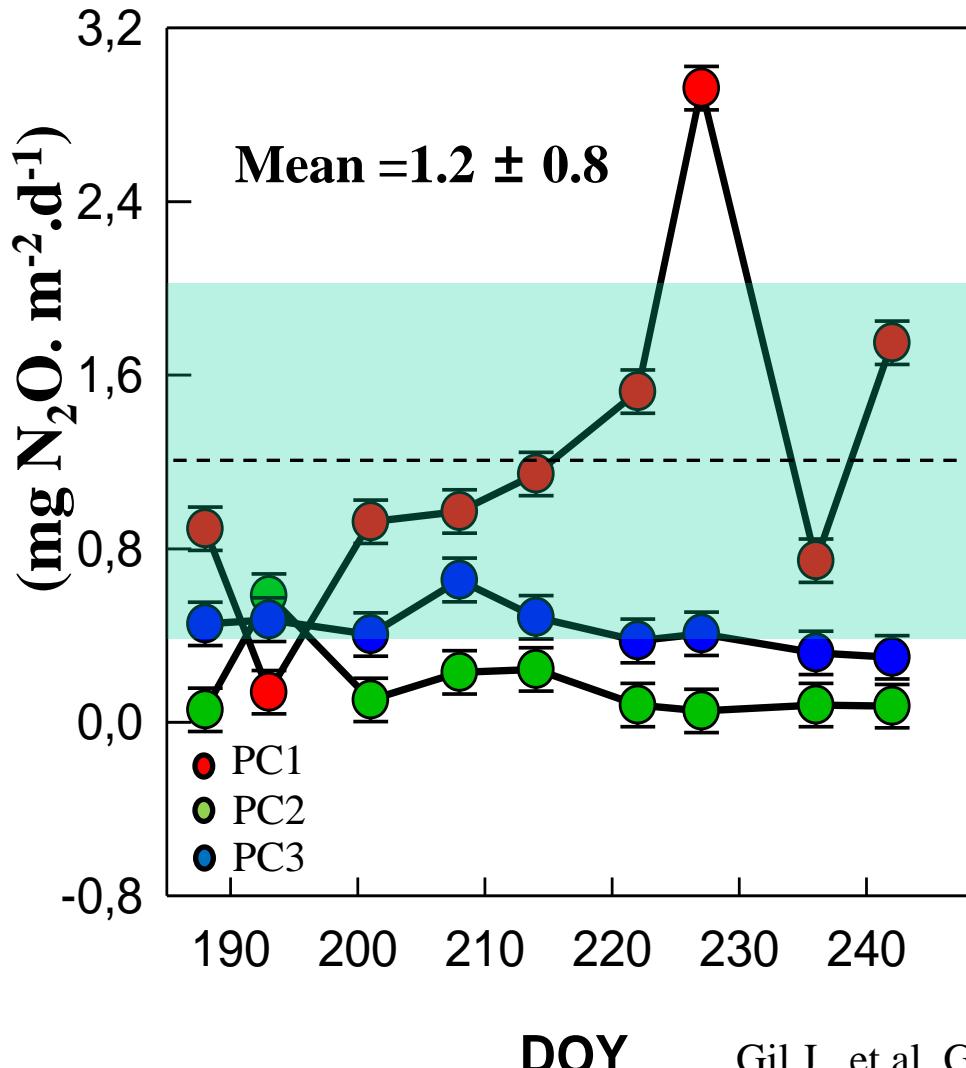


3 bare surface (PC1;PC2; PC3; 5 frames)

N_2O and CO_2 Fluxes
 $\delta^{15}\text{N}_2\text{O}$; $\delta^{18}\text{O}$; ^{15}N -SP
[NH_4^+]; [NO_3^-] and $\delta^{15}\text{N}$
Soil environmental parameters
Weather measurements

Bare peats surface in sub-arctic tundra emit substantial amounts of N_2O

0.1 to 3.4 mg $\text{N}_2\text{O} \text{ m}^{-2} \text{ d}^{-1}$



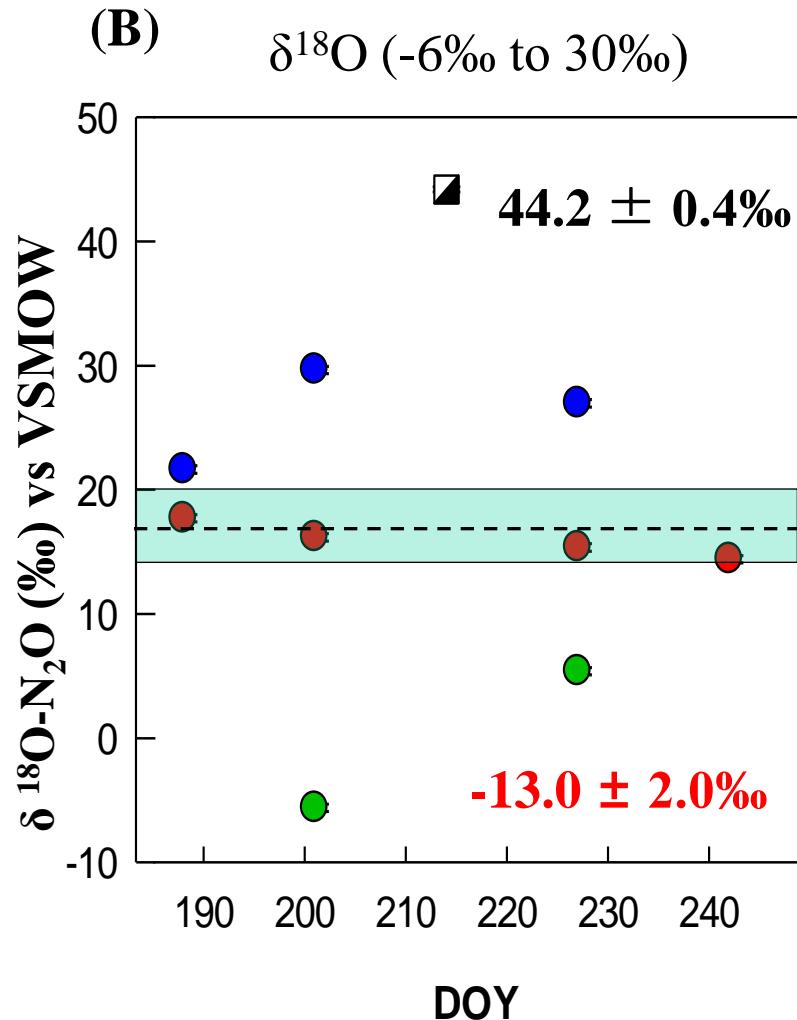
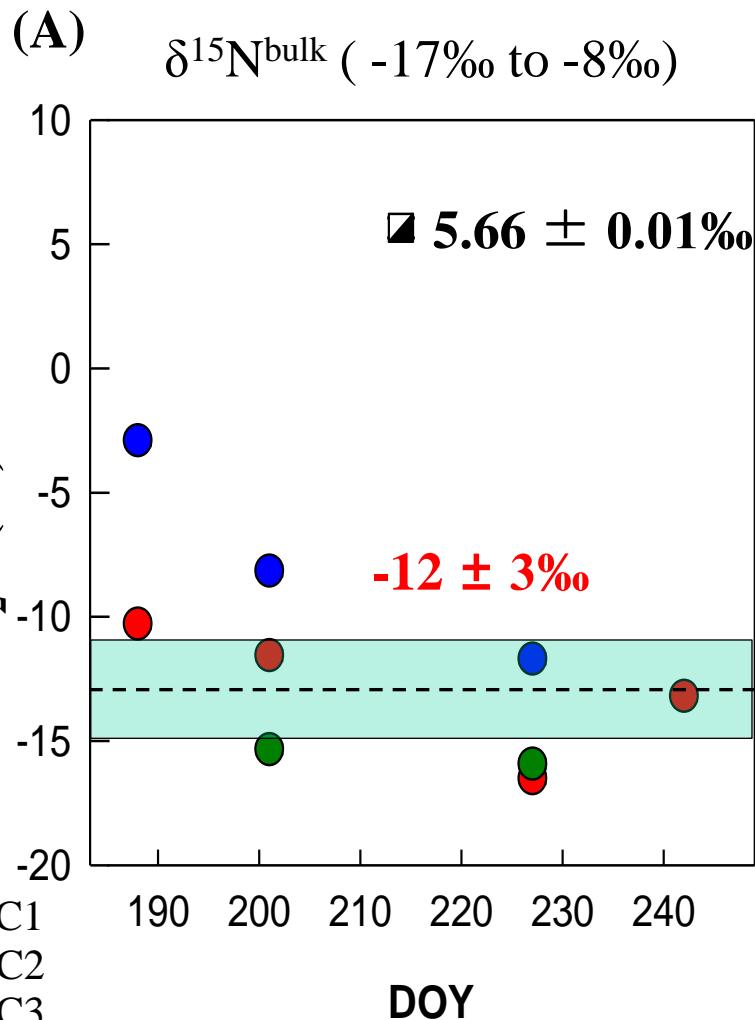
Tropical forests
 $(0.09 - 2.5 \text{ mg } \text{N}_2\text{O} \text{ m}^{-2} \cdot \text{d}^{-1})$

Drained boreal
 peatlands/agriculture
 $(0.1 - 15.1 \text{ mg } \text{N}_2\text{O. m}^{-2} \cdot \text{d}^{-1})$

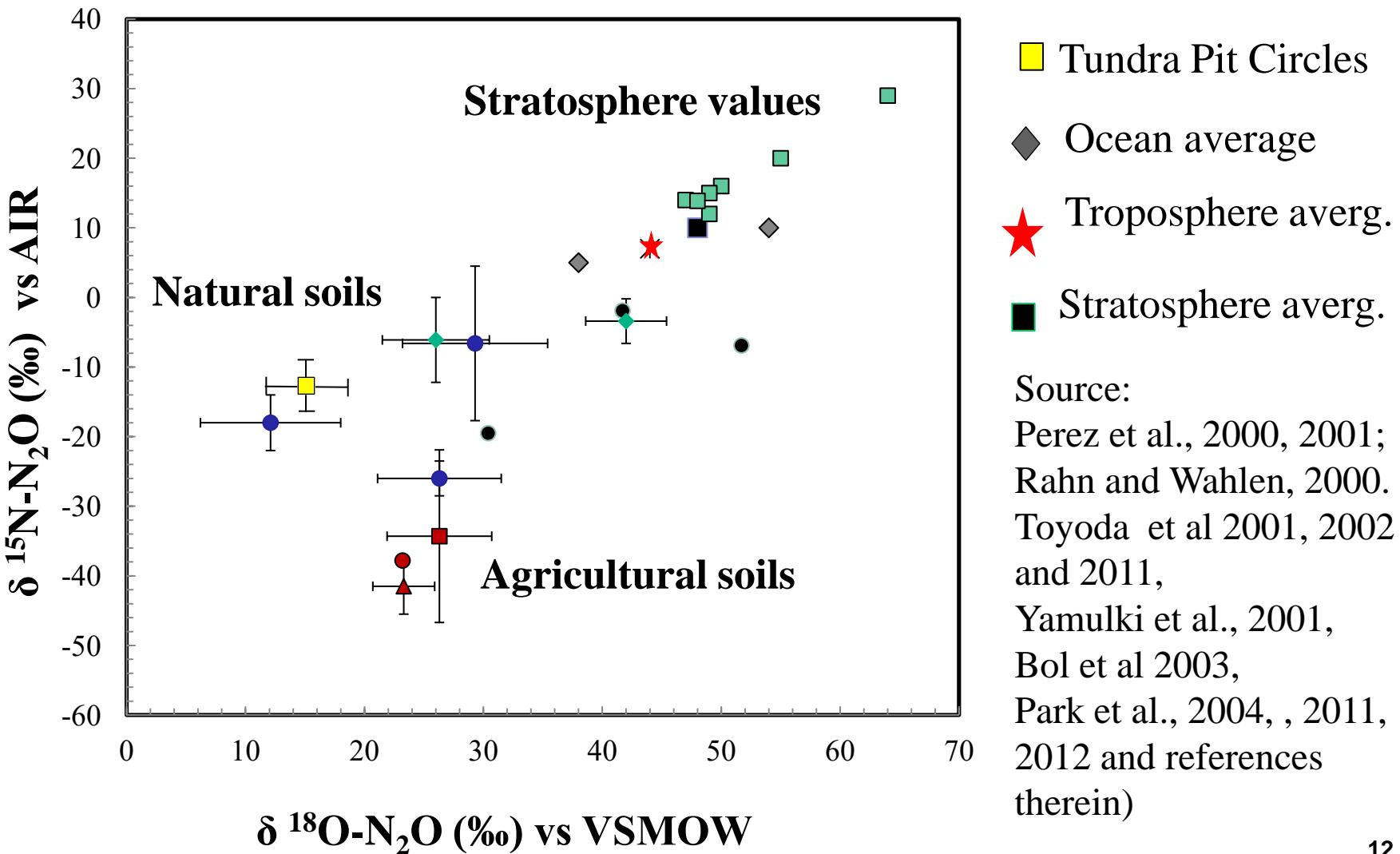
2007 ($1.9 - 31 \text{ mg } \text{N}_2\text{O. m}^{-2} \cdot \text{d}^{-1}$)

2008 ($3.7 - 13.9 \text{ mg } \text{N}_2\text{O. m}^{-2} \cdot \text{d}^{-1}$)

The first data for $\delta^{15}\text{N}^{\text{bulk}}$ of N_2O emitted from Arctic tundra so far...



Natural ecosystems emitted N₂O that is enriched in ¹⁵N compared to fertilized soils

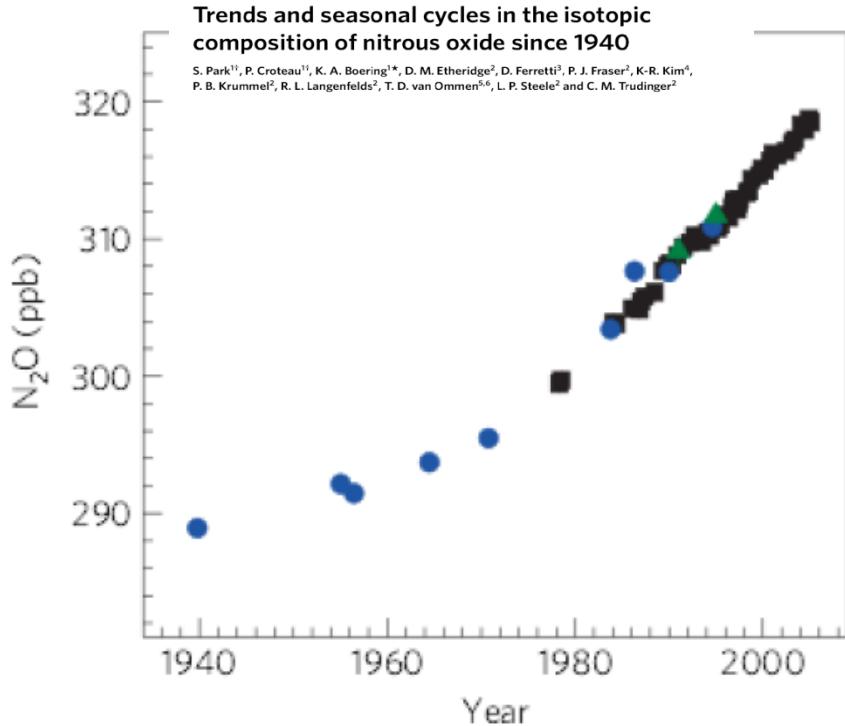
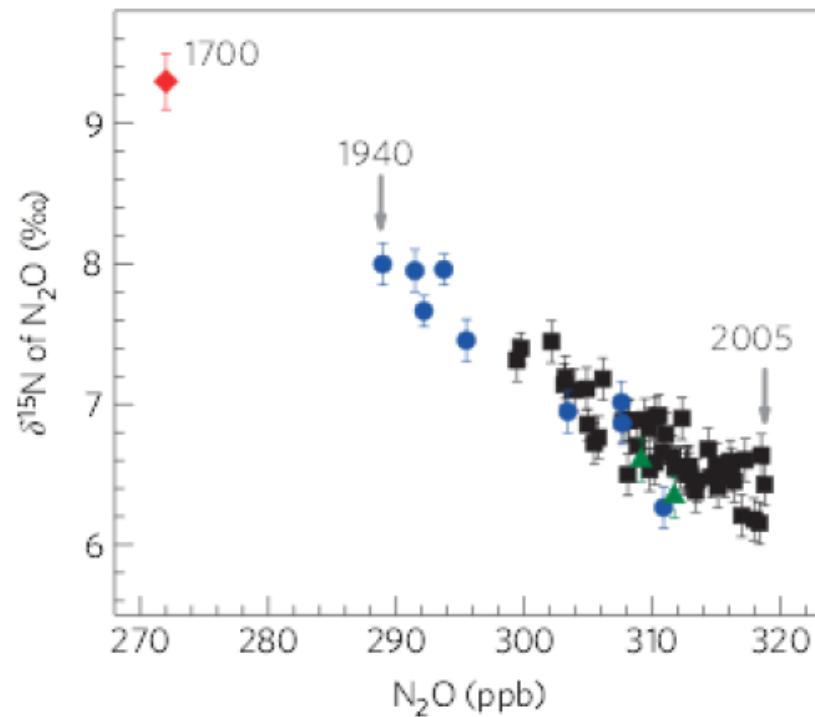


