

**Quantitative Analysis of Reduced Nitrogen Processing in
Marine Aerosols by Fog
and
the Indoor Air of New Canadian Homes**

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ABSTRACT

Reduced nitrogen species, including ammonia (NH_3) and alkylamines (NR_3), are ubiquitous in the atmosphere and play important roles in new particle formation, aerosol growth, multiphase chemical processing, and air quality. However, their quantitative analysis across aerosol and gas phases remains analytically challenging. This thesis develops and applies ion chromatographic (IC) methods to quantify reduced nitrogen to investigate its processing in marine aerosols during fog events and in the indoor air of newly built Canadian homes. An IC method was developed to separate and quantify NH_3 and the ten most abundant atmospheric NR_3 with high selectivity and separation efficiency using 4 μm packed columns and resin-based suppressors, alongside stabilized NR_3 calibration standards. Suppressor performance was improved by stepped-current operation and an external water supply, resulting in enhanced linearity, accuracy, precision, and lower detection limits than conventional suppression modes. The optimized IC method was applied to marine aerosol samples collected during the Fog and Turbulence Interactions in the Marine Atmosphere (Fatima) 2022 campaign over the Northwest Atlantic Ocean. Aerosol chemistry, microphysics, physical processing, and meteorological conditions were analyzed to investigate fog–aerosol interactions. Size-resolved chemical measurements showed a reduction in coarse mode sea salt ions during fog, attributed to their growth into fog droplets, while fine mode processed-S (e.g., nss-SO_4^{2-} and MSA^-) and reduced-N species increased due to enhanced aqueous-phase processing. Consistent reductions in coarse sea salt mass loading across more than a dozen fog events confirm their role as effective fog condensation nuclei and demonstrate the impact of fog processing on aerosol mass loading. The developed IC method was further applied to quantify indoor gas-phase reduced nitrogen in 48 newly built Canadian homes as part of the New Home Air Quality Study (NHAQS) from 2019 to 2024. Indoor NH_3 mixing ratios decreased from pre- to post-occupancy and remained relatively stable over 12 months following, consistent with reduced emissions from new materials and increased partitioning surface area upon occupancy. Overall, this thesis develops a new analytical method to quantify reduced nitrogen in marine fog aerosols and indoor air, improving understanding of aerosol–fog chemistry, fog forecasting models, and indoor air quality.

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List of Symbols and Abbreviations

1°	Primary
2°	Secondary
3°	Tertiary
A	Cross-sectional area of the sampler
A	Eddy diffusion coefficient
ADRS	Anion dynamically regenerated suppressor
a. s. l.	Above sea level
a _{H+}	Proton activity
AR(1)	Autoregressive covariance structure of order one
B	Longitudinal diffusion coefficient
Br ⁻	Bromide
C ₂ O ₄	Oxalic acid
C ₆ H ₈ O ₇	Citric acid
CA	Collected amount
CASCC2	Celtech active strand cloudwater collector
CCN	Cloud condensation nuclei
CD	Conductivity detector
CDRS	Cation dynamically regenerated suppressor
CE	Capillary electrophoresis
C _e	External concentration of the analyte
CERS	Cation electrolytically regenerated suppressor
Chl-a	Chlorophyll-a
CI	Confidence interval
Cl	Chlorine radical
Cl ⁻	Chloride
C _m	Mass transfer coefficient (mobile phase)
C ₀	Concentration at sorbent interface
CO ₂	Carbon dioxide
C _s	Mass transfer coefficient (stationary phase)
D	Diffusion coefficient in air
D	Dynamic suppressor mode
D-CAMS	Deck-mounted cloud aerosol measurement system
DEA	Diethylamine
DIW	Deionized water
DMA	Dimethylamine
DMS	Dimethyl sulfide
DMSO	Dimethyl sulfoxide
DMSP	Dimethylsulfoniopropionate
D _p	Residual particle diameter
E	External water supply
E-AIM	Extended Aerosol Inorganics Model
ESI(-)	Negative electrospray ionization
Fatima	Fog and turbulence interaction in the marine environment
FCN	Fog condensation nuclei
FLD	Fog layer depth

FM	Fog monitor
GCCN	Giant cloud condensation nuclei
GC	Gas chromatography
GFS	Global forecast system
GBT	Glycine betaine
Gg N a ⁻¹	Gigagrams nitrogen per year
GLMM	Generalized Linear Mixed Model
h	Hour
H	Theoretical plate height
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulfuric acid
H ₃ O ⁺	Hydronium
HCl	Hydrochloric acid
HDPE	High-density polyethylene
HNO ₃	Nitric acid
HONO	Nitrous acid
HPLC	High-performance liquid chromatography
HPMTF	Hydroperoxymethyl thioformate
HYSPLIT	Hybrid single-particle lagrangian integrated trajectory
I	Indoor
I	Suppressor current
IC	Ion chromatography
IOP	Intensive operation period
K ⁺	Potassium
K _a	Acid dissociation constant
K _{eff}	Effective equilibrium constant (K _a /K _H)
K _H	Henry's law constant
L	Column length
L	Legacy suppressor mode
L	Length of diffusion path
Li ⁺	Lithium
LOD	Limit of detection
Log	Logarithm
LWC	Liquid water content
mA	Milliampere
MBA	Monobutylamine
MBL	Marine boundary layer
MEA	Monoethylamine
MEtA	Monoethanolamine
Mg ²⁺	Magnesium
Min	Minute
MODIS	Moderate Resolution Imaging Spectroradiometer
MOUDI	Micro-Orifice Uniform Deposit Impactor
mp	Particle mass
MS	Mass spectrometer
MSA	Methanesulfonic acid

MSIA	Methanesulfinic acid
MSLP	Mean sea-level pressure
MTMP	Methylthiomethyl peroxy radical
MW	Molecular weight
N	Plate number
Na ⁺	Sodium
NaOH	Sodium hydroxide
NaOCl	Sodium hypochlorite
NanoMOUDI	Nano micro-orifice uniform deposit impactor
NCl ₃	Nitrogen trichloride
N _d	Number concentration
NE	Northeast
NH ₃	Ammonia
NH ₄ ⁺	Ammonium
NHCl ₂	Dichloramine
NHAQS	New home air quality study
NR ₃ H ⁺	Aminium
NR ₃	Amine
N _r	Reactive nitrogen
nss-SO ₄ ²⁻	Non-sea-salt sulfate
N ₂ O	Nitrous oxide
N ₂ O ₅	Dinitrogen pentoxide
NO	Nitric oxide
NO ₂	Nitrogen dioxide
NO ₂ ⁻	Nitrite
NO ₃	Nitrate radical
NO ₃ ⁻	Nitrate
NOBM	NASA ocean biogeochemical model
NOAA	National oceanic and atmospheric administration
NW	Northwest
O	Outdoor
O ₃	Ozone
OH	Hydroxyl radical
OH ⁻	Hydroxide
P	Significant value
PBL	Planetary boundary layer
pH	Potential of hydrogen
PM _{2.5}	Particulate matter <2.5 μm
PM ₁₀	Particulate matter <10 μm
ppbv	Parts per billion by volume
ppmv	Parts per million by volume
ppqv	Parts per quadrillion by volume
pptv	Parts per trillion by volume
PP	Polypropylene
P _p	Particle density
Processed-S	nss-SO ₄ ²⁻ and MSA ⁻

QA	Quality assurance
QC	Quality control
QTOF-MS/MS	Quadrupole time-of-flight tandem mass spectrometry
R	Recycle water supply
R^2	Coefficient of least-squares regression
RE	Relative error
RH	Relative humidity
RSD	Relative standard deviation
Reduced-N	NH_4^+ , DMAH^+ , and DEAH^+
r	Pearson correlation coefficient
SE_b	Standard error of intercept
σ	Standard deviation
SMPS	Scanning mobility particle sizer
SO_4^{2-}	Sulfate
SOA	Secondary organic aerosol
SSA	Sea salt aerosol
T_{ss}	Sea surface temperature
SVOCs	Semi-volatile organic compounds
SW	Southwest
T/T_{air}	Temperature of the air
TEA	Triethylamine
Tg S a^{-1}	Teragrams sulfur per year
t	Collection time / Sampling time
t_{NR}	Total gaseous reactive nitrogen
TMA	Trimethylamine
TMAO	Trimethylamine N-oxide
TWA	Time-weighted average
t_R	Retention time
VIF	Variance inflation factor
VOCs	Volatile organic compounds
V_p	Particle volume
W	Peak width
W	Shapiro–Wilk test
WD	Wind direction
WS	Wind speed
μ	Flow rate
$\mu\text{g m}^{-2}$	Column mass
$\mu\text{g m}^{-3}$	Mass loading
μm	Micrometre
μS	Microsiemens
neq m^{-3}	Nanoequivalent ionic loading
α	Concentration conversion coefficient
β	Fixed-effect coefficients
χ	Gas-phase mixing ratio
χH^+	Mole fraction of protons

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PREFACE

This thesis consists of a series of manuscripts that have been published, accepted, submitted, are currently under peer review, or are in preparation for submission to peer-reviewed scientific journals. Consequently, some repetition of introductory and experimental details was inevitable. All manuscripts were authored by Leyla Salehpoor, with editorial guidance and critical feedback provided by Trevor C. VandenBoer. The specific contributions of all co-authors are outlined below.

Chapter One – Atmospheric chemistry of reduced nitrogen in indoor air and marine aerosols

Contributions- Prepared by Leyla Salehpoor with editorial comments by Trevor C. VandenBoer

Chapter Two - Suppressor and calibration standard limitations in cation chromatography of ammonium and 10 alkylamines in atmospheric samples

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Author Lists - Leyla Salehpoor and Trevor C. VandenBoer

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Chapter Five - Controls on indoor ammonia in new Canadian homes during the first year of occupancy with reduced nitrogen case studies

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Chapter Six – Conclusions and future directions

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Lao, M.; Crilley, L.R.; **Salehpoor, L.**; Furlani, T.C.; Bourgeois, I.; Neuman, J.A.; Rollins, A. W.; Veres, P.R.; Washenfelder, R.A.; Womack, C.C.; Young, C.J.; VandenBoer, T.C. A portable, robust, stable and tunable calibration source for gas-phase nitrous acid (HONO). *Atmospheric Measurement Techniques*, **2020**, 13(11), 5873-5890. doi: 10.5194/amt-13-5873-2020

CHAPTER ONE – Atmospheric chemistry of reduced nitrogen in indoor air and marine aerosols

Author Contributions:

Leyla Salehpour prepared the contents of this chapter, and Trevor C. VandenBoer provided editorial comments.

1.1 The atmosphere and built environments from a chemical perspective

The Earth's atmosphere is divided into four layers based on temperature changes with altitude above the Earth's surface: the troposphere (0–15 km), stratosphere (15–50 km), mesosphere (50–80 km), and thermosphere (80–100 km).^{1,2} The atmosphere is composed of gases, particulate matter, and aqueous phases associated with cloud and fog droplets. In the gaseous phase, the main components are molecular nitrogen (N₂, ~78%) and oxygen (O₂, ~21%).³ Minor constituents include argon (Ar, ~0.93%), water vapour, and trace organic compounds. In addition, a diverse suite of trace gases exists at significantly lower concentrations, ranging from parts per quadrillion by volume (ppqv) to parts per million by volume (ppmv), yet these species play a critical role in governing atmospheric chemical reactions.

The lower layers, the troposphere and stratosphere, contain most of the atmospheric mass and mediate physical and chemical processes connected to Earth's surface, including the emission, transport, lifetimes, and fates of anthropogenic and biogenic chemicals. In the troposphere, the planetary boundary layer (PBL) is the lowest part, directly influenced by surface conditions, controlling near-surface air composition through turbulence and vertical mixing over short periods.⁴ Over oceans, this layer is called the marine boundary layer (MBL), which is typically shallower and more stable, characterized by high humidity and frequent cloud or fog formation.⁵ These conditions enhance multiphase chemical processing and influence the transport and fate of reactive trace species.

Atmospheric composition is governed by emissions, dispersion and transport, chemical and physical transformations, and removal processes (Figure 1-1).⁶ Gases and particles originate from natural sources, such as oceans, soils, vegetation, and wildfires, as well as from human activities, such as fossil fuel combustion, agriculture, and industry.^{7,8} The impact of these emissions depends on their amount, temporal and spatial distribution, and chemical reactivity. Once emitted, species are dispersed and transported across local to global scales, during which they undergo physical and chemical transformations, including gas–particle partitioning and multiphase chemical reactions.⁹ Atmospheric particles consist of suspended solid and liquid matter in a gas with a wide range of sizes and compositions, and they play significant roles in atmospheric chemistry and climate. Finally, atmospheric constituents are removed through dry deposition onto surfaces and wet deposition via clouds, fog, and precipitation.¹⁰

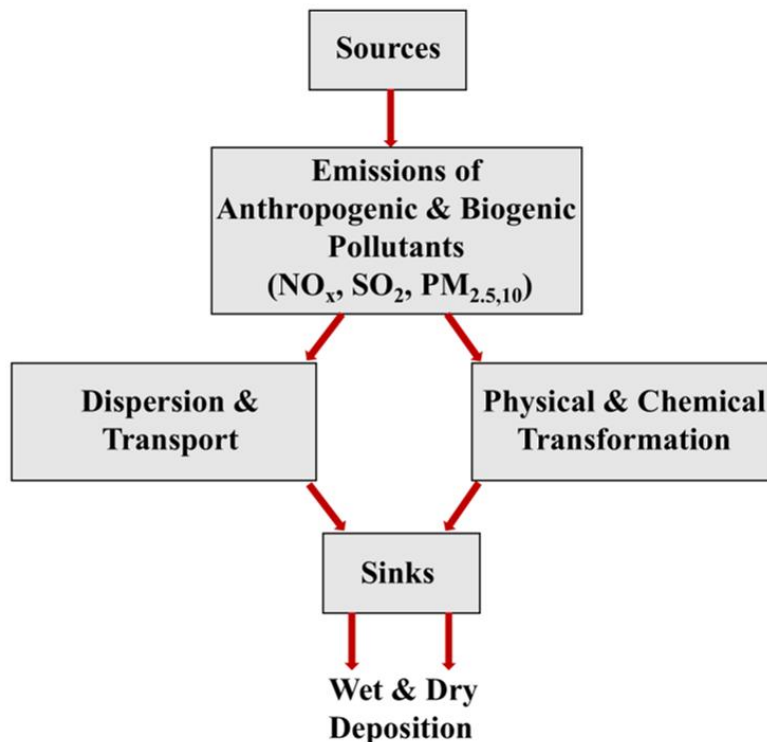


Figure 1-1: Overview of the key processes that control the atmospheric life cycle of trace gases and particles.

Understanding atmospheric chemistry is essential because it directly affects air quality, human health, and climate. Variations in atmospheric composition directly influence human exposure to reactive gases and particles through inhalation in both outdoor and indoor environments. Since people spend most of their time indoors, indoor exposure often has the greatest impact on overall health risks.^{11,12} Indoor air quality is controlled by indoor emission sources, ventilation and infiltration of air from outdoors, surface interactions, and chemical processing and fate.^{13,14} As a result, indoor environments are chemically dynamic systems in which atmospheric processes can modify the composition and lifetimes of trace species, underscoring the need to study indoor atmospheric chemistry and its effects on occupants.

1.2 Reduced reactive nitrogen in the atmosphere

Atmospheric reactive nitrogen (N_r) comprises both reduced (e.g., NH_3/NR_3) and oxidized (e.g., NO , NO_2 , $HONO$, NHO_3 , NO_2^- , NO_3^- , N_2O , and N_2O_4) forms, with reduced nitrogen playing a key role in atmospheric and indoor chemistry. In NR_3 , R denotes an organic substituent, such as an

alkyl group or other carbon-containing organic groups, including amino acids or cyclic species. Although research has focused largely on ammonia (NH_3), the most abundant reduced nitrogen species, the roles of alkylamines (NR_3) remain poorly understood. Due to their high reactivity and basicity, NH_3 and NR_3 participate in multiphase chemical processes, including gas–particle partitioning and secondary organic aerosol (SOA) formation.^{15–19} Through these processes, NH_3 and NR_3 can contribute to new particle formation and aerosol growth. Atmospheric aerosols originate from a variety of natural sources, including sea spray droplets, windblown dust, volcanic emissions, and biogenic material.^{20,21} Primary aerosols originate from anthropogenic sources like soot, smoke, or road salt, while secondary aerosols form through atmospheric processing of precursor gases.²² Aerosol particle sizes span from nanometers to micrometers and are commonly classified into three modes based on diameter: ultrafine (0.01–0.1 μm), fine (0.1–1 μm), and coarse (1–100 μm).²³ In this distribution classification, the ultrafine, fine, and coarse modes comprise the majority of particle number, surface area, and mass, respectively.²⁴ In aerosol chemistry, aerosol surface area and mass distribution are critical properties. Surface area governs the potential rate of heterogeneous chemical reactions, and mass generally indicates whether a substantial fraction of the aerosol mass resides in primary emitted coarse particles or generated chemically in the fine mode. Particles smaller than 1 μm are principally derived from gas-to-particle conversions through nucleation, condensation, acid/base neutralization, oxidation, and coagulation. Conversely, particles larger than 1 μm are produced by mechanical processes such as breaking a bubble and forming sea salt droplets. Aerosol removal processes include dry deposition and wet removal.²⁵ Dry deposition occurs by gravitational settling and particle impaction onto the surface, and in wet removal, particles are eliminated by incorporation into precipitation droplets. The lifetime of aerosols depends on their removal mechanisms. Ultrafine mode particles have a short lifetime of less than an hour, undergoing condensation and coagulation into the fine mode. Fine mode particles have a longer atmospheric lifetime, lasting for days to weeks, and are primarily removed through wet deposition, with dry deposition serving as an additional sink in the absence of precipitation. In contrast, coarse mode particle lifetimes range from minutes to a day, mainly influenced by the dry deposition mechanism.²⁶ Aerosol size, chemical composition, and atmospheric persistence govern their activation under supersaturated conditions, enabling aerosols to act as cloud and fog condensation nuclei (CCN/FCN). Therefore, by participating in new particle formation, NH_3 and NR_3 can impact the climate directly through radiative forcing and

indirectly by altering cloud and fog droplet properties.^{27,28} These processes emphasize the need for a comprehensive investigation of NH₃ and NR₃ to better understand their effects on aerosol chemistry, air quality, and climate.

1.2.1 Reduces nitrogen and anthropogenic impacts on the nitrogen cycle

Nitrogen is an essential element for all forms of life, and the atmosphere is Earth's largest reservoir of nitrogen. Atmospheric dinitrogen (N₂) comprises approximately 78% of atmospheric volume but is highly unreactive due to the high bond energy of the N≡N triple bond (≈950 kJ mol⁻¹).²⁹ As a result, N₂ must be converted into N_r, primarily as ammonium (NH₄⁺) or nitrate (NO₃⁻), before it can be assimilated by plants and microorganisms.

Natural conversion of atmospheric N₂ to N_r happens via two processes: lightning and biological nitrogen fixation (Figure 1-2).³ During lightning, the high temperatures cause molecular nitrogen and oxygen to dissociate and react, producing nitric oxide (NO; R1-1). This NO is rapidly oxidized to nitrogen dioxide (NO₂) via reaction with O₃ (R1-2).³⁰ The NO₂ subsequently undergoes atmospheric oxidation through reaction with hydroxyl radicals (OH), forming nitric acid (HNO₃) (R1-3).



Biological nitrogen fixation (BNF) is a major pathway for introducing N_r into ecosystems (Figure 1-2). In terrestrial soils, specialized prokaryotes (e.g., Azotobacter and Rhizobium) reduce N₂ to NH₃ via the enzyme nitrogenase (R1-4).^{31,32} In surface waters, nitrogen fixation is primarily carried out by cyanobacteria (e.g., Trichodesmium).³³ Globally, terrestrial BNF is estimated at approximately 100–130 Tg N a⁻¹, while marine BNF ranges from 87–156 Tg N a⁻¹, indicating that both environments contribute comparably to the global nitrogen cycle.³⁴



In addition, ammonification supplies N_r by converting organic nitrogen to NH₄⁺ through microbial degradation of organic matter in soils and aquatic environments (Figure 1-2).³⁵ The NH₄⁺ produced through nitrogen fixation or ammonification can be directly assimilated by plants, phytoplankton, and microorganisms to form amino acids and proteins.

Under aerobic conditions, NH_4^+ undergoes nitrification, a two-step microbial oxidation process in which NH_4^+ is first converted to nitrite (NO_2^- ; R1-5) and then to NO_3^- (R1-6; Figure 2-1).³ The produced NO_3^- can be assimilated by plants and other organisms or transported through terrestrial and aquatic systems.

