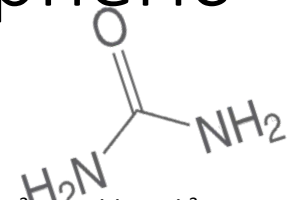
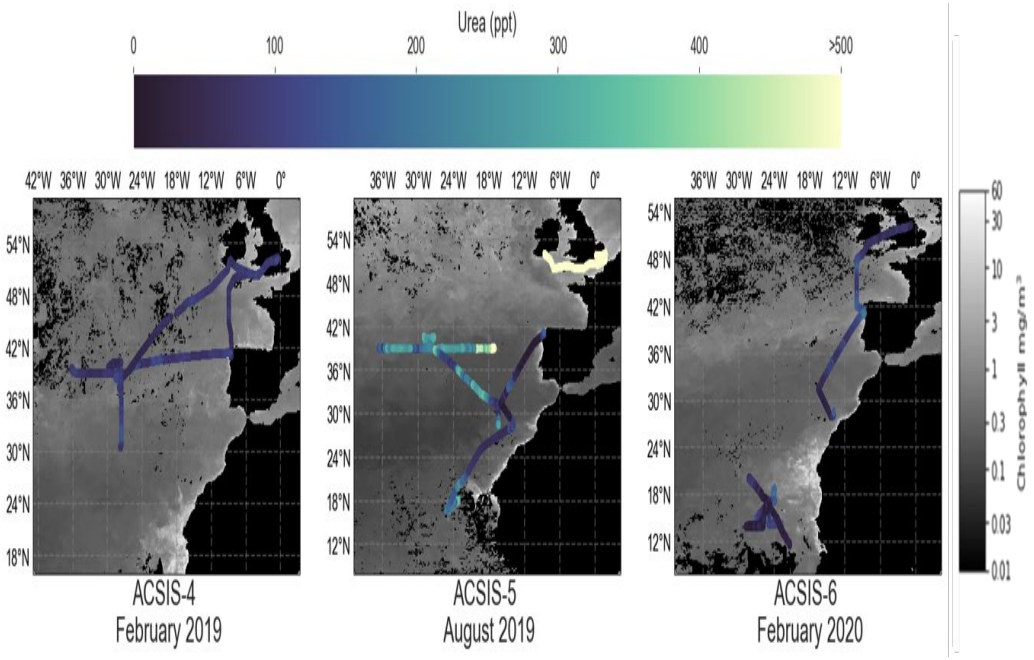
Natural Environment Research Council

The University of Manchester

Airborne observations over the North Atlantic Ocean reveal urea is a missing component of atmospheric reduced nitrogen





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Iodide ion chemical ionisation mass spectrometer (I-CIMS)

Main Species Measured:

Halogens (e.g. BrO, BrOH, ClO, ClOH, $ClNO_2$, Cl_2)

- Impact air quality and ozone formation
- Important oxidizers for tropospheric chemistry

Biomass Burning Markers (e.g. HCN/HCNO)

- Impact air quality
- Sources of greenhouse gases

Organic Acids (e.g. Acetic/Lactic/Formic Acid)

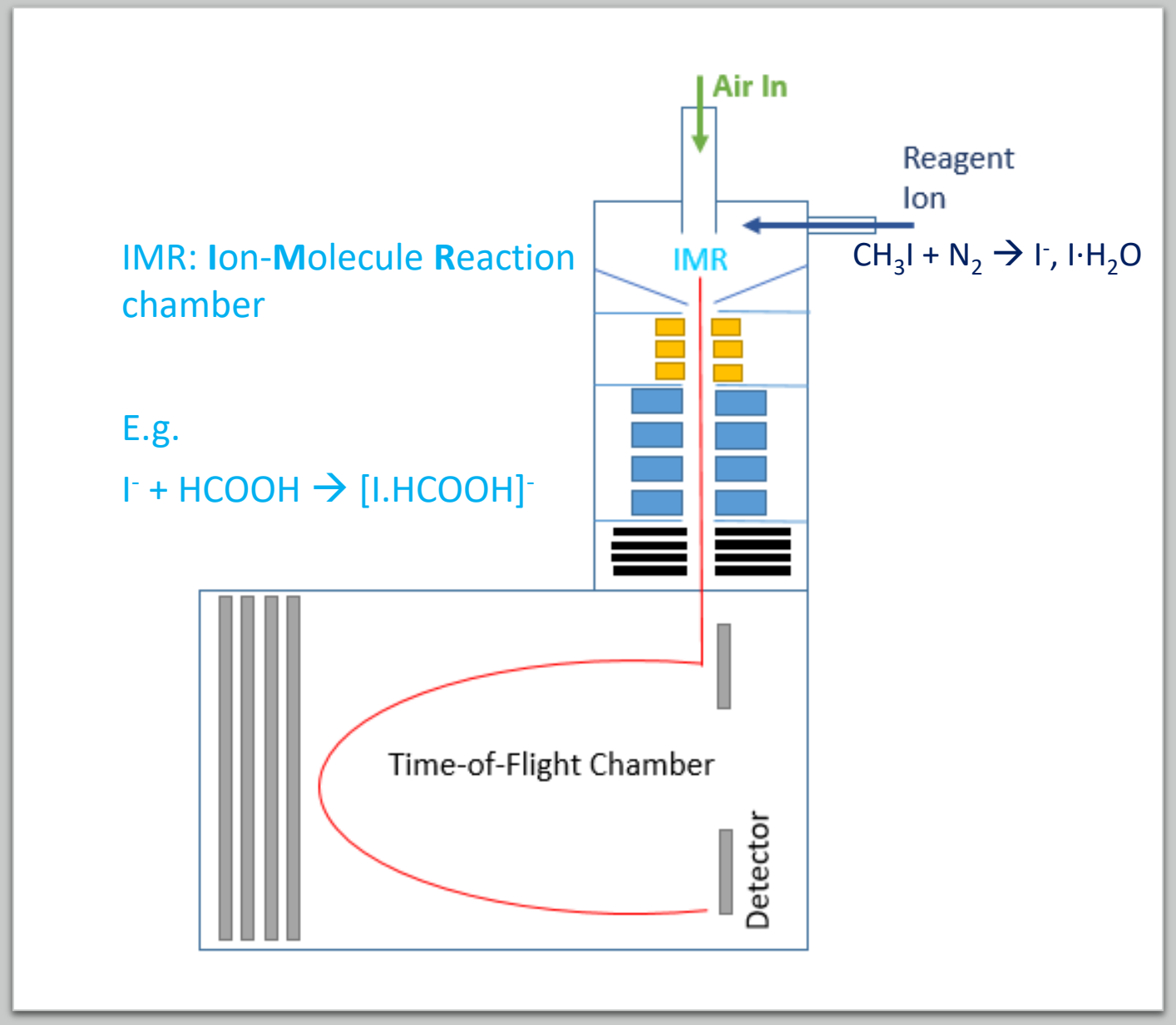
- Important for new particle formation
- Impact Earth's radiation budget

Nitrates (e.g. HONO,HNO_3,N_2O_5)

- Key role in night-time tropospheric chemistry
- Important for aerosol formation
- Impact ozone formation

Hydrocarbons (e.g. Isoprene/Terpene oxidation products)

- Important for secondary organic aerosol (SOA) formation



Aircraft Campaigns

ACSIS: North **A**tlantic **C**limate **S**ystem **I**ntegrated **S**tudy

- Focuses on understanding recent changes in the ocean, the atmosphere (including its composition), the cryosphere and the interactions between these constituent components
- Profiling over the North Atlantic Ocean from 200-8000 m above the ocean
- 4 aircraft campaigns with I-CIMS; ACSIS-4 (February 2019), ACSIS-5 (August 2019), ACSIS-6 (February 2020) and ACSIS-7 (May 2022)