N_2O isotope trend might slow down due to global warming of artic tundra

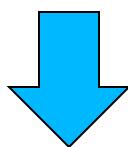
nature
geoscience

LETTERS

PUBLISHED ONLINE 11 MARCH 2012 | DOI: 10.1038/NGEO1423

a**b**

Decrease in $\delta^{15}\text{N}$
of 0.3 ‰/decade



Fertilizer use



Reactive Nitrogen (Nr) in the troposphere

Ecosystem relevant nitrogen species

Reactive nitrogen (Nr-trace levels)

Inorganic

NH_3
NH_4^+
$\text{NO}_x(\text{NO}+\text{NO}_2)$
HNO_3
N_2O
Radical NO_3

Organic

Urea
Aminoacids
Proteins
Nucleic acids
Organic nitrates
Plant derived part

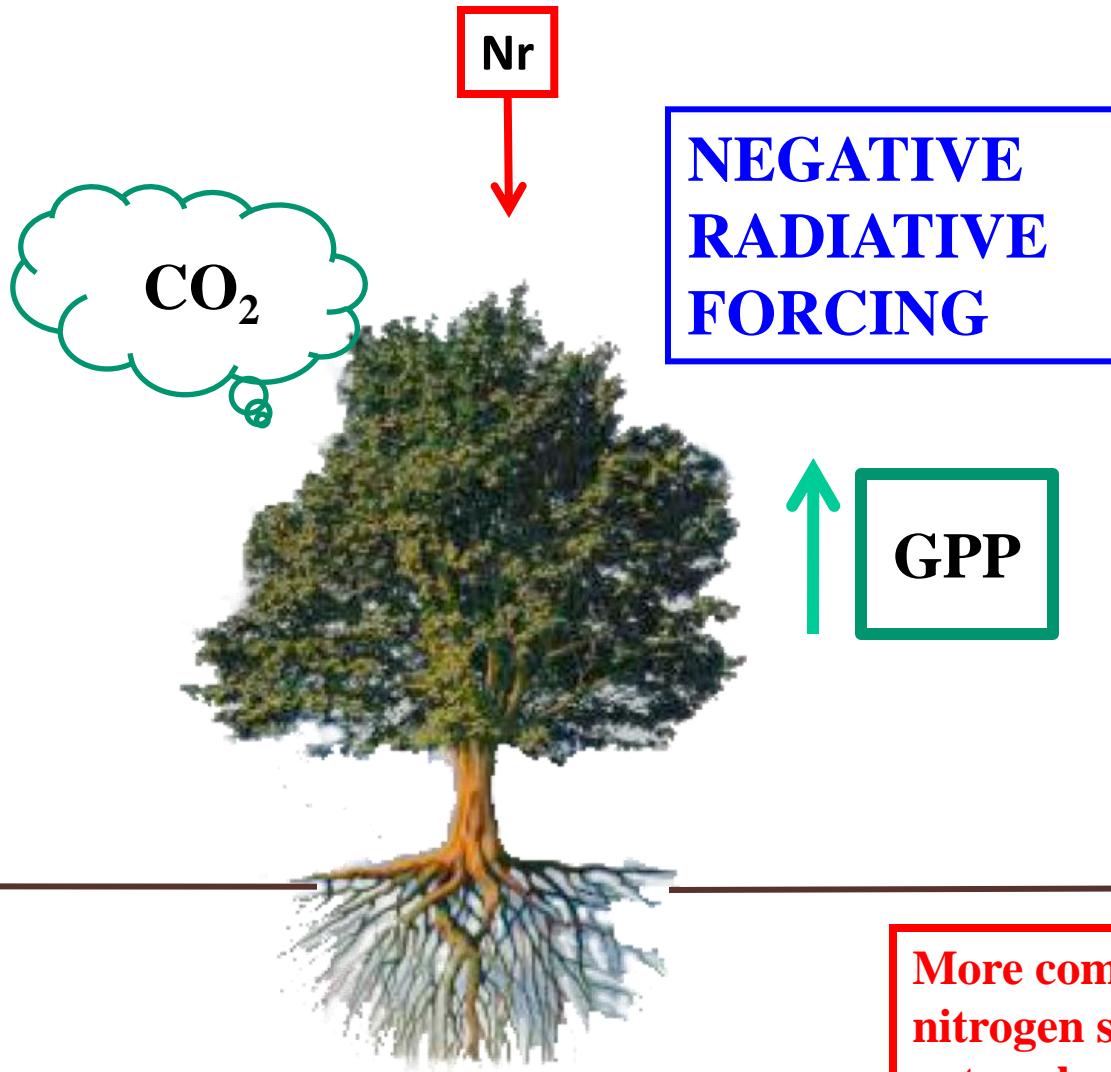
WSIN ($\text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$):

WSON:



TOTAL DISSOLVED NITROGEN (TDN)=WSIN_{NH4+}+ WSON

Why Nr matters on an global perspective



FLUXNET temperate evergreen needleleaf forest sites.

NPP \uparrow with \uparrow nitrogen deposition (up to 8Kg N/ha yr).

Tropical forest (not N limited) sites need more information particularly systematic Nr atmospheric deposition network

More comprehensive measurements of nitrogen stocks and cycling at the global network of carbon monitoring sites are required

All the Nr species have been considered?

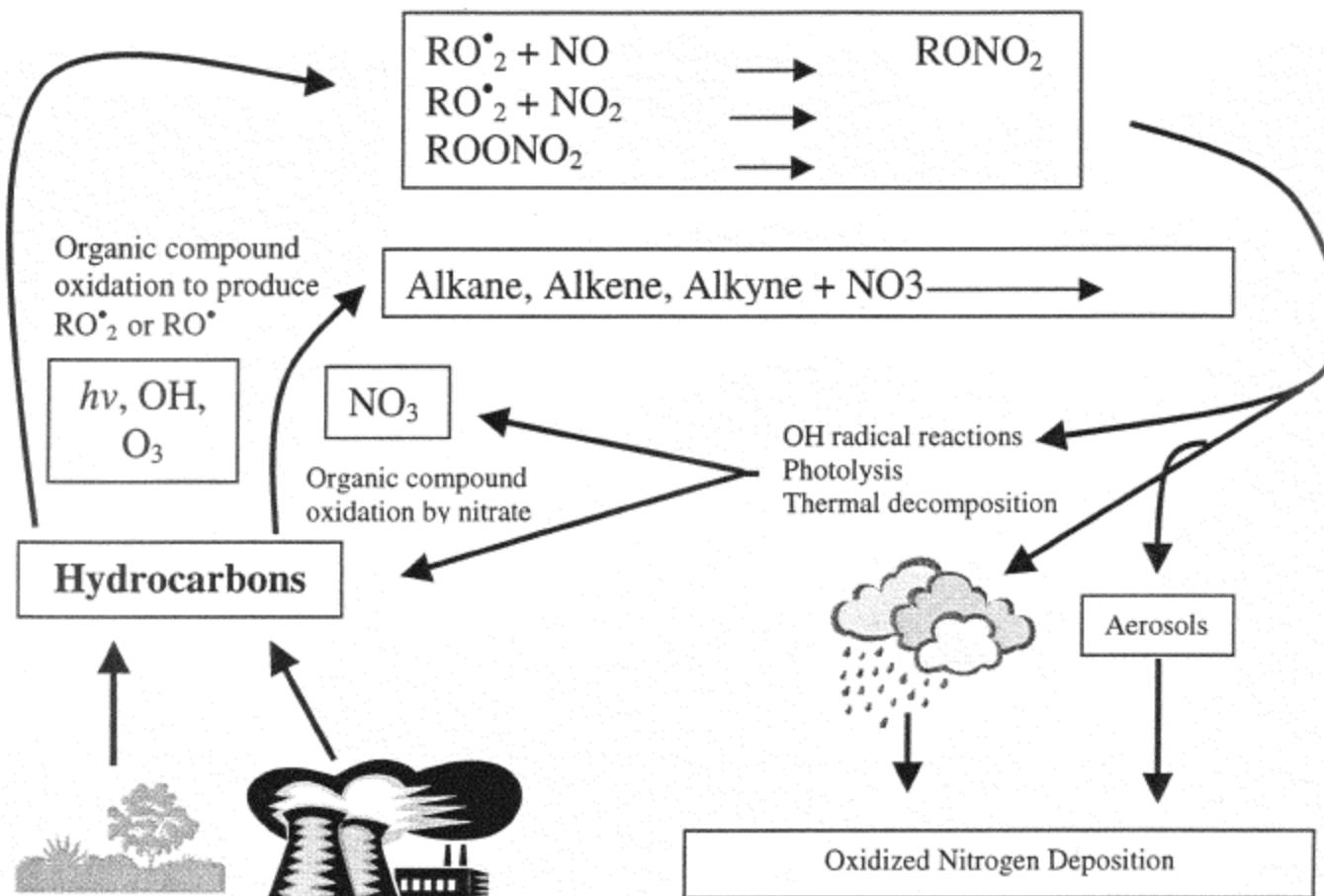
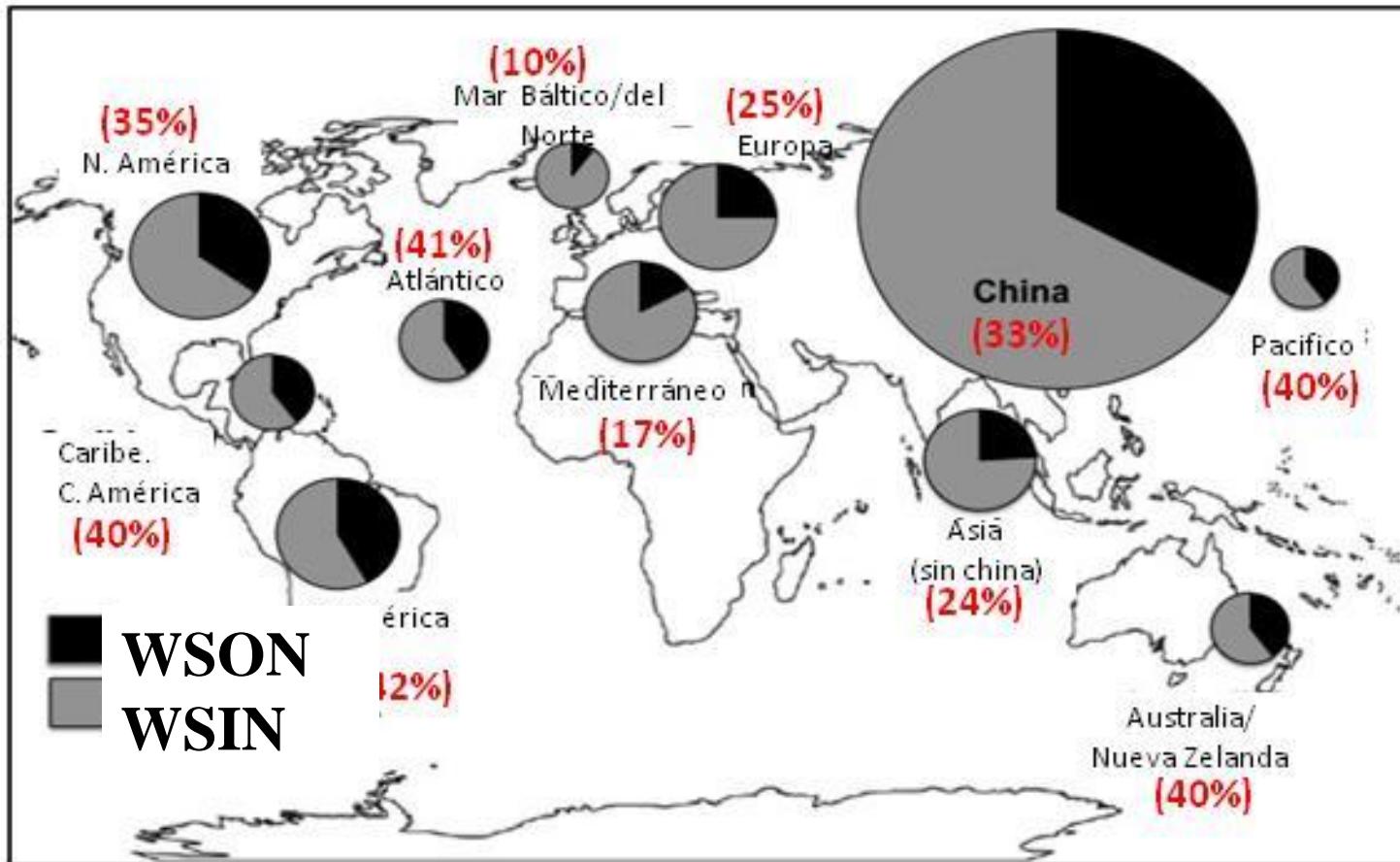


Figure 1. Simplified gas phase formation reactions and removal processes for organic, oxidized N species.