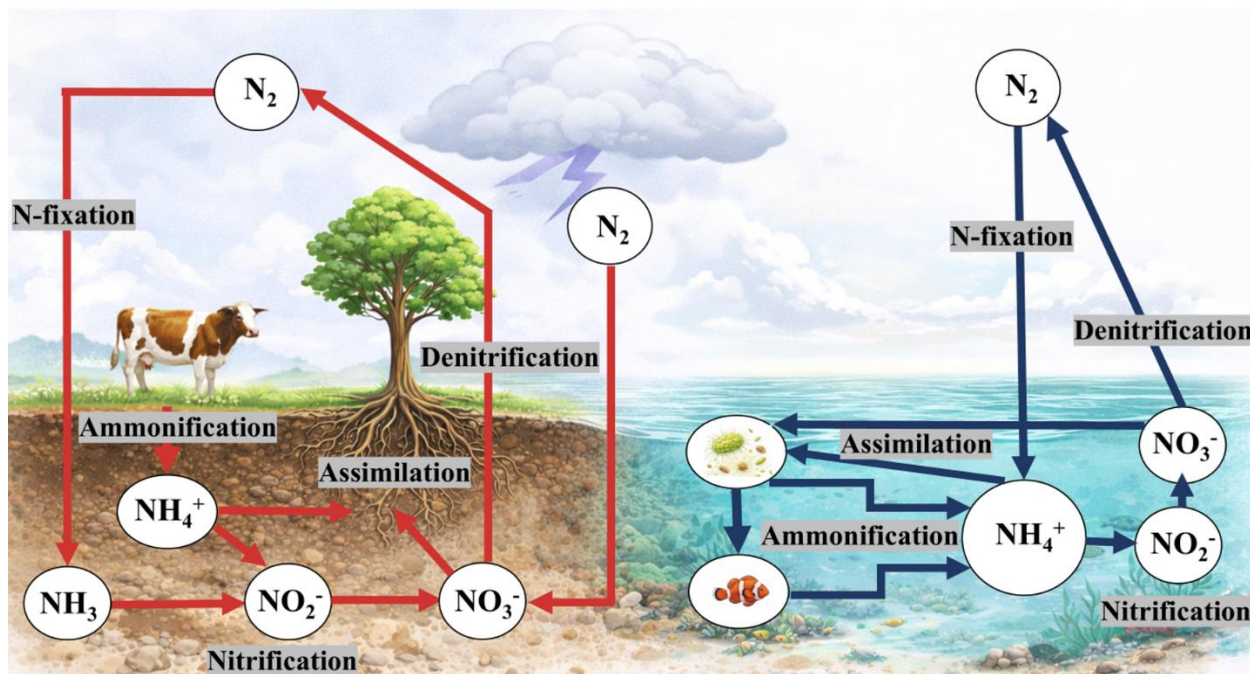
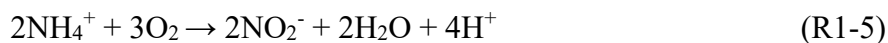
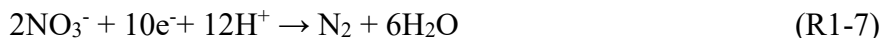


Figure 1-2: Nitrogen cycle in terrestrial and marine environments, highlighting reduced nitrogen ($\text{NH}_3/\text{NH}_4^+$) and the pathways of nitrogen fixation, ammonification, assimilation, nitrification, and denitrification.

Under anaerobic conditions, nitrate can be reduced back to molecular nitrogen (N_2) via denitrification (R1-7), a series of enzymatic reactions performed by heterotrophic microorganisms (Figure 1-2).³⁶ This process is a key pathway for nitrogen loss from terrestrial and marine ecosystems, returning N_2 to the atmosphere and completing the nitrogen cycle.



Reactive nitrogen plays a central role in regulating the composition, diversity, dynamics, and functioning of both terrestrial and aquatic ecosystems. Many ecosystems have evolved under nitrogen-limited conditions, and plant species are adapted to low background levels of available nitrogen. Herbivores that depend on these plants, as well as their predators, rely on the

interconnectedness of the nitrogen cycle.³⁷ Since the 1960s, human activities have substantially altered the global nitrogen cycle, doubling N_r in global ecosystems through fossil-fuel combustion, nitrogen-fertilizer production, and nitrogen-fixing legume cultivation.³⁸ Elevated nitrogen inputs have disrupted the natural nitrogen cycle, causing a range of environmental impacts. In terrestrial and aquatic environments, atmospheric NH_3 deposition initially increases surface pH due to its basicity and conversion to NH_4^+ ; however, subsequent biological processing of NH_4^+ through nitrification produces NO_3^- and releases H^+ (R1-5 and R1-6), contributing to soil and water acidification, and thereby impairing plant growth and increasing susceptibility to pests.^{39,40} In aquatic systems, excess NH_4^+ can cause eutrophication, stimulating excessive phytoplankton growth, oxygen depletion, and the subsequent loss of biodiversity as aerobic organisms perish.⁴¹ Therefore, increased availability of NH_4^+ can reduce biodiversity in both terrestrial and aquatic ecosystems by favoring nitrogen-demanding species while displacing species adapted to low-nutrient conditions.

1.2.2 Sources and atmospheric fate of reduced-N: Ammonia and alkylamines

Ammonia and NR_3 are ubiquitous reactive nitrogen species in the atmosphere, with NH_3 mixing ratios spanning from parts-per-trillion by volume (pptv) to parts-per-billion by volume (ppbv).^{42–44} Ammonia mixing ratios vary by environment, typically <1 ppbv in remote marine and continental regions,^{45,46} ~ 0.01 – 1 ppbv over the open ocean,⁴⁷ ~ 0.5 – 5 ppbv in coastal and rural environments,^{48,49} and ~ 5 – 20 ppbv in urban and agriculturally influenced regions,^{50–52} with mixing ratios exceeding 24 ppbv in intensive agricultural areas. Sources include diverse biogenic processes (Figure 1-3), such as marine biological activity, biomass burning, protein degradation, and vegetation, as well as anthropogenic activities, including animal husbandry, tobacco smoke, industrial emissions, combustion, vehicular exhaust, and wastewater treatment.^{42–44,53–57} Marine emissions are driven by biological degradation of organic matter, particularly phytoplankton grazing and microbial remineralization, linking oceanic sources to marine aerosol formation and growth.⁵⁸ Globally, NR_3 emissions are estimated at 285 ± 87 Gg $N\ a^{-1}$, with approximately 72% from terrestrial sources and 28% from oceanic sources. Methyl- and ethyl amines (mono-, di-, and tri-) are the most abundant atmospheric NR_3 with higher concentrations in rural areas than in urban environments.^{59,60}

Atmospheric removal of NH_3 and NR_3 occurs via gas-phase oxidation, gas-to-particle partitioning through acid–base chemistry, chemical reactions that lead to secondary organic aerosol formation, and wet deposition via rainwater and fogwater due to their high solubility and acid-neutralizing capacity.^{18,61,62}

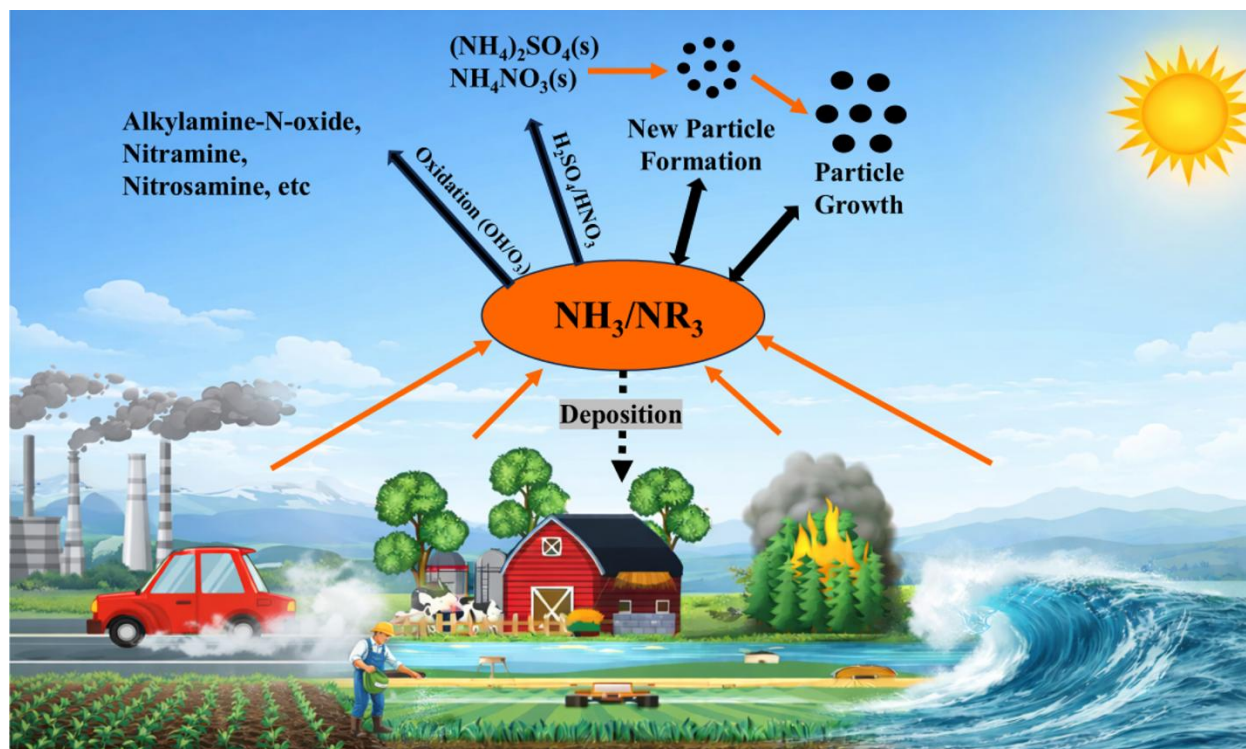
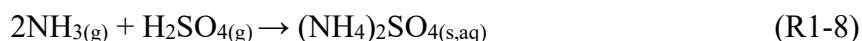
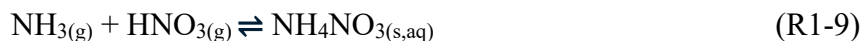


Figure 1-3: Atmospheric sources and sinks of ammonia and alkylamines.

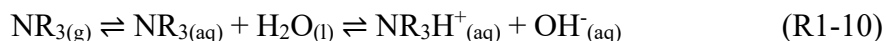
1.2.3 Chemical and physical properties governing the reactivity of ammonia and alkylamines

Ammonia and NR_3 ($\text{C}_1\text{--C}_6$) are important atmospheric bases, with NH_3 being an inorganic compound and NR_3 representing organic derivatives with alkyl substitutions on the nitrogen atom. Both molecules contain a lone pair of electrons, enabling them to act as Lewis bases and nucleophiles. Although NR_3 concentrations are 1–3 orders of magnitude lower than those of NH_3 in the atmosphere, NR_3 often outcompete NH_3 in acid–base reactions due to their higher basicity ($\text{pK}_a = 9.25\text{--}10.98$ vs. 9.25 for NH_3).^{18,59} Their high proton affinity enables them to neutralize acidic species like H_2SO_4 and HNO_3 and to form stable ammonium or aminium salts (R1-8 and R1-9).⁶³





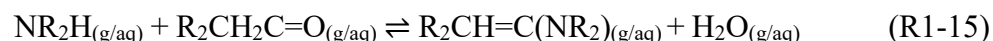
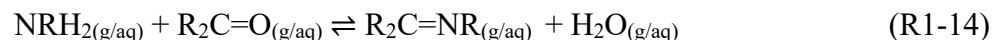
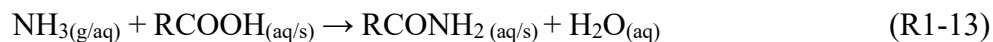
Ammonia and NR_3 readily partition into the gas phase from pure solutions due to their high volatility. Ammonia has a vapor pressure of ~ 860 kPa at 20°C , and short-chain alkylamines ($\text{C}_1\text{--}\text{C}_3$) also exhibit high volatility (>10 kPa at 20°C), which decreases with increasing alkyl chain length due to stronger van der Waals interactions.⁶⁴ Ammonia and NR_3 ($\text{C}_1\text{--}\text{C}_6$) are highly water-soluble due to hydrogen bonding and dipole-dipole interactions, with Henry's law constants (K_H) of ~ 60 M atm⁻¹ for NH_3 and ranging from ~ 4 M atm⁻¹ for trimethylamine to $\sim 10^6$ M atm⁻¹ for monoethanolamine.^{65,66} Solubility generally decreases with increasing alkyl chain length due to hydrophobic and steric effects. For example, monomethylamine ($K_H \approx 10^2$ M atm⁻¹) is about two orders of magnitude more soluble than trimethylamine. In aqueous phases, both NH_3 and NR_3 readily protonate to form NH_4^+ or NR_3H^+ ions (R1-10). The extent of protonation depends on the pK_a of NH_3/NR_3 and the effective pH of the aqueous phase. These ions can then react with a conjugate base (A^-) in solution to form an insoluble salt (R1-11).



Alkylamines can partition into pre-existing particles due to their high solubility and basicity, contributing to particle growth. Their stronger basicity relative to NH_3 also allows them to displace NH_3 from existing acid–base clusters (R1-12).⁶³

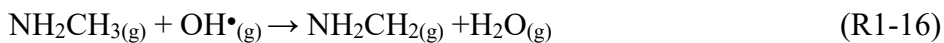


The basic nitrogen in NH_3 and primary (1°) or secondary (2°) NR_3 can react with carboxylic acids to produce amides (R1-13), particularly on aerosol surfaces or in aqueous films, contributing to secondary organic aerosol (SOA) formation.⁶⁷ Additionally, 1° NR_3 reacts with carbonyl compounds to form imines (R1-14), while 2° NR_3 forms enamines (R1-15).⁶⁸ These products can undergo further cyclization to form stable nitrogen-containing heterocycles, such as pyrroles and imidazoles.⁶⁹



Ammonia and NR_3 primarily undergo atmospheric oxidation via hydroxyl radicals (OH ; R1-16), but they can also react with Cl , NO_3 , and O_3 . Ammonia reacts slowly with OH ($k \approx 1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹), yielding an atmospheric lifetime of several days to a week.⁷⁰ In contrast,

NR₃ reacts much more rapidly ($k \approx 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), with gas-phase lifetimes of only a few hours.¹⁸ Although this limits their long-range transport as gases, their tendency to form stable particle-phase salts increases their persistence in the atmosphere.



1.3 Sample collection and analytical methods for quantifying reduced nitrogen in gas and aerosol phases

Reduced nitrogen species are present in the atmosphere in both gas and aerosol phases. Accurate quantification requires sampling approaches that account for the physicochemical properties and chemical reactivity of the target analytes, with collection methods matched to the relevant phase and sampling environment. Following collection, quantitative analytical techniques are required to determine ultratrace-level concentrations in atmospheric matrices.

1.3.1 Sample collection of gas and aerosol-phase reduced nitrogen

Appropriate sampling strategies are required before analysis and depend on the target phase and measurement environment. Gas-phase reduced nitrogen species can be measured using direct in situ spectroscopic techniques or mass spectrometry, or through collection-based approaches followed by offline analysis. In a collection-based approach, gas-phase species can be collected using active or passive sampling methods, both of which rely on acid–base interactions between basic nitrogen compounds and acidic collection substrates. In active sampling, controlled airflow transports NH₃ and NR₃ to a collection or detection interface, including acid-coated denuders for rapid chemical uptake onto acid-coated surfaces (e.g., phosphorus or citric acid),⁷¹ as well as (near) real-time instrumentation such as the Ambient Ion Monitor coupled with Ion Chromatography (AIM-IC), Cavity Ring-Down Spectroscopy (CRDS), Quantum Cascade Tunable Diode Laser Absorption Spectroscopy (QC-TDLAS), and Chemical Ionization Mass Spectrometry (CIMS) for active measurements of NH₃ and NR₃.^{72–76} Passive diffusive samplers, such as Ogawa samplers, rely on molecular diffusion to transport gaseous species to an acid-coated surface (e.g., citric acid), where irreversible protonation of reduced nitrogen drives collection without the need for pumps or power.⁷⁷ Although both approaches provide chemical selectivity for reduced nitrogen, passive samplers are generally preferred indoors because their unobtrusive,

power-free operation enables long-term time-weighted average (TWA) measurements in occupied spaces with minimal disturbance.^{78,79}

Atmospheric aerosols are typically collected by drawing ambient air through sampling devices that remove particles from the airstream either by filtration or impaction onto a substrate for subsequent chemical analysis. The Micro-Orifice Uniform Deposit Impactor (MOUDI) is engineered explicitly for size-resolved aerosol sampling, which is important for linking aerosol chemical composition to sources and atmospheric processing.^{80–82} The MOUDI functions as a cascade impactor that separates particles by aerodynamic diameter through inertial impaction. This involves passing aerosol through multiple stages with arrays of micro-orifice nozzles of decreasing sizes, each stage corresponding to a specific aerodynamic cutoff diameter. These stages span a wide particle size range, from submicron ($<1\ \mu\text{m}$) to supermicron ($>1\ \mu\text{m}$). Particles with sufficient inertia deviate from airflow streamlines and impact on collection substrates, while smaller particles remain in the airflow and travel to the next stage. A notable aspect of MOUDI is its numerous micro-orifice nozzles per stage, which reduce jet velocity and pressure drop, maintain predominantly laminar flow, and ensure uniform particle deposition.⁸³ As a result, bounce and re-entrainment are minimized, enhancing collection efficiency across different size ranges and enabling reliable size-resolved aerosol collection across a wide range of atmospheric environments.

1.3.2 Analytical methods for quantitative analysis of reduced nitrogen

Accurate quantification of NH_3 and NR_3 in both gas and aerosol phases is essential for understanding their roles in atmospheric chemistry in indoor and outdoor environments. A range of analytical approaches has been developed to quantify reduced nitrogen species across multiple phases. Amine-containing particles have been detected using several on-line mass spectrometric techniques, including aerosol time-of-flight, atmospheric pressure interface time-of-flight, and thermal desorption chemical ionization methods.^{16,84–87} These approaches provide insights into particle composition and sources; however, they are mostly qualitative because structural isomers cannot be distinguished solely by mass-to-charge ratios, and measurements are subject to substantial ionization efficiency matrix effects.

Quality assurance and quality control (QA/QC) are integral to the development and validation of analytical methods. Quality assurance prevents errors throughout sampling and analysis,

whereas quality control detects and quantifies errors through systematic evaluation of method performance. The QA/QC processes aim to reduce both random errors, evaluated through precision (variability of replicate measurements), and systematic errors caused by calibration bias, matrix effects, or analyte loss. Analytical performance is assessed using quantitative metrics such as precision (e.g., relative standard deviation of replicate analyses), accuracy (e.g., percentage relative error of check standards), reproducibility, and blank assessments (e.g., reagent, field, and sample blanks) to detect background contributions and potential contamination. Additional measures include validation of calibration standards, determination of detection limits, and intercomparison with established analytical methods. Reproducibility further characterizes method robustness by assessing consistency across varying analytical conditions, including measurements conducted over time. The stability of calibration standards is also evaluated to quantify potential analyte loss and its impact on method accuracy. These considerations are particularly critical for reduced nitrogen species, where volatility, reactivity, ultra-trace concentrations, and matrix effects can introduce analytical uncertainty. Implementation of rigorous QA/QC protocols ensures reliable quantification and provides a robust framework for method validation, including the assessment of precision, accuracy, reproducibility, standard stability, calibration performance, and the application of methods to real atmospheric samples (Chapter 2).

Quantitative analysis of NH_3 and NR_3 in atmospheric samples is most commonly achieved using chromatographic techniques, including gas chromatography (GC), high-performance liquid chromatography (HPLC), capillary electrophoresis (CE), and ion chromatography (IC). Chromatographic separation is based on the distribution of analytes between two phases: a mobile phase (gas or liquid) and a stationary phase (a solid or a liquid immobilized on a solid support).^{88–90} After injection, the mobile phase carries the sample through the stationary phase, and analytes partition between the phases according to their molecular structures and intermolecular interactions. Analytes with higher affinity for the stationary phase migrate more slowly, whereas those with weaker interactions elute more rapidly with the mobile phase. These differences in migration rates separate the analytes as they move through the system, enabling subsequent detection and quantification. Although all chromatographic techniques are based on differences in analyte partitioning between a mobile and a stationary phase, they differ in the physical characteristics and chemical functionality of these phases, as well as in their separation processes. In GC, analytes are carried by an inert gas and mainly separated based on volatility and interactions

with the stationary phase. High-performance liquid chromatography employs a liquid mobile phase, with separation primarily achieved through partitioning and adsorption between analytes and the stationary phase. Capillary electrophoresis separates charged species in a liquid medium based on differences in their electrophoretic mobility under an applied electric field. Ion chromatography is a liquid-phase method in which separation primarily occurs via electrostatic interactions between charged analytes and ion-exchange functional groups on the stationary phase. The GC, HPLC, and CE methods often require extraction and derivatization to enhance sensitivity, selectivity, and the limit of detection; however, these additional steps increase analytical time and complexity and can introduce uncertainty when handling volatile, highly reactive compounds such as reduced nitrogen.^{91–93} Ion chromatography is regarded as one of the most robust quantitative techniques for analyzing low molecular weight NR₃, including tertiary amines, because it enables direct analysis of aqueous extracts, minimizes sample preparation, and reduces contamination, analysis time, and systematic errors.⁹⁴ Despite these advantages, earlier IC methods were limited by low resolution and separation efficiency, which restricted the quantification of NR₃ and often led to co-elution of highly abundant atmospheric species such as diethylamine (DEAH⁺) and trimethylamine (TMAH⁺).^{76,95–97} Accurate quantification of NR₃ species remains challenging due to their ultra-trace pptv range ambient concentrations, high reactivity and volatility, susceptibility to sampling artifacts, instability of calibration standards, and reduced reproducibility. These challenges reveal a key knowledge gap in the literature and highlight the need for improved ion chromatographic method development capable of separating the most abundant atmospheric NR₃ with high selectivity and separation efficiency, and of quantifying them with higher accuracy and precision, with lower limits of detection, in both gas- and particle-phase samples.