Aircraft Campaigns

ACRUISE: **A**tmospheric **C**omposition and **R**adiative forcing changes due to **U**N **I**nternational **S**hip **E**missions regulations

- In 2015 the International Maritime Organization (IMO) ordered a reduction in the maximum ship sulphur emissions in coastal Sulphur Emission Control Areas (SECAs) of Europe and North America
- ACRUISE aims to quantify the impact on atmospheric chemistry and climate due to the new IMO regulations
- 2 Aircraft campaigns with I-CIMS; ACRUISE-2 (September 2021) and ACRUISE-3 (May 2022)

Aircraft Campaigns

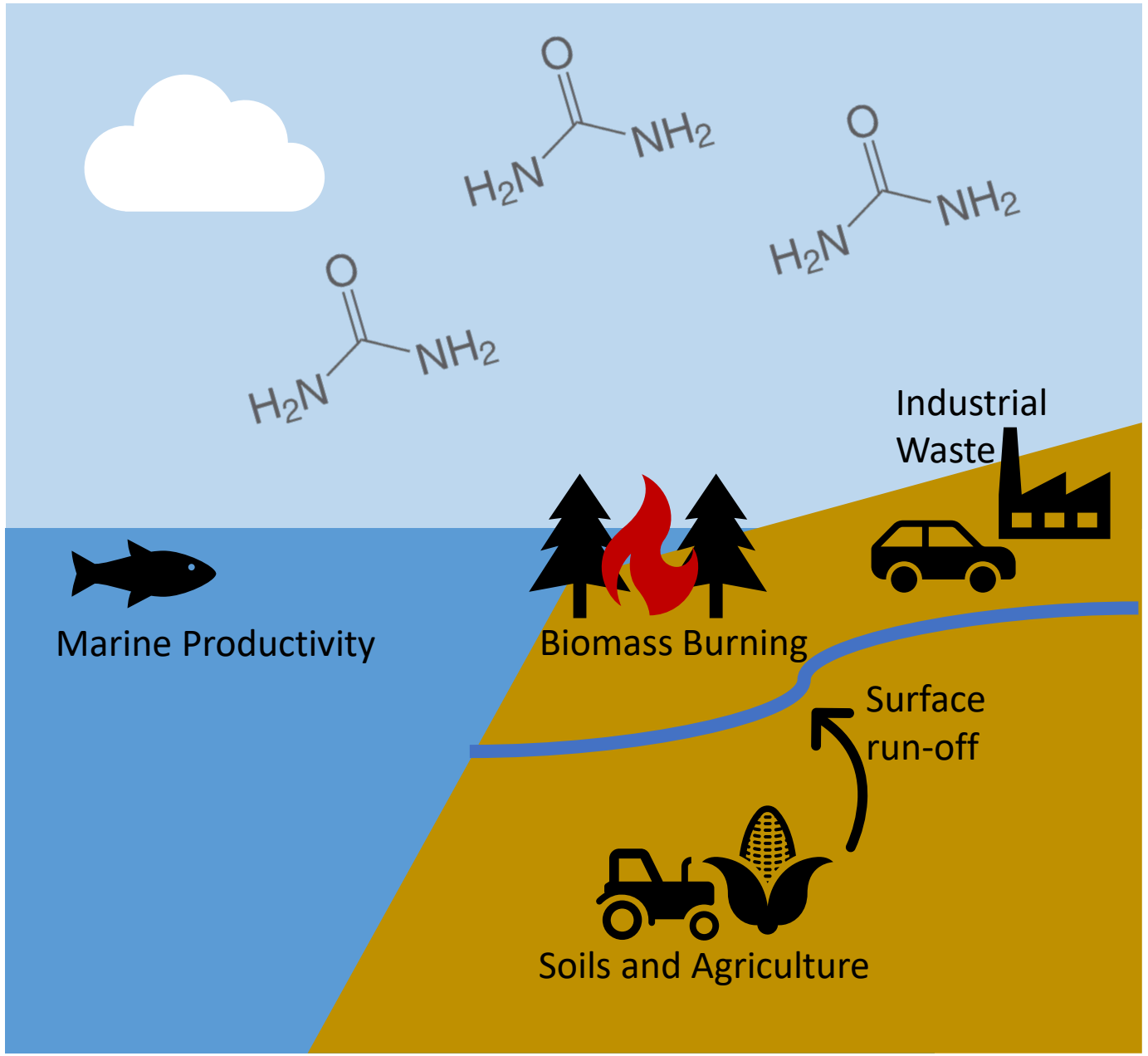
MOYA: **M**ethane **O**bservations and **Y**early **A**ssessments

- Aims to move towards closing the global methane budget through the undertaking of new observations and further analysis of existing data
- 1 aircraft campaign with I-CIMS in January 2019 over East Africa
- Various environments surveyed; agricultural lands, biomass burning events, lakes, urban and wetlands

Atmospheric Urea

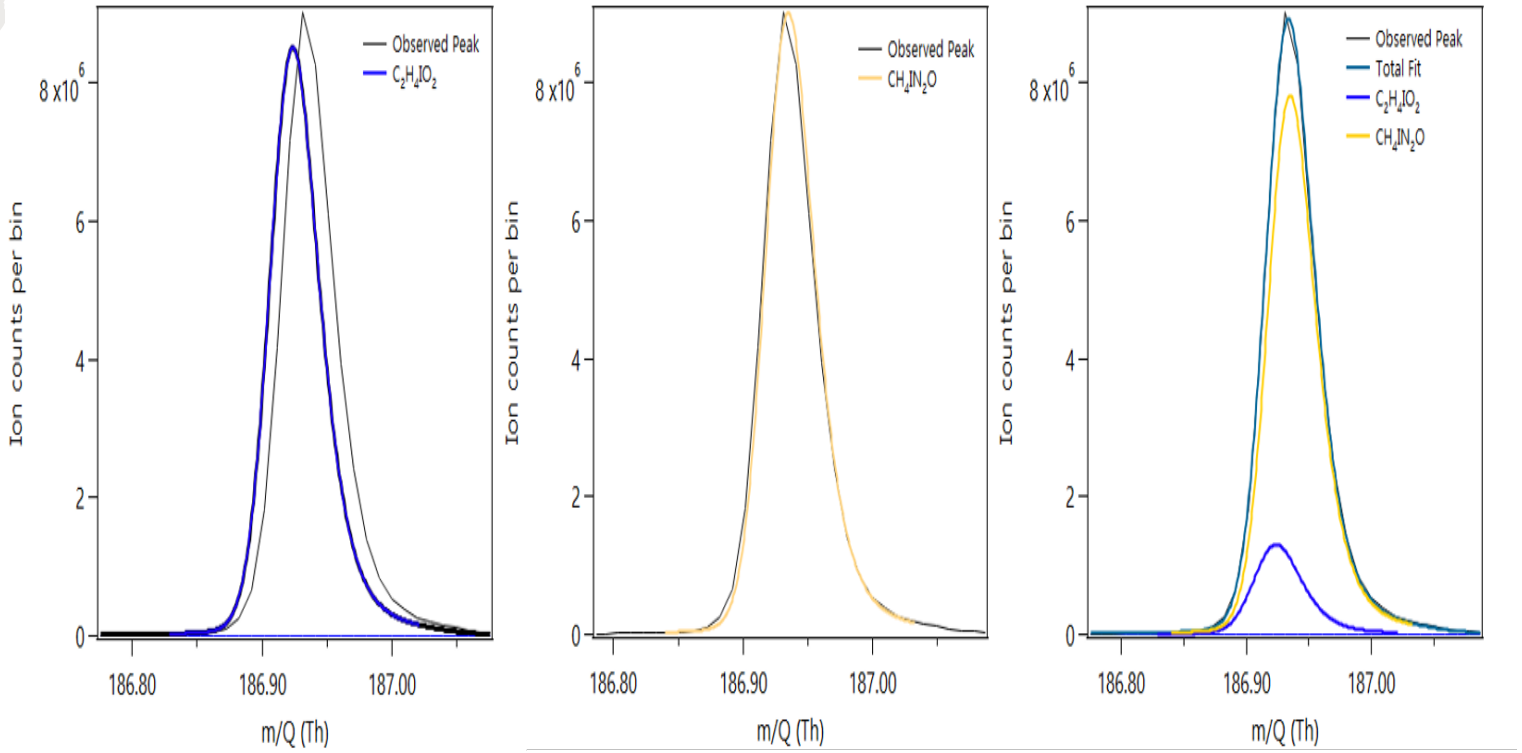
- Urea has shown to contribute a significant proportion of water soluble organic nitrogen (WSON) in both aerosols and rainwater
- Natural sources primarily arise from marine biological activity
- Anthropogenic sources include animals, fertilisers, industrial waste and biomass burning