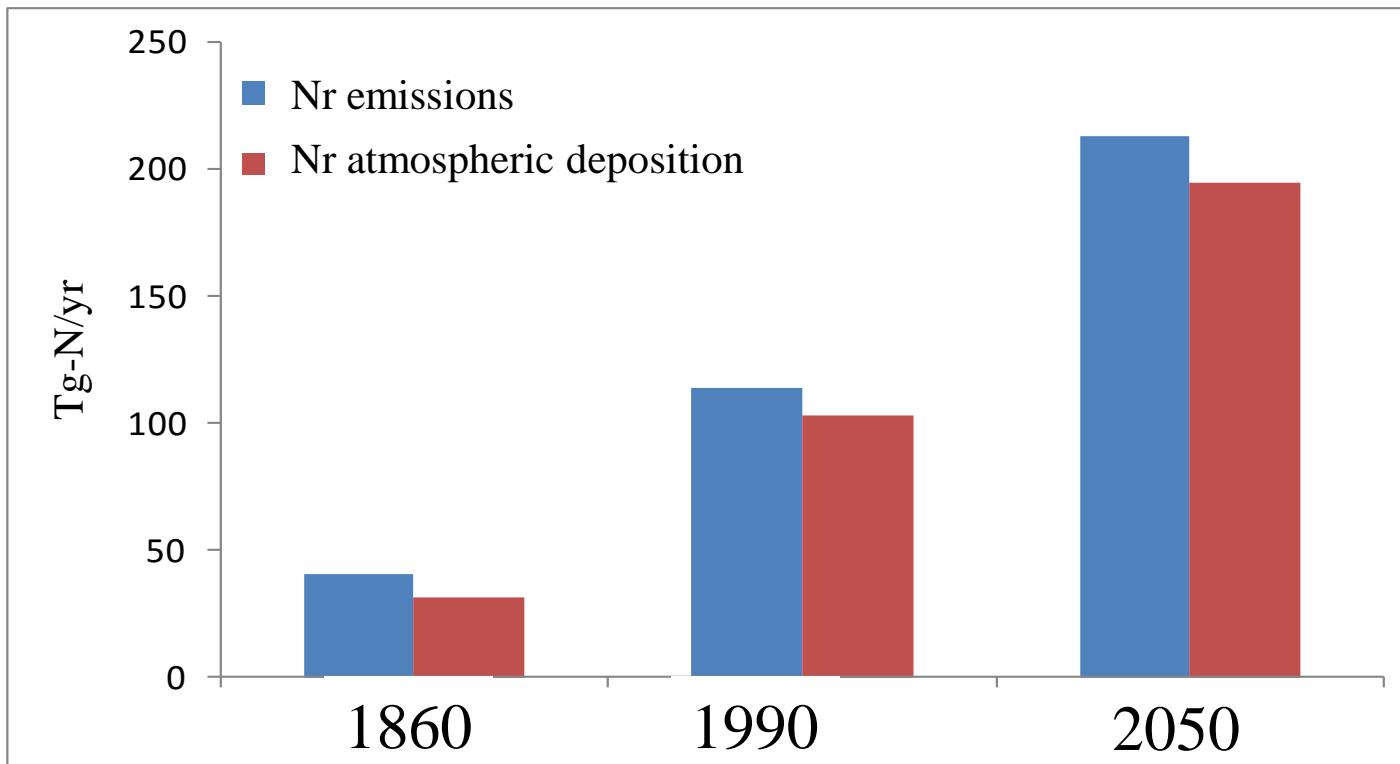
Relative contribution of WSON to Nr in wet deposition

(32 ± 11)%



Cornell (2011). Environmental Pollution 159:2214

Global reactive nitrogen (Nr) change through time



WSON is not included

Bioavailability of WSON

Plants →



Tansley review

Uptake of organic nitrogen by plants

Author for correspondence:

Torgny Näsholm¹, Knut Kielland² and Ulrika Ganeteg³

Soils →

Soil microbial decomposition
of bioavailable organic
nitrogen

Ocean

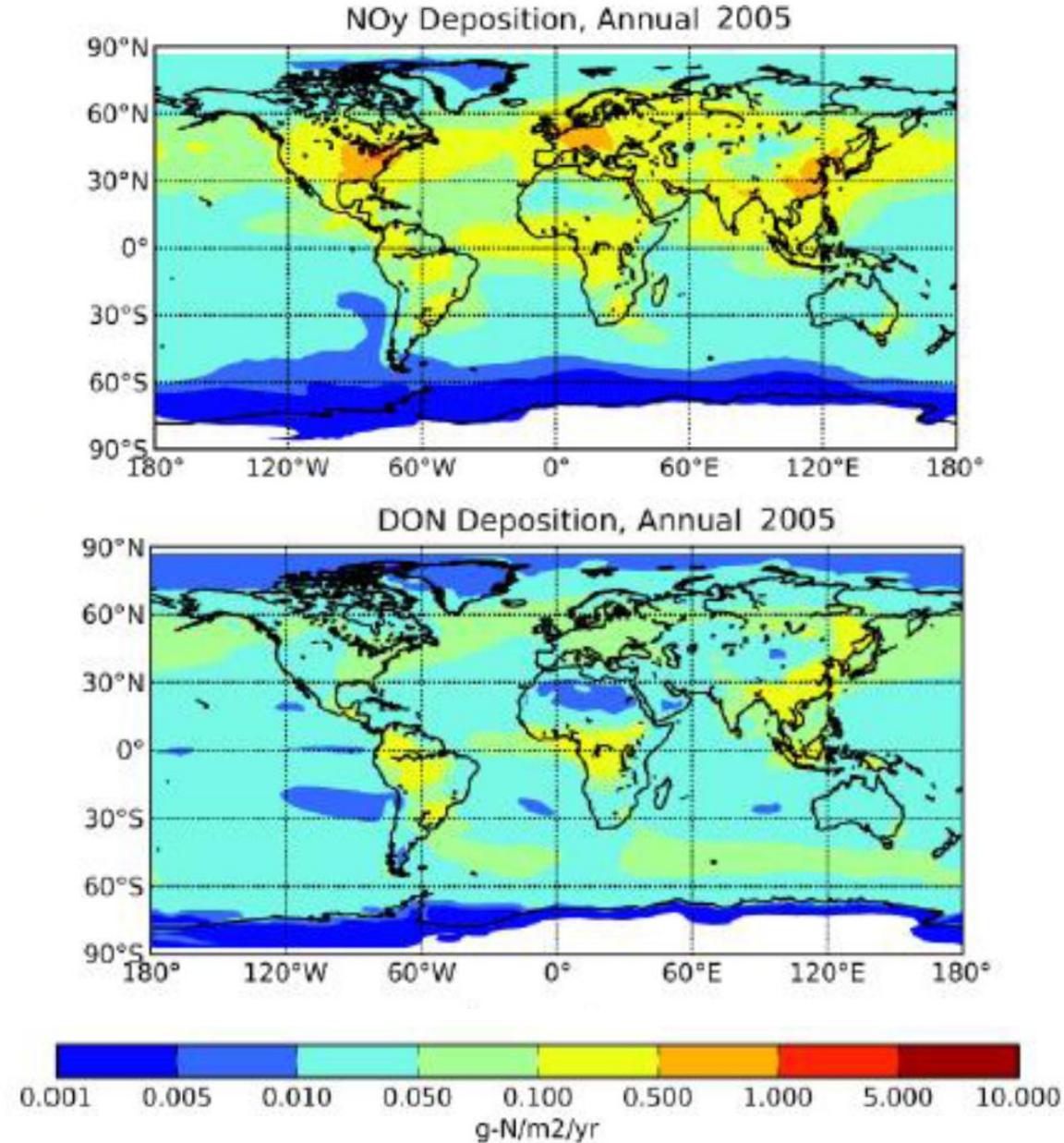


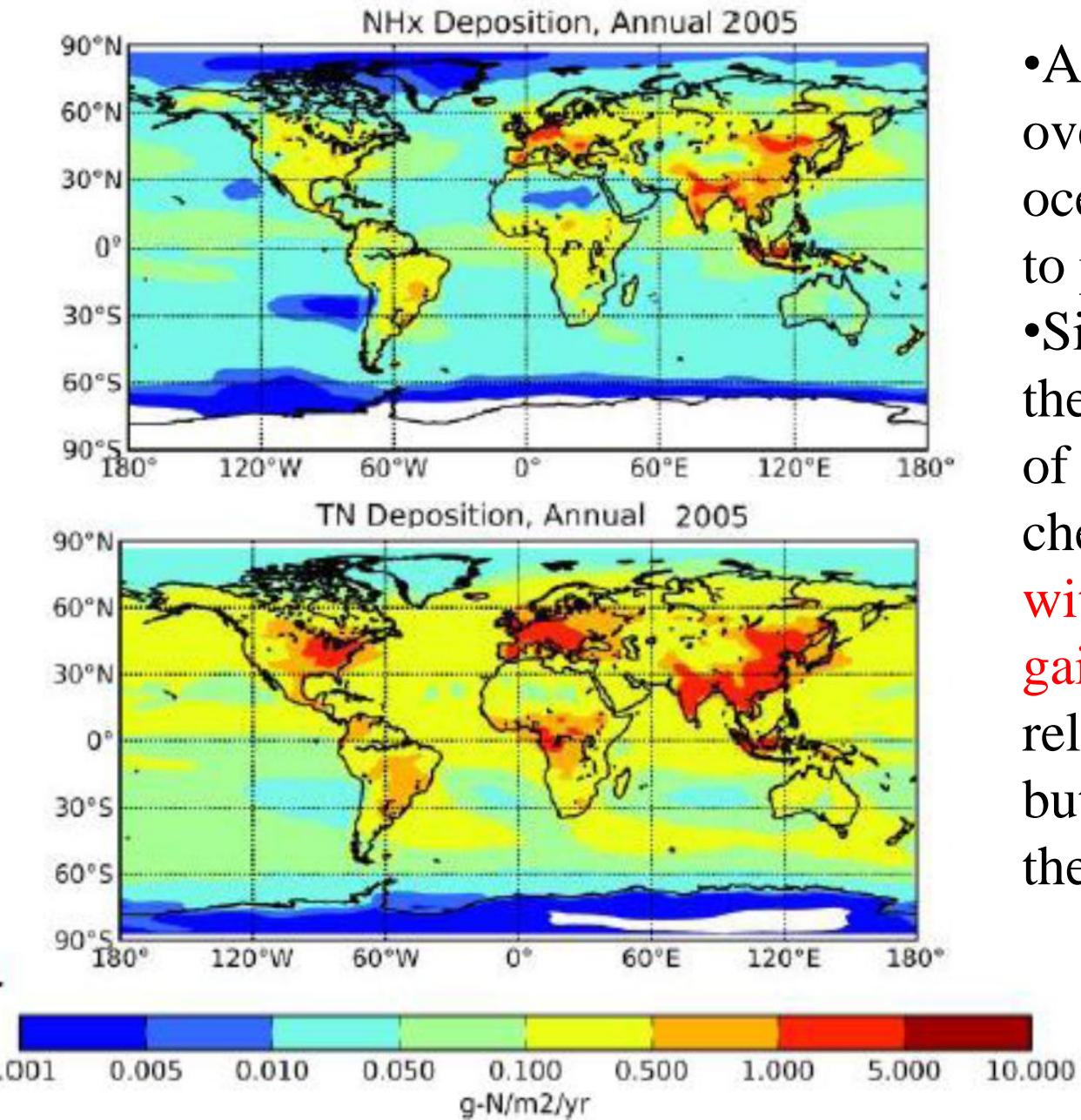
Bioavailability of DON

DON	bioavailability of DON (%)	Time of uptake	References
Estuarines	40-72	10-15 days	Seitzinger and Sanders 1999
Aquatic Systems	12-72	Days –weeks	Bronk 2002
Marine ecosystem	20-30	-	Violaki et al., 2009
Marine ecosystem	46-80	-	Wedyan et al., 2007
Marine ecosystem	20-30	hours –few days	Peierls and Paerl, 1997

Atmospheric chemistry-transport model (TM4-ECPL)

- Organic nitrogen **60%** anthropogenic.
- Total N deposition estimate increases by about 20% relative to simulations without ON.
- About **20-25%** of total deposited N is ON.
- About **10%** of the emitted nitrogen oxides are deposited as ON instead of inorganic nitrogen(IN) **as is considered in most global models**.

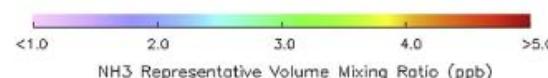
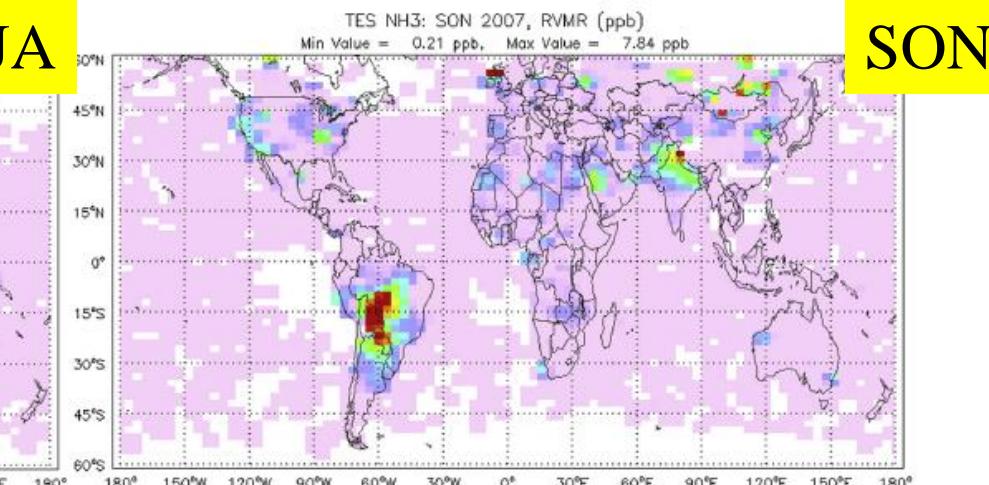
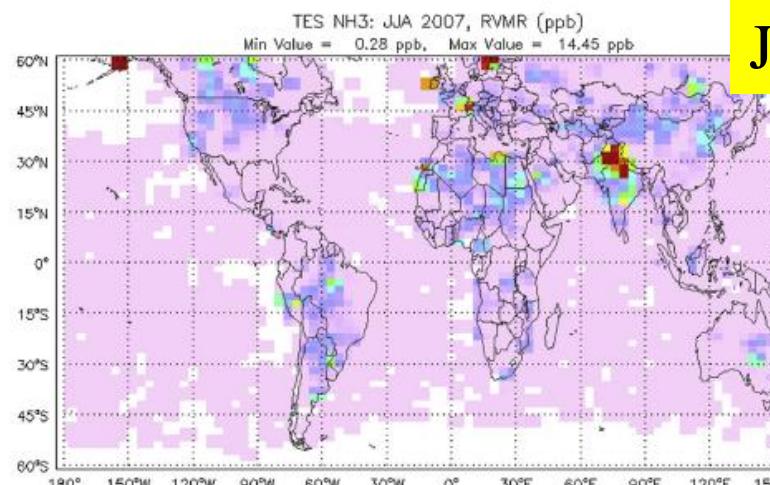
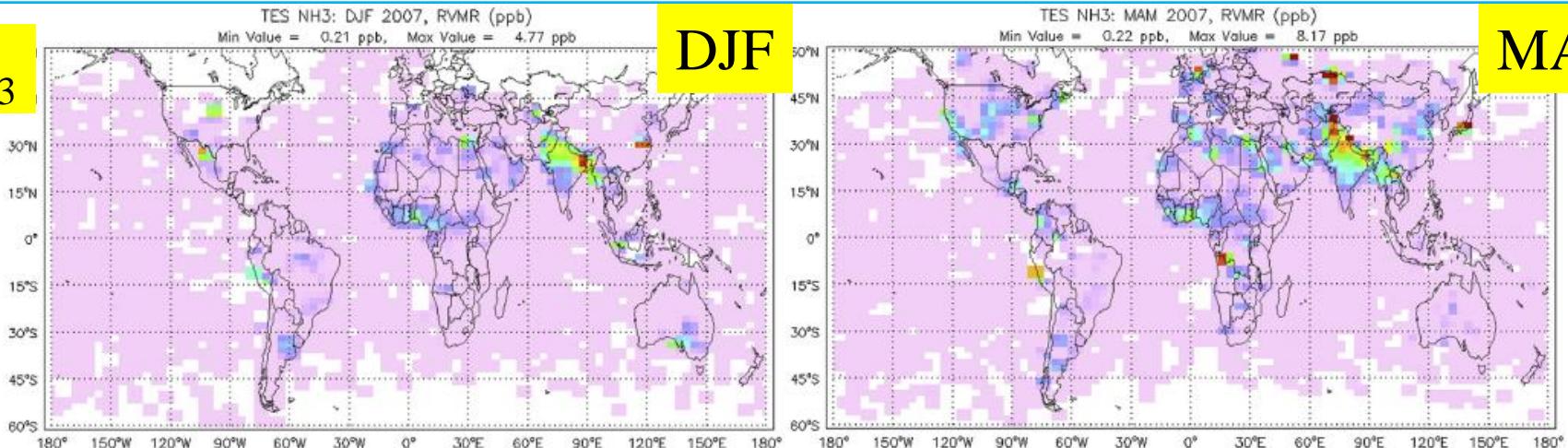




- Almost a 3-fold increase over land (2-fold over the ocean) of TN from 1850 to present.
- Significant changes in the regional distribution of N deposition and chemical composition, **with reduced compounds gaining importance** relative to oxidized ones, but very small changes in the global total flux.

