Stable isotopes as tracers of anthropogenic nitrogen sources, deposition, and impacts

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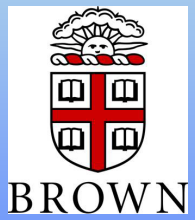
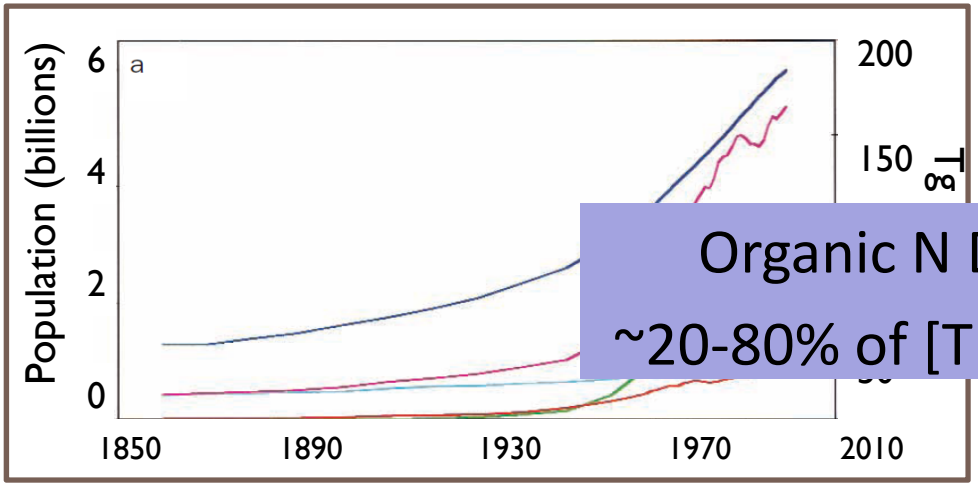


Increased emissions, Increased Deposition

N deposition = NO_3^- + NH_4^+ + Org N

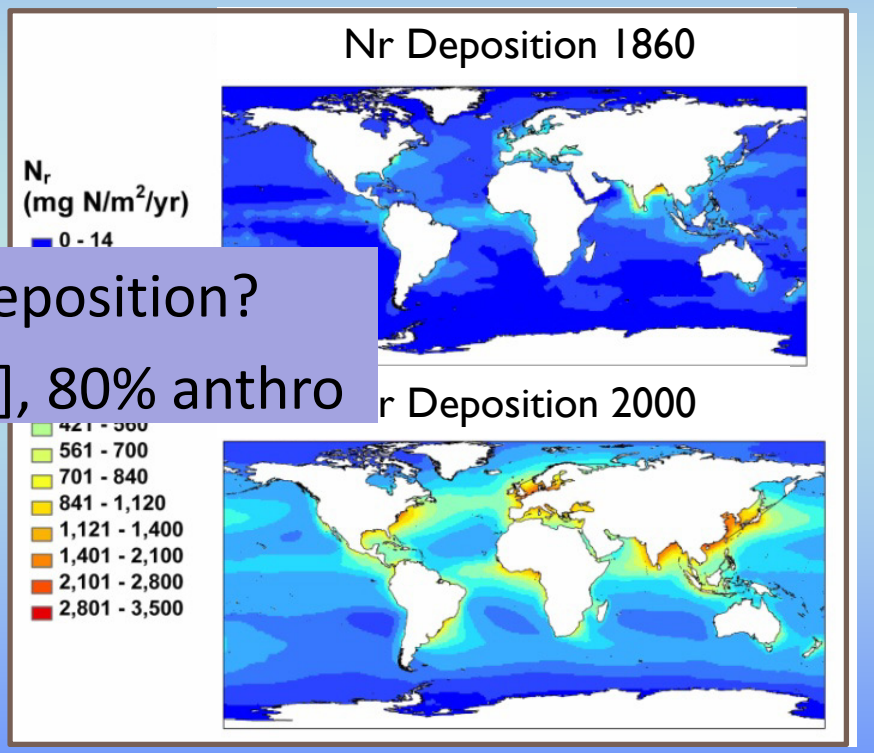
- ↑ Nitrogen oxides (NO_x)
- ↑ Ammonia (NH_3)
- ↑ Nitric Acid/Nitrate (HNO_3/NO_3^-)
- ↑ Ammonium (NH_4^+)



Galloway et al., 2003

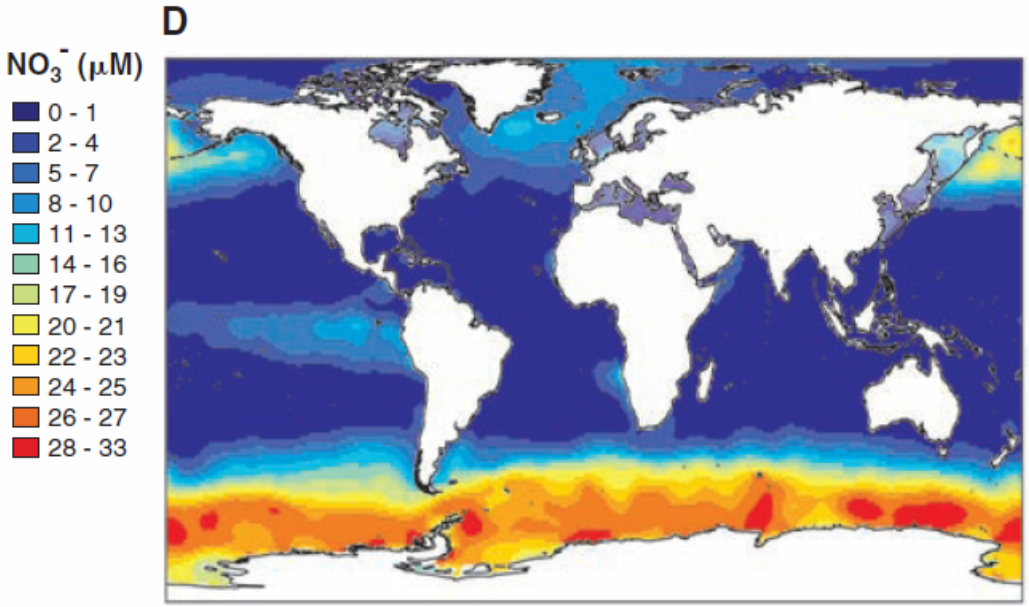
Organic N Deposition?

~20-80% of [TN], 80% anthro



Duce et al., 2008

Implications for the Marine N Cycle



Note: Surface concentrations of NO_3^- are ~μM, NH_4^+ are ~nM

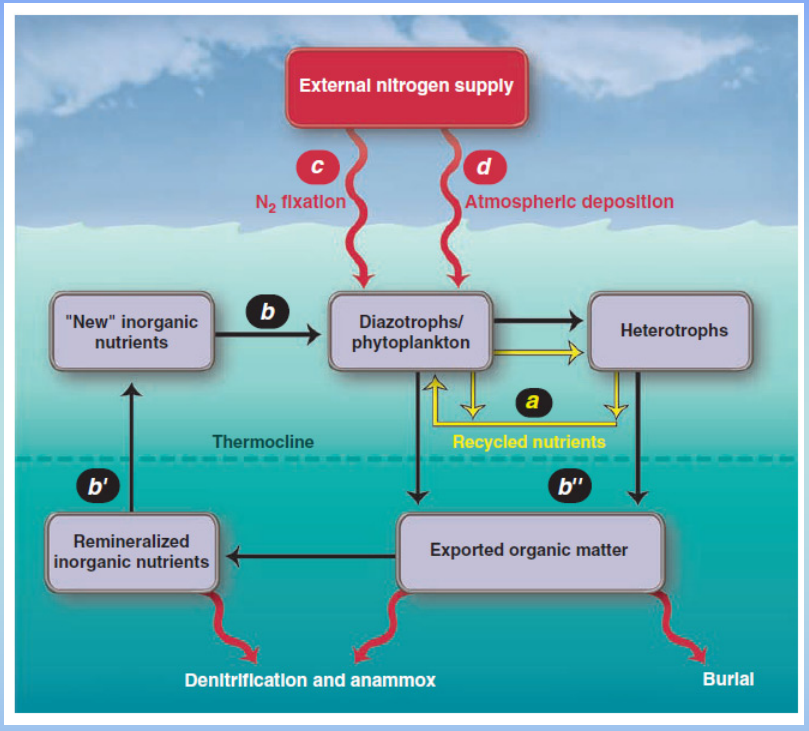
External N Supply to Ocean

Biological N_2 Fixation 60-150 Tg N/yr

Atmospheric Deposition 38-96 Tg N/yr

Duce et al., Science, 2008

Implications for the Marine N Cycle



Duce et al., 2008

Increasing External N Supply to Ocean

- N is a limiting nutrient in the ocean
- Stimulate oceanic productivity (↑CO_2 uptake, ↑POC export)
- Alter surface water alkalinity, pH and inorganic C storage
- Change phytoplankton community composition (++ w/ concomitant nuts deposition)

Predicted Impacts on the Marine N Cycle

Some examples:

- Globally, modern atmospheric input of N accounts for 5.1% of biogenic export from the euphotic zone (up to 7-9% if ON is bioavailable) (Krishnamurthy et al. 2010)