Currently no reported ambient measurements of gas-phase urea



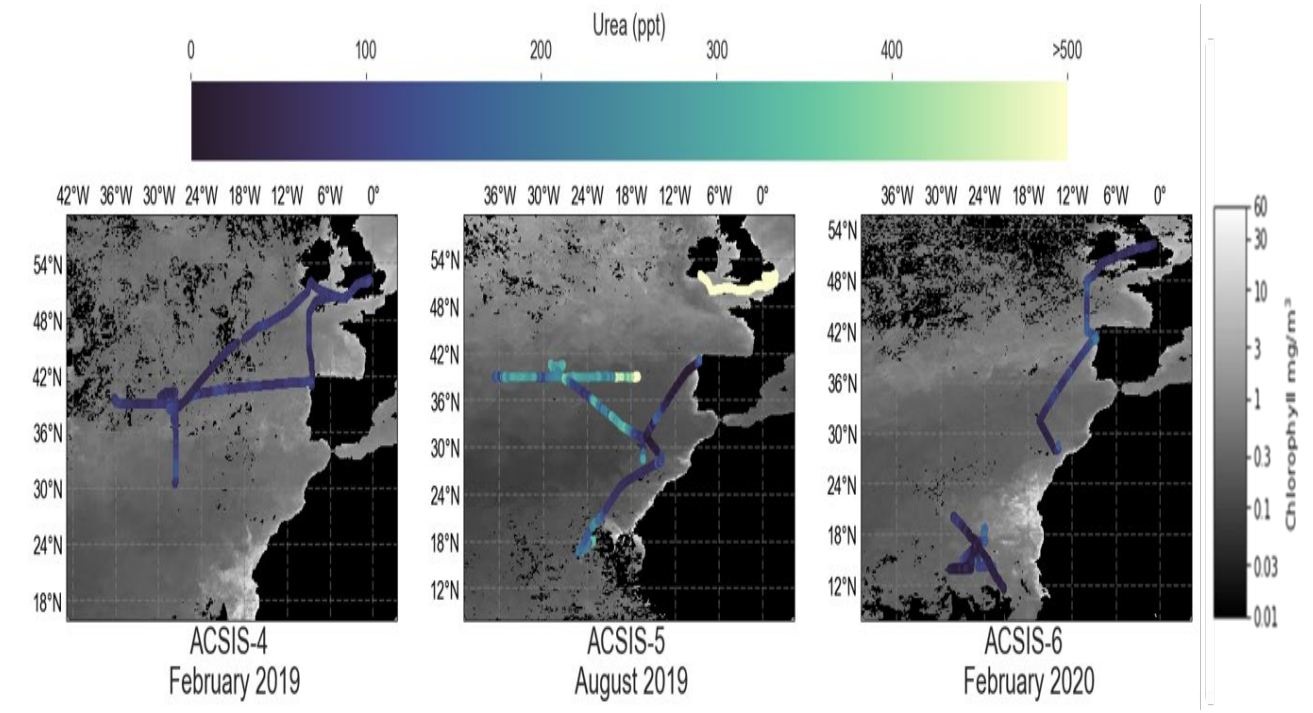
Large signal at m/z 187

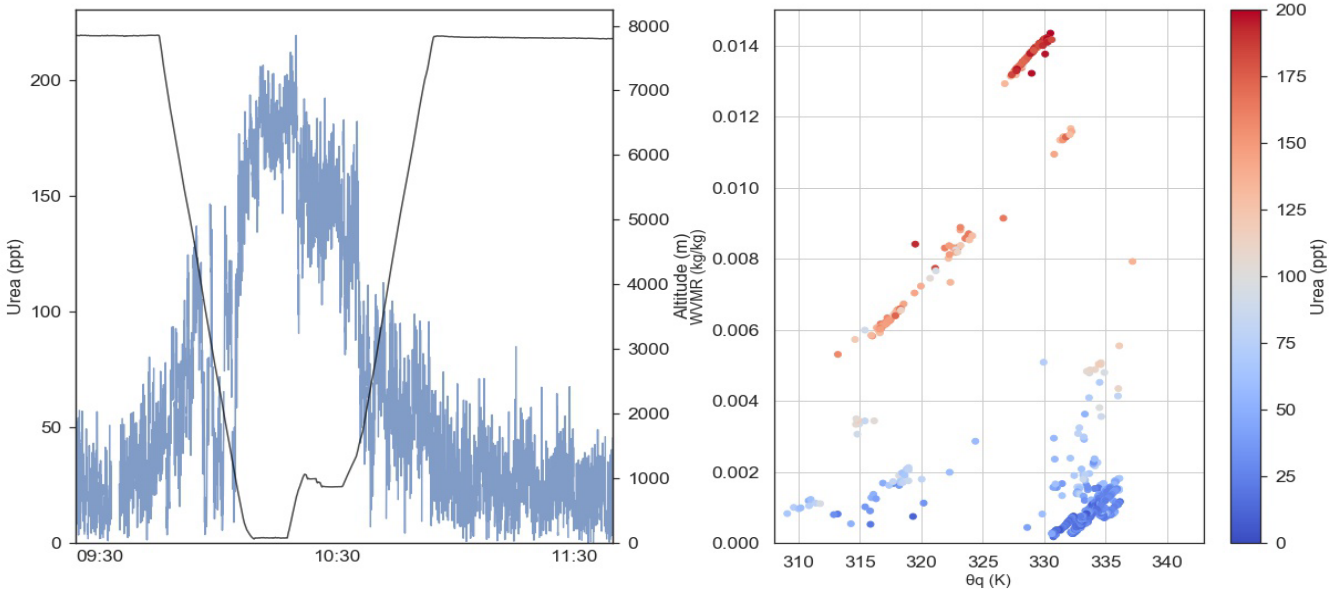
- Identified a large signal at m/z 187 that is dominated by urea and not acetic acid
- Worked to calibrate and verify measurements