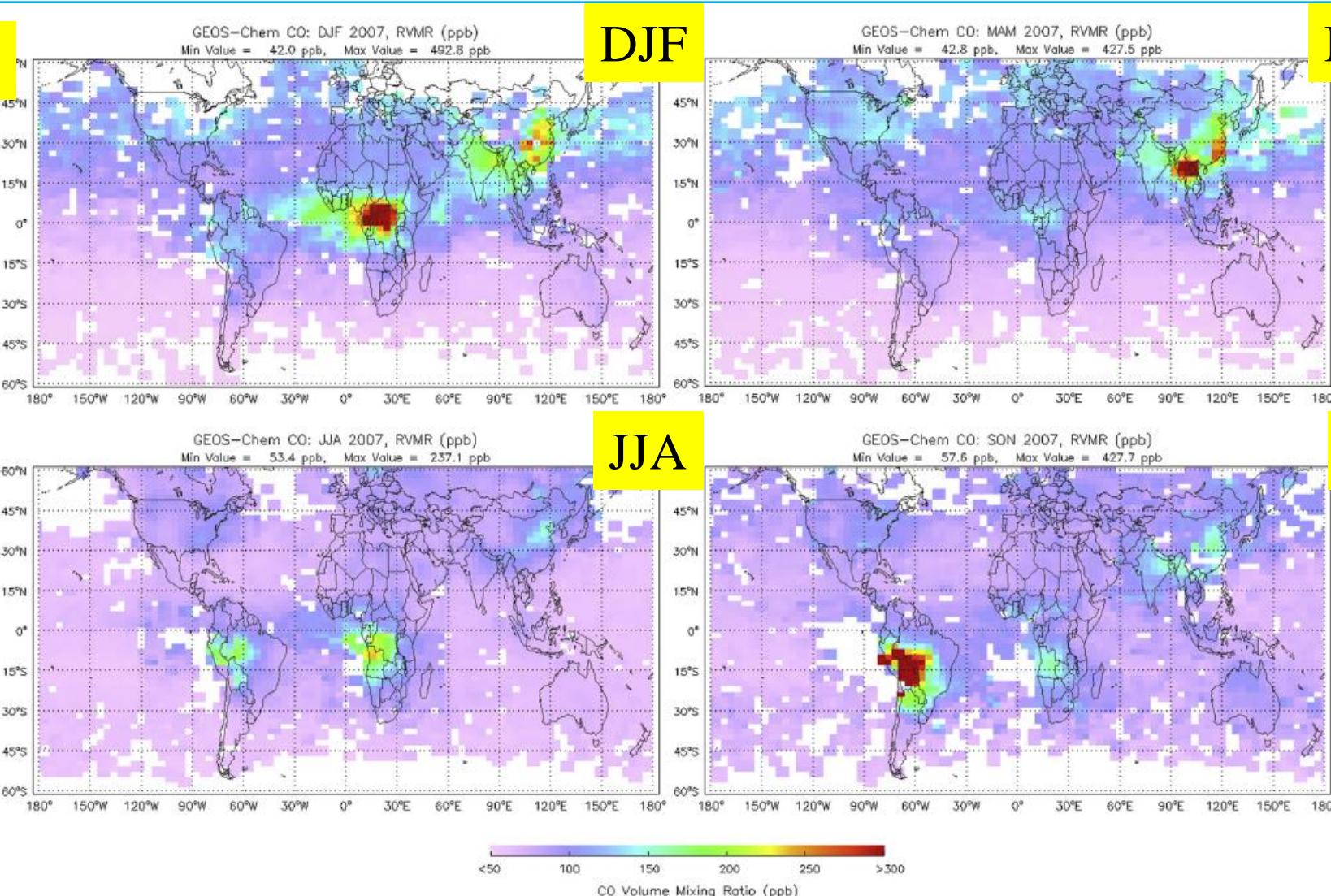
Satellite information a valuable tool for global Nr estimates

NH₃



Satelite information a valuable tool for global Nr estimates

CO



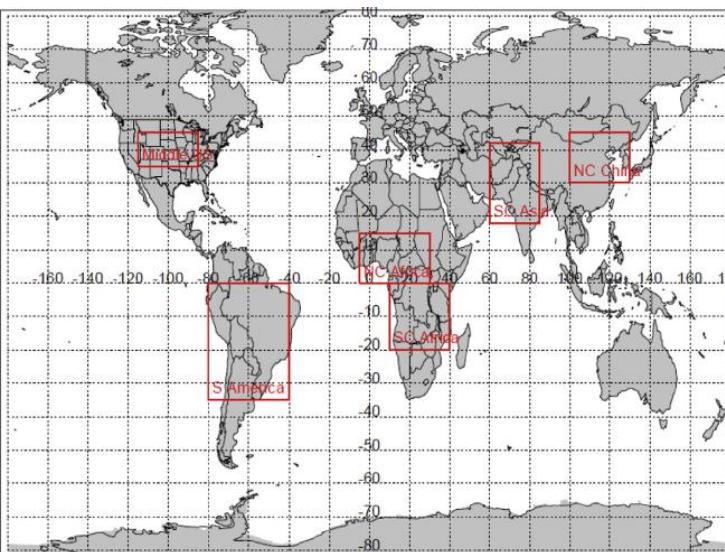
M. Luo et al. / Atm

osphere

Environment 106 (2015) 262–277

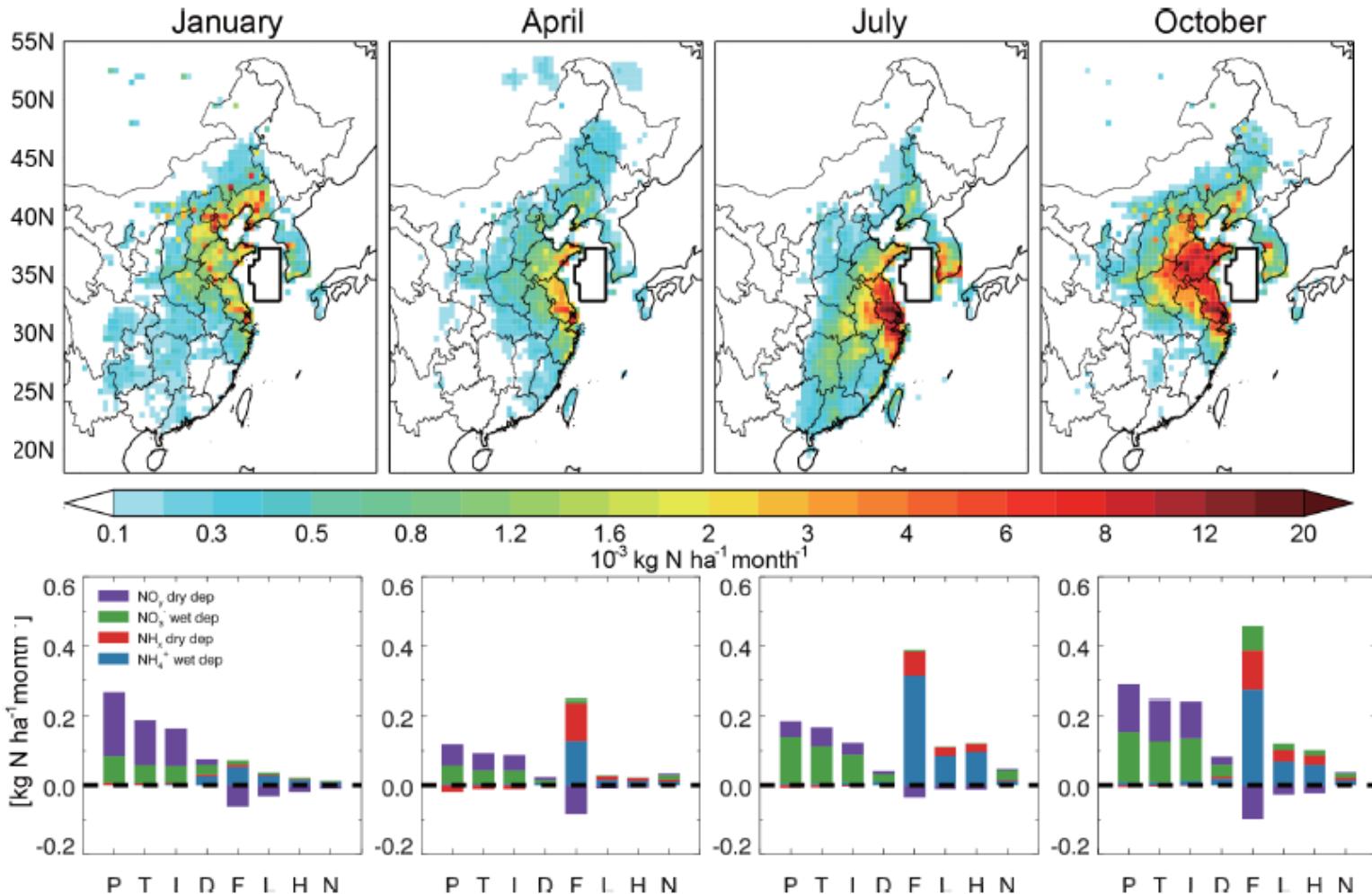
Partitioning NH₃ sources

NH₃/CO

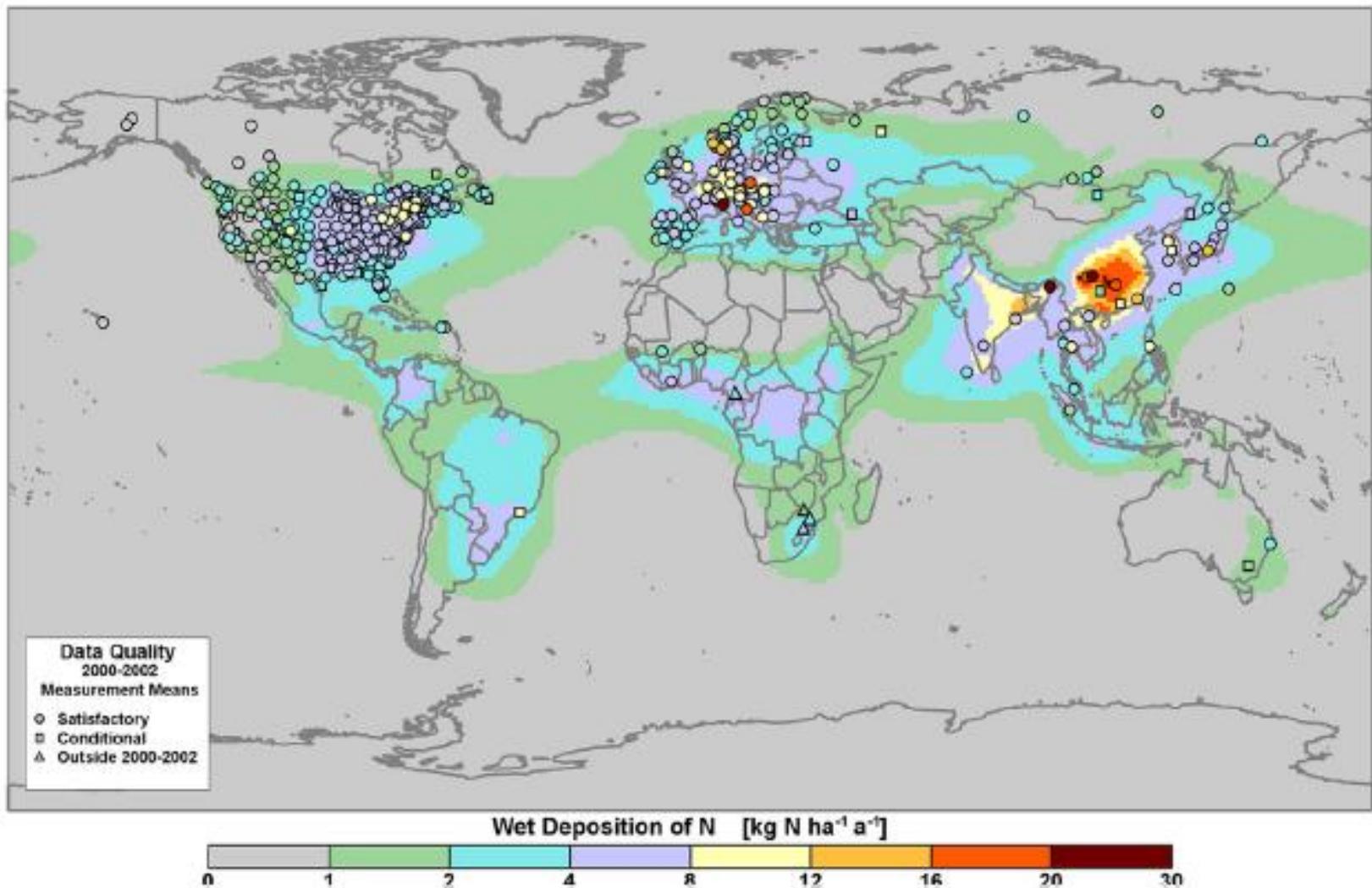


Region	Season	TES		GC		Class
		Slope	Corr Coef	Slope	Corr Coef	
SC Asia	DJF	0.052±0.002	0.61	0.019±0.001	0.61	High NH ₃
	MAM	0.041 ±0.002	0.38	0.029±0.001	0.46	High NH ₃
	JJA	0.120 ±0.005	0.44	0.082 ±0.003	0.37	High NH ₃
	SON	0.047±0.002	0.45	0.027±0.001	0.52	High NH ₃
NC China	DJF					
	MAM	0.015±0.001	0.24	0.017±0.002	0.14	High NH ₃
	JJA	0.018±0.001	0.09	0.032 ±0.001	0.45	High NH ₃
	SON	0.038±0.001	0.12	0.026±0.002	0.44	High NH ₃
Mid US	DJF					
	MAM					
	JJA	0.049±0.002	0.28	0.041 ±0.002	0.34	High NH ₃
	SON	0.082±0.009	0.12	0.048±0.004	0.55	High NH ₃
Average		0.051±0.003		0.036±0.002		High NH ₃
S America	DJF					
	MAM					
	JJA					
	SON	0.015±0.000	0.64	0.011±0.000	0.74	BB
SC Africa	DJF					
	MAM					
	JJA	0.013±0.001	0.11	0.014±0.001	0.62	BB
	SON	0.011±0.001	0.19	0.016±0.001	0.70	BB
NC Africa	DJF	0.014±0.001	0.52	0.008±0.000	0.73	BB
	MAM	0.023±0.001	0.38	0.017±0.001	0.37	BB
	JJA					
	SON					
Average		0.015±0.001		0.013±0.001		BB