1.4 Indoor atmospheric chemistry of gas-phase ammonia and alkylamines

Ammonia and NR₃ are highly volatile reduced nitrogen gases that are generally present at elevated mixing ratios indoors compared with outdoors. In the outdoors, NH₃ mixing ratios typically range from <1 ppbv in remote regions to ~5–20 ppbv in urban and agriculturally influenced areas reflecting atmospheric dilution, dry and wet deposition, and gas–particle partitioning.^{18,46} By contrast, indoor concentrations typically range from 10 to 70 ppbv. This indoor enhancement reflects continuous and proximal emission sources, limited ventilation, and reduced atmospheric removal mechanisms.^{13,98}

Indoor sources of NH_3 and NR_3 include humans and pets, tobacco smoke, meat cooking, ammonia-based cleaning products, and emissions from building materials, such as curing agents used in concrete (Figure 1-4).^{98–102} Because NH_3 and NR_3 are dominant indoor alkaline species, they readily neutralize acidic gases such as CO_2 and HNO_3 in both the gas phase and surface water films, thereby promoting secondary aerosol formation through multiphase acid–base reactions.¹³ At high concentrations, these compounds are classified as hazardous air pollutants because of their irritant and toxic effects.¹⁰³ Even at lower levels, NH_3 exposure can cause sensory irritation, and higher exposures may lead to respiratory symptoms such as coughing, headaches, and asthma-like responses.¹⁰⁴



Figure 1-4: Overview of indoor NH_3 emissions and their transformation through surface reactions (Table of contents figure adapted from Chapter Five of the manuscript on indoor NH_3 submitted to *ACS ES&T Air*, with a revision requested).

In addition to their direct toxicity, NH_3 and NR_3 can generate hazardous secondary pollutants indoors via chemical reactions at the surface of water films. A well-known example is the formation of monochloramine when NH_3 -based cleaning products are mixed with oxidizing hypochlorite bleach (NaOCl), producing this volatile respiratory irritant (R1-17), along with NHCl_2 and NCl_3 in the presence of excess oxidants.^{105–107}



Chloramines may also form unintentionally during kitchen cleaning when chlorinating agents react with ammonium, aminium ions, or amino acids on indoor surfaces. A second critical pathway involves the formation of nitrosamines, highly carcinogenic compounds produced by the nitrosation of NR_3 with nitrous acid (HONO) in surface water films (R1-18).



Indoor HONO and nitrite (NO_2^-) come from the deposition of combustion-generated $\text{HONO}_{(\text{g})}$ and nitrogen dioxide released during activities like gas stove cooking, smoking, and candle burning.^{108–}

¹¹⁰ Nitrosamines can cause serious health risks, including mutations and tumors, by alkylating DNA.

Therefore, NH_3 and NR_3 are critical indoor air pollutants, as they are volatile bases and precursors of hazardous reaction products; however, their chemical processes and impacts in indoor environments remain poorly understood. In North America, people spend most of their time indoors, so inhalation of indoor air pollutants is the primary route of exposure.¹² Accordingly, identifying and reducing indoor sources of NH_3 and NR_3 is essential not only to reduce direct exposure but also to limit their subsequent chemical transformations indoors. However, source control alone is insufficient to explain observed indoor concentrations, as the indoor concentrations of reduced nitrogen are largely determined by its fate following emission. The fate of indoor NH_3 and NR_3 is governed by coupled physicochemical and environmental processes, including air exchange, surface chemistry in water films, and interactions with solid surfaces.¹³ Unlike the outdoor environment, the high indoor surface-to-volume ratio prioritizes surface-mediated, multiphase processes in determining the fate of reduced nitrogen compounds. Once NH_3/NR_3 partitions from the gas phase into surface water films, various chemical pathways can be followed. First, NH_3/NR_3 is readily protonated to form $\text{NH}_4^+/\text{NR}_3\text{H}^+$ through acid–base equilibrium (R1-10). Second, protonated $\text{NH}_4^+/\text{NR}_3\text{H}^+$ can neutralize deposited inorganic acids, such as HNO_3 and H_2SO_4 , forming ammonium/aminium salts (R1-8 and R1-9) that may reside on surfaces or in particle-associated water. Third, in the presence of reactive organic compounds, particularly carboxylic acids and carbonyl compounds, reduced nitrogen species form amides, imines, and enamines (R1-13 – R1-15). In addition to chemical reactions, NH_3/NR_3 can undergo physical sorption onto indoor materials independently of aqueous-phase processes.¹¹ Surfaces such as drywall, concrete, wood, textiles, carpets, and dust can adsorb and retain NH_3/NR_3 either within their structure or on surface functional groups. This adsorbed fraction serves as a dynamic reservoir

that stores reduced nitrogen and can subsequently release it back into the gas phase. Desorption is controlled by material microstructure (e.g., permeability and porosity) and is promoted by higher temperatures, lower relative humidity, and increased ventilation, which enhance concentration differences between surface reservoirs and the surrounding indoor air.^{111,112} These interconnected chemical and physical mechanisms govern the persistence, transformation, and removal of NH_3/NR_3 in indoor environments.

1.5 Reduced nitrogen in the marine boundary layer: aerosol–fog interactions

Aerosols play a key role in regulating Earth's energy balance through direct radiative forcing and indirect effects by acting as cloud condensation nuclei (CCN).^{27,28} Aerosols can promote fog formation by growing through water uptake when relative humidity exceeds 100%, whereas fog can modify aerosol populations through coupled physical and chemical multiphase processes.^{113,114} In this aerosol–fog system, reduced nitrogen is particularly important because of its high basicity, abundance, and reactivity in the marine atmosphere; however, its influence on fog formation, persistence, and associated aerosol processing remains poorly understood.

1.5.1 Marine sources, formation, and size distributions of aerosols

Marine aerosols can originate from both primary and secondary sources.¹¹⁵ Primary aerosols originate from sea spray produced by sea bubble bursting after wave breaking, and from the direct mechanical disruption of wave crests due to wind action on the ocean surface (Figure 1-5). These primary aerosols at the air–sea interface produce three distinct types of droplets: film, jet, and spume, which differ in formation mechanisms and size distributions.²⁰ Film and jet droplets form under moderate wind speeds ($\sim 5 \text{ m s}^{-1}$).¹¹⁶ Film droplets arise from the breakup of thin bubble films and contribute primarily to the chemical composition of fine mode aerosols. These droplets are enriched in organic matter derived from marine biological activity, including polysaccharides, proteins, and phytoplankton fragments, as well as inorganic sea salt ions.^{68,117,118} Simultaneously, jet droplets form through the collapse of bubble cavities and typically generate coarse mode aerosol from bulk seawater. Under stronger wind conditions ($\sim 10 \text{ m s}^{-1}$), direct shearing of wave crests produces spume droplets ranging from tens of micrometers to millimeters.¹¹⁹ Sea surface temperature further affects sea spray aerosol production: lower temperatures reduce emissions, while higher temperatures increase emissions for both fine and coarse aerosols modes.¹²⁰

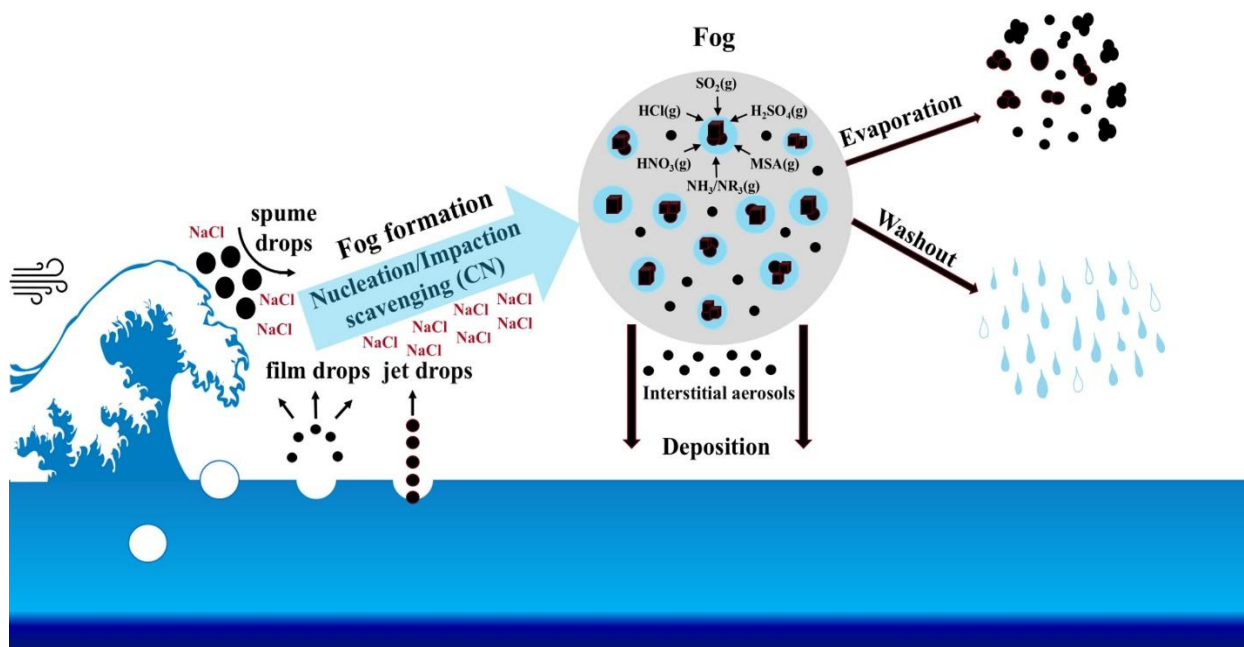


Figure 1-5: Marine aerosols derive from sea spray generated by bubble bursting and disruption of the wave crest, resulting in the formation of film, jet, and spume droplets (primary) and through gas-to-particle conversion (secondary). In a supersaturated atmosphere, primary aerosols can act as condensation nuclei, leading to fog formation via nucleation or impaction scavenging, which produces fog droplets. The uptake of gaseous species by fog droplets through aqueous phase reactions contributes to the formation of secondary aerosols. Aerosol loading can increase due to fog droplet evaporation or decrease through precipitation or deposition (Table of contents figure adapted from Chapter Three of the manuscript on microphysical chemistry of aerosol-fog interaction published in *QJRMS*).

Secondary marine aerosols are produced through gas-to-particle conversion processes that involve volatile gaseous precursors released by marine biological activity, such as the phytoplankton life cycle (Figure 1-5).⁵⁸ In the marine atmosphere, oxidation and partitioning of these biogenic gases yield low-volatility products, including processed sulfur species (e.g., non-sea-salt sulfate (nss)- SO_4^{2-} and methane sulfonic acid) and reactive reduced nitrogen compounds (e.g., NH_3 and NR_3).^{121–125} In addition to marine-derived aerosols, anthropogenic particles containing acidic (e.g., SO_4^{2-} and NO_3^-) and basic (e.g., NH_4^+) species are transported from continental regions over the oceans and deposited into surface waters. This deposition can alter surface seawater chemistry by changing pH and nutrient availability, with important implications for marine biogeochemistry and biological productivity.^{126,127} Therefore, marine and

anthropogenic sources supply processed sulfur and reduced nitrogen species to the MBL, providing precursors for secondary aerosol formation and subsequent aerosol processing.

1.5.2 Marine fog in the boundary layer

Fog is a collection of suspended water droplets that reduces horizontal visibility at the surface to less than one kilometer. Fog formation results from a complex interplay of radiative, thermodynamic, microphysical, chemical, and surface-driven processes, coupled with microscale air mixing and turbulence, and influenced by synoptic-scale meteorological factors, including air mass movement, temperature variations, surface wind direction, and sea-level pressure changes.¹¹³ In marine environments, fog typically forms within a shallow boundary layer capped by a temperature inversion, where cooling and moistening of near-surface air led to saturation and droplet activation on ambient aerosol particles.¹²⁸ In marine environments, fog is typically classified as either advection fog or cloud-base-lowering fog.^{113,129} Advection fog occurs when air moves over an ocean surface with a different temperature. Warm sea fog forms when warm, moist air passes over colder waters, cooling down and becoming saturated. This process was first recorded over the Grand Banks by Taylor (1917),¹³⁰ where air from the Gulf Stream encounters the colder Labrador Current. Conversely, cold sea fog occurs when cold air is advected over warmer ocean surfaces, becoming saturated through enhanced evaporation and turbulent mixing, as observed in coastal regions like southern California. Another key type of marine fog is cloud-base-lowering fog, which forms when low marine stratus descends to the surface due to subsidence and strong boundary-layer inversions.¹³¹

The Grand Banks and Sable Island regions of the Northwest Atlantic Ocean are the second-largest marine fog area globally, with fog occurring most frequently in the summer months (June–August), which account for approximately 45% of observed fog events from 1950 to 2007.¹²⁸ This elevated frequency is driven by persistent interactions between warm, moist air masses associated with the Gulf Stream and the cold surface waters of the Labrador Current, which create favorable conditions for frequent warm sea fog formation. The high frequency and persistence of fog in this region pose a significant safety hazard to marine transportation, aviation, and offshore operations, highlighting the need to resolve uncertainties in aerosol activation and fog formation. In particular, determining which aerosol size fractions activate to form and sustain fog droplets, and how size-resolved composition influences fog formation and persistence, is critical to improving marine fog

forecasting in the Northwest Atlantic.^{132,133} There is an intricate relationship between aerosols and fog, because all atmospheric droplets nucleate on or grow from existing aerosols (Figure 1-5). Aerosol properties, particularly size, chemical composition, and hygroscopicity, directly influence fog droplet activation, growth, and persistence, while fog droplets affect aerosol loading and chemistry.¹¹³

1.5.3 Aerosol-fog interactions and reduced nitrogen processing

Fog droplets have competing effects on atmospheric aerosol populations.¹³⁴ On the one hand, aerosol concentrations are reduced through scavenging processes, including nucleation, in which aerosols are activated and grow into fog droplets, and impaction (collection), whereby aerosols are collected by droplets via collision-coalescence and are subsequently removed through deposition or precipitation.^{114,135,136} On the other hand, aerosol mass loading can increase through the uptake of gas-phase species into fog droplets, followed by aqueous-phase reactions that form secondary aerosol mass.^{137,138} These aerosols are then released into the atmosphere through droplet evaporation and the repartitioning of gases from the aqueous phase. The relative importance of these processes depends on environmental conditions governing fog formation, including meteorology, aerosol and gas-phase chemical composition, and fog duration. Consequently, aerosol-fog interactions play a fundamental role in controlling fog evolution and persistence, making them critical for improving fog prediction. Despite extensive research, key knowledge gaps remain regarding which aerosol populations dominate fog microphysics in marine environments. It remains unclear whether fog droplet activation and long-term persistence are primarily controlled by fine-mode aerosols, such as ammonium sulfate, which have high number concentrations, or by coarse mode aerosols, such as sea salt, which have lower number concentrations but are strongly hygroscopic and ubiquitous in marine air. The mechanisms by which coarse mode aerosols initiate fog droplet formation and subsequently sustain large droplet populations through nucleation and other microphysical processes are poorly constrained. Moreover, it is not well understood which aerosol populations persist throughout and/or sustain fog droplet populations during prolonged marine fog events (>24 h) and actively maintain fog droplet populations over time.

Reduced nitrogen species (NH_3 and NR_3) are the most abundant basic compounds in the marine atmosphere and readily neutralize acidic species such as sulfuric and nitric acids, thereby

contributing to secondary aerosol formation. In marine fog, liquid water enhances aqueous-phase chemical processing, promoting the partitioning of reduced nitrogen into fog droplets and facilitating acid–base reactions.^{139,140} Despite this reactivity, questions remain regarding the role of reduced nitrogen in marine fog microphysics. It is unclear if or how reduced nitrogen influences the initial activation of aerosols into fog droplets and whether its aqueous-phase partitioning contributes to sustaining droplet populations during prolonged marine fog events and its potential chemical impacts. These uncertainties limit our understanding of how reduced nitrogen processing within fog droplets affects aerosol populations, their chemical properties, and fog persistence in marine environments.

1.6 Reduced nitrogen research in this thesis

This thesis presents a quantitative analysis of reduced nitrogen species, including NH_3 and the most abundant atmospheric NR_3 , in marine boundary layer aerosols under fog conditions and in the indoor air of newly built Canadian homes during the first year of occupancy. Reduced nitrogen plays a central role in atmospheric chemistry due to its abundance, high basicity, and reactivity, influencing aerosol formation and growth, multiphase chemical processing, and air quality in both outdoor and indoor environments. Despite its importance, significant uncertainties remain about the role of reduced nitrogen in aerosol–fog interactions, particularly its processing within aerosols during fog events, as well as the sources, transformations, and fate of gaseous reduced nitrogen in indoor environments. This is largely driven by the difficulty in making quantitative measurements of these trace gases from atmospheric samples.

A central component of this thesis is, therefore, the optimization and development of an IC method coupled with conductivity detection (CD) for the quantitative analysis of NH_3 and the ten most abundant atmospheric NR_3 species in both aerosol and gas phases (Chapter 2). The methodological advances address key analytical challenges, including chromatographic selectivity and separation efficiency, calibration stability, suppressor performance, and overall analytical accuracy, precision, and detection limits. Method validation was achieved by applying the method to real aerosol and gas-phase samples. Collectively, these improvements establish a robust analytical method for quantifying reduced nitrogen species in marine boundary layer aerosols and indoor air.

The developed IC–CD method was applied to analyze marine aerosol samples collected over the Northwest Atlantic Ocean during the fog and turbulence interactions in the marine atmosphere (Fatima) 2022 ship-based field campaign. Chapters 3 and 4 examine the chemical and microphysical processes governing fog-aerosol interactions. Chapter 3 presents a comprehensive investigation of aerosol–fog interactions by combining size-resolved aerosol chemistry with microphysical properties, physical processing, and meteorological and oceanographic parameters. This chapter investigates the impact of fog on the ionic mass loading of aerosols across both coarse and fine modes, including coarse mode sea salt ions (e.g., Cl^- , Na^+ , Mg^{2+} , ss-SO_4^{2-} , K^+ , and NO_3^-) and fine mode processed sulfur species (e.g., nss-SO_4^{2-} and MSA^-) and reduced nitrogen species (e.g., NH_4^+ , DMAH^+ , and DEAH^+). These analyses elucidate how fog affects aerosol mass distributions and identifies which aerosol size act as fog condensation nuclei. In addition, three chemically distinct fog types were identified using size-resolved ion mass distributions, particle number concentrations, and meteorological conditions, thereby providing insight into the drivers of aerosol chemical composition for each type. Chapter 4 focuses on the impact of fog on the chemical composition and properties of fine mode aerosols and fog water, with particular emphasis on processed sulfur and reduced nitrogen species. This fog influence is assessed by quantifying changes in the equivalent ionic loadings of processed sulfur and reduced nitrogen species under ambient and fog conditions, and by quantifying their corresponding equivalent ionic loadings in fog waters. The Fatima 2022 dataset is the most extensive marine fog dataset to date for studying aerosol–fog interactions from a chemical perspective. These findings have direct implications for improving marine fog forecasting models to support safer marine transportation.

The optimized IC–CD method was also applied to quantify reduced nitrogen in the indoor gas phase. Chapter 5 examines the influence of NH_3 on indoor air and surface chemistry. As part of the New Home Air Quality Study (NHAQS), temporal changes in indoor reduced nitrogen, especially NH_3 , from pre-occupancy through the first 12 months of resident occupancy were quantified in 48 new homes with non-smoking residents in the Ottawa-Gatineau area of Ontario, Canada from 2019 to 2024. Passive samplers collected target analytes quantified by ion chromatography and liquid chromatography with mass spectrometry, and occupant surveys were integrated into a generalized linear mixed model to identify potential sources and sinks of NH_3 . This chapter extends the application of the developed analytical methods to indoor settings and addresses sources and temporal variability of reduced nitrogen in the built environment to provide

new insight on how homeowners may recognize and reduce NH_3 sources to improve indoor air quality.