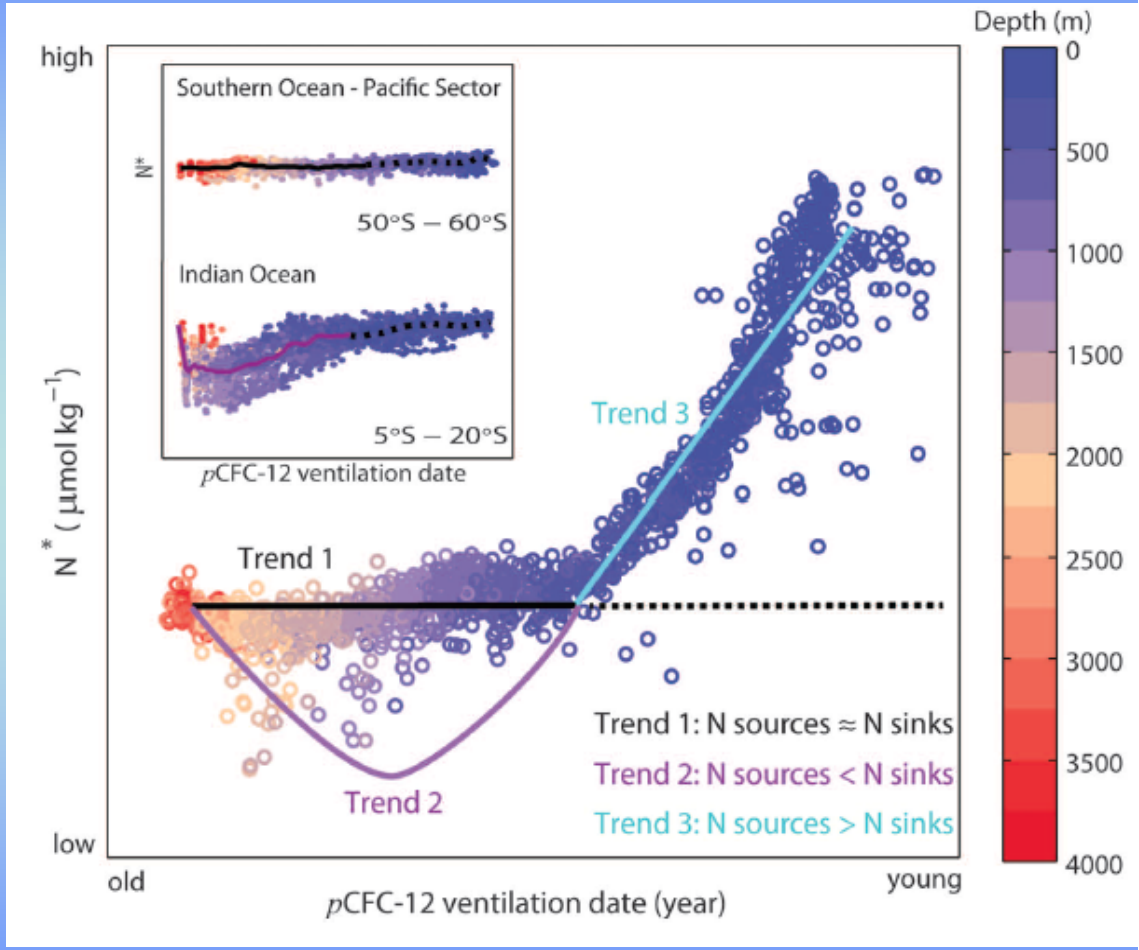
- Regionally, "extra" N input can influence export production by
  >25% (Krishnamurthy et al. 2010)
  ~19% in North Atlantic SG (not including ON) (Zamora et al., 2010)
  4-10% in East China Sea/East Sea (Kim et al., 2011)

- N accumulation observed in NASG thermocline – est. 19% of annual excess N from N dep (Zamora et al., 2010)

- Globally, atmospheric N deposition is responsible for 3% annual new production (Duce et al., 2008)

“Observed” Impacts on the Marine N Cycle

- Number of coastal studies (near Canada, U.S., Western Europe and East Asia) show clear impacts of high rates of N dep
- Open ocean – Increasing N* (mostly in surface layer) across entire NPO (for waters <30 y.o.)

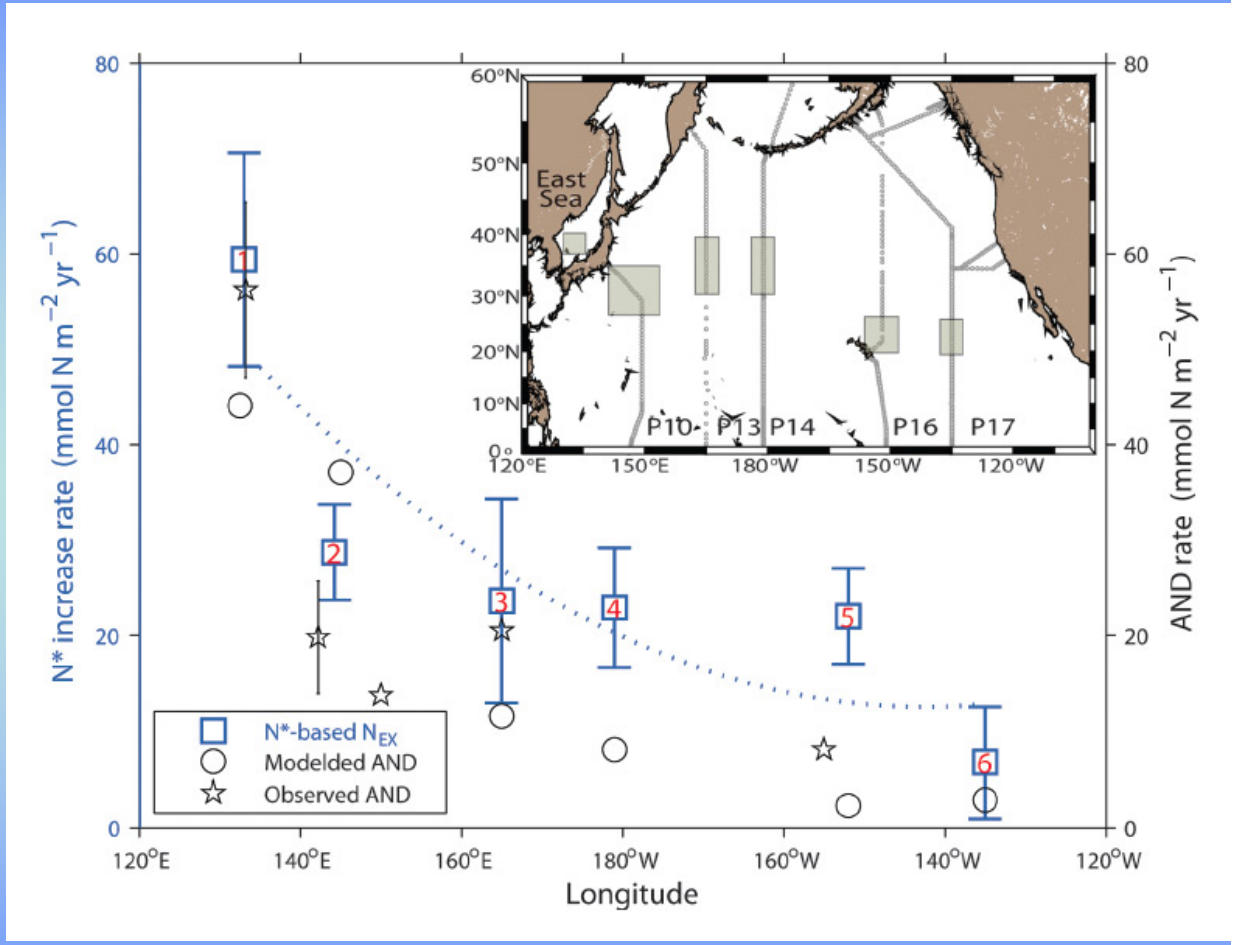


Kim et al., Science, 2014

How well do we understand influence of N dep?

Some key assumptions:

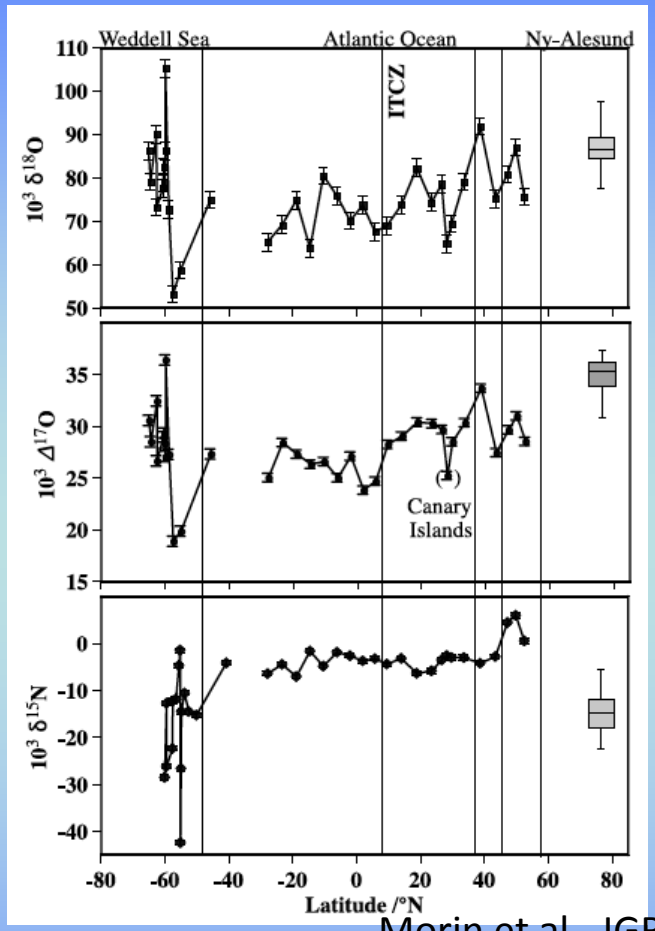
- N deposition is an external, new N input to the open ocean
- Organic N (ON) is typically not included, not bioavailable, or assumed to be a constant (~30%) of total N deposition
- N deposition is assumed to be 80-100% anthropogenic in origin



Kim et al., Science, 2014

How can isotopes contribute?