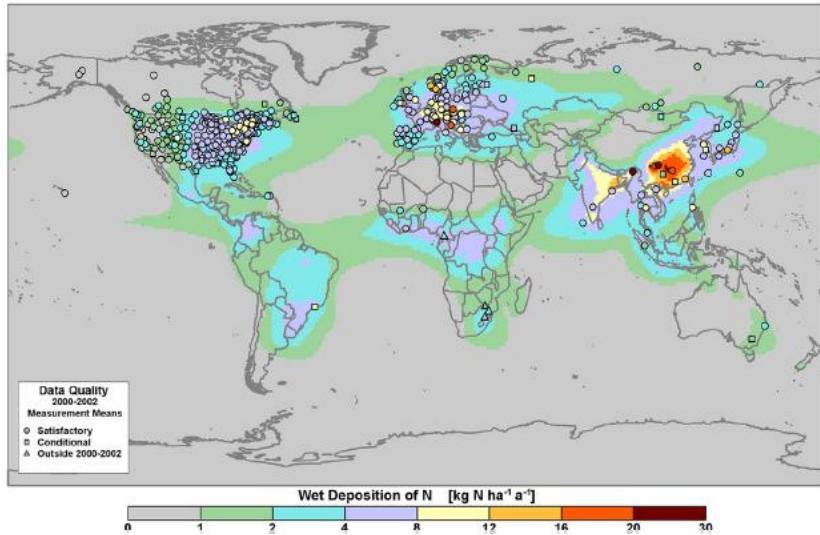
Partitioning N_r sources



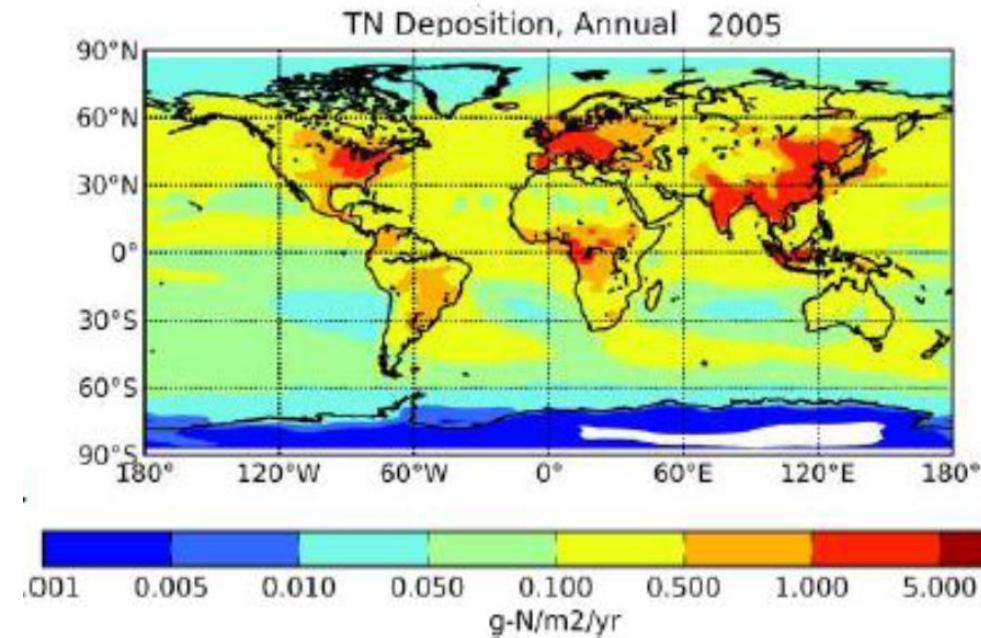
Ground based N_r monitoring



Comparison between estimates



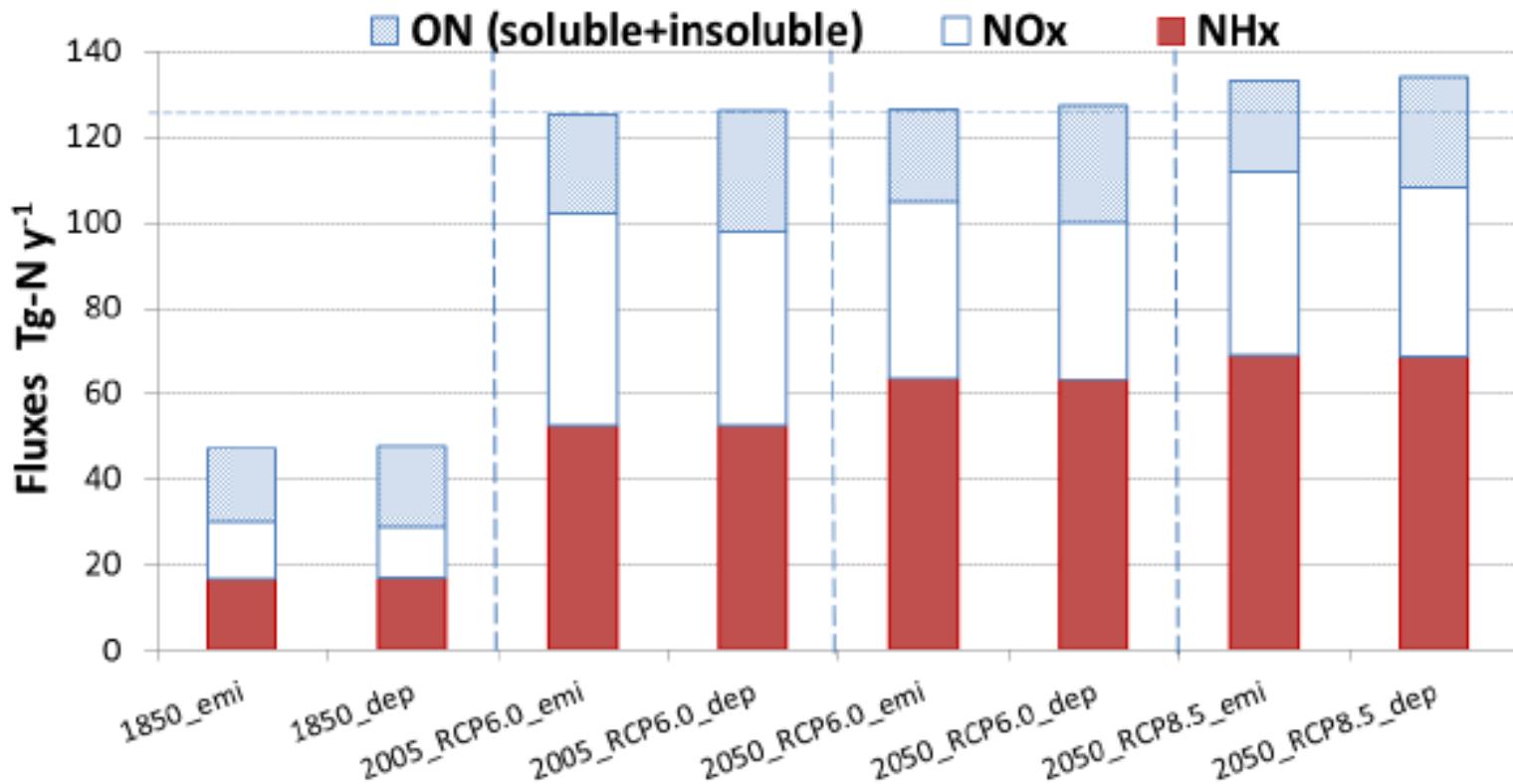
Vet, R. et al (2014). A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric Environment* 93. 3-100.



Kanakidou, M., S. et al 2016: Past, Present and Future Atmospheric Nitrogen Deposition. *J. Atmos. Sci.* doi:10.1175/JAS-D-15-0278.1, in press.

Inclusion of WSON in new estimates!

N atmospheric emissions & deposition 1850-2050





How to assess N deposition in Latin America and the Caribbean?

www.sciencemag.org SCIENCE VOL 340 12 APRIL 2013

Published by AAAS

ENVIRONMENT

Latin America's Nitrogen Challenge

A. T. Austin,¹ M. M. C. Bustamante,² G. B. Nardoto,² S. K. Mitre,² T. Pérez,³ J. P. H. B. Ometto,⁴ N. L. Ascarrunz,⁵ M. C. Forti,⁴ K. Longo,⁴ M. E. Gavito,⁶ A. Enrich-Prast,⁷ L. A. Martinelli^{8*}

Human impacts on the N cycle require sustainable ecological solutions to preserve ecosystem and human health.



Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in
Environmental
Sustainability

Innovations for a sustainable future: rising to the challenge of nitrogen greenhouse gas management in Latin America

Mercedes MC Bustamante¹, Luiz A Martinelli²,
Jean PHB Ometto³, Janaina Braga do Carmo⁴,
Víctor Jaramillo⁵, Mayra E Gavito⁵, Patricia I Araujo⁶,
Amy T Austin⁶, Tibisay Pérez⁷ and Sorena Marquina⁷



Nitrogen Cycling in Latin America: Drivers, Impacts and Vulnerabilities (Nnet)

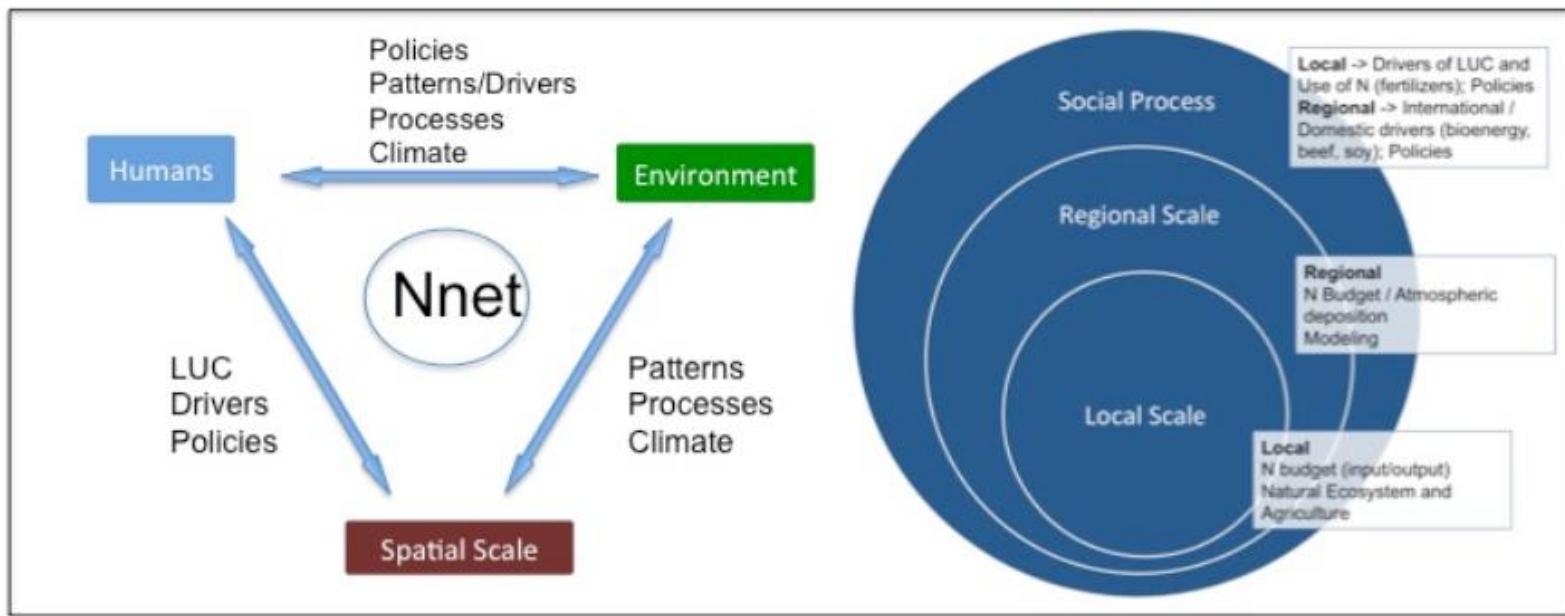


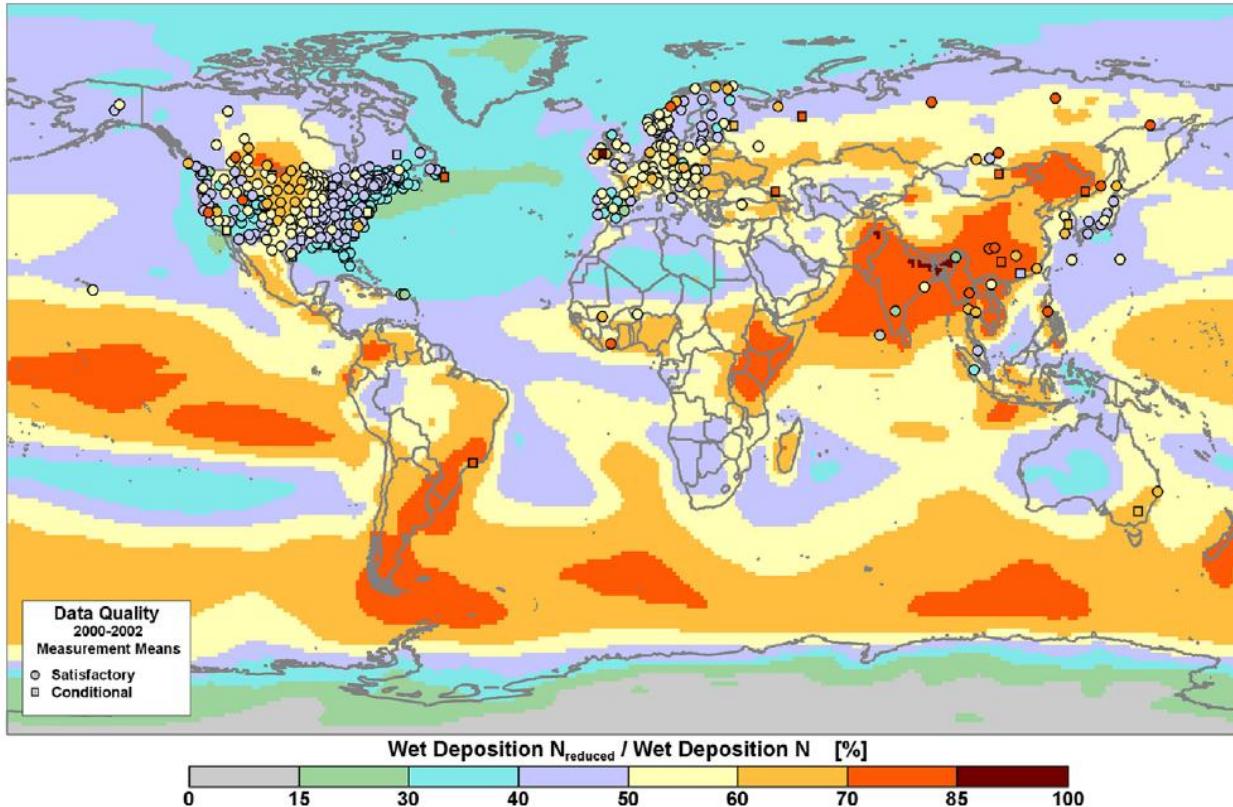
Figure 1.: Integration of different components of the Nitrogen Human Environment Network (Nnet) and the different levels of study with interdependent and interconnected drivers.