1.7 References

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CHAPTER TWO – Suppressor and calibration standard limitations in cation chromatography of ammonium and 10 alkylamines in atmospheric samples

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Abstract

Ammonia (NH_3) and alkylamines are ubiquitous in the atmosphere and have been suggested to play important global roles through new particle formation and aerosol growth. In this work, we optimized an ion-chromatographic (IC) method to separate and quantify the ten most abundant atmospheric alkylamines with high selectivity and separation efficiency, using 4 μm packed columns and resin-based suppressors, alongside stabilizing amine standards. Modern resin suppressors operating on a gradient elution program affected the linear response of this IC technique. Calibration statistical analyses found a loss of analytes in these cation-exchange devices. Suppressor operational longevity was optimized by using a stepped current and an external water supply, which improved precision, accuracy, and LODs compared to other suppression modes. When this new method was applied to real samples, amines were found ubiquitously in size-resolved marine aerosol samples; monpropylamine, isomonpropylamine, and monobutylamine were detected and quantified in these samples, which have not been reported before. The molar ratio of the sum of aminium to ammonium ranged from 0.02 to 0.2, showcasing the application of the developed method towards studying the diversity and importance of alkylamines in coastal marine particle composition. The new analytical method also found NH_3 present in a suite of new homes with a mean mixing ratio of 25 ± 15 ppbv; a common level reached between homes across the study during the first year of occupation which can then be transported outdoors.

2.1 Introduction

Ammonia and alkylamines are reactive species ubiquitous in the atmosphere, emitted to the gas-phase in both outdoor and indoor air.¹ Outdoor sources originate from a variety of processes, both biogenic (ocean organisms,² biomass burning,³ protein degradation,⁴ and vegetation⁵) and anthropogenic (animal husbandry,⁶ tobacco smoke,⁷ industries,⁸ combustion,⁹ automobiles,¹⁰ and treatment of sewage and waste¹¹). The oceans emit these nitrogen-containing gases to the atmosphere due to biological degradation of organic matter, such as grazing of phytoplankton and remineralization of microorganisms, allowing them to contribute to the formation and growth of marine aerosols.¹² Global amine emissions are estimated at $285 \pm 87 \text{ Gg N a}^{-1}$ with 72% of terrestrial origin (205 Gg N a^{-1}) and 28% derived from oceanic sources (80 Gg N a^{-1}).¹³ Methyl and ethyl amines (mono-, di-, and tri-) are the most abundant alkylamines in the atmosphere, with higher concentrations in rural areas than in urban environments.¹⁴ For example, global emissions of methylamines have been estimated at $150 \pm 60 \text{ Gg N a}^{-1}$ from animal husbandry operations.⁵ Removal of amines from the atmosphere can proceed through gas phase chemical reactions, gas-to-particle partitioning, and wet deposition.¹⁵ Amines are oxidized by reacting with the hydroxyl radical (OH), chlorine radical (Cl), nitrate radical (NO₃), and ozone (O₃) with short atmospheric lifetimes on the order of hours, mainly via loss to OH.¹⁶ Amines can condense into the particle-phase and undergo neutralization reactions with acids such as HNO₃ and H₂SO₄, a process which has been suggested to play an essential role in new particle formation and aerosol growth.¹⁷ Even though alkylamine concentrations are 1 – 3 orders of magnitude lower than NH₃ in the atmosphere, they compete with NH₃ to participate in these acid-base reactions.¹⁵ This is in part due to alkylamines having higher basicity (pK_a = 9.25–10.98) than NH₃ (pK_a = 9.25), resulting in the formation of more stable salts, and by extension more rapid atmospheric particle formation. Amines can also undergo reactions with other organics in particles, like carbonyls, to form light-absorbing species such as imines, enamines, and even polymerized materials.¹⁸ Formation of these high molecular weight nitrogen-containing products depends on the structure of the precursor amines (i.e. primary or secondary) and the presence of carbonyl compounds that can facilitate such particle formation or aerosol growth. De Haan *et al.*¹⁹ measured the condensed-phase reactions between monomethylamine (MMA) and glyoxal to form oligomers, imidazole, and light-absorbing compounds that identified a new contribution for MMA to be involved in particle formation. In both cases, amines participating in the formation of new particles can go on to

directly impact climate through their radiative forcing and indirectly by changing cloud droplet properties.^{20,21} Changes in aerosol sizes and morphologies impact scattering and absorption of light, resulting in changes to aerosol photochemistry and the energy balance of Earth. Displacement reactions of ammonium by alkylamines, in contrast, improves sulfate aerosol water uptake and thereby their propensity to form cloud condensation nuclei (CCN). The formed CCN impact cloud formation and lifetime, and ultimately climate forcing through their radiative properties. Finally, gaseous amines can also be removed from the atmosphere through wet deposition in the form of rainwater and fogwater due to their high water solubility and acid-neutralizing capacity,^{22,23} alongside scavenged aerosols.^{24,25}

The study of ammonia and amines as atmospheric pollutants is also critical in indoor environments since people in North America spend more than 90% of their time inside yet the sources and processes governing indoor air quality are poorly understood.²⁶ Ammonia and alkylamines have a number of indoor sources: tobacco smoke,⁷ humans,²⁷ pet excrement,²⁸ cooking meat,²⁹ cleaners,³⁰ a host of consumer products,³⁰ and concrete curing agents.³¹ The fate of indoor pollutants depends on environmental parameters such as humidity, temperature, the concentration of emitted compounds, air mixing, and air exchange by the ventilation system.³² Ammonia and amines as gases or as components of inhalable particles have been associated with detrimental effects on respiratory health such as occupational asthma.³³ In indoor environments where nitrous acid is also abundant, amines may react to form toxic and carcinogenic nitrosamines.³⁴ Therefore, high quality analytical methods can play an important role in quantifying ammonia and amines indoors to help occupants recognize sources and reduce exposure to hazardous reaction products.

Analytical techniques to quantify NH_3 and alkylamines are essential in both aerosol and gas phases. Consequently, quantitative measurement of NH_3 and amines is required to understand their role in both phases in outdoor and indoor atmospheric environments. Amine-containing particles have been detected by multiple on-line mass spectrometric methods such as aerosol time-of-flight, atmospheric pressure interface time-of-flight, and thermal desorption chemical ionization.^{35–38} The drawback of mass spectrometric measurements is that they provide qualitative results due to an inability to differentiate structural isomers by their mass to charge ratio. These techniques can also be subject to substantial ionisation efficiency matrix effects. For example, Murphy *et al.*³⁹ observed increased ionisation efficiency of ammonia and amines in a C-TOF-AMS

when methylamine was added to a chamber containing ammonium sulfate seed. Quantitative analysis of atmospheric alkylamines in gas and particle phases is challenging because of their low ambient concentrations (parts per trillion by volume (pptv)) in various environmental matrices.¹³ Quantitative measurements of alkylamines have been obtained most often by chromatography methods such as gas chromatography (GC), high-performance liquid chromatography (HPLC), capillary electrophoresis (CE), and ion chromatography (IC). Most of these approaches (GC, HPLC, and CE) require extraction and derivatization to improve sensitivity, separation selectivity, and limits of detection, which is time-consuming and requires special handling when working with volatile compounds.^{40–42} IC is regarded as one of the most common quantitative methods to analyze low molecular weight alkylamines, including tertiary amines, with the advantage of direct analysis of aqueous extracts, reducing sample preparation and contamination, analysis time, and systematic errors.⁴³ However, previously developed IC methods could only analyze a few atmospheric alkylamines or struggled with coelution of pairs of cations (e.g. diethylamine (DEAH^+) and trimethylamine (TMAH^+)). Because of the low resolution and separation efficiency of prior IC methods,^{39,44–47} Place *et al.*⁴⁸ developed the first successful IC method to separate the DEAH^+ and TMAH^+ pair, amongst others, by modifying the analytical column temperature for the separation. As a result, they could separate and quantify ammonium and the nine most abundant atmospheric alkylamines. Here we build on this prior work to develop an ion chromatographic method with conductivity detection (CD) to separate and quantify the ten most abundant atmospheric alkylamines (including MEtA) and six inorganic cations using the next generation of 4 μm stationary phase packing and dynamic suppression with resin-based ion exchange devices. Herein, we demonstrate an increase of separation efficiency and better peak resolution with gradient and temperature programming, an assessment of how to prepare stable calibration standards of alkylamines, an exploration of statistical approaches to recommend an appropriate calibration method that retains high accuracies for these analytes, an optimization of the suppression mode to obtain calibrations with the highest accuracy and precision outcomes alongside the lowest LODs, and application of the developed method to real atmospheric samples of aerosol and the gas phase to validate the IC method.

2.2 Experimental

2.2.1 Materials and Chemicals

A premixed cation standard concentrate (Dionex six-cation II, P/N: 046070, Thermo Scientific, Sunnyvale, CA, USA) of Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} was used to prepare inorganic cation stock solutions. Primary standard solutions of the following alkylamines: monomethylamine (MMA, 40% w/w), dimethylamine (DMA, 40% w/w), trimethylamine (TMA, 45% w/w), monoethylamine (MEA, 70% w/w), diethylamine (DEA, $\geq 99.5\%$ w/w), triethylamine (TEA, $\geq 99.5\%$ w/w), monopropylamine (MPA, $\geq 99\%$ w/w), isomonopropylamine (iMPA, $\geq 99.5\%$ w/w), monobutylamine (MBA, 99.5% w/w), monoethanolamine (MEtA, $\geq 98\%$ w/w), and methane sulfonic acid reagent (0.1 M) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Two analytical grade primary standard solutions of TMA and TEA chloride salts with concentrations of 1000 mg L^{-1} were purchased from the RICCA chemical company (CAT# RV010950-100N and RV010949-100N, Arlington, TX, USA).

2.2.2 Method Development for Separation of Alkylamines and Inorganic Cations

The chromatography method developed was based on a prior cation separation method using 5.5 μm particle sizes, electrolytic eluent generation, and an electrolytically regenerated suppressor.⁴⁸ Re-optimization of this IC method was required to separate and quantify the ten (including MEtA) most abundant atmospheric alkylamines and six inorganic cations. Therefore, several new innovations could be attempted to improve separation efficiency further and reduce method operating costs: 4 μm particle sizes in the analytical and guard columns, separated temperature controlled compartments for the columns and suppressor, the capacity to use a quarternary mixing valve to control eluent composition, and dynamically regenerated resin-based anion exchange suppressors. Samples were analyzed using a Thermo Scientific ICS-6000 IC-CD. A CS19-4 μm cation-exchange column was used to separate the suite of ten alkylamines and six inorganic cations (including ammonium, NH_4^+) by systematically exploring isocratic methane sulfonic acid (MSA) concentrations (1 to 10 mM), mobile phase flow rates (1.25 to 1.75 mL min^{-1}), and column temperatures (35 to 55 $^{\circ}\text{C}$). Maximum peak resolution was then further optimized by using a constant mobile phase flow rate of 1.25 mL min^{-1} and a 55 $^{\circ}\text{C}$ column temperature. An eluent gradient was then constructed that resulted in optimized combination of peak resolution and run time as follows: initially hold at 1 mM over the first 20 mins, followed by a step increase to 4 mM

before ramping exponentially to 8 mM over 5 mins, and holding for an additional 5 mins. Finally, the eluent was stepped back to 1 mM for equilibration over 5 mins before the next sample injection, yielding a total run time of 35 mins. Each sample injection consisted of 1 mL aqueous sample loaded onto a concentrator column (i.e. an inline cation exchange solid phase extraction column; TCC-ULP1; 5 x 23 mm, P/N: 01726065) and was performed with an autosampler (AS-DV). Analytes were injected by eluting them from the concentrator column with mobile phase and these were then separated on the guard (CG19-4 μm , 4 x 50 mm, P/N: 078840) and analytical columns (CS19-4 μm , 4 x 250 mm, P/N: 078837). The analytes were quantified using a conductivity detector (DS6 heated conducting cell at 35 °C) after they passed through a resin-based anion exchange suppressor (CDRS 600, 4mm, P/N: 088668) temperature controlled at 15 °C and operated in: i) dynamic mode, with a constant voltage of 4.4 V, or ii) legacy mode, with a stepped gradient current between 4 to 30 mA. Chromeleon™ v7.2.10 software was used to obtain the peak areas from each chromatogram. The data handling and calculation of concentrations were performed using a combination of Excel (O365, Microsoft Corp.) and Igor Pro (v8, Wavemetrics). Some real atmospheric samples were analyzed using an isocratic method with an MSA concentration of 8 mM and a flow rate of 1 mL min⁻¹ at a column temperature of 30 °C where simple or known sample compositions were investigated. The same instrument components were employed for this isocratic method with the exception of larger packing sizes for the guard and analytical columns: CG19-5.5 μm (4 x 50 mm, P/N:076027) and CS19-5.5 μm (4 x 250 mm, P/N: 076026).

2.2.3 CDRS 600 Suppression Optimization

A dynamically regenerated suppressor was used for removal of eluent competing ions prior to the detection of inorganic cations and alkylamines (Figure 2-1). Analytes are detected in their charged form in a water background. This technique dramatically improves instrument detection limits and is critical to optimize for trace analysis. Modern electrolytic suppressors can operate in two suppression modes to control the electrolytic current that replaces and neutralizes the eluent competing ions: i) dynamic, which applies a constant voltage to generate a responsive current based on eluent competing ion concentration and ii) legacy, which utilizes a current that is held constant. In a gradient method, dynamic suppression is considered more ideal than legacy because it adjusts current based on the competing ion concentration, thereby avoiding excess current being

applied at lower starting eluent concentrations in gradients. There is no difference between the application of dynamic and legacy modes in isocratic methods, since both will maintain a constant current. The suppression of analytes eluting from the column with competing ions was initially performed with dynamic mode and water recycling (i.e. eluent exiting the detector was used for electrolysis of water in the suppressor) at a constant voltage of 4.4 V. Unfortunately, sensitivity of the method decreased over time, with concomitant loss of Mg^{2+} and Ca^{2+} ions occurring under routine suppressor operation. Alternatives to the suppressor methodology were explored for improved instrument performance.

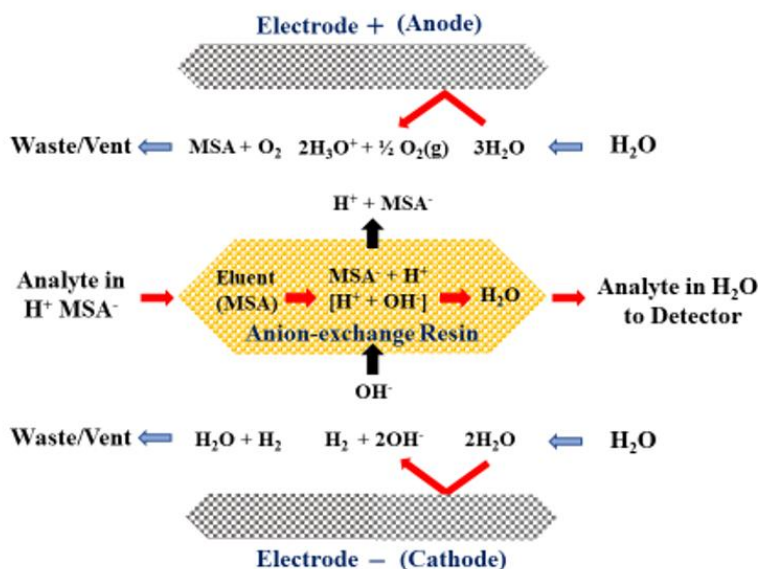


Figure 2-1: Schematic of a cation dynamically regenerated suppressor (Thermo Scientific, CDRS 600). Deionized water is reduced to hydroxide ions electrolytically in the regenerant channel on the cathode surface by the constant applied voltage. Hydroxide ions move toward the anion exchange resin and neutralize H⁺ competing ion in the eluent to form H₂O. Eluent anions (MSA⁻) pass through the anion exchange resin by electromigration toward the anode where water is oxidized to produce hydronium ions that pair with the MSA⁻ to maintain electroneutrality. The analytes remain in the eluent stream because they are repelled at the positively charged anion-exchange resin, moving to the detector in pure water as a result, and measured as their conductive ions. Figure adapted from scheme for AutoSuppression found in Dionex CDRS 600 user's manual.⁴⁹

To address this issue, the suppressor operation was changed from dynamic to legacy mode, programmed with different suppressor currents within legacy mode to effectively suppress the changes in eluent concentration in the IC gradient method, in addition to using water recycling or

an external supply. In the cases where currents were modified, those used were calculated using formula (E2-1) recommended by the manufacturer, using the known eluent strength and typically applied as a constant to isocratic separations.

$$I = \mu \times C \times 2.94 \quad (\text{E2-1})$$

Where, suppressor current (I , mA) depends on mobile phase flow rate (μ , mL min⁻¹), eluent concentration (C , mN), and specific factor of 2.94 (mA min mL⁻¹ mN⁻¹) that is based on sample counterion and mode of operation. As a result, step-wise changes in current over time were used as eluent ion increased in the gradient of a given IC separation method. For example, in our gradient approach with a flow of 1.25 mL min⁻¹, this corresponds to: 4 mA for 1 mM MSA, 15 mA for 4 mM, and 30 mA for 8 mM, as used below. A Chromeleon data file of the above-developed method is provided in Appendix A (Figure A-1).

Finally, the water supply of the suppressor in stepped-legacy mode was changed between being recycled or delivered from an external water supply. The aim was to obtain higher suppression capacity by more effectively removing all competing and analyte cations from the electrolytic compartments within the device (Figure 2-1). Water provided from an external source was explored to reduce (or eliminate) the accumulation of low solubility salts in the suppressor that could damage the exchange resin (e.g., Mg(OH)₂ from Mg²⁺ in standards and samples) and other related processes (Section 2.3.5).

2.2.4 Quality Assurance and Quality Control (QA/QC)

2.2.4.1 Standards Preparation

Amine primary standard solutions were stored in 16 mL amber glass bottles because we observed their loss by volatilization was mitigated in these containers compared to high-density polyethylene (HDPE) bottles. There was also observable alteration of the HDPE containers (e.g. discolouration of material) as the analytes appeared to be permeating through the material, with reactive losses to impurities within it (e.g. reaction with carbonyls to form brown carbon products, such as in aerosol systems).¹⁹ Aqueous working standards were stored in HDPE bottles cleaned with HPLC grade methanol and ultra-pure milli-Q water (DIW; resistivity of 18.2 MΩ·cm) by rinsing six times sequentially with each solvent. Standards were prepared in 50.0 ± 0.1 mL Nalgene™ class B polypropylene volumetric flasks with closure. To clean volumetric flasks, they were rinsed sequentially with methanol and DIW six times each before making standards.

2.2.4.2 Inorganic Cation Calibration Standards

Five calibration standards were prepared for inorganic cations by parallel dilution in DIW with the following ranges: Li^+ (5 to 99 ng), Na^+ (20 to 394 ng), NH_4^+ (25 to 498 ng), K^+ (50 to 990 ng), Mg^{2+} (25 to 502 ng), and Ca^{2+} (49 to 988 ng). The ranges describe the mass injected due to our use of a concentrator column. Two check standards were prepared within the calibration range positioned between the two highest (Li^+ :74 ng, Na^+ :296 ng, NH_4^+ :374 ng, K^+ : 743 ng, Mg^{2+} :377 ng, and Ca^{2+} : 741 ng) and two lowest (Li^+ :7 ng, Na^+ :30 ng, NH_4^+ :37 ng, K^+ : 74 ng, Mg^{2+} :38 ng, and Ca^{2+} : 74 ng) standards to evaluate method quality across the instrument working range. Specifically, they were used here to determine accuracy through their percentage relative error (%RE) compared to the known concentration ($n = 5$).

2.2.4.3 Amine Standard Stability

We have previously noted that a limit on the accuracy in quantifying amines by IC is derived from the stability of standard solutions and potential losses of analytes from these standards.^{44,48} The issue remains open and potential resolutions to improve quantitative analysis were explored. Three aqueous solutions of a mixture of alkylamines were prepared in both DIW and 1 mM MSA to assess whether improved stability in quantitation could be obtained by fixing the protonation of these basic analytes in an acidic solution matched to the matrix of the mobile phase under the starting conditions of the separation. The stability of alkylamine mixtures were tested by aging 10 mg L⁻¹ stock solutions over short-term (up to 19 days) and long-term (>19 days) periods. The first mixture contained MEtA, DMA, DEA, and TEA, the second contained MMA, iMPA, and TMA, and the third contained MEA, MPA, and MBA. Amine analyte mixtures analyte were designed based on their determined elution order from single analyte standards, such that retention times for amines in a mixture were separated a few minutes from each other. In addition, solutions denoted TMA.HCl and TEA.HCl were prepared from chloride salts and compared to those made from their primary standard solutions (denoted TMA and TEA above) in terms of stability as these analytes have demonstrated the lowest accuracy and precision in our prior work. Five standard solutions of the amine mixtures were made by combination of both parallel and serial dilution, to practically reduce error in both DIW and MSA matrices, with calibration ranges between 5 to 500 ng injected on-column. The stability of the amines standard stock solutions was tested first by measuring instrumental sensitivity through calibration standards and then by comparing the experimental

decay rates to the relative effective volatilities of the analytes ($K_{\text{eff}} = K_a/K_H$) in both matrices over 90 days. This comparison explores the idea that the main loss in our prepared amine standards is through volatilization. One check standard was prepared from stock standards that was made freshly with mass of 50 ng from primary standard solutions with a concentration of 50 ng mL⁻¹ to assess the accuracy of the resulting amine calibration curves (n = 5).