- *Potential to trace anthropogenic versus natural sources of NO_3^-, NH_4^+, ON (WSON=water-soluble org N)
- Most studies combine transport modeling (origin of air masses) and difference in isotopes to assess most likely sources
- Potential to trace fate of species following deposition
- Most studies via cruise collections of aerosols (+ rain)



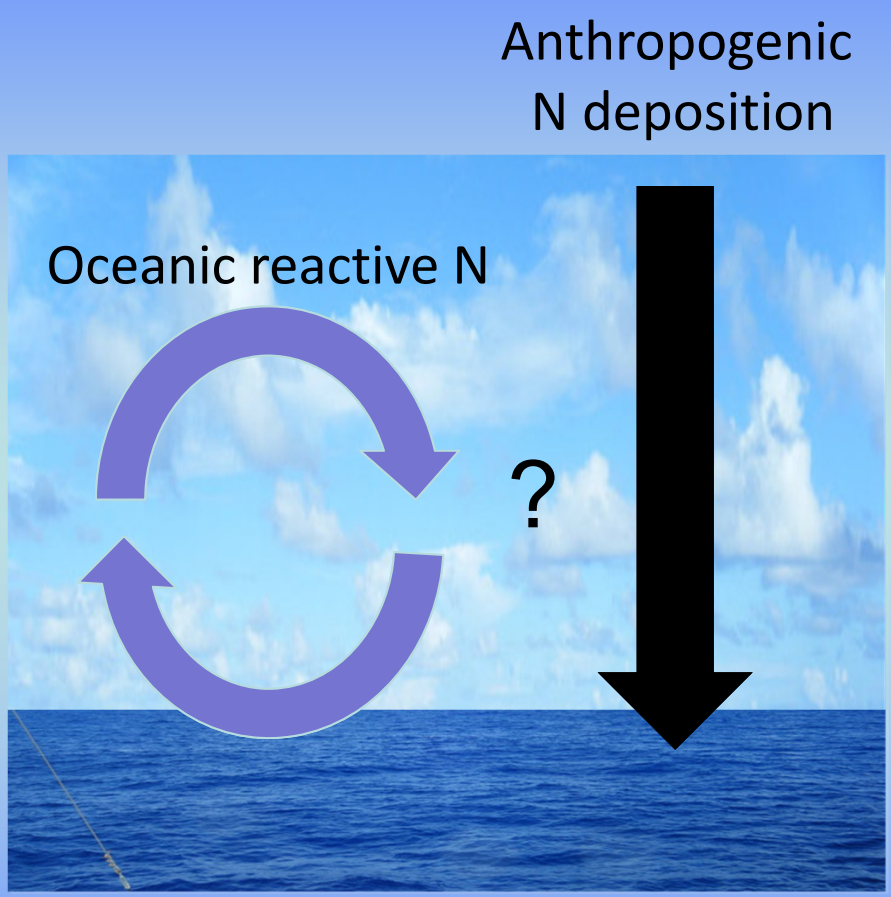
Morin et al., JGR, 2009

**e.g. Lots of important work by Alex Baker, Tim Jickells, Sarah Cornell; More recent work by Scott Wankel, Samuel Morin, Will Vicars*

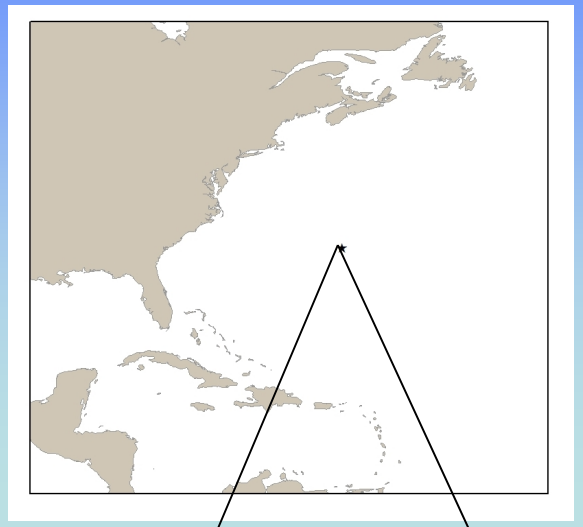
How can isotopes contribute?

<u>18-month study at Bermuda:</u>

- Quantify composition of atmospheric nitrogen deposition to the ocean (incl. NO_3^-, NH_4^+, WSON)
- Investigate sources (anthropogenic vs natural) of atmospheric N deposition
- Is the ocean simply a receptor of anthropogenic N pollution?



Study Location - Bermuda



- Event based rainwater collections
- Weekly, size segregated, sector controlled aerosol collections

Methods

- Major ion concentrations
- Transport Modeling (HYSPLIT Air Mass Back Trajectory)
- Isotopes of NO_3^- ($\delta^{15}N$, $\delta^{18}O$, $\Delta^{17}O$)*

  Denitrifier method
- $\delta^{15}N$ NH_4^+

  Hypobromite/azide method

$$*\delta^{15}N = \frac{[(^{15}N/^{14}N)_{sample} - 1]}{(^{15}N/^{14}N)_{air\text{-}N2}} \times 1000‰$$

$$\delta^{18}O = \frac{[(^{18}O/^{16}O)_{sample} - 1]}{(^{18}O/^{16}O)_{VSMOW}} \times 1000‰$$

$$\Delta^{17}O = \delta^{17}O - 0.5 \times \delta^{18}O$$

- Box model of NH_3/NH_4^+ in seawater and $NH_{3(g)}$ and $NH_4^+{}_{(p)}$ in atmosphere
- Organic N chemical composition

  Bulk $\delta^{15}N$ -WSON

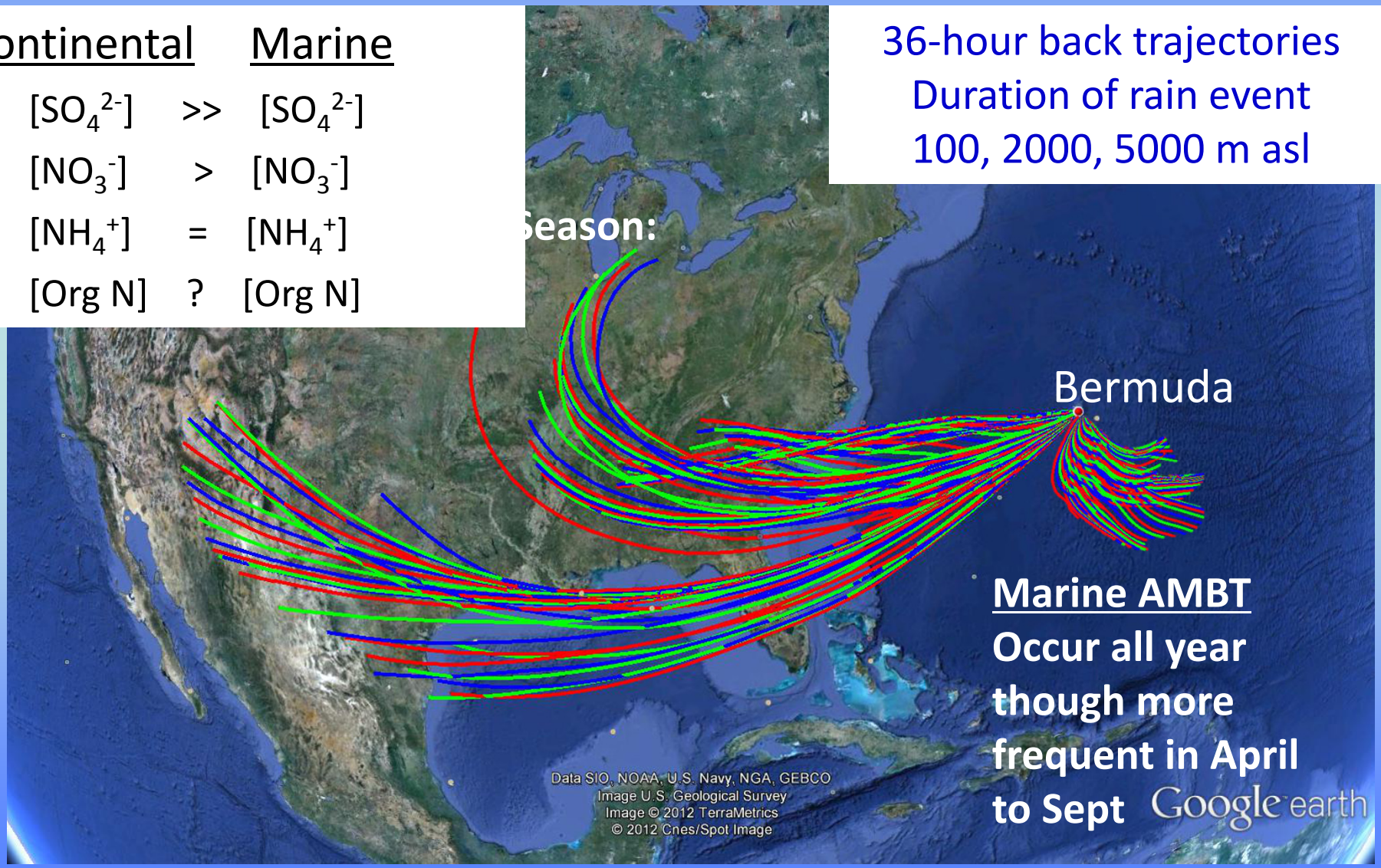
  Ultra-high resolution ESI FT-ICR MS

Transport to Bermuda

Two distinct air mass back trajectory (AMBT) regimes

Continental		Marine
$[SO_4^{2-}]$	>>	$[SO_4^{2-}]$
$[NO_3^-]$	>	$[NO_3^-]$
$[NH_4^+]$	=	$[NH_4^+]$
[Org N]	?	[Org N]