A significant ocean source

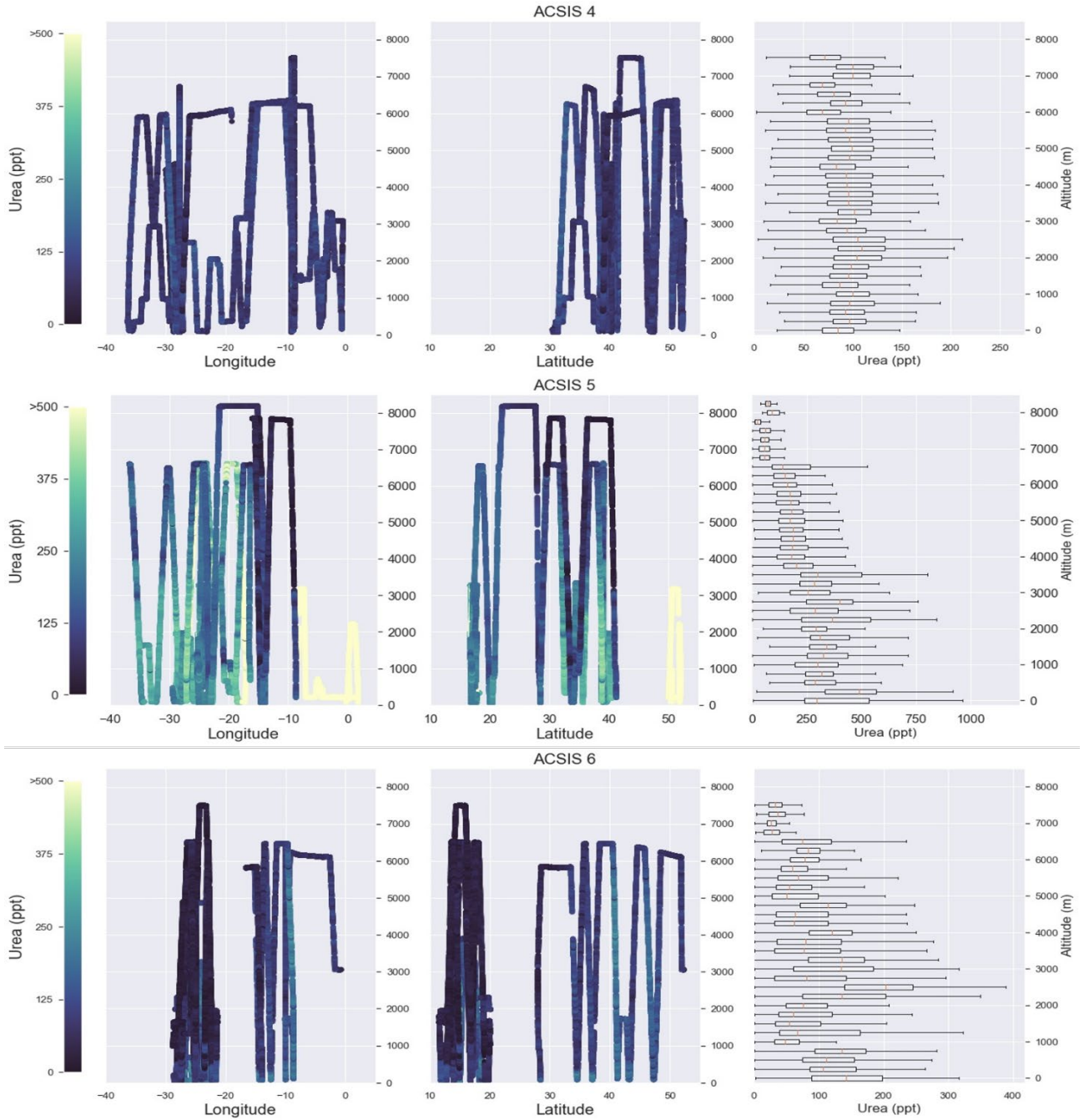
- Enhancements of urea were frequently observed within the atmospheric marine boundary layer (MBL) across the North Atlantic
- Ubiquitous across the lower troposphere and in significant quantities
  - Frequently exceeding 100 pptv
  - Similar mixing ratios to DMS
- Strong seasonality; winter average = 95 pptv, summer average = 310 pptv, spring average = 15 pptv*
- Most abundant in air masses with warm and moist properties and as such indicates an ocean source





Vertical Distribution

- Vertical distribution driven by local physical state of the atmosphere
  - Consistent for a trace gas originating from the sea-water surface



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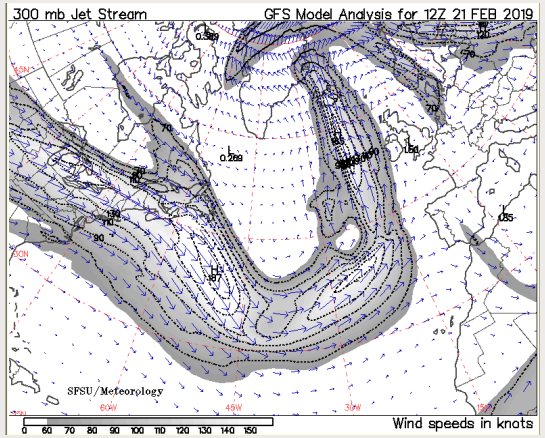
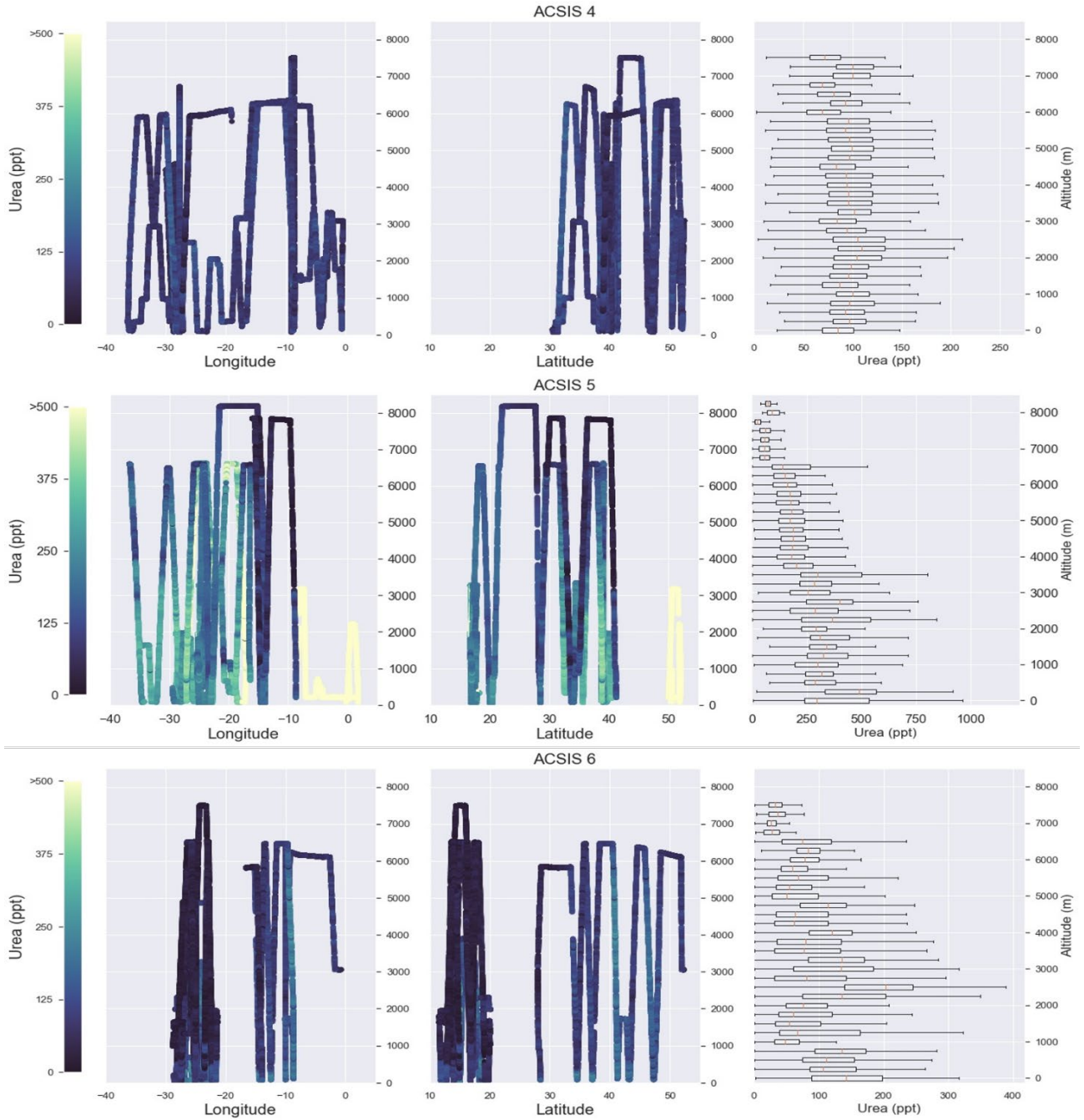
- In presence of frontal systems (i.e. jet streams), urea is observed to be mixed throughout the atmospheric column