2.2.4.4 Precision and Limits of Detection

The method precision of inorganic cations and amine calibration standards was calculated using the standard deviation (σ) in the slope (sensitivity) of the linear calibration curves across multiple analyses spanning several months. Method precision was alternatively calculated through the replicate analysis of check standards in the cases where there were not enough replicates of full calibrations using standards due to clear and rapid damage of the suppressor (i.e. total loss of function after tens of injections, indicated below with an asterisk*; called *critical failure* henceforth). Precision was determined for each of the configurations in suppressor operation and regenerant water provision: dynamic recycle (n = 3 inorganic cations, n = 5* amines), stepped-legacy recycle (n = 5* inorganic cations, n = 5* amines), and stepped-legacy external (n = 5 inorganic cations, n = 3 amines).

Limits of detection (LOD) for inorganic cations and alkylamines were determined using calibration standards and three reagent blank chromatograms under all three suppressor configurations. The LODs were calculated in nanomoles (nmol) using the ratio of three times the standard deviation of the blank signal height from the detector (μS) within the analyte retention time window where no peaks were observed. The resulting value was divided by the slope of the calibration curve when plotting standard peak height versus nmol of analyte injected ($\mu\text{S nmol}^{-1}$). The LOD determinations were performed using a brand-new suppressor with a detector data collection rate of 10 Hz, and resulted in up to 358 data points within the various analyte retention windows (e.g. n = 263 for Li⁺ and n = 188 for K⁺, where the retention windows were determined from the average ion retention time across the calibrated linear range $\pm 3\sigma$).

2.2.4.5 Assessment of the Calibration Approach for Quantitative Analysis

Method validation indicates whether the performance of a newly developed method is reliable and consistent for data analysis.⁵⁰ Calibrations are one of the most important parameters where

mistakes can be made in regression when including the zero-point (0,0) and forcing the line through the origin. Without the incorporation of reagent blank analyses, including (0,0) in a calibration curve can be a source of error since most analytical instruments generate a non-zero background signal. The only exception of using the zero-point is chromatographic techniques where a reagent blank has been run and no signal has been detected (i.e. <LOD).⁵¹ Regression through the origin is usually used for simplicity of the calculation, as there is no y-intercept value. There has been controversy about this topic without clear conclusions.⁵² One consensus is that a calibration curve can only be forced through the origin when there are no significant differences between y-intercept and zero from a unrestricted linear least-squares regression. In this study, injection of DIW as a reagent blank and statistical approaches from the literature were performed to evaluate the best practice in use of inorganic cation and alkylamine calibration curves with the modern components of cation-exchange chromatography instrumentation. Details of statistical approaches considered for the regression analysis are presented in Appendix A (Section A2).

2.2.5 Analysis of Real Samples

Our developed IC methods were applied to quantify NH_3 and alkylamines in real samples of outdoor aerosols and the gas phase indoors to demonstrate its sensitivity and robustness.

2.2.5.1 Size-Resolved Coastal Aerosol Sample Analysis

Analysis of particulate-phase NH_4^+ and amines in marine aerosols with an improved IC-CD method is essential to further our understanding of the sources and sinks of reduced nitrogen in the marine atmosphere. Size-resolved aerosol samples were collected with a Micro Orifice Uniform Deposit Impactor (MOUDI, model 100-NR, MSP Corp., Shoreview, MN, USA) during the Coastal Fog cruise that travelled along the coast of Eastern Canada in September 2018.⁵³ The MOUDI was operated at a sampling flow rate of 30 L min^{-1} with 9 impaction stages set-up to capture particle fractions with aerodynamic diameters centred at 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10, and $18 \mu\text{m}$. Nine rounds of 24-hour aerosol sampling were conducted across various parts of the Grand Banks region, including the open ocean (5 samples), the Gulf of the St. Lawrence (2 samples), and in urban harbours (2 samples). Samples were collected on pre-cleaned 47 mm aluminium foils, which were soaked in DIW for 10 – 60 min and then sonicated for 20 min, followed by sampling, and then extraction in to 15 mL of deionized water with 45 min of sonication and centrifugation at

6000 rpm for 20 min. The extracts were then analyzed using the best IC-CD gradient method available at that time (see Section 2.3.7). More detailed information about MOUDI samples, their broader chemical composition, and impacts on coastal and marine atmospheres can be found in Chisholm *et al.*⁵⁴

2.2.5.2 New Home Air Quality Sample Analysis

The developed IC-CD methods were used to measure the indoor concentration of NH₃ and amines to explore their temporal variability and the effect of occupant activities and household components on their levels in the first-year of occupancy in new homes. The mixing ratios of gaseous NH₃ and amines were measured in 18 newly constructed homes in the Ottawa-Gatineau (Ontario, Canada) census metropolitan area between 2018 and 2022. Samples were collected before and immediately upon occupancy (24-hour duration) and at 3-month intervals thereafter (each 5 days in duration) for the first year, using Ogawa passive samplers (PS-154, Ogawa & Co. USA, Inc., Pompano Beach, Florida) with citric acid-coated reactive substrates.⁵⁵ A total of 7-8 sample substrates were collected indoors (n=4), outdoors (n=2) and as field blanks (n=1-2) at each home, for each timepoint. All the substrates were extracted by being placed in 15 mL deionized water and mixed intermittently by several inversions over an hour, followed by analysis using IC-CD. Half of the samples were analyzed with the gradient method and the remainder with the isocratic method, to preserve suppressor function (Section 2.3.8).

2.3 Results and Discussion

2.3.1 Advancing Separation of Alkyl Amines

An improvement in resolution and quantitation of alkylamines, expanding the analyte suite to include MEtA, was explored based on the cation gradient separation of Place *et al.*⁴⁸ applied to various modifications to the analytical column and suppressor. These modifications including using the newly available 4 µm packing instead of 5.5 µm in the CS19 analytical column, utilizing separated temperature controlled compartments for the column and suppressor instead of a single compartment, incorporating a quarternary mixing valve, and using a dynamically regenerated resin based suppressor instead of an electrolytically regenerated suppressor that was limited to legacy mode. The selectivity of the stationary phase was exploited for this compound class, starting from the optimal hydronium ion (H₃O⁺) gradient and flow rate determined in our prior work. From this

point, temperature modulation spanning 35 °C to 55 °C in 10 °C increments was optimized, as we have also previously determined that this parameter exerts a strong effect on selectivity.⁴⁸ The effect of the temperature on peak separation was then assessed by calculating the peak-to-peak resolution (E2-2) for each consecutive pair of cations.⁵⁶

$$R_s = \frac{2(t_{R2}-t_{R1})}{W_2+W_1} \quad (\text{E2-2})$$

Where t_R is retention time (min) and W is peak width at the base (min). The resolution averages of inorganic cations and ten alkylamines were 1.10 ± 0.97 , 1.45 ± 0.82 , at 35 °C, 45 °C, and 1.52 ± 0.81 (dynamic recycled water) and 2.30 ± 1.69 (legacy external water) at 55 °C, respectively (Table 2-1).

Table 2-1: Peak-to-peak resolution of inorganic cations and ten alkylamines from the following analyte at different column temperatures increases the selectivity of the stationary phase.

Cation	Resolution			
	35 °C (DR) ^c	45 °C (DR) ^c	55 °C (DR) ^c	55 °C (LE) ^d
Li ⁺	3.71	2.98	2.68	4.24
Na ⁺	2.03	1.72	1.69	2.83
NH ₄ ⁺	1.33	1.32	1.27	1.01
MEtAH ⁺	0.51	1.36	0.86	1.42
MMAH ⁺	1.18	1.04 ^a	0.88 ^a	1.20 ^a
MEAH ⁺ (K ⁺) ^a	0.98	0.64 ^a	0.71 ^a	0.77 ^a
K ⁺ (MEAH ⁺) ^a	0.98	0.46 ^a	1.02 ^a	1.12 ^a
DMAH ⁺	0.02	1.56	1.35	1.94
iMPAH ⁺	0.38	1.77	1.66	1.05
MPAH ⁺	0.46	0.97	1.11 ^b	1.26 ^b
DEAH ⁺	0.15	0.24	0.95 ^b	0.84 ^b
TMAH ⁺	1.32	2.76	3.43 ^b	4.01 ^b
MBAH ⁺	1.27	2.07	2.17	6.08
TEAH ⁺	---	---	---	4.81
Mg ²⁺	---	---	---	1.90
Ca ²⁺	---	---	---	---
Average	1.10	1.45	1.52	2.30

^a K⁺ elutes before MEAH⁺. R values calculated between MMAH⁺ and K⁺, K⁺ and MEAH⁺, and MEAH⁺ and DMAH⁺.

^b TMAH⁺ elutes before DEAH⁺. R values calculated between MPAH⁺ and TMAH⁺, TMAH⁺ and DEAH⁺, and DEAH⁺ and MBAH⁺.

^c Peaks evaluated at a mass of 326–991 ng (alkyl amines) and 74–743 ng (inorganic cations) with the suppressor operated in dynamic recycle mode (DR).

^d Peaks for final optimized method (stepped-legacy external water = LE) evaluated at a mass of 500 ng (amines) and 74–743 ng (inorganic cations) for comparison to method performance of Place et al.⁴⁸

Resolution between inorganic cations and amines was enhanced by increasing the temperature and changing suppressor modes from dynamic with recycled water to stepped-legacy with externally supplied water (Table 2-1). Coelution between K^+ and its neighbouring amines was a consistent issue at temperatures below 50 °C, which was overcome above this value. The greatest resolution improvement was observed between $DEAH^+$ and $TMAH^+$, which had poor separation below 55 °C. The chromatograms of the suite of four inorganic cations and ten alkylamines expected in atmospheric samples shows their successful separation from a modest change in column temperature to 55 °C from 45 °C (Figure A-2). The chromatograms demonstrate improvement in peak shape and separation efficiency at 55 °C, consistent with prior findings that the biggest driver of selectivity in modern cation separation of alkylamines is temperature, as selectivity is insufficient at the weakest possible competing ion concentrations in the mobile phase. Additionally, the suppressor operational mode impacts the resolution at the optimized temperature of 55 °C; changing the suppressor from dynamic recycled water to stepped-legacy external water resulted in an average resolution improvement by a factor of 1.5 (Table 2-1).

Drawing from the fundamental components of the van Deemter equation (E2-3), the improved resolution in the cation separation by increasing temperature can be better understood.

$$H = A + \frac{B}{\mu} + (C_S + C_M) \mu \quad (E2-3)$$

Where H is the theoretical plate height (inversely proportional to plate number), A is the eddy diffusion coefficient, B is the longitudinal diffusion coefficient, C is the mass transfer coefficient in the stationary (C_S) and mobile (C_M) phases, and μ is the flow rate.⁵⁷⁻⁵⁹ By increasing the column temperature, the viscosity of the mobile phase was decreased, and mass transfer increased with diffusion through the stagnant mobile phase inside the porous particles.^{60,61} Increasing temperature also enhances the ion desorption kinetics of the stationary phase.⁶²⁻⁶⁴ The cumulative impact of these effects reduces the C_S term. An increase in analyte diffusion in the mobile phase also results in a decrease of C_M term. Together both decreasing C terms lead to increased efficiency. In this experiment, an increase in peak resolution resulted when the mobile phase had greater diffusivity, with best separation efficiency at a temperature bordering on the limit for the CS19 column (60 °C). Elevated temperature further reduces retention time by changing the retention enthalpy of the analyte and/or the degree of ionization of the solute and functional group of the stationary phase.^{59,61} For example, here the retention times of the cation analytes decreased anywhere from

0.25 (Na⁺) to 2.43 (TMAH⁺) minutes when increasing the temperature from 45 °C to 55 °C with the suppressor operated in dynamic recycled water mode (Figure A-2). Also, increasing temperature affected peak widths by reducing them from 0.02 (Li⁺) up to 0.41 (MPAH⁺) minutes, suggesting substantial mass transfer band broadening effects (C-term) in these separations. Lastly, increased temperature resulted in an improvement of the peak shape, with a reduced extent of peak tailing particularly for early eluting analytes, as quantified by the asymmetry factor, which is the sum of the left and right peak widths at 5% of the peak height in minutes, divided by the left peak width at 5% of peak height in minutes multiplied by 2. These decreased from 1.59 to 1.14 for MMAH⁺ and up to 2.53 to 1.01 for Li⁺, improving across the entire analyte suite. In a previous study, it was shown that a change in temperature (60 °C) elicits an effect similar to that of adding an organic modifier (6% acetonitrile) to improve the separation efficiency of amines.⁶⁵ However, there are organic solvent limitations for suppressors and electrolytic eluent generators used on modern IC systems, so temperature alterations provide the benefit of similar improvements in selectivity, while remaining compatible with these components. In summary, elevated temperature improved chromatographic peak shape with better symmetry and reduced peak width. Overall, the higher temperature of the final method strongly altered the selectivity of the CS19 column, perhaps best indicated by the reversal of the elution order for DEAH⁺ and TMAH⁺.

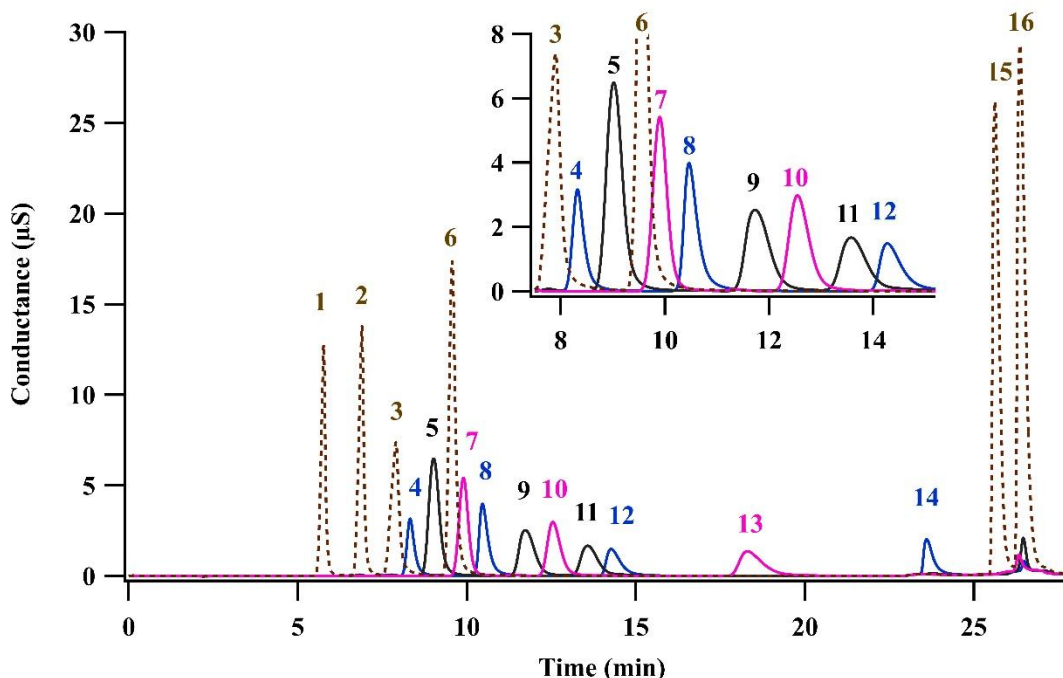


Figure 2-2: Separation of inorganic cations and three amine mixtures with an MSA gradient from 1-8 mM and flow rate of 1.25 mL min⁻¹ at 55 °C. Analytes were passed through a suppressor in stepped-legacy external water mode before detection (final optimized method). Inorganic cations and three amine mixtures are coloured separately: dashed trace (inorganic cations), blue solid trace (MEtAH⁺, DMAH⁺, DEAH⁺, TEAH⁺), black solid trace (MMAH⁺, iMPAH⁺, TMAH⁺), and pink solid trace (MEAH⁺, MPAH⁺, MBAH⁺). The identity, numeric order of elution, and mass of each cation separated are: Li⁺ (1, 74 ng), Na⁺ (2, 296 ng), NH₄⁺ (3, 374 ng), MEtAH⁺ (4, 500 ng), MMAH⁺ (5, 500 ng), K⁺ (6, 743 ng), MEAH⁺ (7, 500 ng), DMAH⁺ (8, 500 ng), iMPAH⁺ (9, 500 ng), MPAH⁺ (10, 500 ng), TMAH⁺ (11, 500 ng), DEAH⁺ (12, 500 ng), MBAH⁺ (13, 500 ng), TEAH⁺ (14, 500 ng), Mg²⁺ (15, 377 ng), and Ca²⁺ (16, 741 ng).

In this work, we tried to improve the IC method further in its application to separate the atmospherically relevant suite of six inorganic cations and ten alkylamines at 55 °C in stepped-legacy external water mode (Figure 2-2). This separation was performed through the reduced particle size now available at 4 µm instead of 5.5 µm in analytical columns used previously.⁴⁸ Theoretical plate height is directly proportional to the diameter of stationary phase particles ($2d_p + d_p^2$); therefore, it was expected H should decrease by a factor of 1.7.⁶⁶ Improvement in theoretical plate number was observed for most of the analytes (9 out of 16): six inorganic cations, MEtAH⁺, DMAH⁺, and TEAH⁺. For example, the H value of NH₄⁺ was calculated from our method using E2-4 as 0.11 mm using the 4 µm packing, a decrease in H by a factor of 1.4 compared to the value of 0.15 mm using the 5.5 µm packing.

$$H = \frac{L}{N} = \frac{L W^2}{16 t_R^2} \quad (\text{E2-4})$$

Where L is the column length (mm). Separation efficiency did not change in three alkylamines: MMAH⁺, MEAH⁺, and DEAH⁺, while the remaining four (iMPAH⁺, MPAH⁺, and MBAH⁺) had decreased. This IC method also observed an improvement, for example, in the resolution of MEtAH⁺ from NH₄⁺ and MMAH⁺ which had R_s values less than 0.65 increase to 1.01 and 1.42, respectively. Improvement in selectivity is yet required for some of analyte pairs, such as K⁺ and MEAH⁺, but was not possible to achieve within the stationary phase limits here. The expected improvement in separation efficiency from the reduced stationary phase particle size found are consistent with the expected theoretical improvement, a substantial impact for this analyte suite.

2.3.2 Stability of Amine Standards

The stability of amine standards was measured over time to explore the potential impact of volatility driven losses on the accuracy and precision of TMA specifically, which was an outstanding issue reported in our previous IC methods.^{44,48} As a result, an investigation of fixing the ionized state of all the analytes in the samples was designed to ascertain whether this is the case, or if the observed losses are occurring elsewhere in the instrumentation. The stability of standards was tested by changing the pH with MSA or preparing standard solutions from the hydrochloride salts, such as TMA.HCl and TEA.HCl. Instrumental sensitivity to the inorganic cations and amines were measured over 90 days in two groups: short-term (up to 19 days) and long-term (> 19 days) when stored in DIW or MSA and subject to the conditions present from three different suppressor modes (Figure A-3). Stock standard solutions (10 mg L⁻¹) were used to evaluate stability through sensitivity changes, which were quantified using calibration standards prepared from the stock solutions. Potassium sensitivity was observed to change over the course of the IC-CD analyses performed across these varied instrumental configurations and within one suppressor over time, despite it being known to be a conserved ion. As a result, it can account for system performance variability over time. This was exploited to obtain comparability between suppressor operation modes and stock solution matrices in our stability tests and the sensitivities of all analytes prepared in DIW or MSA were therefore normalized to K⁺ sensitivity, in particular to account for the degradation of suppressor performance (Section 2.3.4.2). This is a reasonable approach toward mitigating changing instrument function as the relative difference between DIW

and MSA matrix sensitivities for K^+ were 9 % which is within the typical analytical accuracy reported for IC instrumentation.^{44,48} Furthermore, we selected this particular conserved inorganic cation from our suite because K^+ has the nearest retention time to most of the amines, such that suppressor performance was best accounted for on an injection-to-injection basis (Table 2-1, Figure 2-2).

Under these constraints, it was possible to assess the stability of amine standards over time as well as the potential stabilizing effect of an acidified standard matrix using the same competing ion as found in the mobile phase (MSA, Figure 2-3). Short-term stability is essential to assess if amines have the same stability as inorganic cation standards, where the latter can be stored in a stock solution for up to three weeks.