N atmospheric deposition and BNF components



Figure 2: Sampling sites and precipitation gradient

Nreduced becoming important



N atmospheric deposition from Venezuela

WSON concentrations in total suspended particles (TSP) and wet deposition

Total Suspended Particles

	Concentration ($\mu\text{g-N m}^{-3}$ aire)	WSON/TN (%)
Venezuela	0,07-1,3	35-72%
Other studies	0,01-2,1	10-64%

Wet deposition

	Concentration ($\mu\text{g-N/L}$)	WSON/TN (%)
Venezuela	0,34-0,96	51-92%*
Other studies	0,04-0,31	5-84%

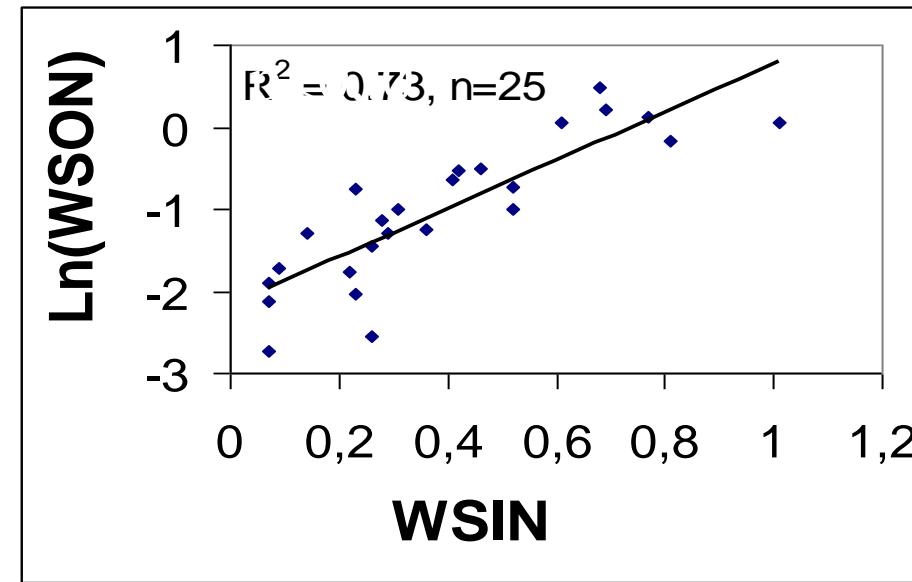
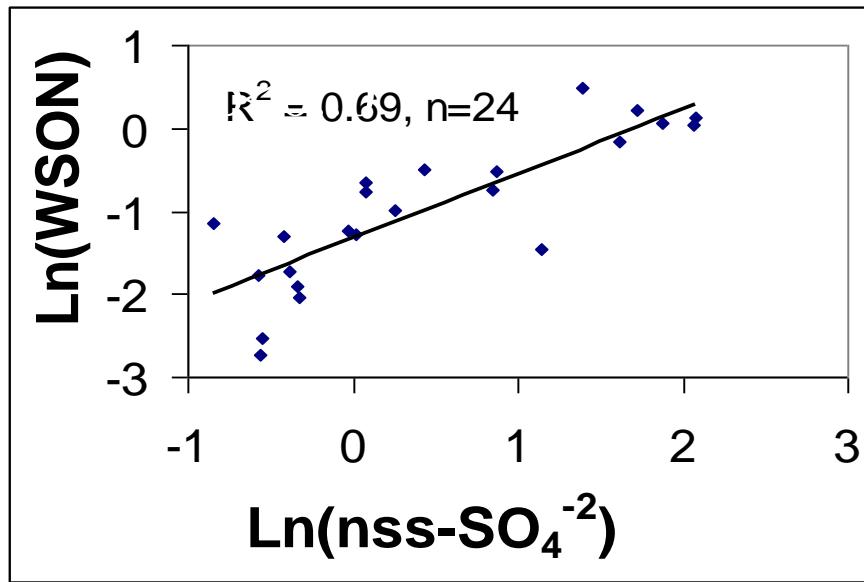
* Maracaibo excluded

Venezuela → ↑ [NOS] %
[NOS] ↑
Canaima National Park
(30.000 km²)

Morales et al., .2001. Water, Air, and Soil Pollution 128, 207-221; Pacheco et al., 2004. Tellus 56B; Canelón et al., 2007 Eos Trans. AGU, 88(52).

N atmospheric deposition from Venezuela

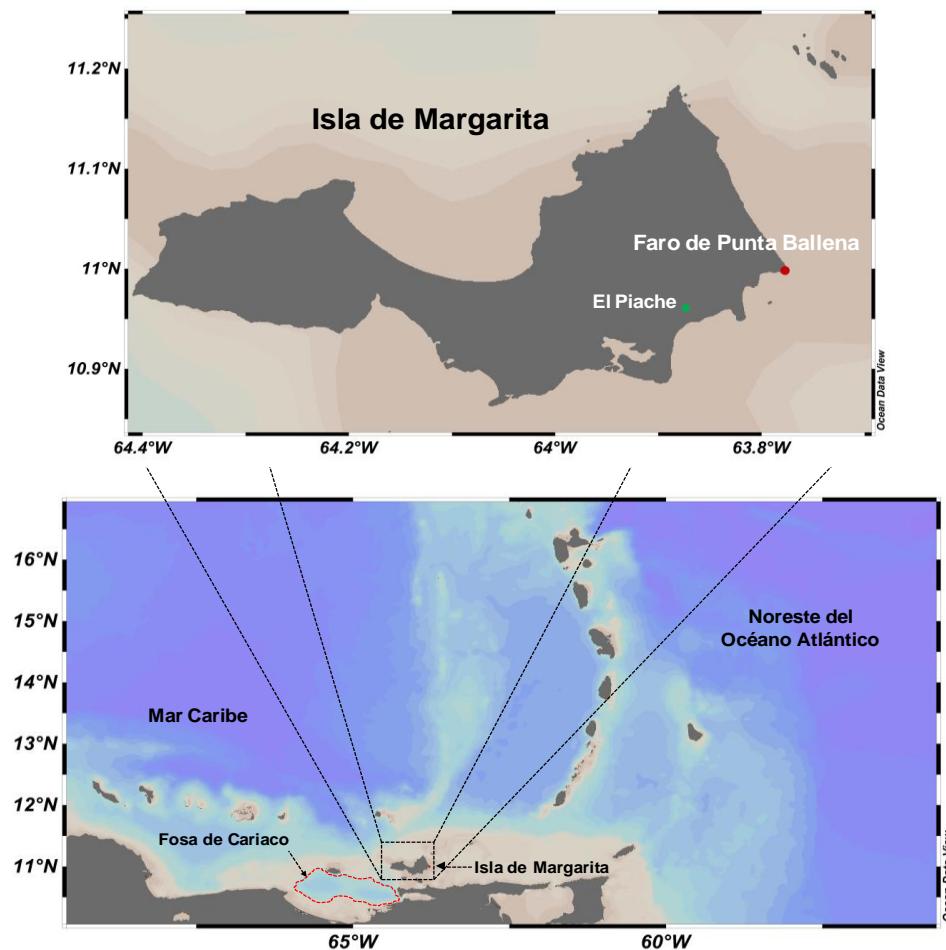
WSON and WSIN from TSP in remote continental and oceanic sites



SOA derived:

- Remote continental sites: biomass burning
- Remote coastal and oceanic sites: Long range transport and tropospheric oxidation of VOCs including DMS

N atmospheric deposition from Venezuela



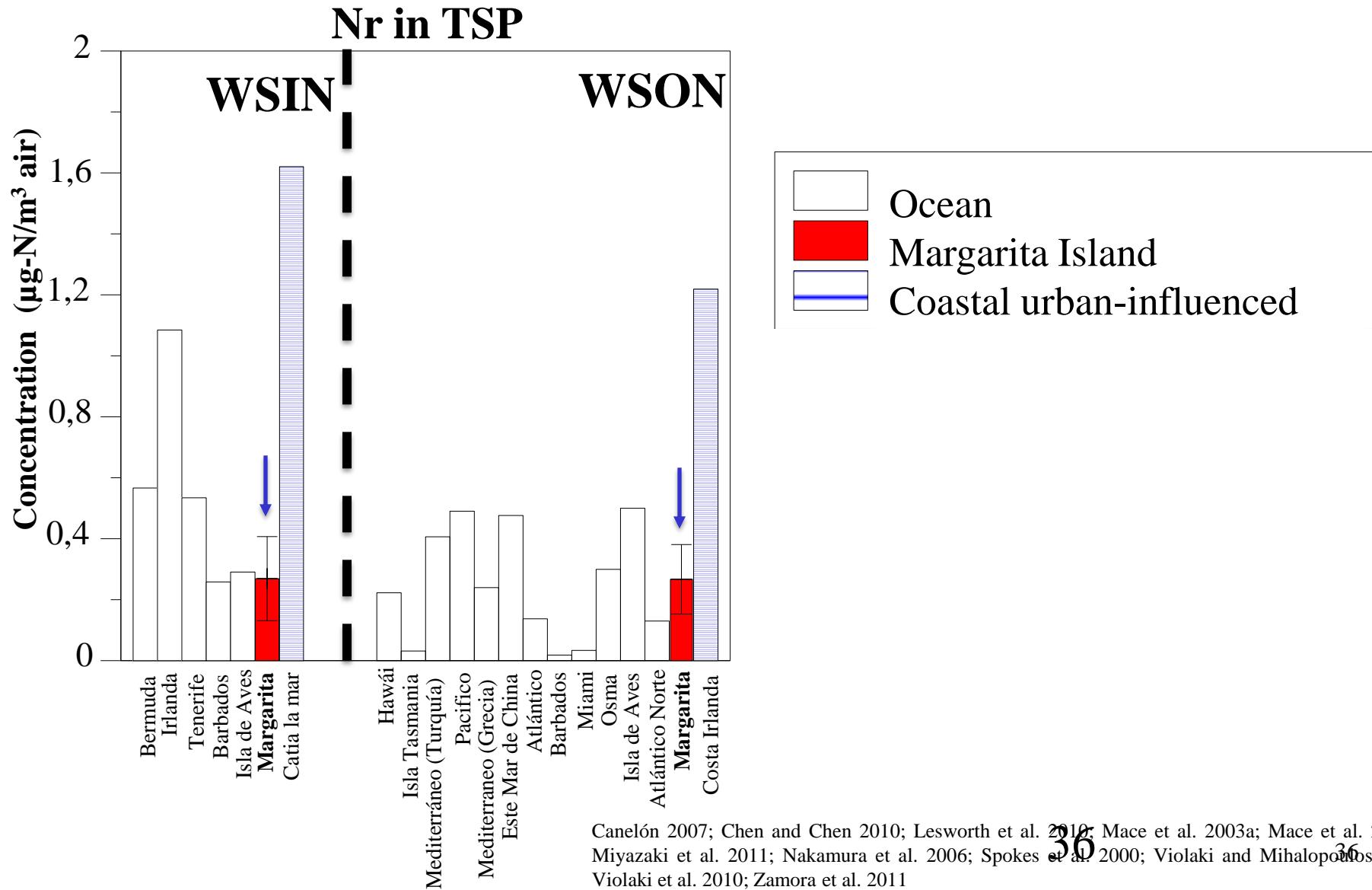
Margarita Island



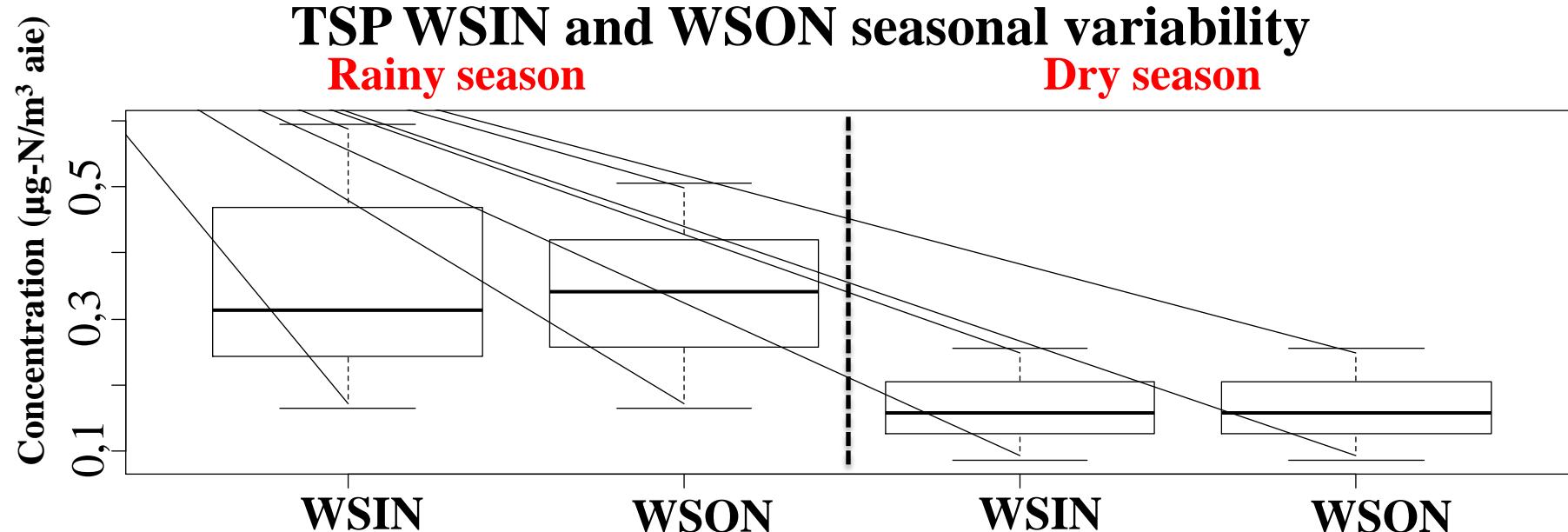
Venezuelan Navy Hidrography Division (DHN)

Rainy season and dry season collection

N atmospheric deposition from Venezuela



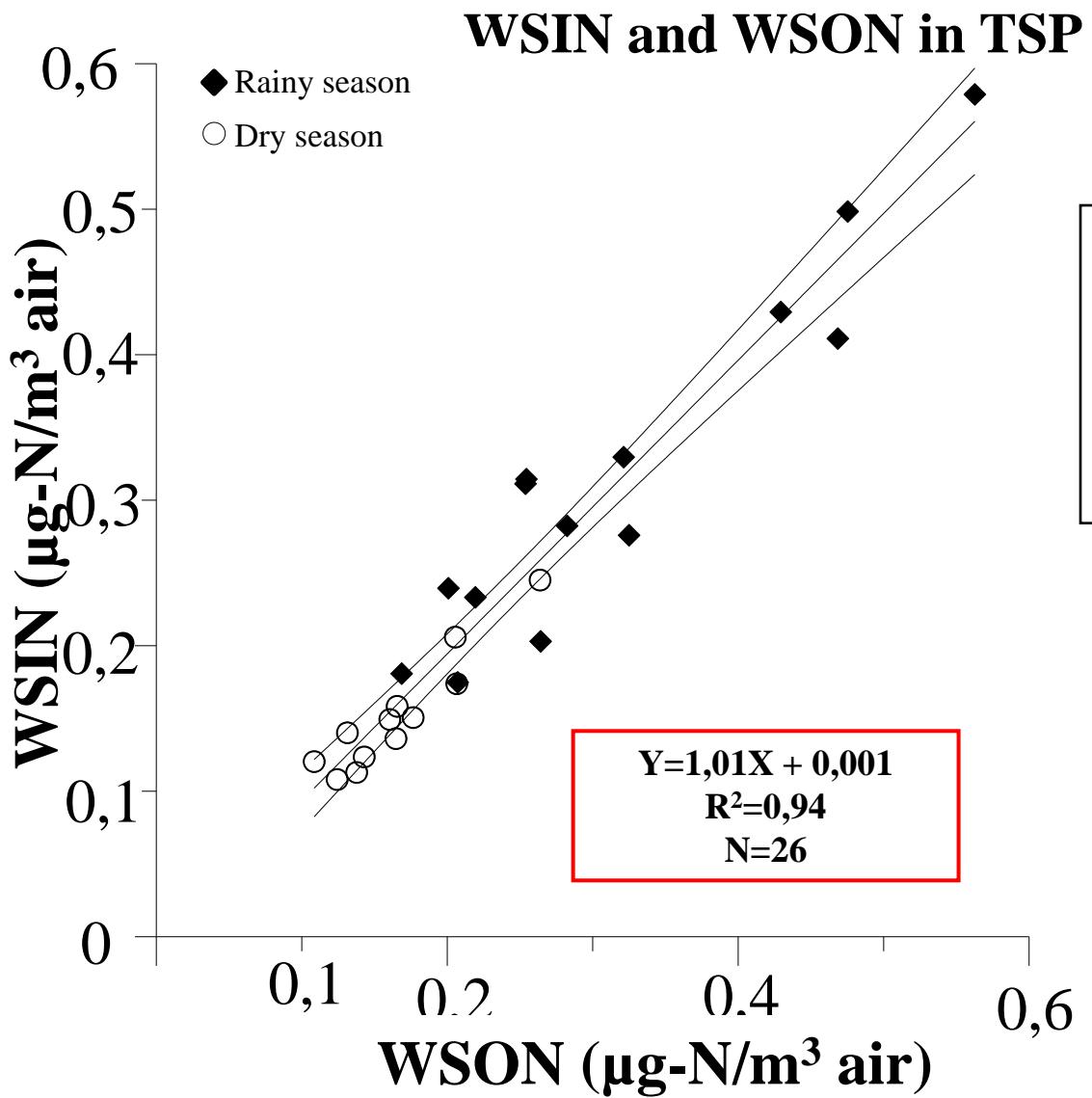
N atmospheric deposition from Venezuela



[WSIN] and [WSON] rainy season > dry season
($p < 0.01$; N = 28)