36-hour back trajectories
Duration of rain event
100, 2000, 5000 m asl



Take Home Points – 3 N Pools

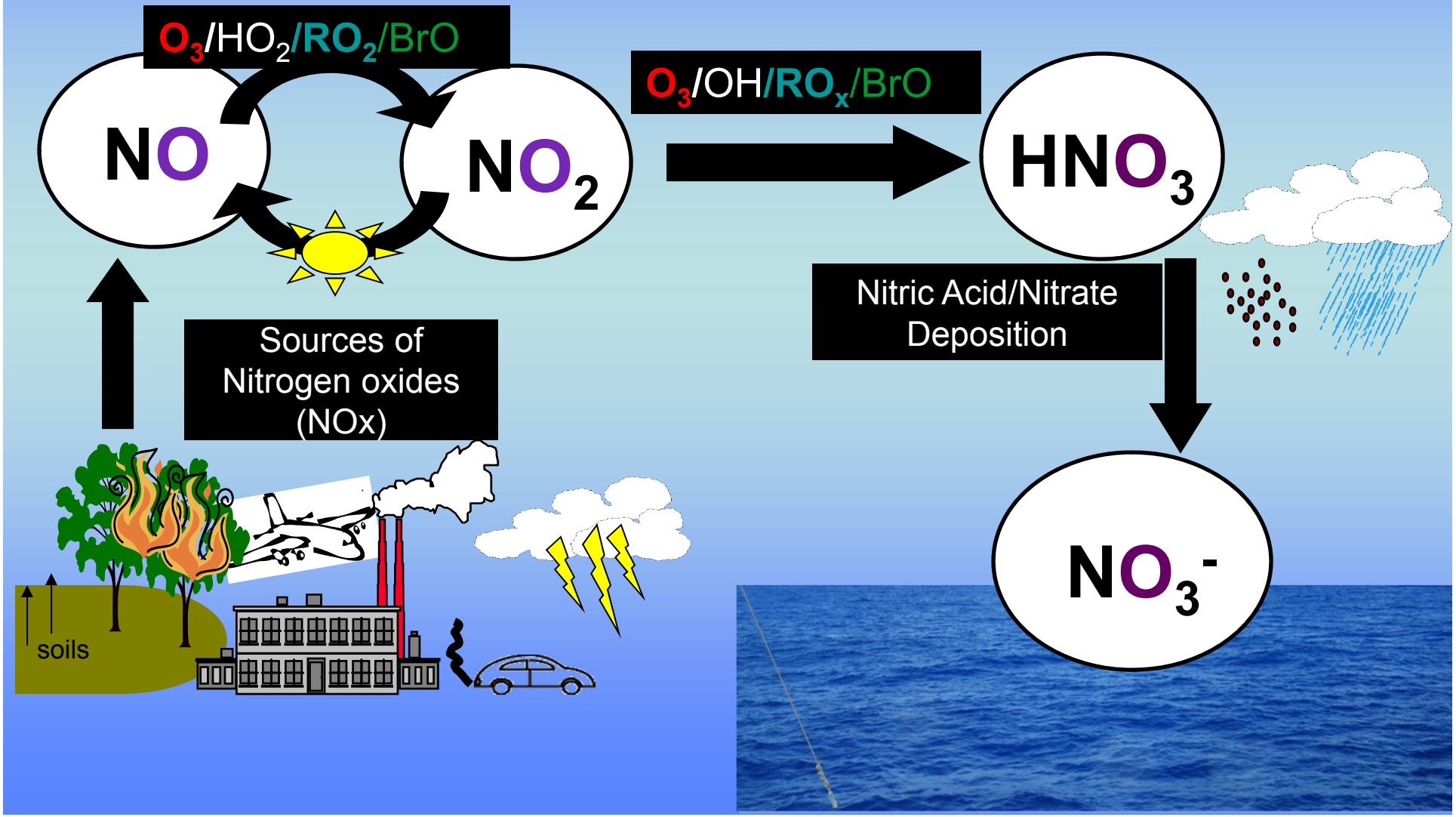
- The concentration and isotopes of **NO_3^-** (rain/aerosol) are clearly influenced by continental versus marine **sources and chemistry**
- Based upon the concentration and isotopes of **NH_4^+**, and a box model, the best explanation for the observations is a **marine source** of NH_3 all year round
- The composition of water soluble organic N (WSON) in rainwater and aerosol is very different. **WSON** represents >700 compounds in each sample and should be largely **bioavailable**.
- **WSON** in **rainwater** is a combination of **anthropogenic** emissions and marine sources+chemistry. **WSON** in **aerosols** are likely derived only from the **marine** system.

Take Home Points – 3 N Pools

- **NO_3^- (rain/aerosol)**: Anthropogenic and natural sources, see an influence of polluted + marine boundary layer chemistry
- **NH_4^+ (rain)**: A marine source of NH_3 all year round
- **WSON (rain)**: Bioavailable, combination of anthropogenic emissions and marine sources+chemistry
- **WSON** (**aerosols)**: Bioavailable, sourced from the marine system.

This work suggests that the ocean influences and even contributes significantly to the reactive N cycle in the marine atmosphere – it is not simply a passive recipient of external N deposition

Atmospheric NO_3^- Sources and Chemistry

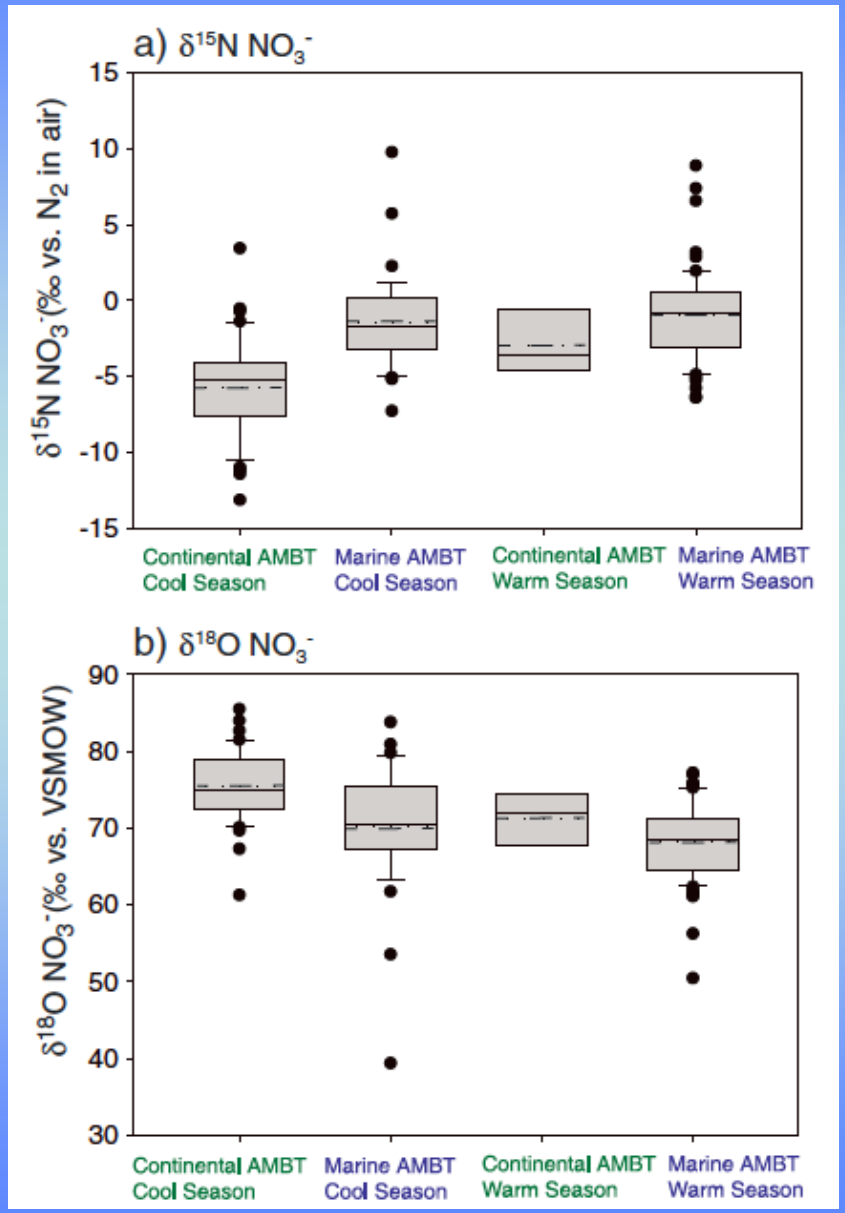


Rainwater $\delta^{15}N\text{-}NO_3^-$

Altieri et al., JGR, 2013

- **Continental air mass back trajectories (AMBT)**
  - Occur in cool season (October to March)
  - High nitrate concentrations
  - Low $\delta^{15}N$ reflects anthropogenic sources and the influence of anthro NO_x + marine halogen chemistry
  - High $\delta^{18}O$ reflects greater influence of ozone-related oxidant chemistry

(see also Gobel et al., GRL, 2013 for aerosol results and interpretation)