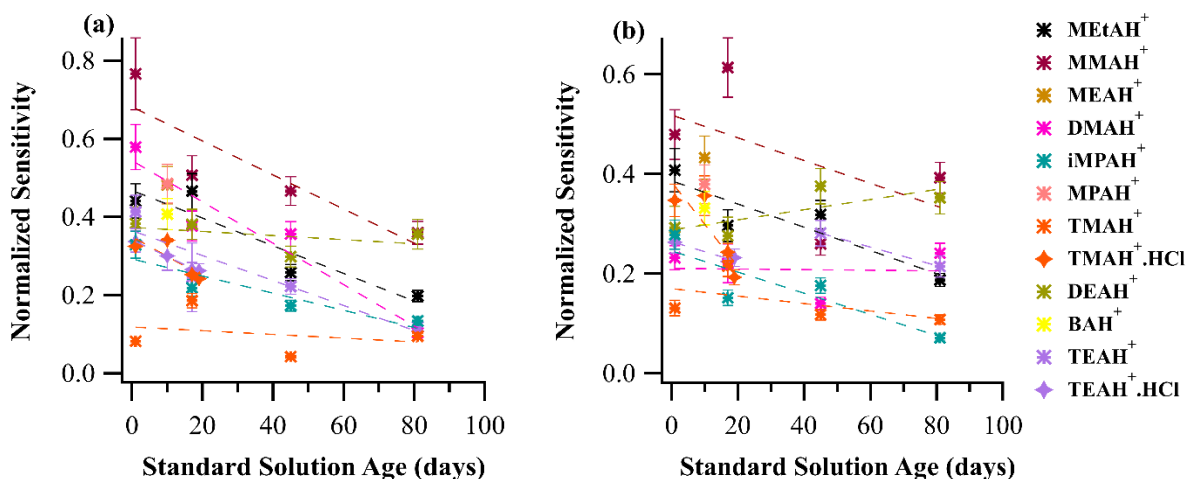


Figure 2-3: Sensitivity of alkyl amines relative to K^+ measured using calibration standards with different ages of the used stock solution in (a) DIW and (b) MSA. Here, all measurements were made by using the same suppressor in dynamic mode with recycled water.

In DIW, the sensitivity of amines decreased over time, and the measured instrument response decreased for MMAH⁺, DMAH⁺, iMPAH⁺, TMAH⁺.HCl, TEAH⁺, and TEAH⁺.HCl indicating analyte degradation or losses – with an average percentage loss of 30 ± 10 % over the short-term experiment (up to 19 days). In contrast, the normalized sensitivities measured for MEtAH⁺ (0.44 ± 0.04 and 0.46 ± 0.04) and DEAH⁺ (0.38 ± 0.04 and 0.38 ± 0.03) demonstrated high stability, without a significant change during the short-term observation period. TMAH⁺ did not show a similar instrument response as the other amines, and its high variance was therefore investigated to be due to its loss from the IC system (Section 2.3.3.2). In the MSA matrix, MEtAH⁺,

iMPAH⁺, TMAH⁺.HCl, and TEAH⁺.HCl showed declining instrument response over time with an average loss of 29 ± 13 % in the short-term. Meanwhile, MMAH⁺ and TMAH⁺ did not show any consistent pattern and they fluctuated by up to 28% and 64% from the initial measurement respectively over the observation period. Finally, DMAH⁺ and DEAH⁺ were observed to have the highest stabilities over the same short-term period. In the short term, storing amine stock standard solutions in DIW resulted in greater retention of instrumental method sensitivity compared to storing them in MSA (MSA/DIW<1; Figure 2-4). In contrast, instrumental method sensitivity of stock solutions in MSA relative to DIW were less impacted at longer timescales (MSA/DIW >1) despite the significant losses observed in both systems over time. In summary, the highest instrumental method sensitivity, accompanied by reproducibility, can only be obtained by preparing freshly made amine stock solutions from the primary standards, on the day of quantitative analysis for samples of unknown composition, using a simple matrix of DIW.

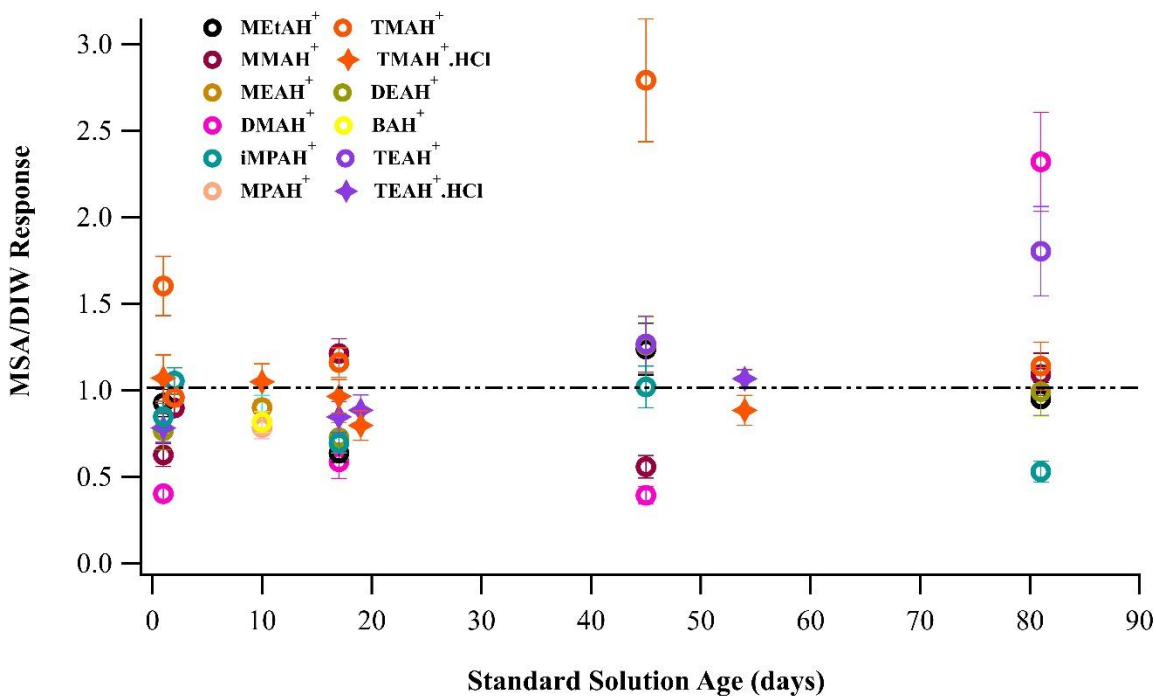


Figure 2-4: Ratio of amine sensitivities in DIW-to-MSA at different stock solution ages, as quantified by one suppressor operated in dynamic mode with recycled.

Amine stock standard solutions of the hydrochloride salts indicated similar instrumental sensitivity in DIW and MSA ($MSA/DIW \approx 1$) over short- and long-term storage. However, due to

the quantities of these analytes lost over time freshly made stock solutions are still required to obtain the correct instrument response with reproducibility.

Decay rate of amines (day^{-1}) were measured by plotting natural logarithm of the normalized amine sensitivities relative to K^+ versus their age in days (e.g. iMPAH^+ in Figure A-4). The loss was first-order in nature and decay rates were determined from the slope. It was expected that the amine decay rates would be slower in MSA than in DIW if volatilization was the dominant loss mechanism, as the analytes would be mostly protonated (99.99 %) in a 1 mM MSA solution ($\text{pH} = 3$) compared to pure water (68% for MEtA to 99% for DEA) (Figure 2-5).

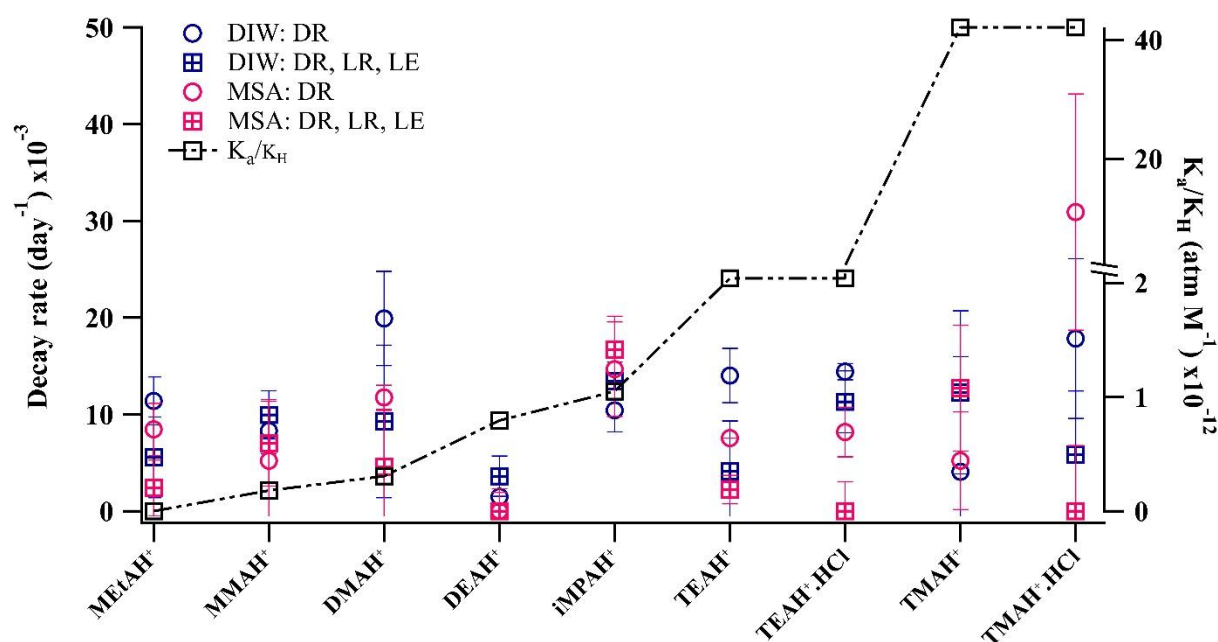
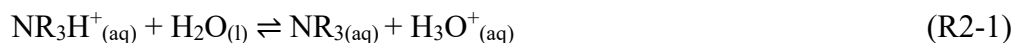


Figure 2-5: The stability of amine standard stock solutions comparing experimental decay rates to a proxy for volatilization loss. Experimentally determined decay rates of the amine analyte suite in both DIW and MSA were measured using the same suppressor in dynamic (D) mode with recycled (R) water as well as other suppressor configurations such as stepped-legacy (L) recycle and external (E) water modes (left axis). The theoretical decay rates via volatilization for the same amines based on their K_a and K_H values were also calculated for comparison (right) axis. Note the axis break on the right changing the order of magnitude in the scale for TMA.

For comparison, we derived the theoretical relative loss potential of each amine by volatilization based on their combined acid ionization constant of the conjugate acid (K_a) and Henry's Law constant ($K_H = M \text{ atm}^{-1}$) (AppendixA, Table A-3).⁶⁷⁻⁶⁹ The degree of amine partitioning from the aqueous to the gas phase at equilibrium is thus based on R2-1 and R2-2.



As a result, it would be expected that the amine decay rates are dependent on the ratio of K_a to K_H if this is the driving process. The order of theoretical loss of amines due to volatilization increases from MEtAH^+ as the lowest to TMAH^+ as the highest (Figure 2-5). Based on the hypothesis that this property is the main driver of analyte loss in standard solutions, it was expected that the stock standard of MEtAH^+ would be the most stable over time with an increase in loss and/or variability towards the more volatile analytes like TMAH^+ ; the most volatile of the analyte suite. The decay rates were compared across different suppressor modes which showed similar variabilities in amine decay rates. Diethylamine (DEAH^+) is the most stable analyte in the suite, with decay rates close to zero, without measurable losses under our instrumental conditions. In contrast, all other amines show high variability with respect to losses during storage of stock solutions with measurable decay rates. The loss of analytes was still observed in cases where the solution pH was lowered, as well as when starting with an ionized reagent through chloride salts, despite the expectation that they would maintain their charged form. Linear regression analysis of amines experimental decay rates versus K_a/K_H showed no correlation ($R^2 < 0.2$ in all cases) between these variables for and of the different suppressor modes. The slope of the regression lines in MSA was positive and higher than DIW; MSA was not more effective than DIW in preventing losses. This result suggests that other factors than volatilization of the neutral amines are affecting the decay rate, such as analyte loss from the suppressor (Section 2.3.3.1). Again, our results suggest that all amine stock standards need to be freshly made from the primary standard solutions prior to each analytical determination to ensure high quality quantitative results.

Place *et al.*⁴⁸ observed lowest accuracy in analytical determinations of TMAH^+ and DMAH^+ (at the lower end of the calibrated range), alongside the largest variations in the slopes of calibration curves of TMAH^+ and TEAH^+ over one to three months. In that prior work, the losses were hypothesized to be driven by volatilization from the standards. In the experiment conducted here, the highest variability is observed in these same three amine standards: TMAH^+ , DMAH^+ , and TEAH^+ , but the effects do not scale with the known effective volatility of these molecules. High variability of the DMAH^+ decay rate could be associated with the loss of this amine from the suppressor, particularly when it was operated under dynamic recycle water mode (Section 2.3.3.1). Standard solutions of TMA.HCl and TEA.HCl from freshly made stock solution were used to

verify the stability of the freshly made standard solutions of TMA and TEA. Stability of TMA and TEA were then explored by comparison to TMA.HCl and TEA.HCl as the stable form of standard solutions under different suppressor modes. The analytical sensitivity of TMAH⁺ was lower by 67% (dynamic recycle), and 28% (stepped-legacy external) when compared to TMAH⁺.HCl. The sensitivity differences between TEAH⁺ and its chloride salt was 18% (dynamic recycle), 1% (stepped-legacy recycle), and 15% (stepped-legacy external). These results indicate that the lower instrumental method sensitivity of TMA compared to TMA.HCl may be due to a combination of factors: i) TMA has higher volatility and is susceptible to loss when preparing stock solutions and ii) the suppressor mode and supply water format lead to amine losses in the eluate from analytical IC column. Therefore, to negate the first issue, and obtain high quality quantitative analysis of high volatility amines like TMA and TEA, we recommend preparation of aqueous stock standards from their hydrochloride salts prior to each instrument calibration.

2.3.3 Optimizing Calibration Approaches with Different Suppression Modes

Regression lines for calibration standards were fitted by applying the calibration method from previous IC studies: forcing the regression line through the origin after background correction for any signal in the reagent blank.^{44,48} Here, we found the linearities of our calibration curves to be much different by assessment of the residuals and through use of check standards, which was eventually linked to the operation parameters of the suppressor. Statistical considerations were then made to evaluate the best practice in quantifying cations when using external calibration curves for the new generation of resin suppressors.

2.3.3.1 Inorganic Cation Standards

Since reagent blanks were injected along with the inorganic cation standards, the resulting calibration peak areas were corrected by background subtraction of any peak areas observed in the reagent blank. As a result, it is analytically acceptable that the zero-point could be used for curve generation in this calibration approach. Three different types of linear calibration curves were then utilized and their regressions were: i) forced through (0,0), ii) not forced through origin but included (0,0) in the regression, and iii) not forced through the origin and not inclusive of (0,0) (Figure A-5). A linear least-squares regression fit (R^2) of the calibration standards ($n = 5$) and the percent relative error (RE %; the difference between the known and calculated concentrations) of

the check standards ($n = 2$) were used to assess accuracy between the three calibration strategies. In the first approach, the regression lines forced through zero resulted in R^2 values ranging from 0.943 to 0.953 and a RE % of $-27 \sim +5$. In the second approach, it was found that not forcing through zero but including (0,0), improved R^2 values between 0.997 to 0.998 and a RE % of $-7 \sim +13$. In the third method, not forcing through zero and excluding (0,0) increased R^2 from 0.998 to 0.999 and had RE % of $-5 \sim +29$. The most accurate calibration strategy was the second approach, where the zero-point was included but the regression line was not forced through the origin. This is consistent with the finding that the analytical accuracy of IC, when data is interpreted with a suitable calibration approach, is generally within 20% of the known value of a suitable check standard.^{44,48}

Even though the second approach gave us the most accurate calibration curves by not forcing through zero, one should statistically test to confirm whether the intercept values of these calibration curves are significantly different from zero. To determine the significance of the y-intercept, three different statistical approaches can be used: i) test statistic (t-statistic), ii) confidence interval of the y-intercept, and iii) standard error of the intercept.^{50,51} The values of all three above-mentioned approaches are presented in Tables A-1 and A-2. The results of approaches i) and ii) used a t-statistic and the confidence interval of the y-intercept to accept the null hypothesis that the y-intercept value is insignificant. However, the approach of iii) rejects this null hypothesis and confirms the y-intercept to be significantly different from the standard error of the y-intercept. Negative intercepts were observed in linear regression lines of the inorganic cations which indicates that analytes were lost in the IC system, something that can only occur in the anion-exchange resin of the suppressor (Figure 2-1). The loss of analytes was calculated for suppressors run in both dynamic recycle ($n = 3$) and stepped-legacy external water ($n = 5$) operation modes, respectively, as follows: 0.85 ± 0.3 and 0.18 ± 0.11 nmol (Li^+), 0.93 ± 0.37 and 0.16 ± 0.13 nmol (Na^+), and 1.24 ± 0.63 and 0.30 ± 0.20 nmol (K^+). We could not easily quantify the loss of NH_4^+ because it typically has a non-linear response over the calibration range.⁴⁴ However, NH_4^+ was observed to have systematically lower peak areas for calibration standards in dynamic recycled water compared to other suppression modes. For example, the peak areas in our 498 ng standards (mass on column) were 6.07, 3.72, and 1.87 $\mu\text{S} \cdot \text{min}$ for stepped-legacy recycle, stepped-legacy external, and dynamic recycle modes, respectively. A negative y-intercept was not observed in the suppressor when operated in stepped-legacy recycled water mode, meaning no loss of the inorganic

cations was observed. As a result, all quantitative determinations of inorganic cations in the final optimized IC method use regression lines that are not forced through zero and the zero-point is retained when obtaining the form of the calibration curves.

2.3.3.2 Amine Standards

The same statistical procedures for calibrations were performed for the amine analyte suite. The results of the regression lines from the first approach showed R^2 values ranging from 0.890 to 0.990 and an RE % of -77 ~ +15. These R^2 values improved to 0.994 to 0.999 with an RE % of -33 ~ +17 using the second approach. The best R^2 values of 0.998 to 0.999 as well as an RE % of -13 ~ +20 were obtained using the third approach. Minimizing the residuals in the linear regression for these analytes was best accomplished by excluding the zero-point from regression data sets was unexpected. As a result, it was concluded here that the origin cannot be considered a valid regression data point. This suggests it is a source of substantial error, meaning that analytes are lost in the analytical system between injection and detection. Its inclusion is clearly detrimental to achieving acceptable accuracy for quantitative analysis. A statistical test of standard error of the intercept supported retaining the y-intercept in the resulting calibration curves, the same as was found for the inorganic cations. The loss of amines can likewise be calculated from the x-intercept of the linear regression in all three suppressor modes ($n = 3$ dynamic recycle and stepped-legacy external water, $n = 1$ stepped-legacy recycle). The loss amounts were between 0.16 – 0.46 nmol (dynamic recycle), 0.03 – 0.37 nmol (stepped-legacy recycle), and 0.13 – 0.32 nmol (stepped-legacy external water). The loss of analytes can occur from damage accumulated in the resin of the suppressor, making the ion-exchange function compromised.

Analyte loss was higher in dynamic compared to stepped-legacy suppressor modes for both inorganic cations and amines. The loss of analytes from the suppressor was found to potentially be associated with high current applied in dynamic mode, leading to over-suppression of the eluent and analytes. For example, in one batch of analyses, an ideal current of 52 mA was automatically calculated by the Chromeleon software for an eluent concentration of 8 mM MSA; meanwhile the result of the recommended calculation is 30 mA (E2-1). In contrast to both of these values, on the first injection in dynamic mode it was observed that the suppressor had an applied current of 110 mA, 2-3 times that required, and this declined to 80 mA over the subsequent injection of 36 more samples; a value still well above either the ideal one or that obtained by E2-1. The suppressor

current operating at more than double the ideal value for the highest eluent concentration will affect the functionality and lifetime of the suppressor. As a result, the use of dynamic mode for gradient separations was found to be highly damaging to suppressor integrity and we used this option minimally in order to obtain the comparisons throughout this work.

We also observed amine loss in stepped-legacy mode with recycled water, but without any detectable loss of inorganic cations. In stepped-legacy external water mode, both the inorganic cations and amines were found to have a similar magnitude of analyte loss, but the longest suppressor lifetime. Overall, from this comprehensive assessment of all possible suppressor operation modes, we have determined that the effect of analyte losses on the linear fitting of calibration curves needs to be considered in any cation gradient separations. By optimizing the functionality of the suppressor, we identified a preferred suppression mode: stepped-legacy external water; this allowed the calibration approach to also be defined. Henceforth, all the amine linear regressions used for quantitation are not forced through zero and the zero-point is excluded from the calibration curves, based on the IC method performance determinations presented in the following section.