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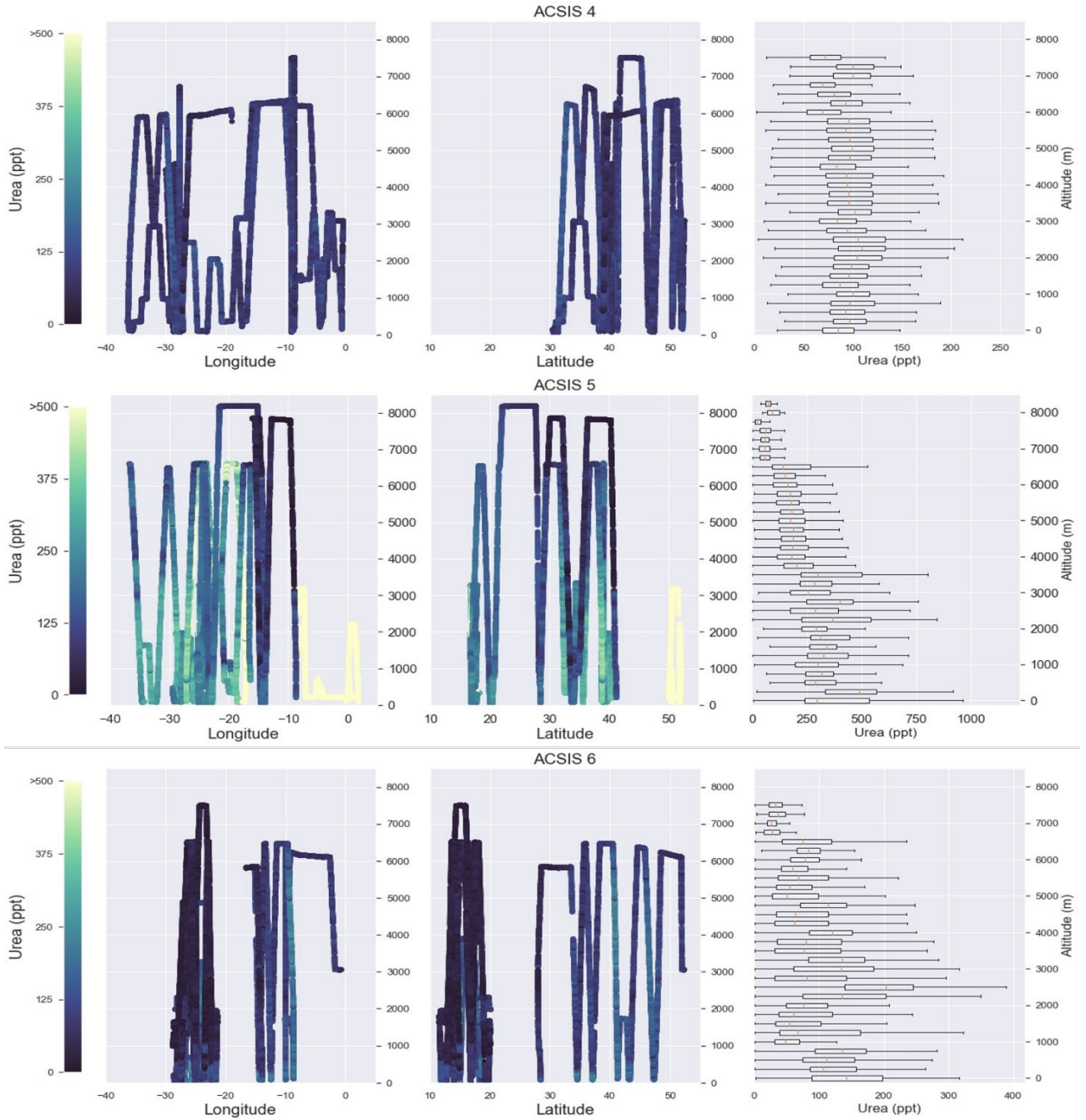
- In regions with a constrained MBL, urea enhancements are confined to the MBL