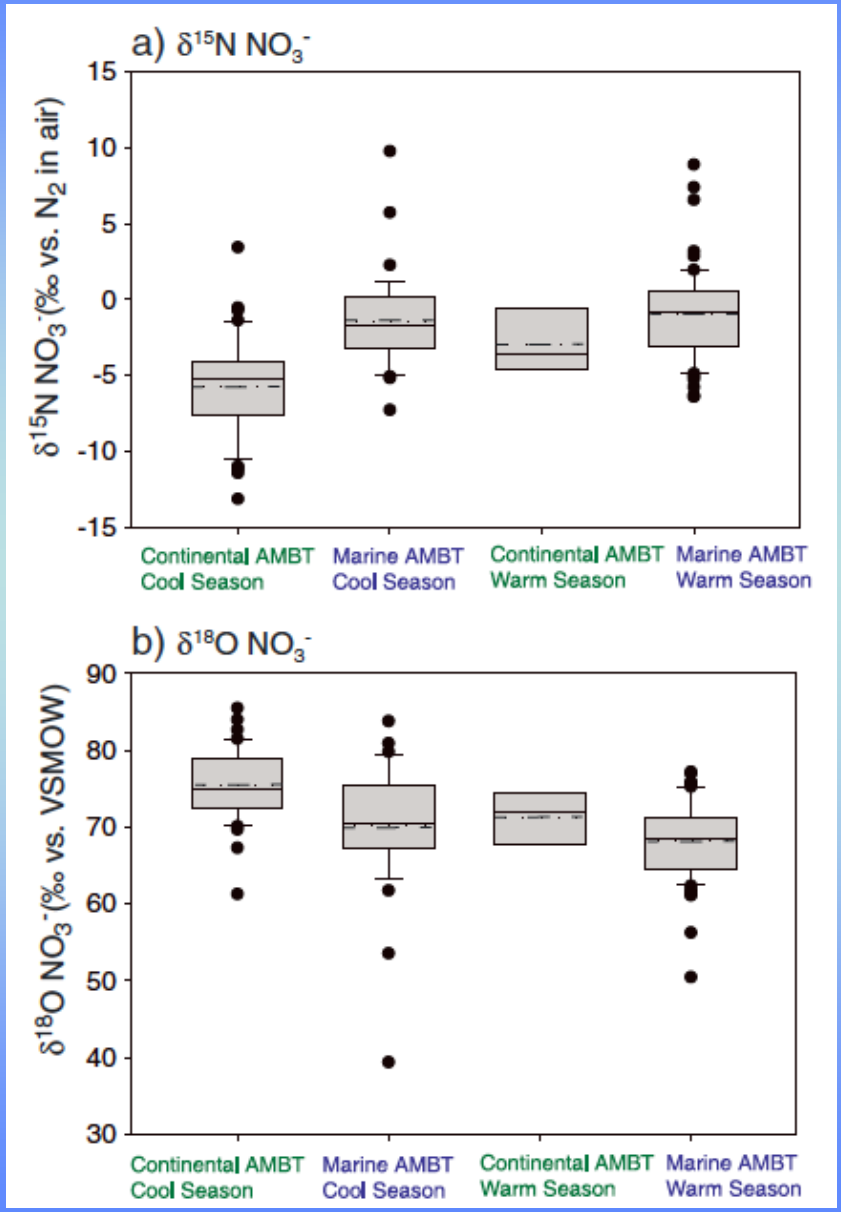


Rainwater $\delta^{15}N\text{-}NO_3^-$

Altieri et al., JGR, 2013

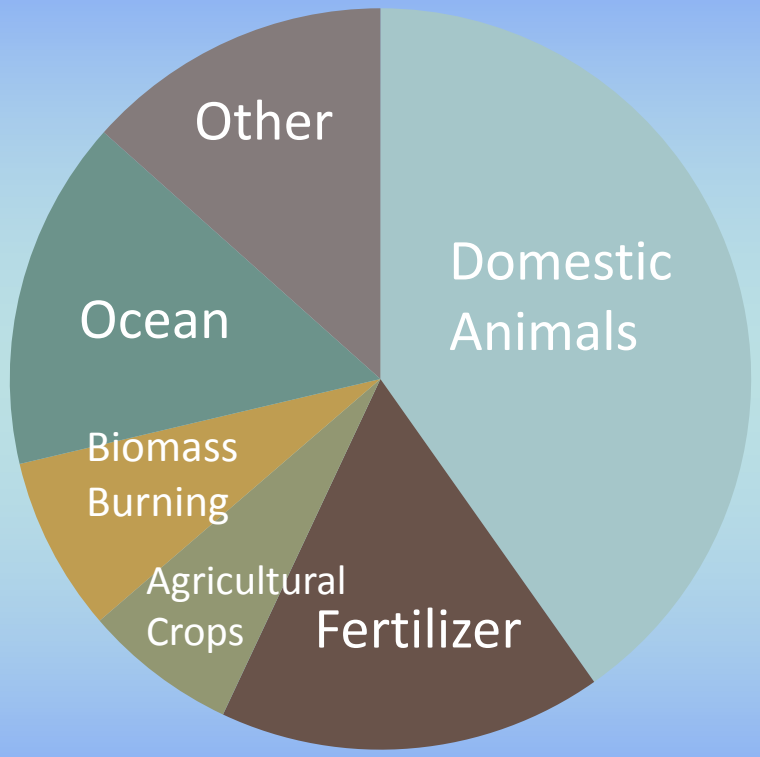
- **Marine AMBT**
  - Occur all year
  - Lower nitrate concentrations
  - Higher $\delta^{15}N$ likely reflects influence of lightning NO_x ($\delta^{15}N \approx 0$) and PAN sourced NO_x (?)
  - Lower $\delta^{18}O$ reflects different atmospheric chemistry (OH-related production dilutes high ozone signal)

- NO_3^- dep. contributes a low-$\delta^{15}N$ signal to the surface ocean which can influence geochemical estimates of N-fixation (Knapp et al., 2009; Wankel et al., 2009; Baker et al., 2007)



Ammonia Sources

Global Atmospheric NH_3 Sources



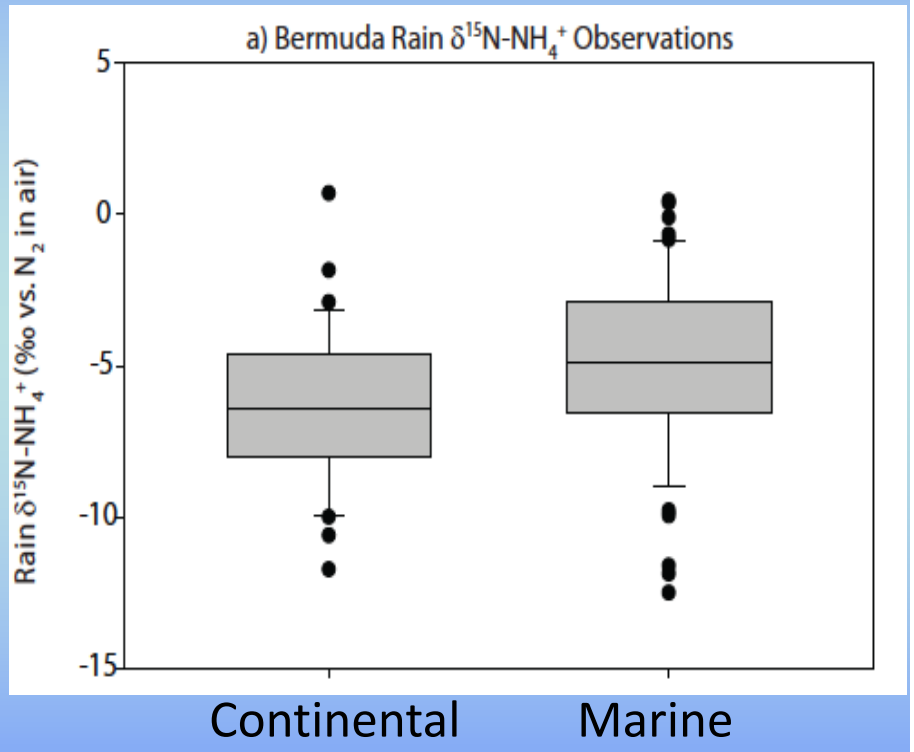
Erisman et al., 2007

- Large uncertainties in NH_3 emissions
  - Few ground based observations and fewer atmospheric measurements
- First satellite estimates in 2009 Clarisse et al., 2009
- Today, ocean is considered a net sink for NH_3, pre-industrial times considered a net source Fowler et al. 2013; Galloway et al., 2003

Rainwater Ammonium (NH_4^+)

- Marine and Continental AMBT:
  - Concentrations not statistically different
    - VWA Marine AMBT = 6.0±4.2 µM
    - VWA Continental AMBT = 5.9±3.2 µM
  - Isotopic composition not statistically different

Altieri et al., GBC, 2014



Hypotheses

The lack of a clear trajectory or seasonal trend in $\delta^{15}N\text{-}NH_4^+$ could be due to:

1) a continental/anthropogenic source overwhelms the regional budget all year-round

2) the source signal of marine and continental ammonium have the same isotopic signature (or the source signal plus isotopic fractionation during transport)