2.3.4 Accuracy, Precision, and Limits with Different Suppression Modes

2.3.4.1 Inorganic Cation Standards

Accuracy and precision improvements for inorganic cations is the most notable driver of our suppressor operation selection, which is stepped-legacy external water mode. This is particularly true when compared to the limitations reported in prior calibration analyses of inorganic cations where the instrumentation all used eluent generation and legacy recycled water mode.^{44,48} Accuracy, precision, and LOD of inorganic cations were measured in three different suppressor modes; results of our preferred method using stepped-legacy external water are presented in the SI (Table A-4). Inorganic cations had measured accuracies of 83% to 99% in dynamic recycle, 87% to 99% in stepped-legacy recycle, and 95% to 99% in stepped-legacy external water, with precisions of $\pm 14\%$, $\pm 13\%$, and $\pm 8\%$, respectively. The divalent cation analytes Mg^{2+} and Ca^{2+} were not possible to detect after running a few (~ 20) samples in dynamic recycle mode, ~ 100 samples in stepped-legacy recycle mode, and ~ 300 samples in stepped-legacy external water when utilizing the optimized gradient elution conditions necessary to separate the target suite of atmospherically relevant alkylamines. Inorganic cations were found to have lower LODs in

stepped-legacy mode compared to dynamic, with the lowest LODs for the optimized separation obtained in stepped-legacy recycled water. For example, independent of injection volume, NH_4^+ was found to have a LOD of 0.99 ± 0.72 nmol (dynamic recycle), 0.07 ± 0.05 nmol (stepped-legacy recycle), and 0.17 ± 0.12 nmol (stepped-legacy external water). These findings are generally consistent with the trend and relative magnitude of losses observed from the suppressor in the preceding section. Inorganic cation analysis demonstrated the highest accuracy and precision with the suppressor operated under stepped-legacy external water mode, with the added advantage of greater robustness in detecting and quantifying Mg^{2+} and Ca^{2+} . Overall, there is improvement in IC separation method performance for this analyte mixture.

2.3.4.2 Amine Standards

Amine standards in DIW were also analyzed for accuracy and precision with suppressors in dynamic recycle and stepped-legacy separation modes with two different water supplies: recycle and external (Figure 2-6). Comprehensive metrics on the performance of the stepped-legacy external water suppressor mode for amines are provided in Table S4. Amine standards were found to have the highest sensitivities when using stepped-legacy mode with recycled water, followed by external water. However, the suppressor had a shorter lifetime prior to critical failure when using recycled (~2 months) versus external water (~6 months). The lowest sensitivities observed in this work arise from operating the suppressor in dynamic recycle mode, probably due to analyte loss within the device, which was also associated with the shortest device lifetime (≤ 2 months).

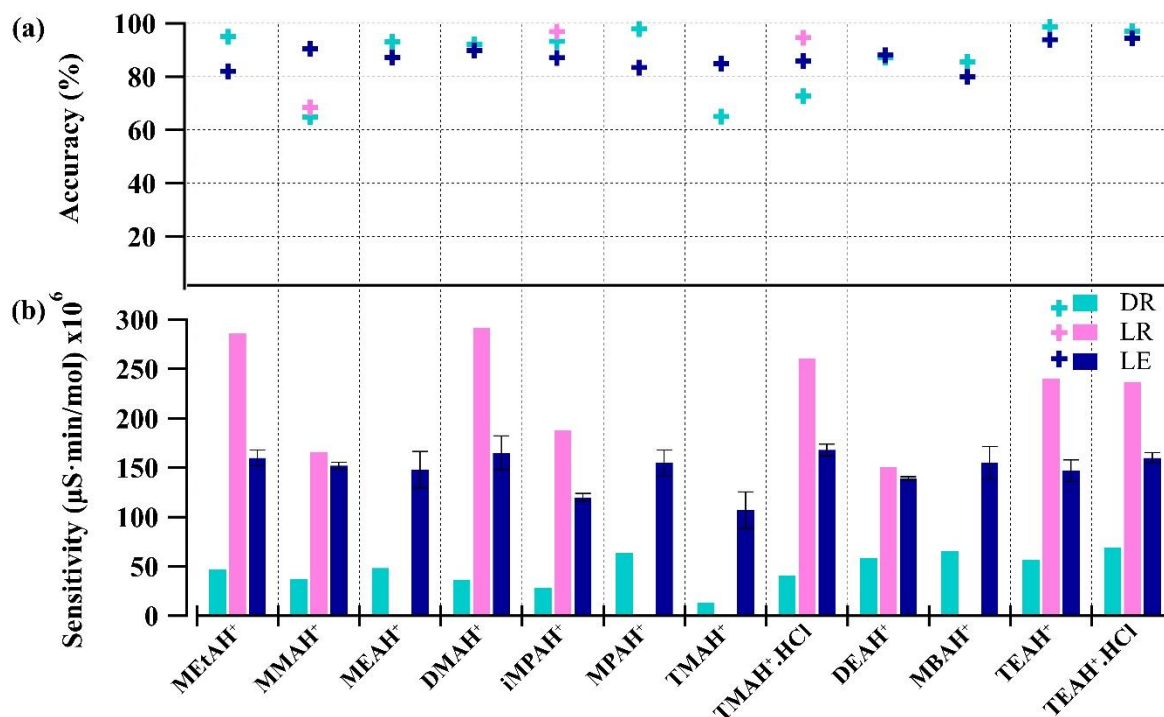


Figure 2-6: (a) Accuracy and (b) sensitivity and calibration precision of alkyl amines for three different suppressor modes: dynamic (D) with recycled (R) water, stepped-legacy (L) with recycled water, and legacy with external (E) water. Replicates were only performed for LE ($n = 3$), while the other two (DR and LR) were only measured once as the devices failed quickly due to damage accumulated by the suppressors.

Accuracy of the method when operating the suppressor under dynamic mode with recycled water was performed exclusively with freshly prepared standards. The accuracy of all amine standards was calculated to be within 65% ~ 99% and precision was $\pm 14\%$ when using dynamic recycled water mode. Instrumental LODs were calculated for all of the target amines with an average of 1.51 nmol per injection (range: MBA = 0.26 ~ TEA = 5.61 nmol). Systematic amine calibrations showed low sensitivities and rapid loss of detection for Mg^{2+} and Ca^{2+} in dynamic recycled mode (Table A-4). The suppressor was changed from dynamic to stepped-legacy mode while keeping the water recycled. This was done to improve sensitivity, LODs, and duration of detection of Mg^{2+} and Ca^{2+} peaks in a gradient method (see Section 2.3.5). The accuracy of freshly made standards were only assessed using the amine mixture of MMA, iMPA, and TMA.HCl which were within 68% ~ 97% under stepped-legacy recycled water (Figure 2-6a). This suite was selected as the analyte retention times span the gradient. Monomethylamine did not show any accuracy improvement when compared to the dynamic-recycle mode; however, the accuracy of the

TMA.HCl improved by 22 %. The precision was measured using the additional analytes MEtA, DMA, DEA, and TEA, with values of ± 15 % and a mean LOD of 0.44 nmol (range: MEtA = 0.08 ~ TEA = 1.87 nmol). Overall, the result of standard analyses showed higher sensitivity for the amine suite, with lower LODs, and it was possible to detect Mg^{2+} and Ca^{2+} peaks in ~100 samples. However, the suppressor also critically failed in this mode when conducting gradient separations after two months and this mode of operation did not improve suppressor lifetime compared to that of dynamic recycled mode. Lastly, the water supply of the suppressor in stepped-legacy mode was switched to an external water supply over recycling eluent from the detector. In this method, the accuracy of all amine standards was much improved to a range spanning 80 % to 94 %, with MMA and TMA particularly benefiting. The precision was calculated to be ± 13 %, a marginal improvement, and the calculated mean LOD as 0.64 nmol (range: MEtA & MBA = 0.13 ~ TEA = 3.41 nmol), a marginal decline. In conclusion, the quantification of alkyl amines showed the highest accuracy when using the stepped-legacy external water mode with a commensurate longer suppressor lifetime, at the sacrifice of some sensitivity (Figure 2-6). Improvement of both precision and accuracy are observed under stepped-legacy external (Table A-4) over the previous amine quantitative analysis reported by Place *et. al.*⁴⁸ which was performed using legacy recycled water suppression. The external water set up additionally reduces the accumulation of exchange materials that can bleed from the column and/or formation of low solubility Mg^{2+} and Ca^{2+} hydroxide salts. This allows these divalent cations to be detected in ~300 samples while simultaneously increasing the suppressor lifetime to six months before critical failure when conducting gradient separations.

2.3.5 Enhancement of Gradient Cation-Exchange Analysis by Suppression Mode Optimization

Quantifying amines in real samples is achieved using the highest IC method performance attainable with the optimum suppressor function and longest lifetime. Suppressor operation must be consistent to obtain sufficient robustness in the developed methodology. To achieve such optimization, cation calibration standards were analyzed using the three different modes of modern electrolytic suppressors and various cleaning procedures. Quantitative analysis of inorganic cations and amines standards were first explored with suppression under dynamic recycle water mode. In this setup, water is reused from the suppressed eluent post-detection for continuous

regeneration of OH^- and H_3O^+ (Figure 2-1). Cation calibrations had the lowest sensitivities, loss of monovalent inorganic cations (Li^+ , Na^+ , K^+ , and NH_4^+) and alkylamines, and the loss of the capability to detect divalent cations Mg^{2+} and Ca^{2+} during gradient elution conditions. There are several potential explanations for this, where they could be occurring simultaneously or in isolation, depending on the suppression mode. First, if there is extra current provided in dynamic mode, this could lead to over-suppression which would produce an excess amount of OH^- compared to that required to neutralize the H_3O^+ competing ion. This excess OH^- could lead to the formation of Mg^{2+} and Ca^{2+} precipitates as highly insoluble hydroxide salts. Excess current can also generate excess heat, leading to the degradation of the anion exchange material, shortening the suppressor lifetime, which results in critical failure. Lastly, the exchange material of the analytical column may be bleeding into the suppressor resin and accumulate there over time, which can facilitate more rapid degradation, in addition to retaining divalent ions irreversibly. The performance of the prior line of resin-based suppressors, the cation electrolytically regenerated suppressor (Dionex CERS 500, 4 mm, P/N: 082542), was previously noted to be compromised by these same lost capabilities in detecting Mg^{2+} and Ca^{2+} when performing gradient cation separations.⁴⁸ Therefore, a variety of methods were tested in this work to formulate effective ways to prevent suppressor-related instrument sensitivity losses and increased LODs: acid (MSA) and base (NaOH) washes, changing from dynamic to stepped-legacy water recycle mode, oxalic acid wash, and changing regenerant water from recycled via the detector to an external water supply (see Section A6 for details). The best outcomes were obtained when we paired stepped-legacy suppression mode with use of external water. No cleanups were required, and the system retained a high sensitivity for all analytes, while detecting Ca^{2+} and Mg^{2+} ions in ~300 samples, and resulted in the longest suppressor lifetime of 6 months before critical failure when performing gradient separations. The only way determined to retain Ca^{2+} and Mg^{2+} quantitative capabilities across thousands of analyses with this stationary phase and suppressor combination was through the use of isocratic separations with an MSA concentration of 8 mM and a flow rate of 1 mL min^{-1} , with a suppressor current of 24 mA and operation in legacy external water mode.

2.3.6 Comparison of Optimized Method to Previous Amine Separations

Ion chromatographic methods utilizing gradients of H_3O^+ to facilitate separations of mixtures of common inorganic cations and alkylamines have been developed over the past decade using

several different cation-exchange columns from Dionex (now ThermoScientific): CS12A (8.5 μm), CS17 (7 μm), CS19 (5.5 μm), and CS19 (4 μm). Methanesulfonic acid gradient programs were used on the CS12A and CS17 cation-exchange columns at 30 $^{\circ}\text{C}$ with the cation self-regenerating suppressor (CSRS 300) under legacy recycle mode.⁴⁴ These methods obtained good resolution and reproducibility but the coelution of $\text{NH}_4^+/\text{MMAH}^+/\text{MEAH}^+$ occurred on CS12A, along with the coelution of $\text{DEAH}^+/\text{TMAH}^+$ on both columns. Five years later, this method was improved to analyze nine alkylamines with successful separation of $\text{DEAH}^+/\text{TMAH}^+$ using the CS19 (5.5 μm) column chemistry by increasing the separation temperature to 55 $^{\circ}\text{C}$, which was paired with a cation electrolytically regenerated suppressor (CERS 500) operated using legacy recycle mode.⁴⁸ In the present work, the IC method development advances to analyze ten alkylamines by improving the selectivity of MEtAH^+ using the CS19 (4 μm) column at 55 $^{\circ}\text{C}$ with cation dynamically regenerated suppressor (CDRS 600) under three different water modes: dynamic recycle, stepped-legacy recycle, and stepped-legacy external.

Three different suppressors were used in these methods: CSRS 300, CERS 500, and CDRS 600; the main differences being in the material of the ion-exchanger in the eluent channel. All were applied to gradient separations. Gasketed screen is used in the CSRS 300 as opposed to the resin beds in CERS 500 and CDRS 600. The CSRS 300 and CERS 500 can only be operated in legacy mode by setting the electric current, ideally using E2-1. The CDRS 600 has an updated resin composition to enable operation in dynamic mode, in addition to the traditional legacy mode, without setting the electric current requirement, but instead applying a constant voltage that should theoretically be current-responsive to changes in eluent conductivity. The highest sensitivities of mixed inorganic cations were observed when using the CERS 500 operated in legacy recycle mode by Place *et al.* (Figure A-7).⁴⁸ In the present study, the lowest sensitivities were observed for the CDRS 600 in dynamic recycle mode with total loss of detection for Mg^{2+} and Ca^{2+} analytes. The suppressor did not work as expected to automatically adjust the current based on the eluent ion concentration and over-suppression at eluent concentrations of 1 mM MSA were often observed. Sensitivity improvement in detection of alkylamines was observed in the stepped-legacy suppressor mode of the present work compared to the prior work of Place *et al.* and VandenBoer *et al.*, where CS19 and CS17 stationary phase chemistries were used, respectively (Figure 2-7).^{44,48} Even though MMAH^+ and MEAH^+ showed high separation efficiency (and sensitivities as a result) when separated using the CS12A, they coeluted with NH_4^+ . Since the latter is ubiquitous in

atmospheric samples, the amines would not be possible to detect as unknown analytes in real samples subject to conductivity detection.

Overall, in the current study, we could detect and quantify the ten most abundant alkylamines and six inorganic cations with the improvement of separation efficiency and resolution, such as DEAH^+ and TMAH^+ by using the new $4\ \mu\text{m}$ stationary phase. Accuracy and precision improvement were achieved mainly in NH_4^+ and TMA.HCl , in addition to identifying optimum suppression function for the CDRS 600 through stepped-legacy external water mode in gradient separations. This overcomes the challenges of losing analytes and exhibits the greatest longevity of electrolytically regenerated resin-based suppressor. This highly selective developed IC-CD method allowed us to separate and quantify inorganic cations in addition to a large suite of amines expected to be present in real samples of atmospheric aerosol and as gases. We demonstrate this through the analysis of size-resolved marine aerosol samples and indoor gas samples.

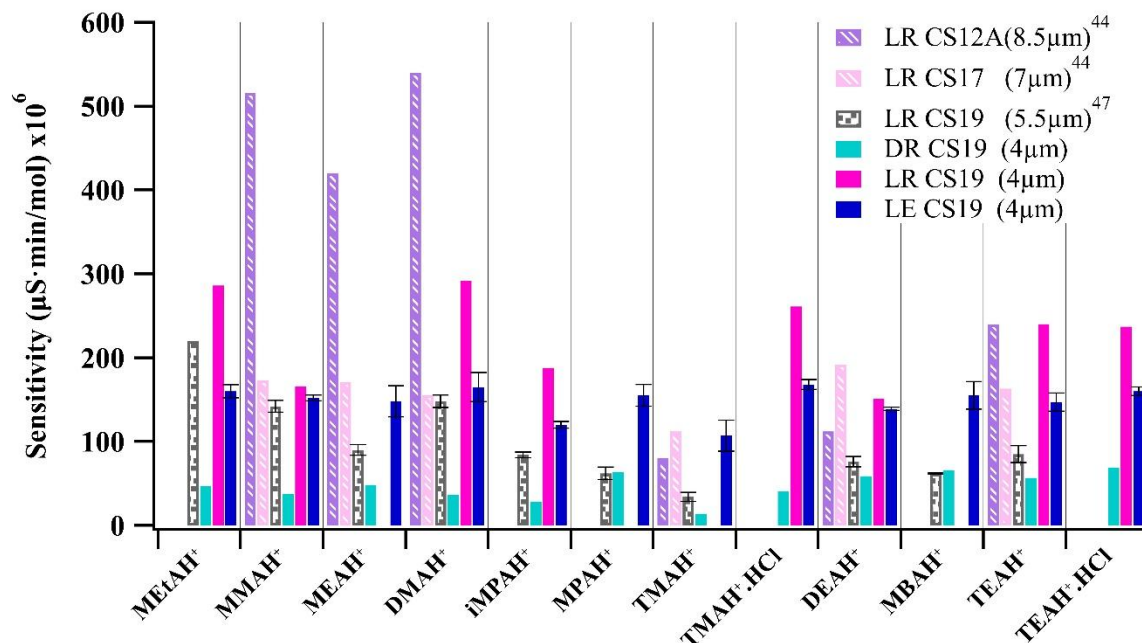


Figure 2-7: Sensitivity of alkylamines by using different cation-exchange columns and suppressors over a decade (legacy or stepped-legacy (L) and dynamic (D) modes, with recycled (R) or externally (E) provided water). The analyte separation and suppression performed by CS12A ($8.5\ \mu\text{m}$) and CS17 ($7\ \mu\text{m}$) analytical columns with a CSRS 300 operated in LR were made by VandenBoer et al.⁴⁴; a CS19 ($5.5\ \mu\text{m}$) analytical column with a CERS 500 operated in LR by Place et al.⁴⁸; and CS19 ($4\ \mu\text{m}$) analytical column with a CDRS 600 with DR, LR, and LE determined in this work.

2.3.7 Quantifying NH_4^+ and Alkylamines in Size-Resolved Marine Aerosols

Sample analysis of size-resolved aerosol was conducted at the beginning of our IC method development, as many of the reported issues herein were not yet identified. Nonetheless, sample analytes were separated with the mobile phase flow rate of 1.25 mL min^{-1} and a column temperature of 35°C . The eluent gradient program was slightly different from the optimized version that we report here. This method added 5 more minutes in the exponential ramp from 4 to 8 mM MSA and used a longer equilibration time for the 1 mM MSA (5 vs 9 minutes). The suppressor was operated using dynamic mode with recycled water to analyze these samples. Due to time constraints, they were immediately analyzed after extraction and insufficient volume remained for reanalysis with the optimized method obtained years later. Despite the conditions not being the best performing obtained, amines were ubiquitously detected in all aerosol samples and were possible to quantify, with several new species detected for the first time.

First, more generally, the molar ratio of the sum of aminium ions to ammonium ranged from 0.02 to 0.2, consistent with the emerging understanding of the importance of amines in marine particle composition. Alkylamines have been detected in marine aerosols and have been implied to make key contributions to new particle formation and aerosol growth.^{70–73} The size-resolved aerosol composition from our MOUDI samples were categorized in a bulk approach based on larger bins of particle diameter: $0.1\text{--}1 \text{ }\mu\text{m}$ (fine mode) and $1\text{--}100 \text{ }\mu\text{m}$ (coarse mode). The results of the fine mode show that cation molar quantities were in excess of anions in these marine aerosol water soluble ion observations, with a charge balance ratio (Σ^+/Σ^-) of 1.58 (Figure 2-8a). Di Lorenzo *et al.*⁷⁴ observed cationic excess with $(\Sigma^+/\Sigma^-) > 2$ in the composition of size-resolved aerosols from aged biomass burning samples that transited the coastal marine atmosphere prior to collection. The excess of cations in this prior work was suggested to be due to the formation of stable salts of reduced nitrogen and small organic acids or carboxylate functional groups found ubiquitously in oxidized secondary organic aerosol.⁷⁵ The reactive uptake of ammonia and amines by carbonyls was another hypothesized pathway, based on findings reported from a number of lab studies.^{19,76} A similar ion imbalance has also been observed as an emerging trend in the chemical composition analysis of continentally-originating cloud water at Whiteface Mountain; where an increasing trend in (Σ^+/Σ^-) was also associated with missing anion measurements in those samples.⁷⁷

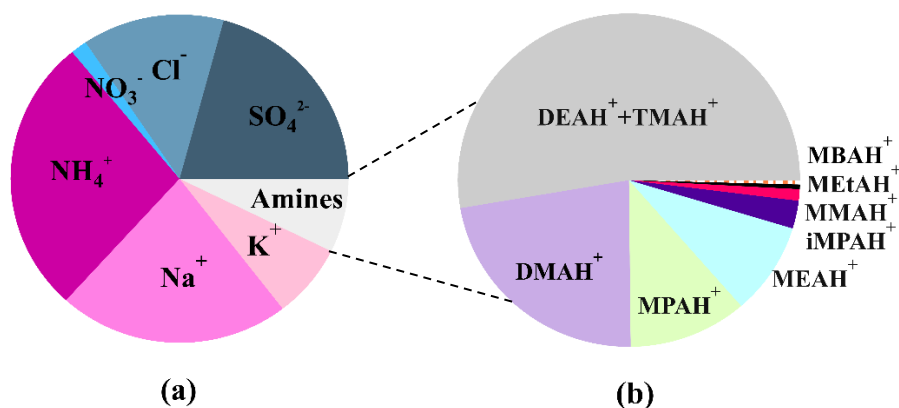


Figure 2-8: Sum of total equivalent ionic loading of (a) cations, and (b) alkylamines in fine mode aerosol. The equivalent ionic loading were 23 and 4 neq m⁻³ for NH₄⁺ and amines, respectively, which were quantified in this MOUDI sample from the coast of Eastern Canada.