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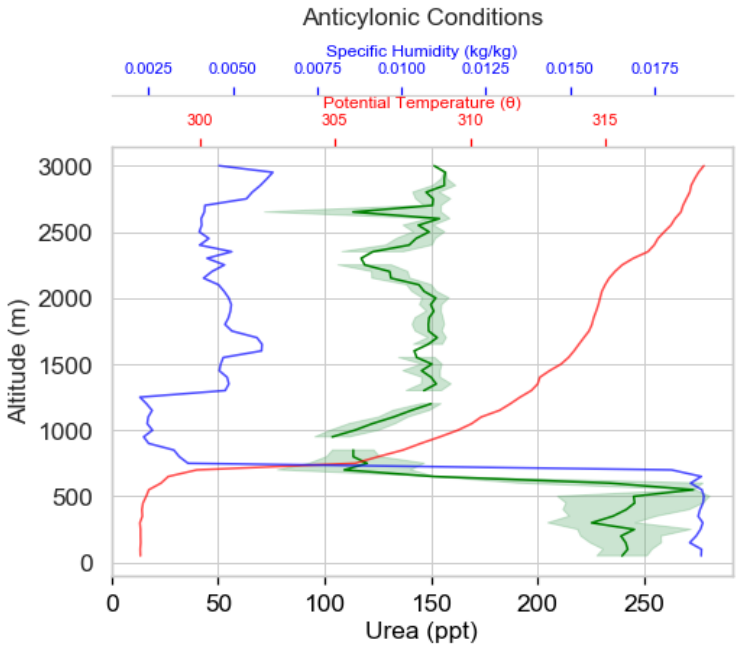
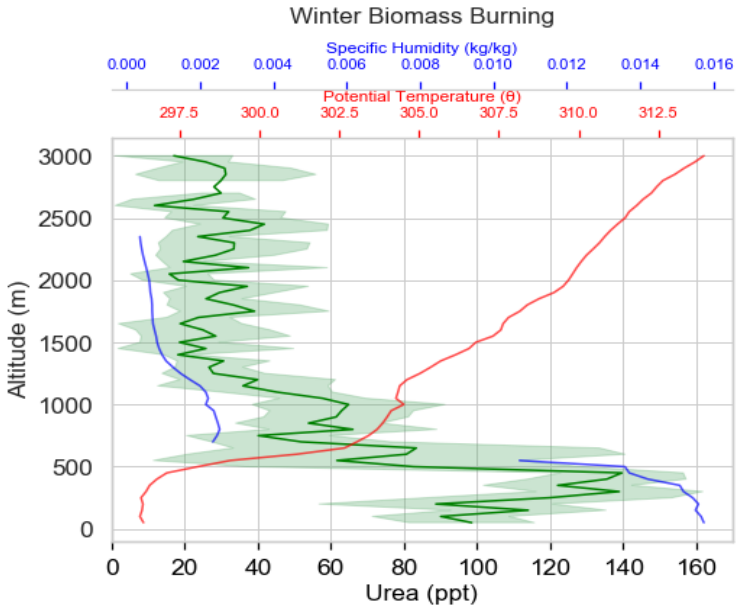
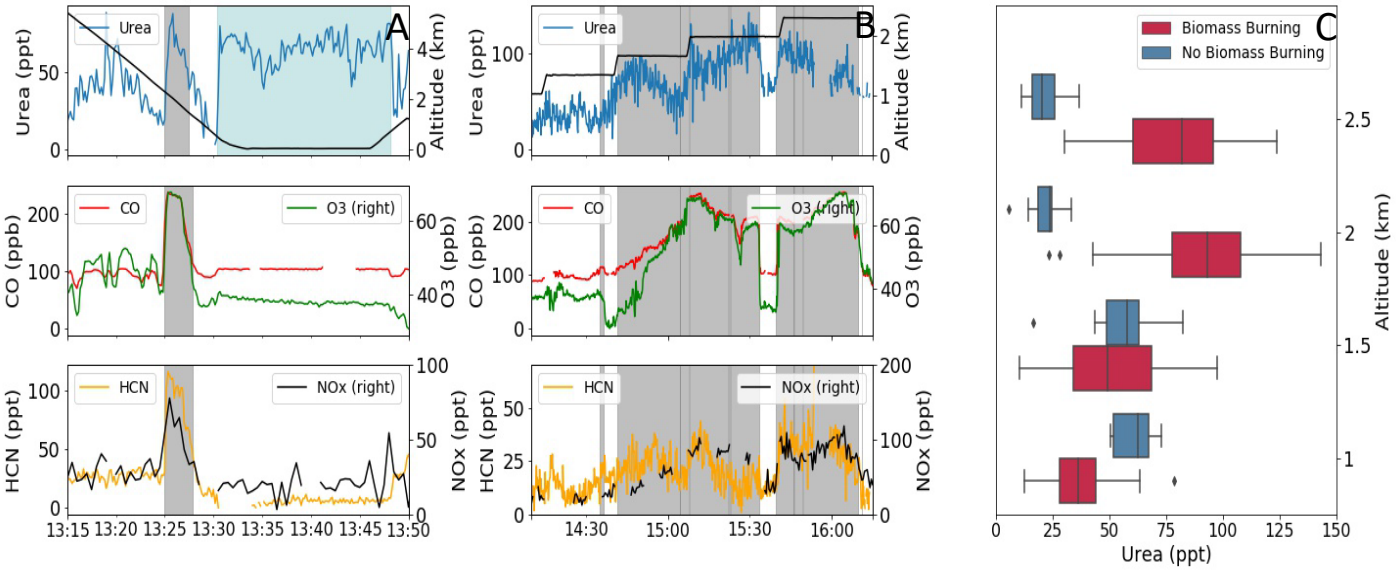




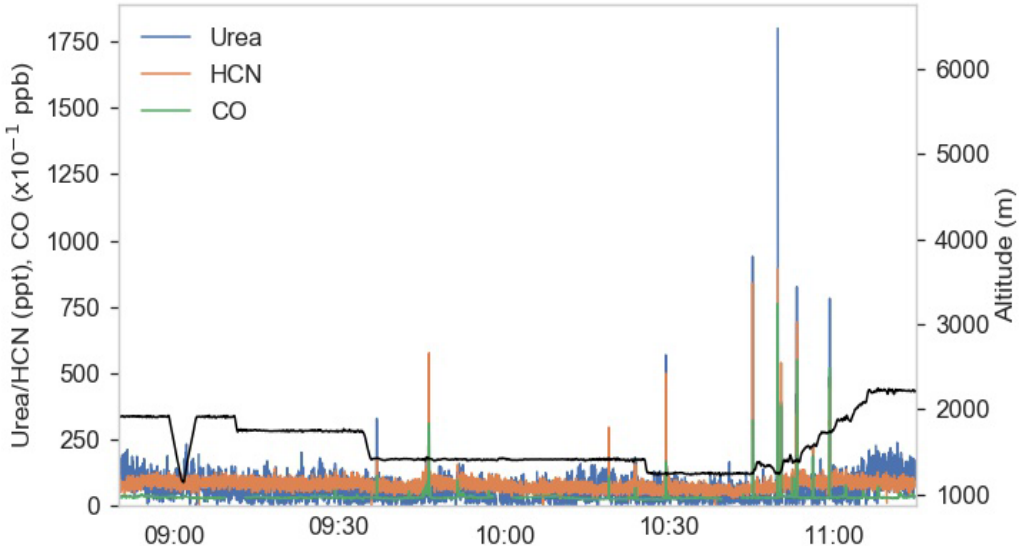
Biomass Burning – An additional source

- During ACSIS-6 (Feb 2020) observed enhancements in both the BL and FT over the tropical North Atlantic ocean
- Region dominated by biomass burning and dust outflow from continental Africa
- Enhancements of urea in the FT were observed exclusively in the presence of biomass burning plumes
- Age of plumes 6-8 days (Lee et al., 2021)

Aged fire plumes over tropical North Atlantic (grey shaded regions)



Fresh fire plumes over Uganda



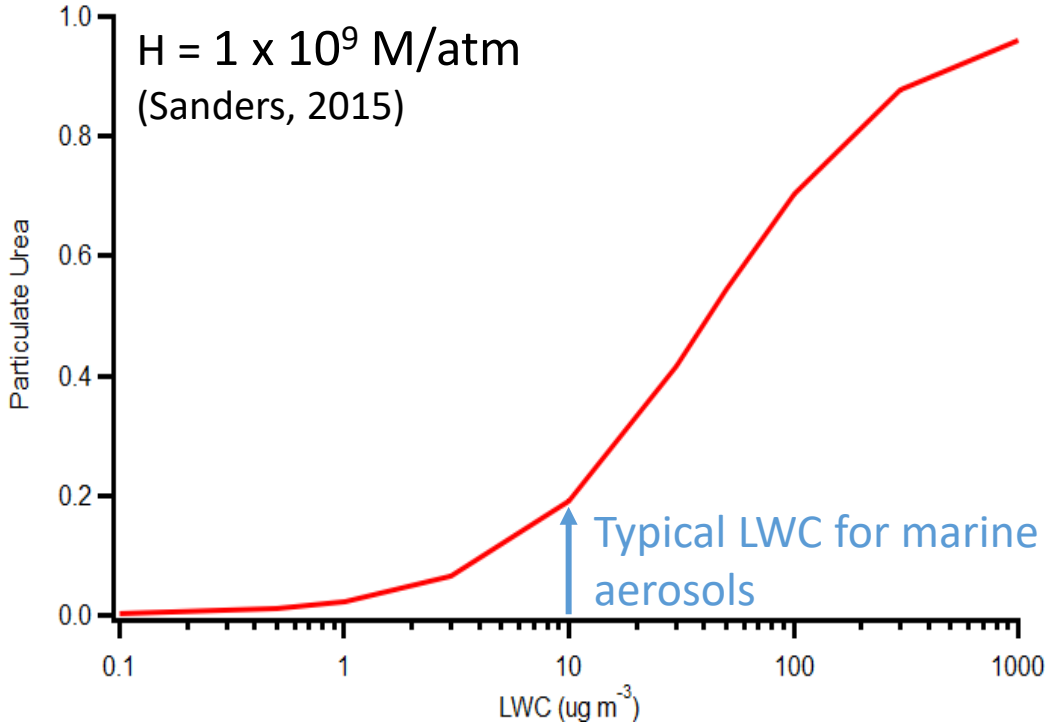
Urea Partitioning

- High Henry's Law coefficient: 1×10^{9} M atm^{-1} (Sanders, 2015)
- Low vapour pressure: 2×10^{-8} atm (Glasoe et al., 2015)

Mechanisms responsible for the exchange of urea from the seawater surface to the atmosphere?