WSON/WSIN ratio ~ 1:1 possible similar sources

N atmospheric deposition from Venezuela



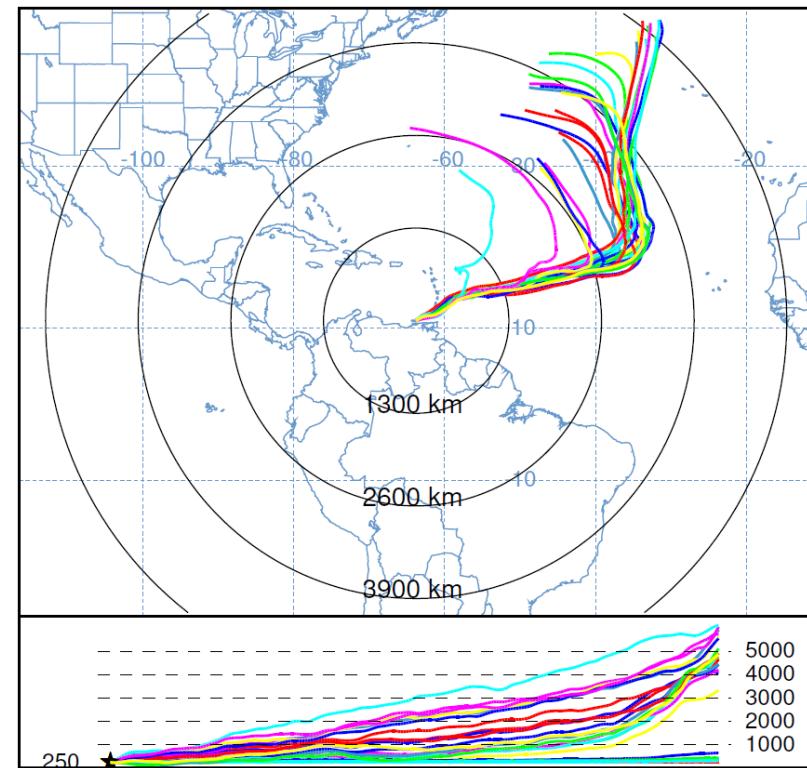
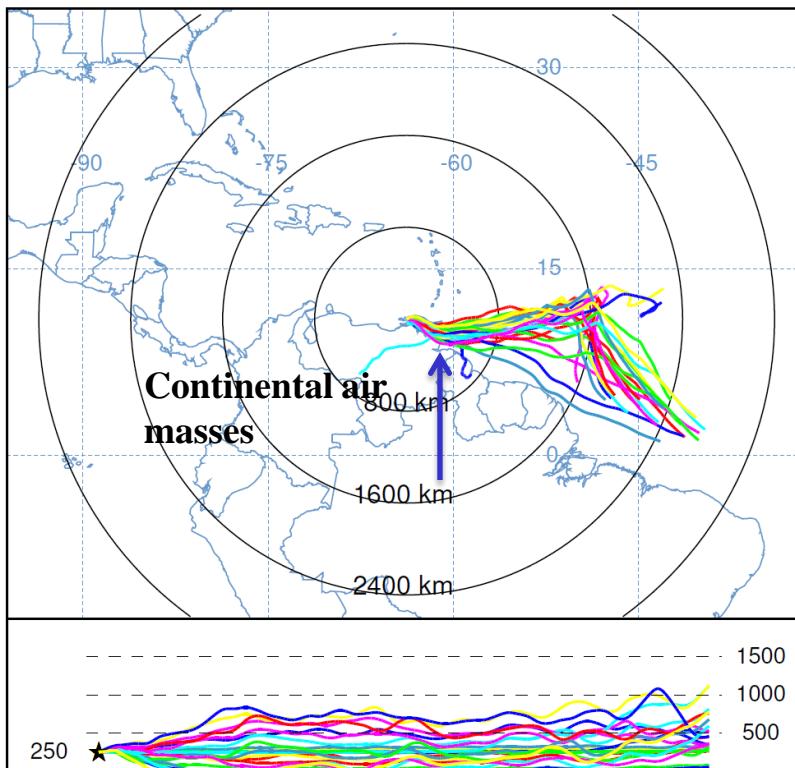
**Mean concentration
values**

[WSIN] and [WSON]
rainy season >
dry season
($p<0,01; N=28$)

N atmospheric deposition from Venezuela

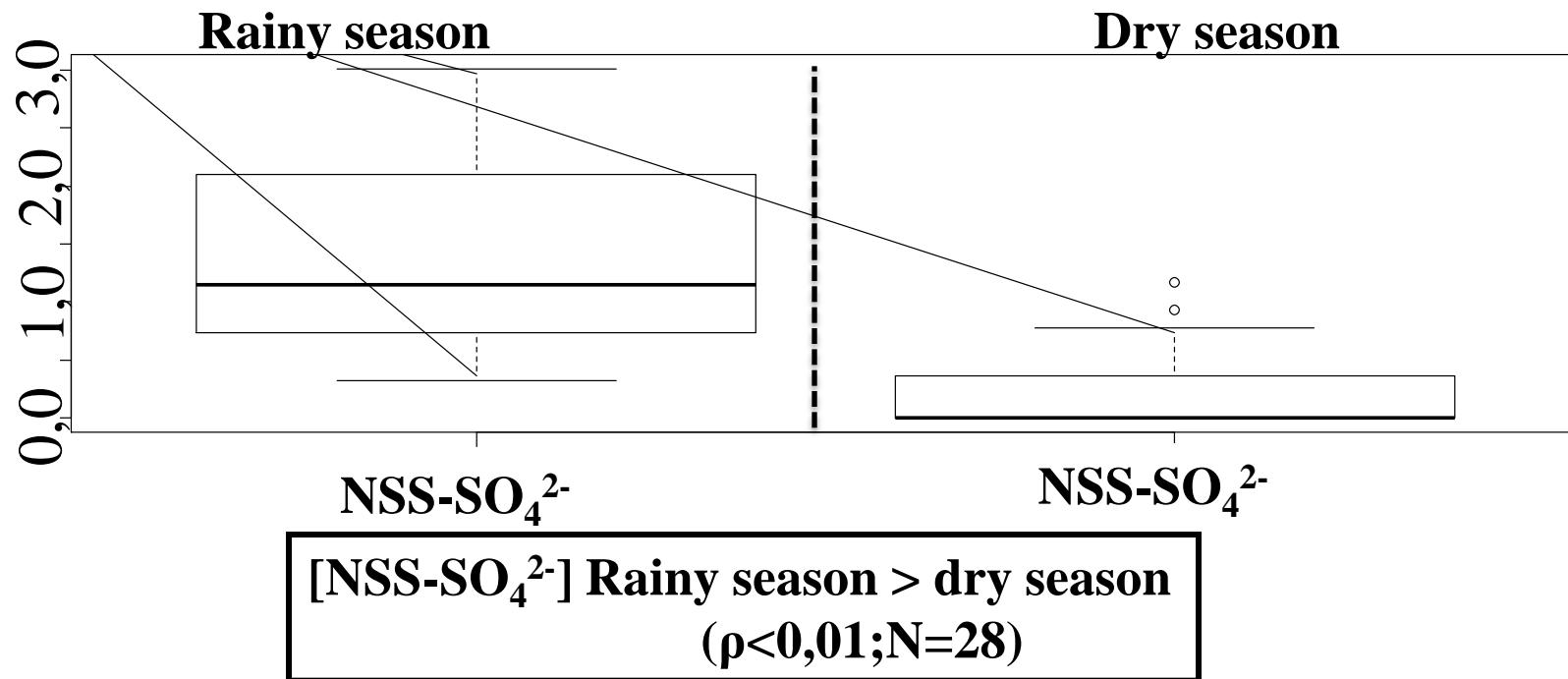
Back trajectories and meteorological data

Rainy season Dry season



N atmospheric deposition from Venezuela

Concentration ($\mu\text{g}/\text{m}^3$ air)



[WSIN] Vs [NSS-SO_4^{2-}] ($R^2 = 0,423$; $p < 0,05$; $N = 28$)

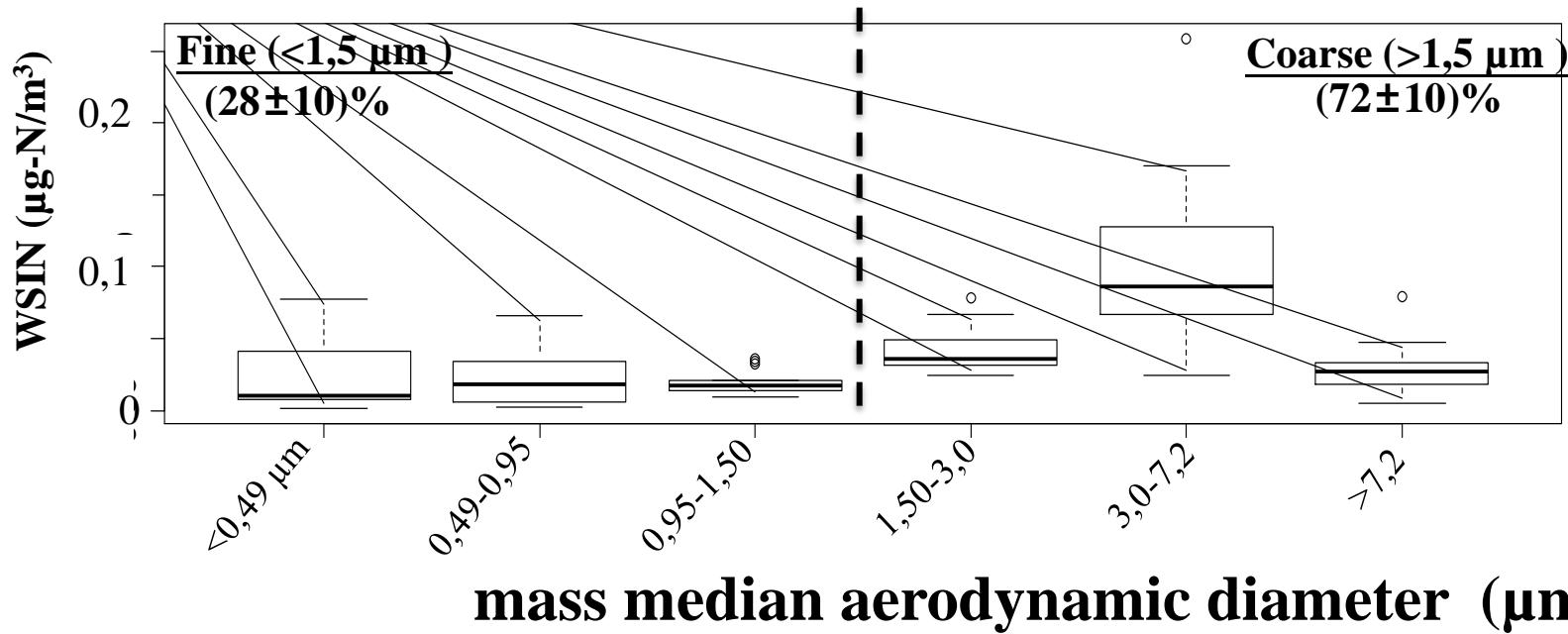
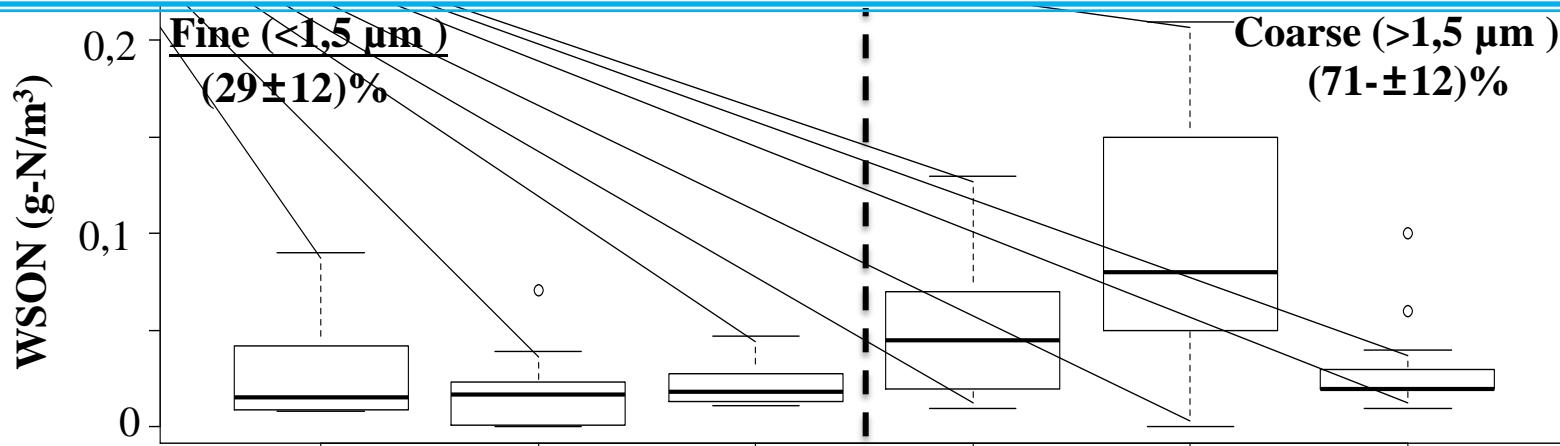
[WSON] Vs [NSS-SO_4^{2-}] ($R^2 = 0,480$; $p < 0,05$; $N = 28$)

Back trajectories, meteorological data, [CO] and [NSS-SO_4^{2-}]

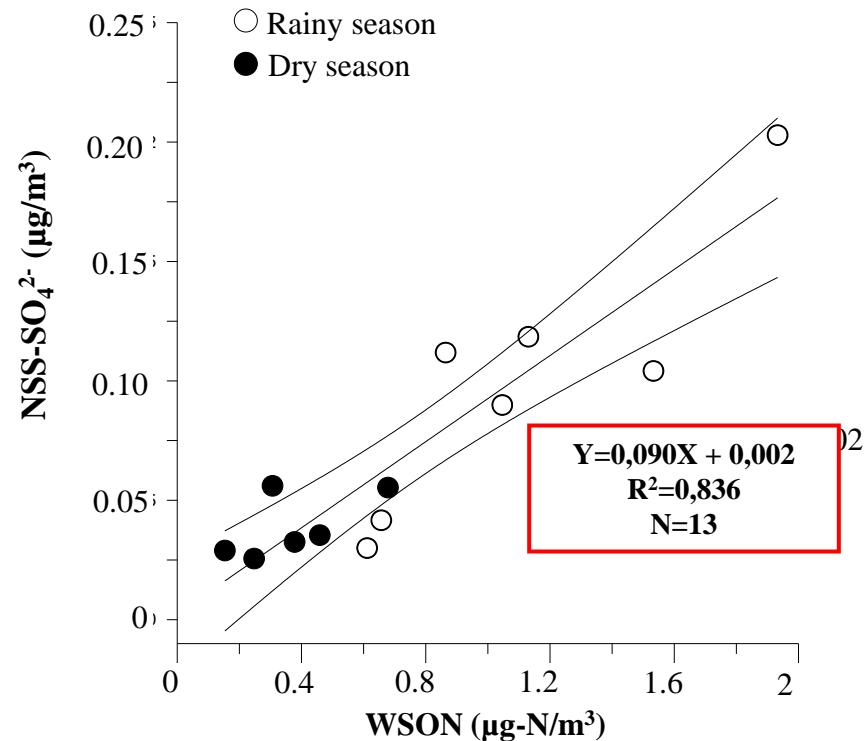
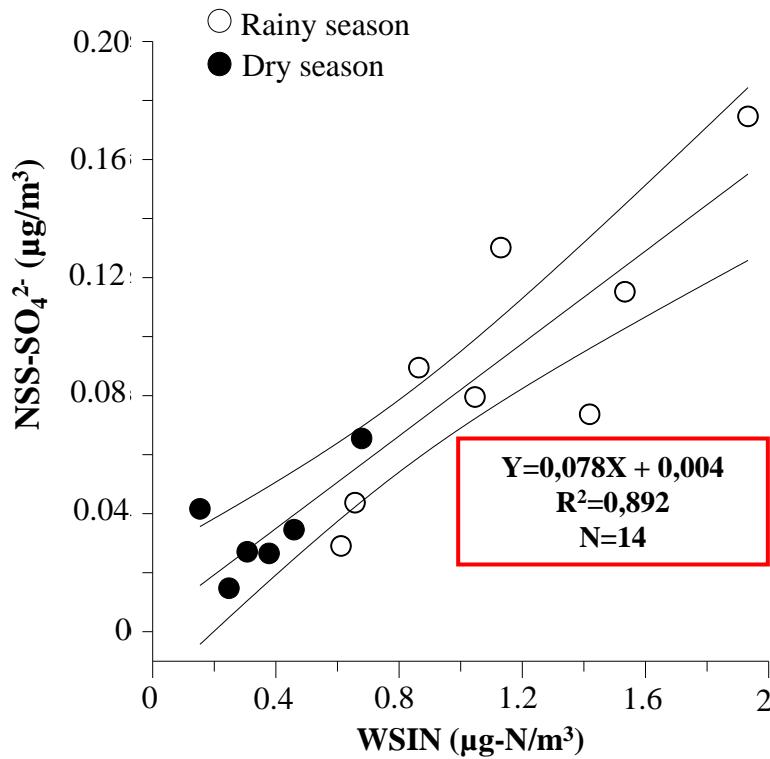