3) a local marine source dominating the NH_4^+ in Bermuda rainwater

Altieri et al., GBC, 2014

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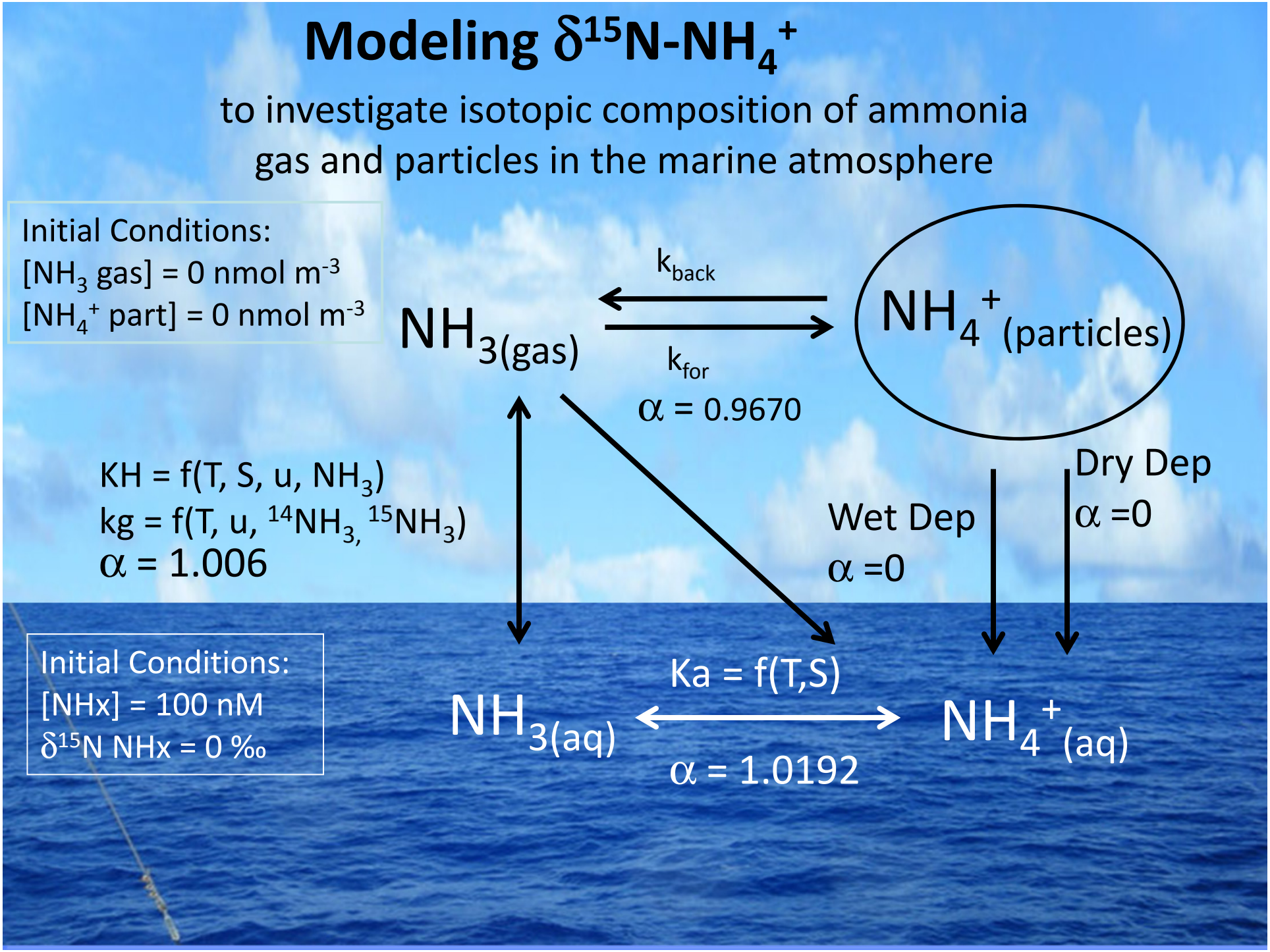
Altieri et al., GBC, 2014

Modeling $\delta^{15}N\text{-}NH_4^+$

to investigate isotopic composition of ammonia gas and particles in the marine atmosphere

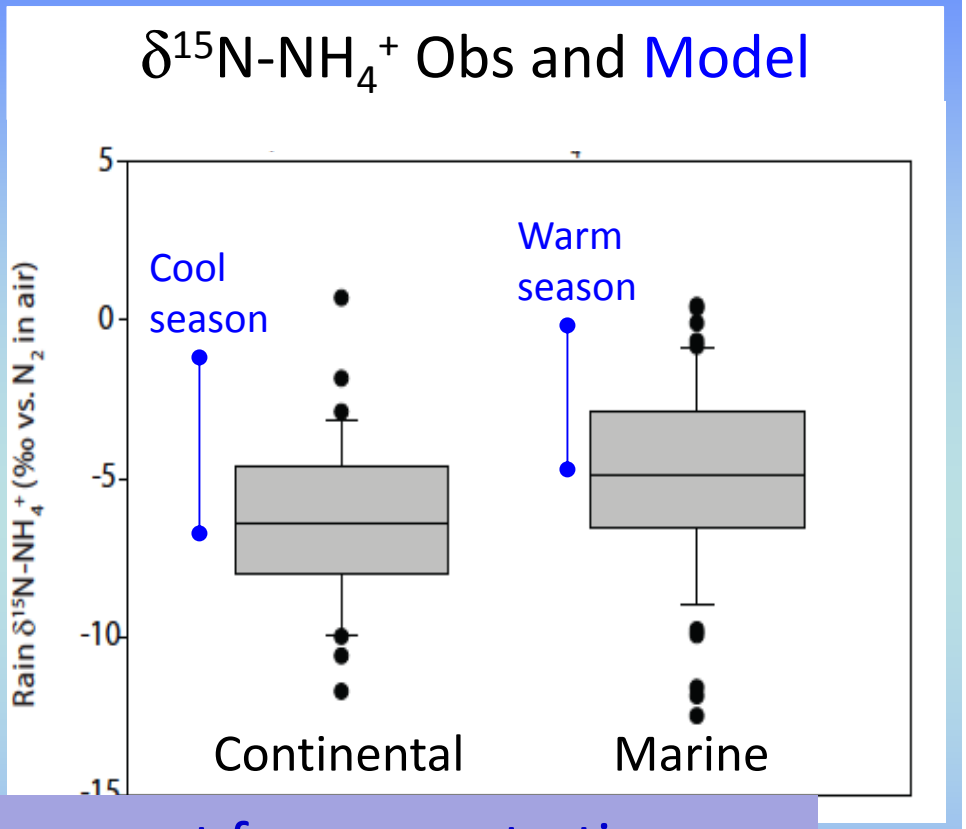
Initial Conditions:
$[NH_3$ gas$] = 0$ nmol m^{-3}
$[NH_4^+$ part$] = 0$ nmol m^{-3}



Model Results and Implication

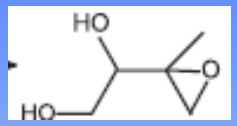
Altieri et al., GBC, 2014

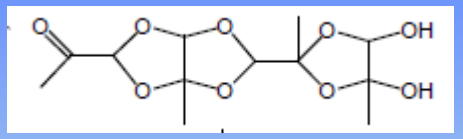
- Assume scavenging efficiency of 100% for $NH_{3(g)}$ and 50-100% for $NH_4^+{}_{(p)}$
  - Predicted range in seasonal concentrations and isotope values matches observed values well and fits with marine aerosol $\delta^{15}N\text{-}NH_4^+$ observations (Jickells et al., 2003)

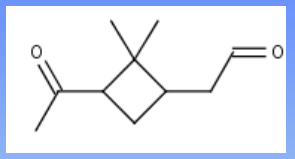


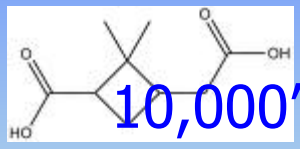
Ocean emissions of NH_3 can account for concentrations and isotopic composition of rainwater ammonium in Bermuda all year regardless of AMBT

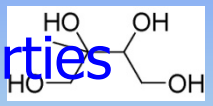
Organic N Sources



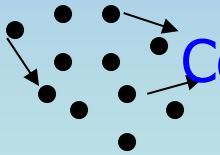








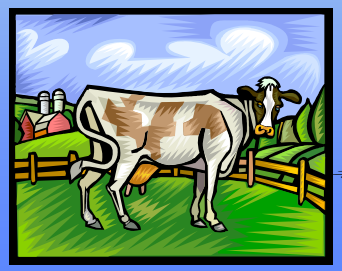
10,000's of (unidentified?) compounds with variable properties



Continuing Oxidation/Partitioning in the Atmosphere

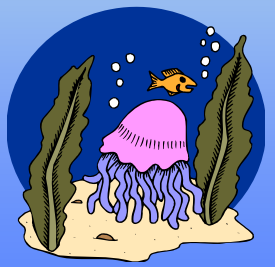
Secondary Aerosols

Uncertain Formation (Missing sources? Poorly understood processes?)



Aerosols
(particulates – PM)

Emissions
(Primary PM)



Organic N Observations

Table 1 Aerosol water-soluble ON (WSON) from selected sites that are remote from local influences to illustrate large-scale patterns of concentrations.

site	WSON (nmol m^{-3})	references
Taiwan	76	[10]
NE India/Bay of Bengal	35, 46	[24]
Northern California	16	[42]
Crete	12	[26]
Delaware	7	[11]
North Atlantic Saharan outflow	14.5	[34]
North Atlantic remote	5.3	[34]
South Atlantic	6	[34]
Miami	3	[14]
Southern Ocean	1–3	[20,34]
North Pacific remote	1.2, 3.3	[19,35]
Barbados	1.5	[14]