Urea Partitioning

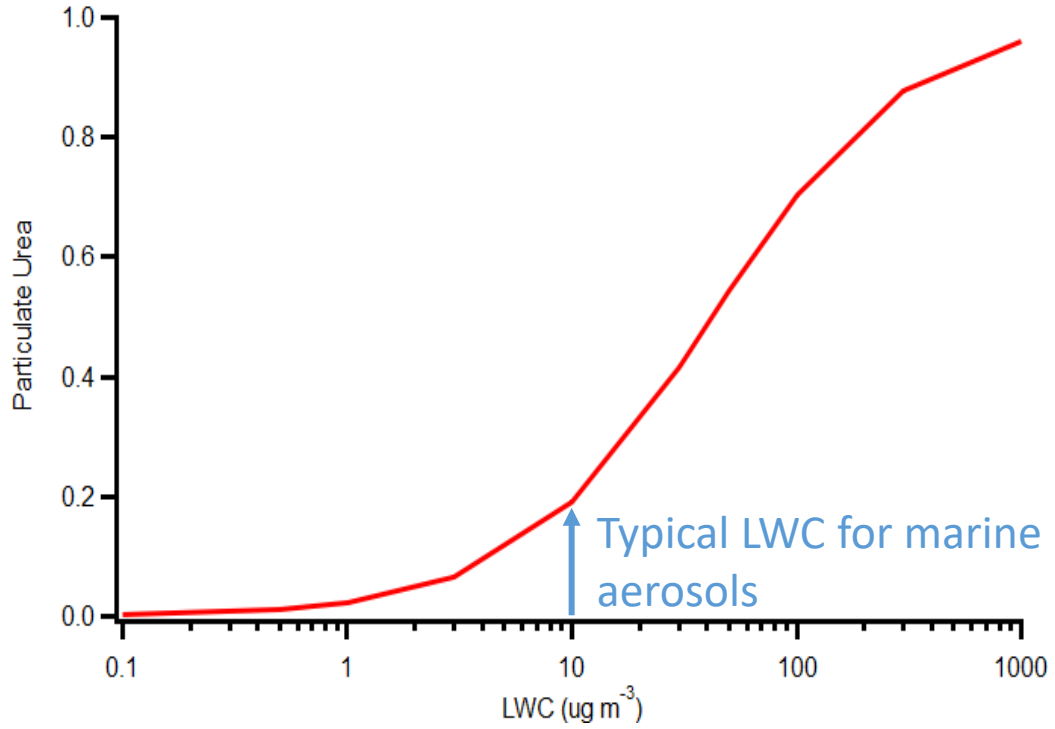
- High Henry's Law coefficient: 1 x 10^9 M/atm (Sanders, 2015)
- Low vapour pressure: 2 × 10^{-8} atm (Glasoe et al., 2015)
- Compared our observations against reported urea concentrations in aerosol phase and surface seawater
- Gas phase measurements consistent with equilibrium partitioning based on literature particulate concentrations
- Large surface enhancements required to explain observations



Observation	Urea conc.	Conc. in liquid water	Reference
Atmosphere - Gas phase	230 ppt	0.26 mol L^{-1}	This study
Atmosphere - Particulate phase	9 nmol N m^{-3}	3.9 mol L^{-1}	(Zamora et al., 2011)
Seawater surface	300 nmol L^{-1}	30-300 umol L^{-1}	(Painter et al.,2008)

Urea Partitioning

- Under dry conditions and low relative humidity most of the urea is in the gas phase.
- At humidities above 95% and in cloud atmospheric urea exists almost exclusively in the aqueous phase.



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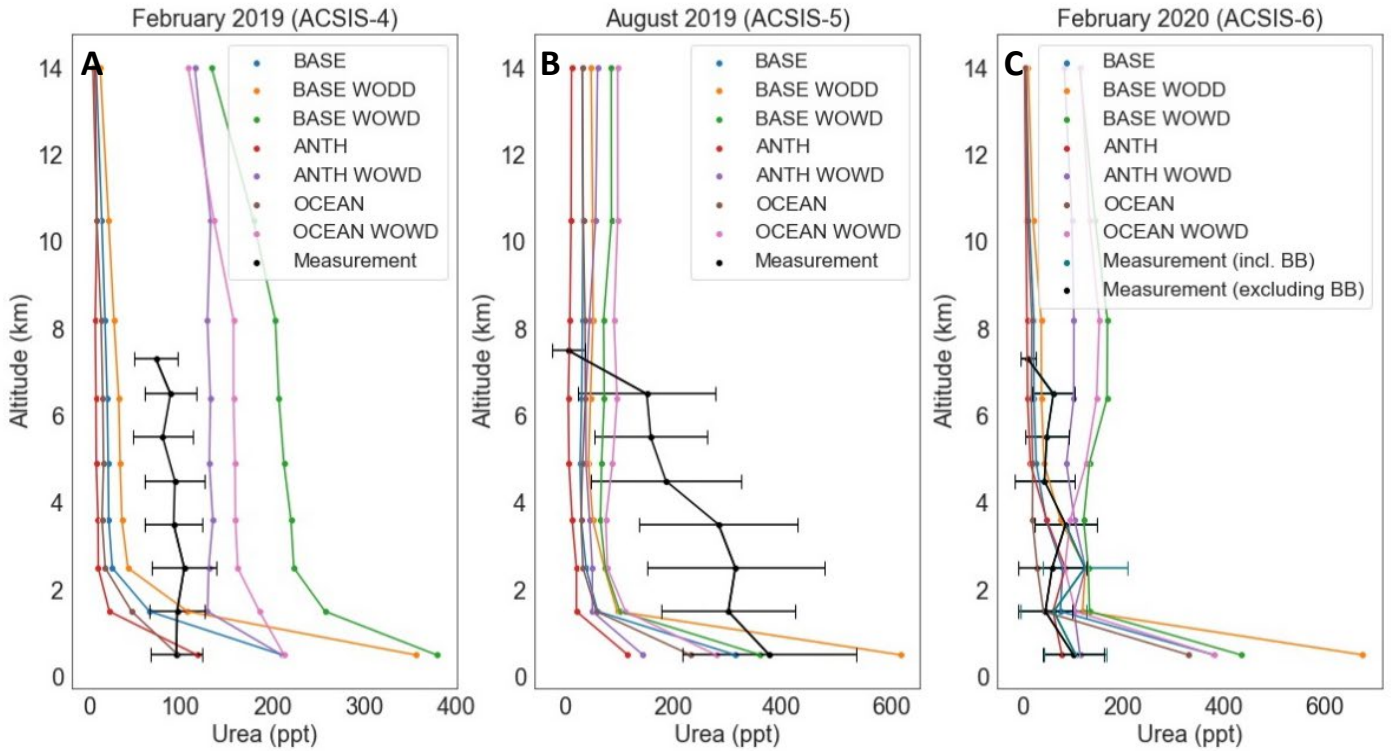
Global burden of urea

- A suite of model simulations were conducted to assess
  - (i) the possible source signature of urea using DMS as an ocean emission and NH_3 for anthropogenic emissions
  - (ii) the impact of individual loss processes on the mixing ratios of urea
  - (iii) the global burden of urea and its contribution to the total reduced nitrogen
- Physical loss processes dominate loss process
  - 50% due to wet deposition and 32% from dry deposition
- Lifetime greater than NH_3
- Increase reduced nitrogen budget by ~50% for BASE case