Fossil fuel combustion and/or Biomass Burning during rainy season

N atmospheric deposition from Venezuela



Identifying sources of WSIN and WSON

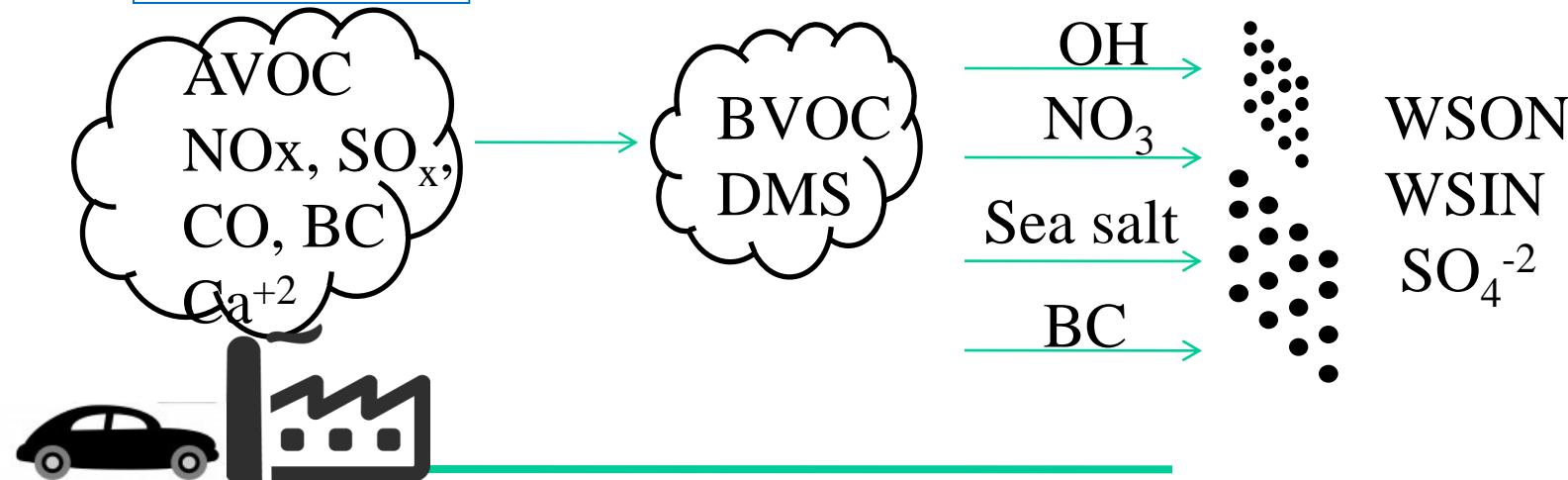


Nitrogen species	nss-SO ₄ ²⁻	nss-K ⁺	nss-Ca ²⁺	WSON
<i>Fine fraction</i>				
WSIN	0.892**	0.326	0.656**	0.898**
WSON	0.836**	0.330	0.659**	-
<i>Coarse fraction</i>				
WSIN	-0.203	0.054	0.325	0.898**
WSON	-0.086	0.092	0.346	-

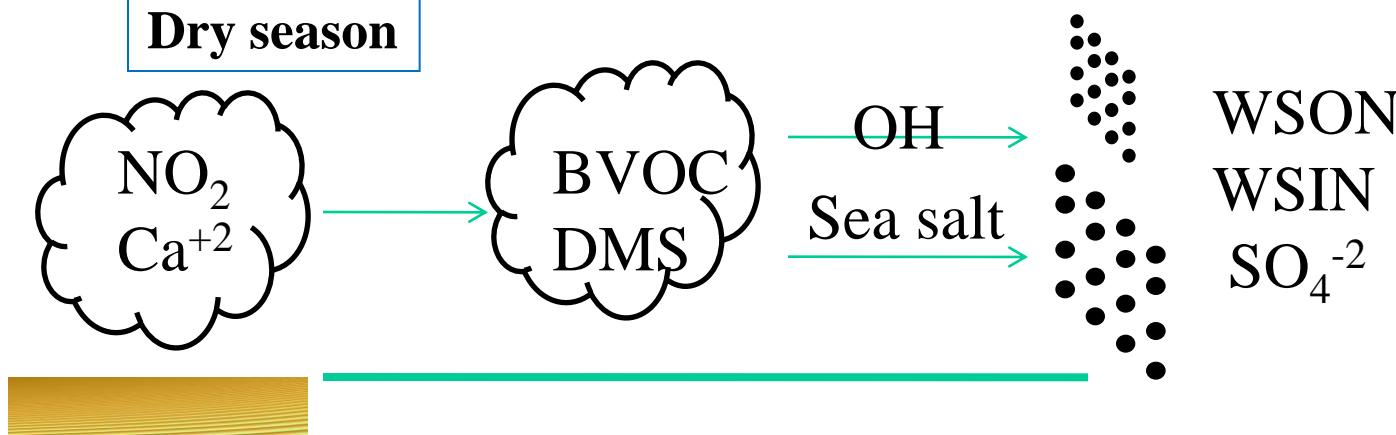
**Correlation is significant at the 0.01 level

Identifying sources of WSIN and WSON

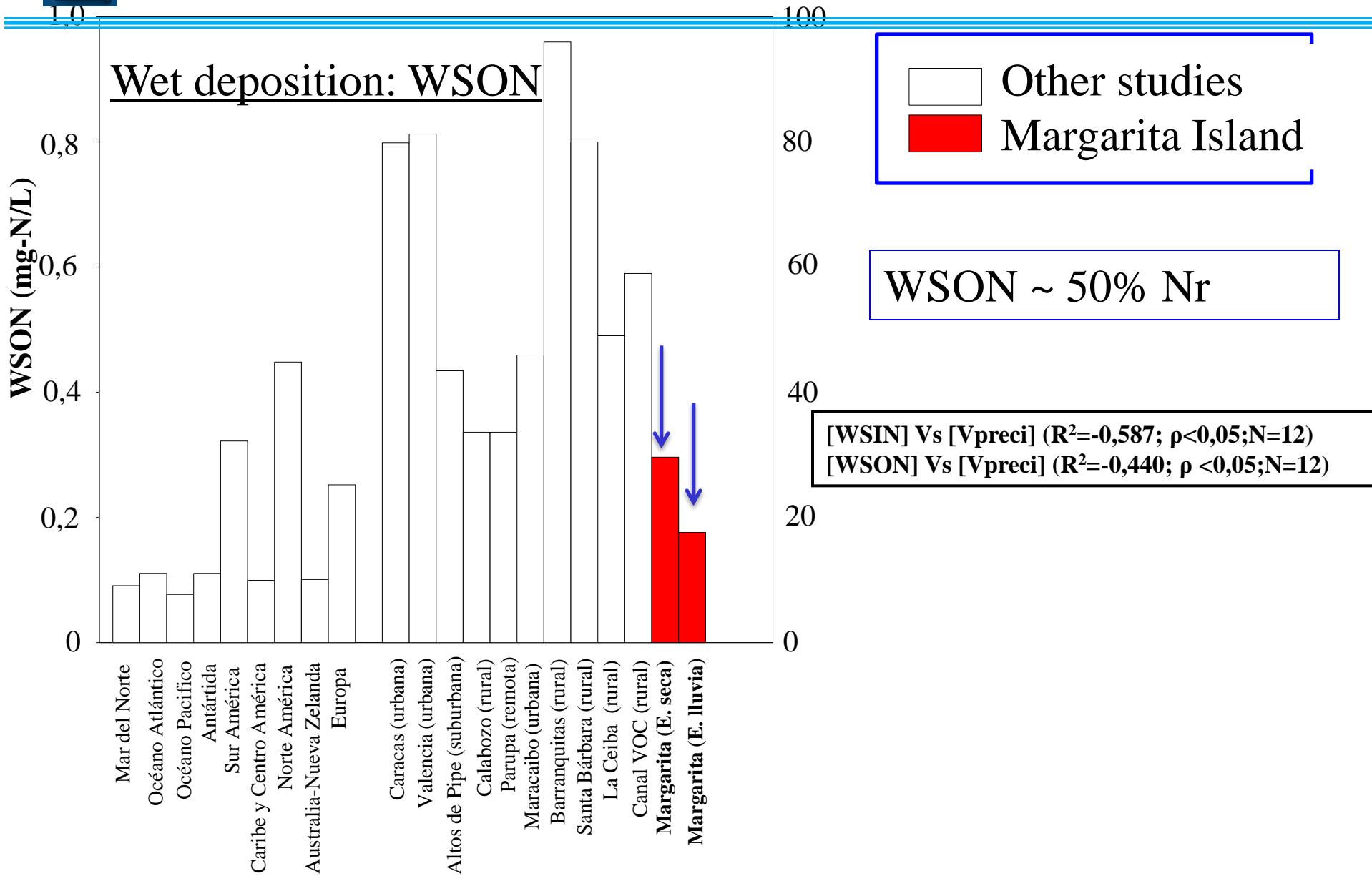
Rainy season



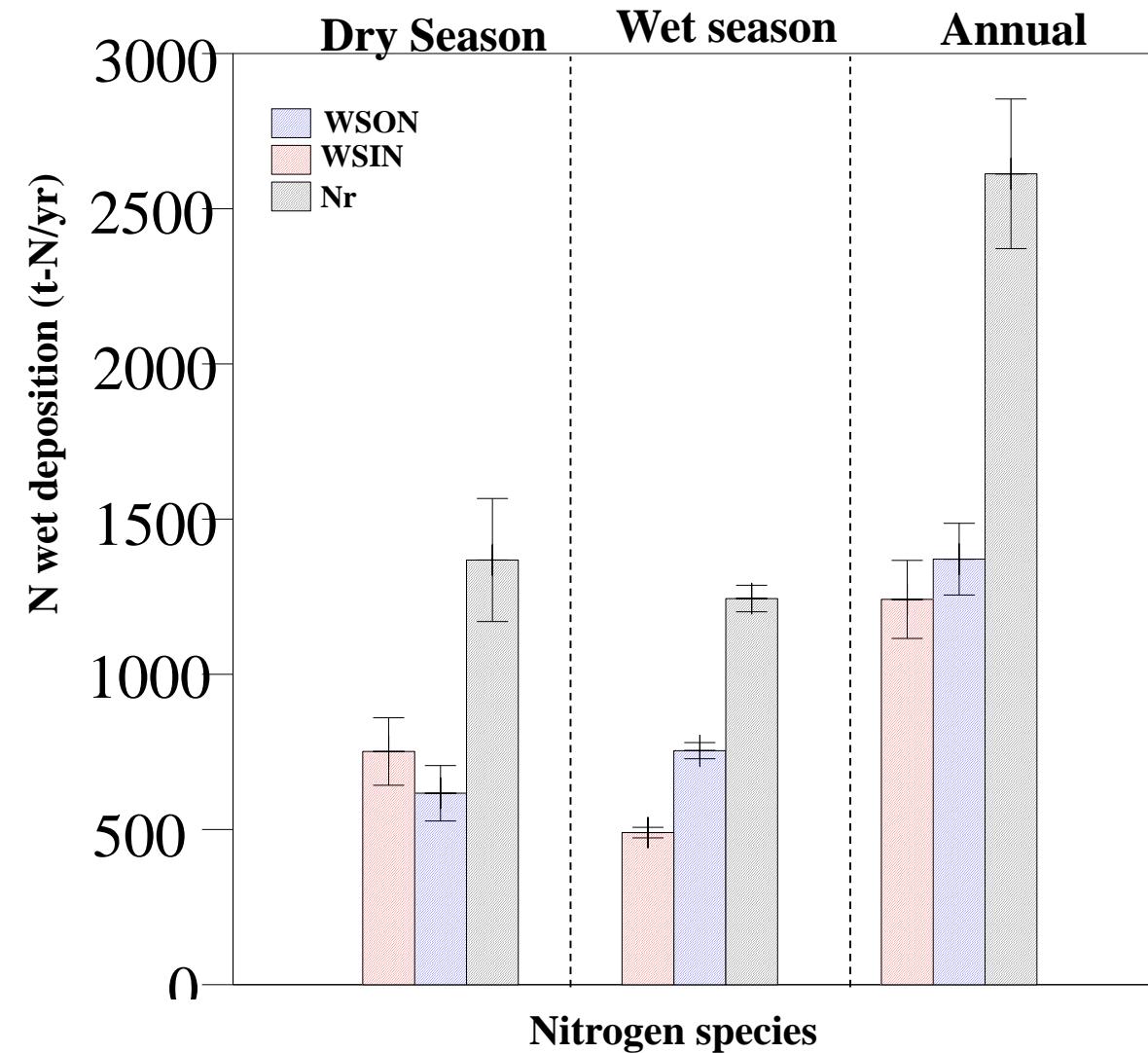
Dry season



Partition of WSIN and WSON



N annual wet deposition (ND_w)



$$ND_w: 2,4 \times 10^3 \text{ t-N/año}$$

No seasonal variation

WSIN: $(48 \pm 5) \%$

WSON: $(53 \pm 4) \%$

N annual dry deposition (ND_d)

$$ND_d = (\sum V_{ni} \times [NS]_{ni}) \times \text{Cariaco basin area}$$

N dry deposition (ND_d)

V_{ni} : constant deposition velocity (cm/s)

$[NS]_{ni}$: N concentration ($\mu\text{g-N/m}^3$)

Cariaco trench basin area: 12600 Km²

Total N atmospheric deposition (ND_t) = ND_w + ND_d

N annual dry deposition (NDd)

Total N atmospheric deposition in the Cariaco Basin

Atmospheric N deposition	T-N/year	%WSIN	%WSON
Dry deposition	$1,2 \times 10^3$	47 ± 22	53 ± 24
Wet deposition	$2,4 \times 10^3$	48 ± 5	53 ± 4
Total deposition	$3,6 \times 10^3$	48 ± 23	53 ± 24

N wet deposition= $(68 \pm 6)\%$
 N dry deposition= $(31 \pm 14)\%$

Comparison of N deposition with satellite and ground based measurements