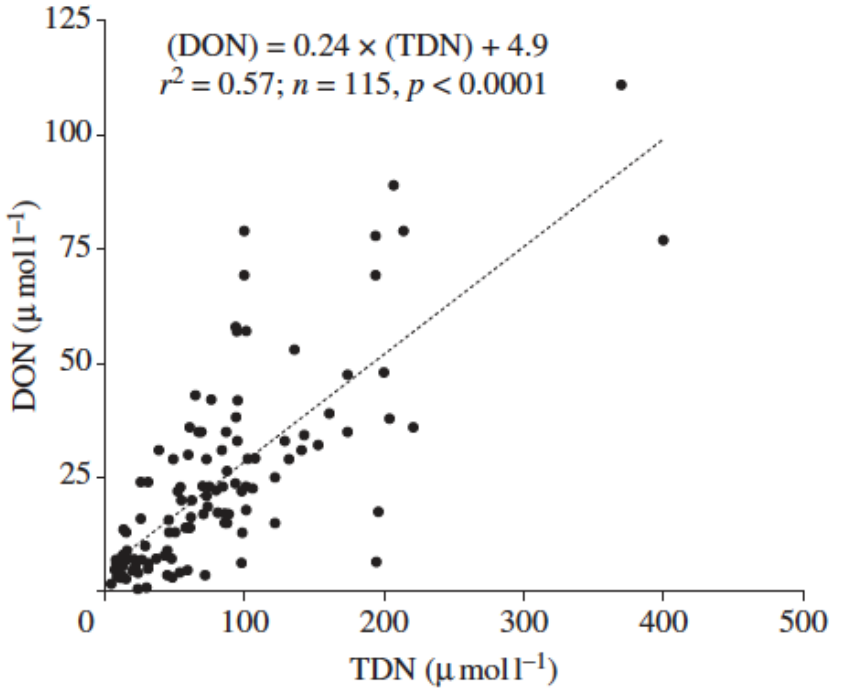
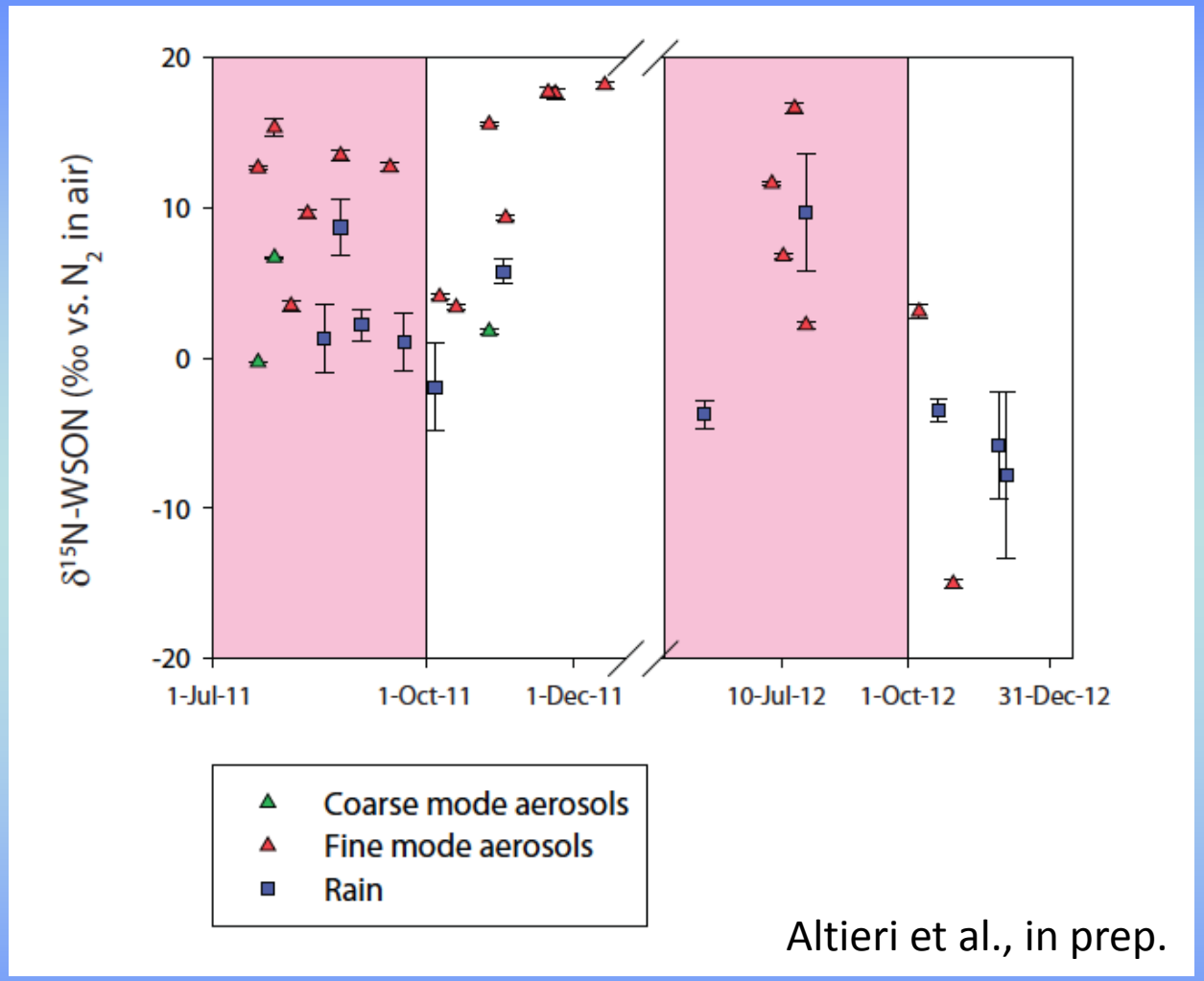


Figure 1. Plot of published long-term average rainwater DON and total dissolved nitrogen (TDN) concentrations from sites around the world, based on the data compilations of references [6,9,23] induding a best fit correlation.

Jickells et al., Phil Trans Soc B, 2013

Rain and Aerosol δ^{15}N-WSON

- δ^{15}N-WSON ranges from -15.8 to 19.7‰
- Aerosol and rain show very different δ^{15}N on average
- No distinct relationship with AMBT



Altieri et al., in prep.

- Continental $AMBT_{rain}$ = 2.6 ± 9‰, $AMBT_{aerosol}$ = 10.5 ± 4.9 ‰
- Marine $AMBT_{rain}$ = -0.4 ± 4.6‰ , $AMBT_{aerosol}$ = 15.9 ± 26.3‰

Organic N in Aerosol

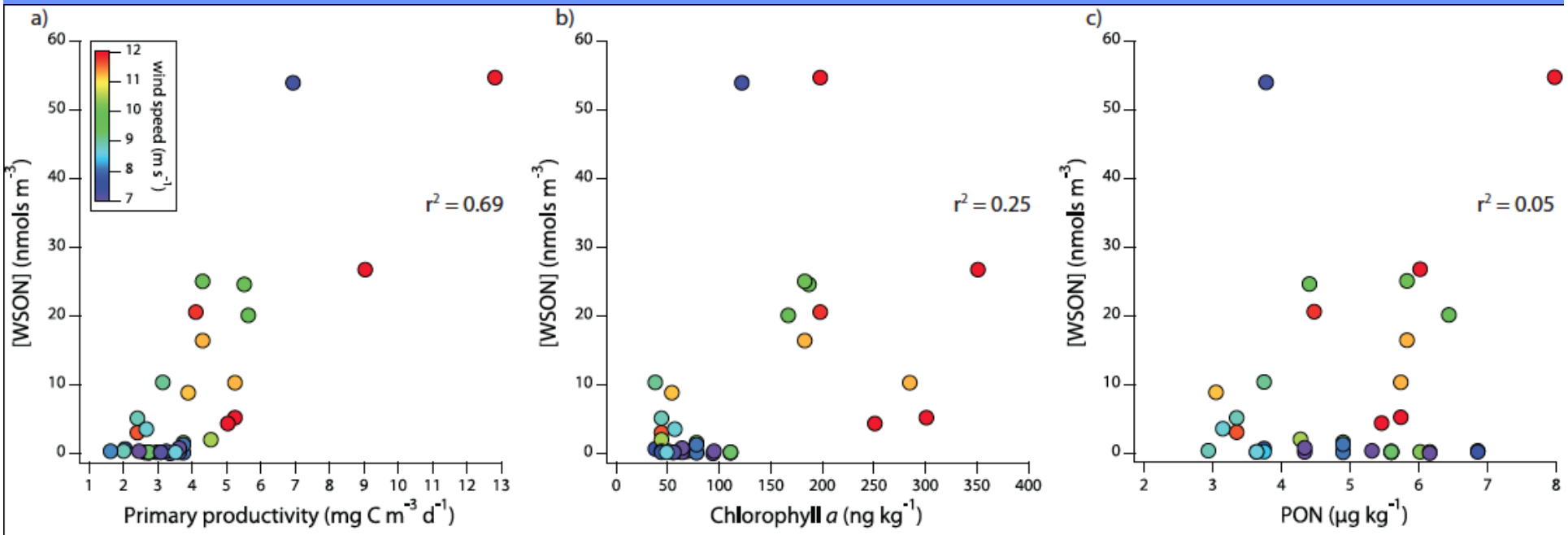


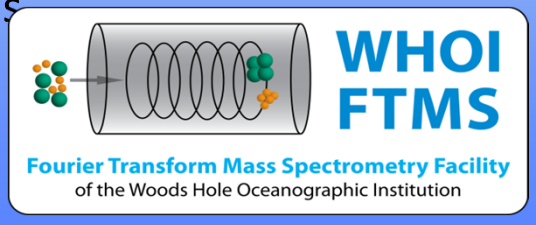
Figure 1. Aerosol [WSON] as a function of a) gross primary production (GPP), b) chlorophyll-a concentration, and c) particulate organic nitrogen (PON) concentration in the surface ocean (i.e., 0-10 m) at BATS. The wind speeds indicated by the color shading are the average of the daily recordings taken by the Bermuda Weather Service (www.weather.bm) for the time period during which the aerosol sampler was deployed (one week).