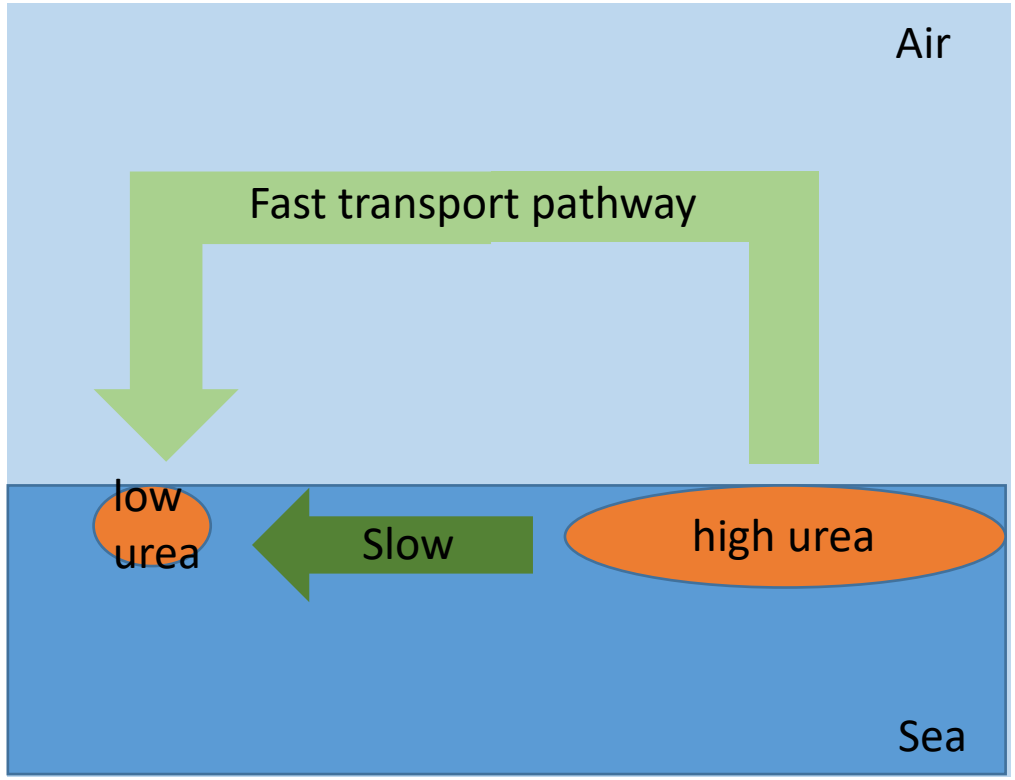
	BASE	BASE_ WODD	BASE_ WOWD	ANTH	OCEAN	ANTH_ WOWD	OCEAN_ WOWD
Emissions (Tg N/yr)	93.3	93.3	93.3	37.1	56.2	37.1	56.2
Losses (Tg N/yr)							
Reaction by OH	16.8	25.6	44.2	6.1	5.3	15.6	21.4
Dry deposition	30.0	n/a	48.9	13.9	17.5	21.4	34.6
Wet deposition	46.2	67.4	n/a	17.0	33.2	n/a	n/a
Global burden (Tg N)	0.26	0.42	0.93	0.13	0.16	0.45	0.82
Lifetime (days)	1.0	1.6	3.7	1.3	1.0	4.4	5.4

BASE = Ocean + Anthropogenic source
WODD/WOWD = without dry/wet deposition

Model simulations work of Dr. Anwar Khan

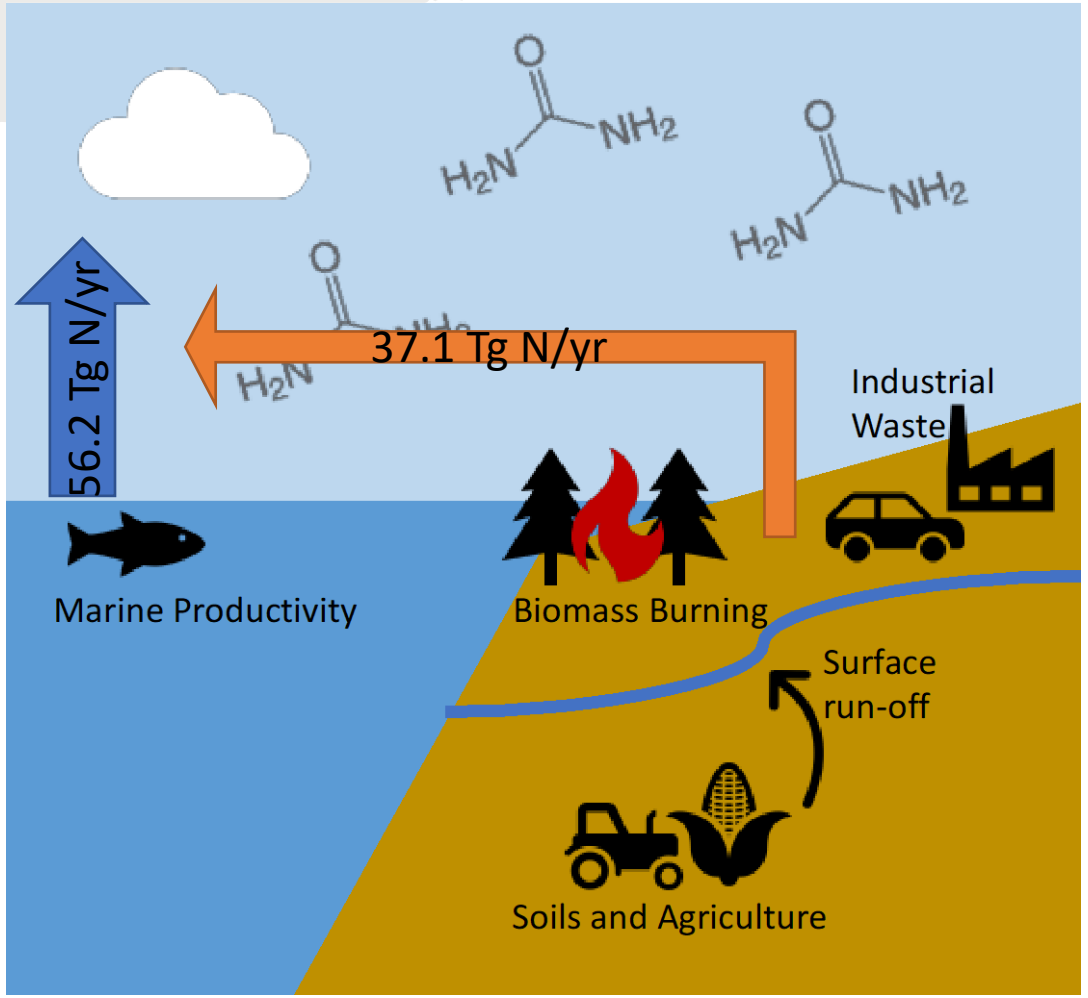
Urea – an important component of the global nitrogen cycle

- Our measurements show urea is ubiquitous throughout the remote marine environment
- Observations and model simulations indicate that urea has a relatively long atmospheric lifetime
- Atmosphere provides an important pathway for the redistribution of reduced nitrogen at rates and scales far greater than ocean transport



Summary

- Ubiquitous throughout the lower troposphere and often high in concentration (similar to DMS)
- Seasonality: Summer > Winter > Spring
- Evidence for long-range transport during:
  - Frontal transport systems
  - Transport of biomass-burning plumes over the remote marine environment
- Modelling studies suggest that presence of gas-phase urea in the atmosphere increases the reduced nitrogen budget by ~50%
- Urea readily partitions between gas and particle phases
- Need further studies to constrain the role of urea in models and to understand the processes driving the significant presence of urea in the marine environment



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