- Aerosol WSON correlated with SST (-), Wind Speed (+), GPP
- **Hypothesis: aerosol organic N derives primarily from surface ocean biology** (with wind speed providing physical mechanism)

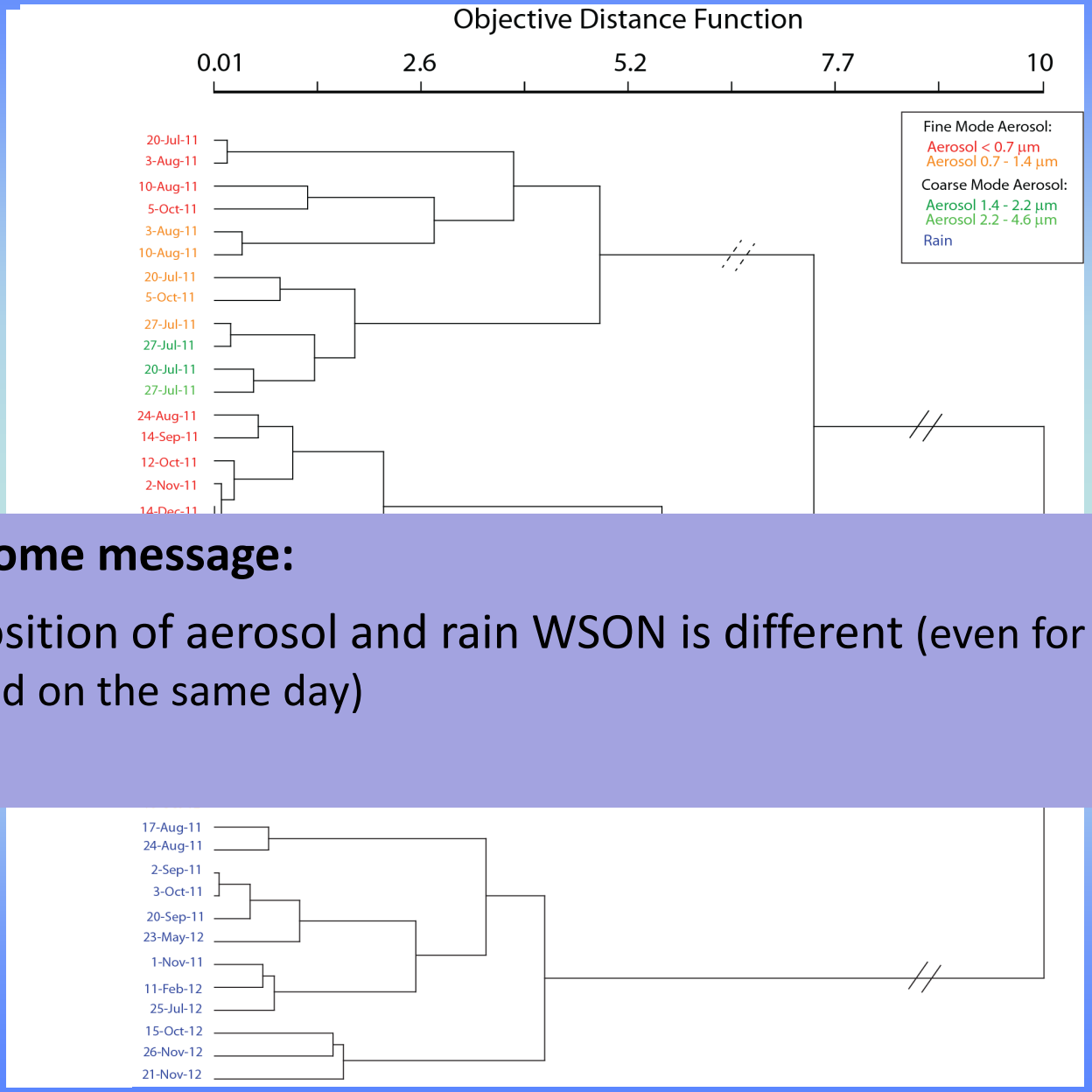
Methods: Mass Spectrometry, Cluster analysis and NMS

- Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
  - Provides molecular weight info as *m/z* (1000s of organic N compounds)
  - Non-quantitative, ultra-high resolution
  - 42 samples → 12 rain and 30 aerosols
  - Average of 747 N containing compounds in each sample over mass range 50-500 Da, smallest # in sample = 465, max = 1245
- Hierarchical cluster analysis:
  - Calculate a matrix of distances or similarities among a set of items in multidimensional space, merge groups
  - Minimize the number of groups, maximize information retained
- NMS (non-metric multidimensional scaling): ordination method
  - Good for non-normal data
  - Doesn't assume linear relationships among variables

Following from Kujawinski et al., 2009



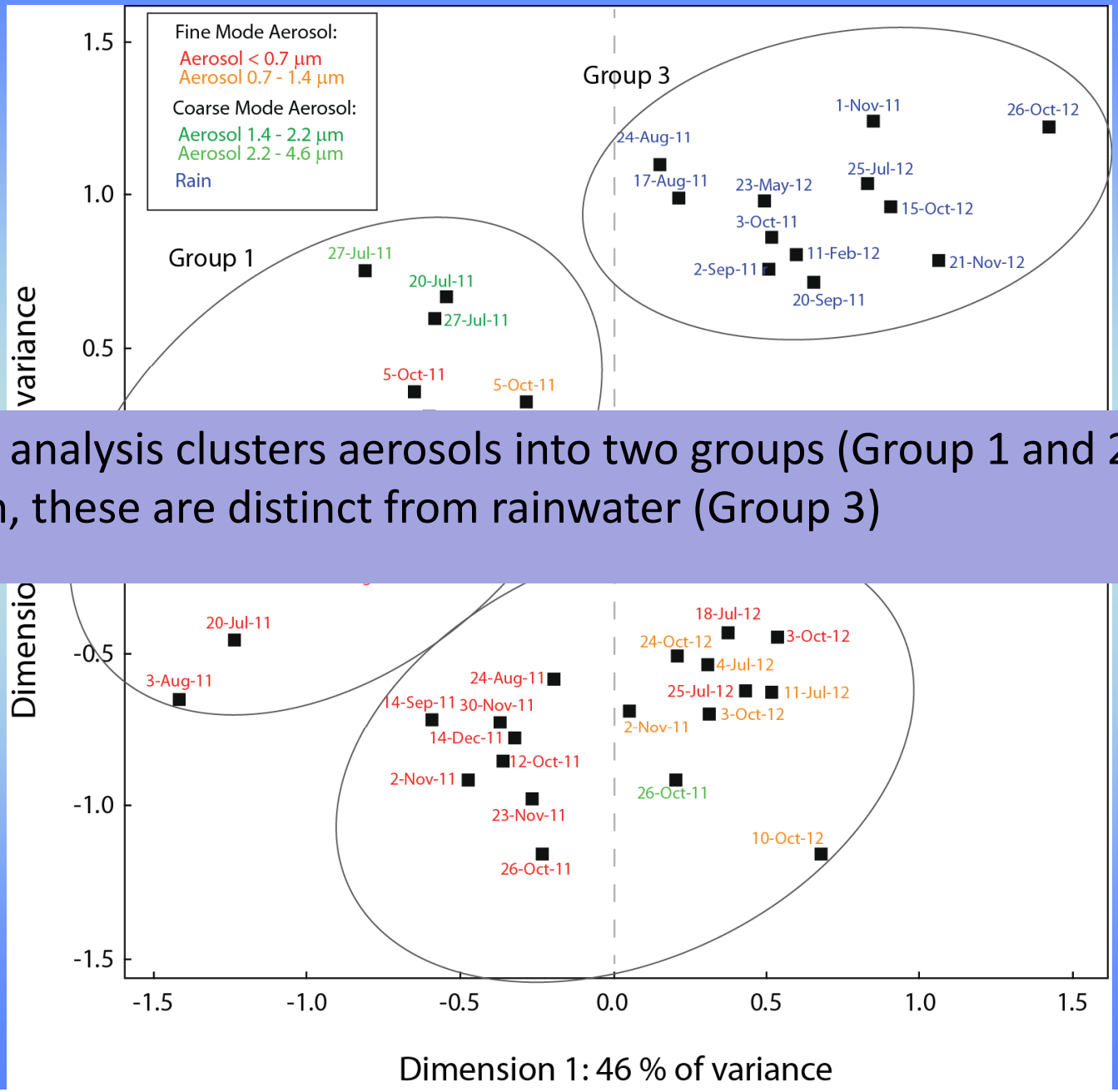
Cluster Analysis: Rain and Aerosol



Take home message:

Composition of aerosol and rain WSON is different (even for samples collected on the same day)

NMS Analysis: Rain v Aerosol



NMS analysis clusters aerosols into two groups (Group 1 and 2), and again, these are distinct from rainwater (Group 3)

Insights: Rain v Aerosol WSON

- Composition of aerosol and rain WSON is different – even for samples collected on the same day

- Aerosols are clustered into two groups

  Differences driven by date, [NH_4^+], [nss-SO_4^{2-}], δ^{15}N-NH_4^+

  Fits with Rinaldi et al. 2010 SOA formation framework

- **"WSON in rain is like nitrate, WSON in aerosol is like NH_4^+"**

  Fits with hypothesis (ocean as a source), and raises two potential

Aerosol WSON formed in marine atmosphere,
via marine biogenic sources

- Or oceanic emissions of organics have N and are emitted with NH_3?

Implications for anthropogenic N deposition

- Duce et al. 2008 (Kanakidou et al. 2012, Jickells et al., 2013) estimates:
  - 80% N deposition to the ocean is anthropogenic
  - 30% (26%, 25%) is organic N

- 18 months of sampling at Bermuda
  - Wet deposition flux is 45% NH_4^+, 41% NO_3^-, 14% WSON
  - 30% anthropogenic
  - Dry deposition flux is 15% NH_4^+, 76% NO , 9% WSON
  - 33% anthropogenic

Revised estimates from our work:

- **32% total N deposition at Bermuda is anthropogenic**
- **11% is organic N**

Deposition fluxes to the ocean are typically interpreted simply as N inputs, whereas the Bermuda work suggests that the ocean influences and (if results are scalable) even contributes significantly to the reactive N cycle in the marine atmosphere

Broader conclusions/observations/questions

- It matters where the deposition occurs and what is deposited (coastal versus open ocean, N-limited vs P-limited, community structure, circulation (subduction/ventilation)
- We have a lot more data on NO_3^- deposition than NH_4^+ and WSON
- Isotopes tell us more than concentration alone, but it's not yet quantitative in terms of sources (still useful esp. in combination with others methods)
- Are Bermuda results scalable? Need similar studies in other locations + modeling based on conclusions regarding marine source emissions

- Where is all the N going? (advection, buried, denitrified?)
- What is the fate of WSON in the ocean?
- How big of an influence does non-Redfield ratio stoichiometry have on conclusions drawn regarding N*?
- Is there a way to quantify the interaction of N deposition and N-fixation ? (could/would decreases in N-fixation offset impact of increasing N-deposition?)

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