Two amines were unresolved in this initial analysis: DEAH⁺ and TMAH⁺ because the column temperature was only 35 °C, which limited the stationary phase selectivity. Compared to the other quantified amines, the analysis of DEAH⁺ + TMAH⁺ was found to have the highest equivalent ionic loading estimated at 2.29 neq m⁻³ (Figure 2-8b). Average calibration slopes and molecular weights (MW) of DEAH⁺ and TMAH⁺ were used to estimate the concentration of the coeluting DEAH⁺ and TMAH⁺. Unfortunately, by the time our final optimized method was achieved, the limited sample volume remaining was insufficient for reanalysis, and they had been in storage for a substantial period of time (> 1 year). Diethylamine (DEA) is one of the most abundant amines detected in marine atmospheres and aerosols, with known biogenic sources,⁷⁸ making it the more likely contributor to our observed peak, which would decrease the 2.29 neq m⁻³ by a factor of 1.2 (if using its calibrated sensitivity and MW) to 1.91 neq m⁻³. In a gas-particle partitioning framework, DEA can form more stable salts than other methyl and ethyl amines (mono-, di-, and tri-) due to its high basicity,⁷⁸ such as in its thermodynamically favorable reaction with HNO₃,³⁹ in addition to the stability of diethylammonium nitrate salt toward oxidation.¹⁶ However, trimethylamine (TMA) is also an abundant and common amine in the atmosphere; it has mainly been found to be emitted from animal husbandry, biomass burning, as well as biological degradation of osmoregulatory compounds such as glycine betaine (GBT), trimethylamine N-oxide (TMAO), and choline in marine organisms with global emissions estimated at 169 ± 33 Gg N a⁻¹.^{5,79,80} If TMA were the sole source of our observation, the 2.29 neq m⁻³ would increase by a

factor of 1.2 to 2.75 neq m^{-3} . In addition, three new amines: MPA (0.49 neq m^{-3}), iMPA (0.12 neq m^{-3}), and MBA (0.02 neq m^{-3}) were detected and quantified in these MOUDI samples, which have not been reported in prior studies of marine particles. Ion mass concentrations of two MOUDI samples show the differences between amine mass loadings in coastal marine and anthropogenically influenced harbour air (Figures 2-9 and A-8). The summed amine equivalent ionic loadings are higher in the marine air than in the harbour air with value of 1.55 and 0.76 neq m^{-3} , respectively. The advantage of applying our highly selective IC method is it can quantify a large suite of amines in marine aerosol samples. Because this method resolved all the amine analytes from the highly abundant sodium in these samples, we were able to identify several new species that have not been previously reported. Therefore, application of this improved IC method can inform future field studies about reduced nitrogen basic species of interest and their importance in Earth's atmosphere. Those results can then inform laboratory studies to better understand the roles physical, chemical, and biological processes have on the composition of aerosol, or in the exchange of gases and particles across the air-sea interface.

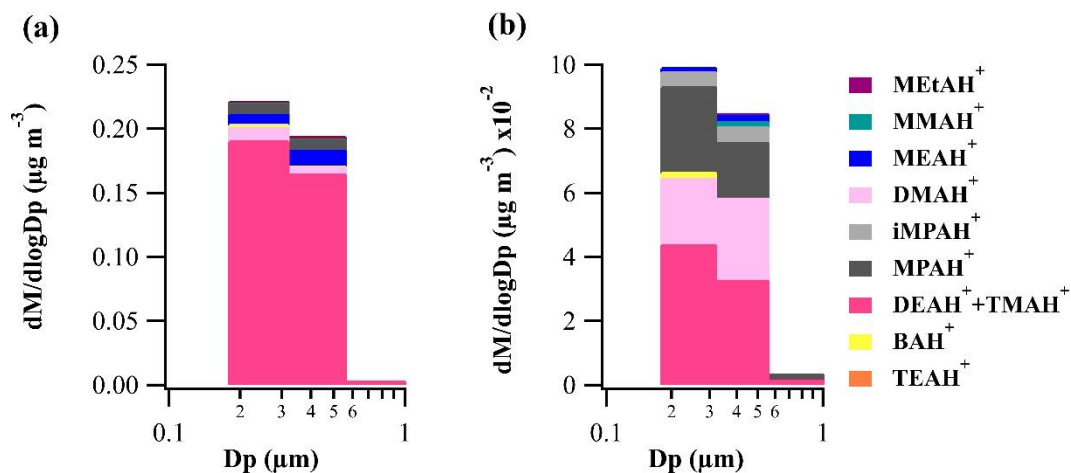


Figure 2-9: Ion mass loadings of MOUDI samples is shown only in fine mode (particle diameter less than $0.1 \mu\text{m}$) in (a) marine air from 15/09/2018 to 16/09/2018, and (b) Halifax harbour air from 18/09/2018 to 19/09/2018 on the Atlantic coast of Nova Scotia, Canada (Fig. S8). The amine mass loading in the coarse mode is not depicted because levels were below detection limits.

2.3.8 Indoor Measurement of NH₃ and Alkylamines

Quantification of indoor NH₃ and amines from passive sample collection was performed with the optimized gradient method at 55 °C and stepped-legacy external water suppression. Ammonia was the dominant basic indoor compound during the New Home Air Quality Study (NHAQS), with a mean mixing ratio of 25 ± 15 ppbv, ranging from 4 – 79 ppbv through the different time periods of occupancy. Unfortunately, amine levels were below the instrumental LODs, and we could not detect and quantify them in either indoor or outdoor samples. The maximum mixing ratios for detectable amines is between 0.34 ppbv for MMA which we detect the most sensitively and 10.50 ppbv for TEA which is the least sensitive for a sampling time of 1 day. These limits decrease to 0.08 ppbv for MMA and 2.59 ppbv for TEA when the sampling time is extended to 5 days. The upper limits for the mixing ratios of the full analyte suite detectable by our optimized IC method are presented in Table A-5.

The concentration of NH₃ in previous studies ranged between 8 – 44 ppbv in a variety of residential buildings (Figure 2-10).^{81–84} Ampollini *et al.*²⁹ measured a mean mixing ratio of 32 ppbv in an unoccupied test house with increasing maximum concentrations of NH₃ during different activities, including cooking meat (130 ppbv), cleaning with ammonia-based products (1592 ppbv), and high-occupancy events (99 ppbv). Indoor measurements of amines have been performed in a few studies, and primarily aromatic amines were reported in a tobacco smoking environment.^{85–87} Akyüz quantified alkylamines in indoor (smoking and non-smoking areas) and outdoor air samples during the summer and winter months at six sampling sites in Turkey. Seasonal mean concentrations of MMA, DMA, MEA, DEA, MPA, and MBA were determined at mass loading levels of ng m⁻³ which are on the same order as pptv mixing ratios.⁸⁸ Our IC method can detect and quantify the ten most abundant atmospheric alkylamines, yet LODs for 24 hr and 5 day integrated sampling when assuming the same sampling rate as for NH₃ range from 0.14 – 30 µg m⁻³, which are equivalent to mixing ratios on the order of ppbv, so this passive sampling technique is more applicable for detecting or quantifying amines from emission sources. Our findings here show that there are not strong sources of alkyl amines in newly built Canadian homes and that they were also not located near any strong outdoor point sources.

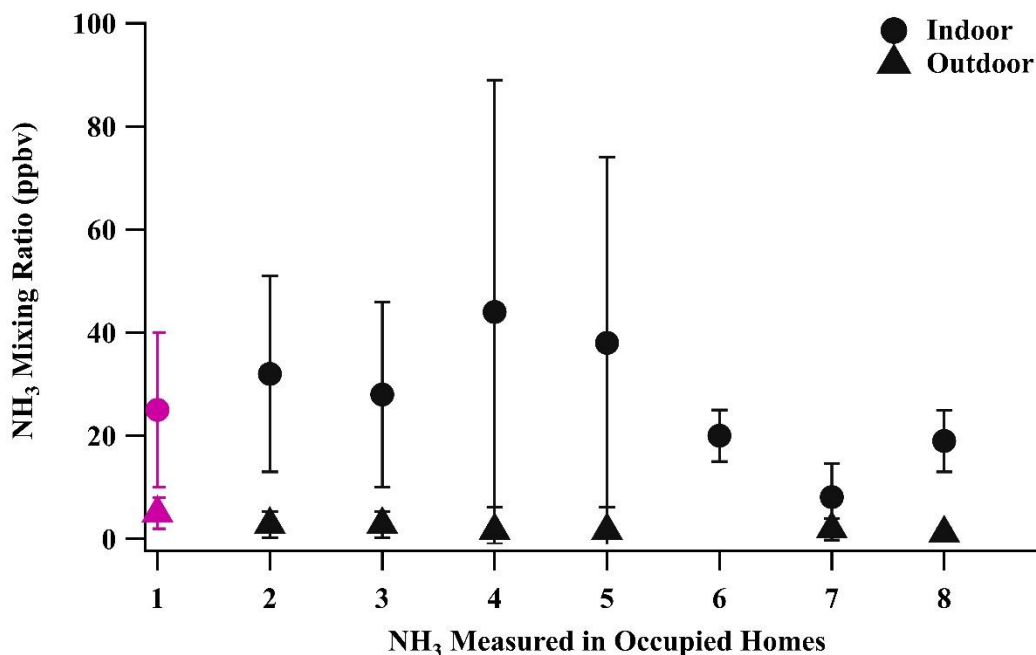


Figure 2-10: Mixing ratios of NH₃ from NHAQS compared to previous studies in different occupied residential buildings: NHAQS (1, this work), Leaderer et al. (2, summer; AC ON),⁸¹ (3, summer; AC OFF),⁸¹ (4, winter; kerosene heater ON),⁸¹ (5, winter; kerosene heater OFF),⁸¹ Spengler et al. (6)⁸², Brauer et al. (7, summer)⁸³, (8, winter)⁸³, and Li and Harrison (9)⁸⁴.

Mixing ratios of NH₃ decreased in the majority of homes after occupancy in the NHAQS (Figure 2-11a), potentially due to either reduction in emissions from new building materials or an increase in surface area from occupancy to which it can partition. When occupants moved in, the surface/volume increased through the addition of furniture, personal materials, and the occupants into the houses. This amplifies the emerging recognition that surface interactions and their influence on the chemical composition of indoor air is important.^{89,90} In a case study, the ammonia mixing ratio in one home decreased significantly from 79 ppbv pre-occupancy to 18 ppbv during the first year of occupancy (Figure 2-11b). The simultaneously measured outdoor mean mixing ratio of NH₃ was 4 ± 2 ppbv. The indoor to the outdoor ratio of NH₃ was typically greater than unity in all 18 houses, consistent with the known indoor sources of NH₃. A more detailed analysis on NHAQS indoor NH₃ is beyond the scope of this work as sample collections from a larger number of homes is ongoing and will be the subject of future work.

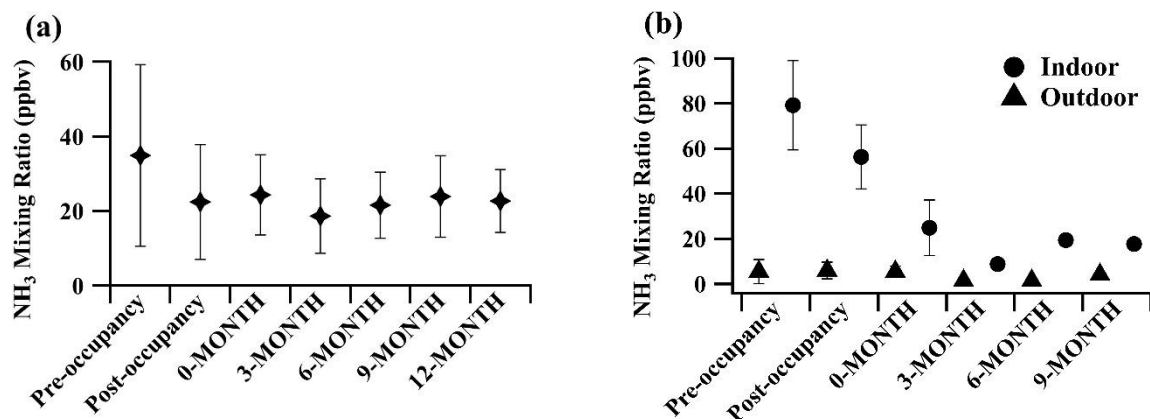


Figure 2-11: NHAQS observations of (a) average indoor mixing ratios of NH₃ ($\pm 1\sigma$) from pre-occupancy through the first-year occupancy in 18 houses (b) outdoor and indoor mixing ratios of NH₃ ($\pm 1\sigma$) from pre-occupancy to 9-MONTH in the case study home.

2.4 Conclusions

The ion-chromatographic method was developed with high selectivity and separation efficiency to quantify six inorganic cations and ten most abundant alkylamines found in the atmosphere, including MEtA, which was not measured in previous reports. This method was optimized in separation efficiency and resolution of cations using a smaller particle size of 4 μm on a CS19 cation-exchange column and a resin-based suppressor operated in stepped-legacy external water mode. The stability of amine standards was not improved overtime by decreasing the pH and fixing the ionized state of standards as hydrochloride salts; amine standards must be made freshly from stock solutions from the primary standards prior to quantitative analysis in DIW to achieve the highest instrument reproducibility and method accuracy. TMA standards have been previously reported for high variability between days due to its high volatility; in this study, we found that a freshly made stock solution of its hydrochloride salt improves IC method performance and recommend the same for quantitation of TEA. Despite losing analytes in the modern anion-exchange resin suppressors operating on a gradient elution program, the most accurate calibration curves of cation standards were obtained using regression lines that are not forced through zero. For inorganic cations, the zero-point was retained, whereas for amines, the zero-point was excluded. Analysis of calibration of inorganic cations and alkylamines was then optimized using a suppressor operated with stepped-legacy external water to obtain higher accuracy and precision,

while also detecting the divalent cations Mg^{2+} and Ca^{2+} with the longest suppressor lifetime prior to critical failure.

Overall, this highly selective developed IC-CD method allowed us to separate and quantify inorganic cations and large suites of amines in real samples. The result from size-resolved aerosols suggests that NH_3 and amines are diverse and abundant in the marine environment; MPA, iMPA, and MBA were detected and quantified in these samples, which have not been reported before. Therefore, more research will be required to understand the chemical composition of aerosol in the exchange of gases and particles across the air-sea interface. The result from NHAQS will be used to explore associations between homeowners' activities and observed NH_3 mixing ratios to better understand the controls on their emission sources, and to set initial upper limits on indoor amines. These estimates are important for ongoing regulate of NH_3 and amine emissions from new building materials that could lead to occupant exposure and subsequent health effects.

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CHAPTER THREE - Microphysical chemistry of fog-aerosol interactions over the Northwest Atlantic Ocean during Fatima 2022

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Abstract

A comprehensive study of aerosol chemistry, microphysics, physical processing, and meteorological parameters was conducted to investigate fog-aerosol interactions over the Northwest Atlantic Ocean during the fog and turbulence interactions in the marine atmosphere (Fatima) 2022. Chemical analysis of size-resolved aerosols and fog droplets revealed a reduction in coarse mode sea salt ions (e.g., Cl^- , Na^+ , Mg^{2+} , ss-SO_4^{2-} , K^+ , and NO_3^-) compared to ambient conditions, attributed to their growth into fog droplets. In contrast, fine mode aerosol processed-S (e.g., nss-SO_4^{2-} and MSA^-) and reduced-N (e.g., NH_4^+ , DMAH^+ , and DEAH^+) increased during fog events. Three distinct fog types were identified based on size-resolved ion mass distributions, combined with particle number concentrations and meteorological parameters, to provide insight into the drivers of aerosol chemical composition during each chemically distinct fog type. Type I fog was the most common, characterized by depleted coarse mode sea salt aerosols, with fog droplets initially formed from freshly emitted coarse mode aerosols and most likely sustained by growth of fine mode aerosols. Type II fog was least common, sustained by ongoing production of coarse mode sea salt aerosols due to elevated winds, and supplemented by fine mode aerosol contributions. Type III fog had highest mass loadings of sea salt ions at fog droplet sizes, with droplet formation primarily driven by coarse mode growth with minor contributions from fine mode aerosol. Reduction of coarse sea salt mass loadings during more than a dozen fog events confirms their expected role as effective fog condensation nuclei and the physical impact of fog processing in reducing their atmospheric mass loading. This dataset shows these aerosols are scavenged (~70%) in a supersaturated atmosphere to form droplets. This is the most extensive marine fog dataset to date to study fog-aerosol interactions from a chemical perspective, with the potential to improve marine fog forecasting models to provide safer marine transportation.

3.1 Introduction

Aerosols play an important role in regulating the Earth's energy balance directly and indirectly by impacting radiative forcing and cloud condensation nuclei, respectively (Lohmann and Feichter, 2005; Bellouin *et al.*, 2020). Fog is a collection of suspended water droplets that reduces horizontal visibility at the surface to less than one kilometer. Fog formation results from a complex interplay between radiative, thermodynamic, microphysical, chemical, and surface processes, along with dynamical micro-scale air mixing and turbulence in addition to larger scale meteorology such as air mass movement and temperature variations (Gultepe *et al.*, 2007). Aerosols can promote fog formation through growth by water uptake as cloud condensation nuclei (CCN) when the relative humidity (RH) exceeds 100%. Since fog is a ground level cloud, these activated aerosols will henceforth be referred to as CCN.

Aerosol can originate in the atmosphere from various natural sources, such as sea spray droplets, windblown dust, volcanic emissions, and biogenic material (Judson, 1968; Mitchell Jr., 1970; Lewis and Schwartz, 2004). Primary aerosols originate from anthropogenic sources like soot, smoke, or road salt, while secondary aerosols form through atmospheric processing of precursor gases (Singer, 2012). The dimensions of aerosols range from nanometers to micrometers and can be classified based on their diameter into three modes: ultrafine (0.01–0.1 μm), fine (0.1–1 μm), and coarse (1–100 μm) (Willeke and Whitby, 1975). Marine aerosols can originate from primary and secondary sources (Quinn *et al.*, 2015). Primary aerosols originate from sea spray produced by sea bubble bursting after wave breaking, and from the direct mechanical disruption of wave crests due to wind action on the ocean surface. These primary aerosols generate three types of droplets: film, jet, and spume (Lewis and Schwartz, 2004). Both film and jet droplets emerge at wind speeds of approximately 5 m s^{-1} (Wang *et al.*, 2017). Film droplets are produced by breaking apart the thin film of bubbles and they are direct contributions to the chemical composition of fine mode aerosol. These include organic components such as polysaccharides, protein, and fragments of phytoplankton derived from marine biological activity, as well as inorganic sea salt ions (O'Dowd *et al.*, 2004; Hawkins and Russell, 2010; Frossard *et al.*, 2014). Simultaneously, jet droplets form through the collapse of the bubble cavity, generating coarse mode aerosol from bulk sea water. With an increase in wind speed above 10 m s^{-1} , wave crests can begin to shear, forming spumes ranging from tens of micrometers to millimeters (Monahan *et al.*, 1983). Sea surface temperature affects sea salt aerosol production, reducing both fine and coarse

modes at lower temperatures and increasing them at higher temperatures (Hu *et al.*, 2024). Secondary marine aerosols, on the other hand, are formed through the process of gas-to-particle conversion (Carpenter, Archer and Beale, 2012). In the marine atmosphere, secondary aerosols are often produced from partitioning or oxidation of gases of biological origin. Gaseous precursors which are emitted by phytoplankton throughout their life cycle form low volatility products such as processed sulfur (e.g., non-sea salt (nss)-SO₄²⁻ and methane sulfonic acid) or reactive reduced nitrogen (e.g., NH₄⁺ and alkylamines) (Charlson *et al.*, 1987; Schwartz, 1988; Bode *et al.*, 2004; Stefels *et al.*, 2007; Kilgour *et al.*, 2024). Anthropogenic aerosols, including acidic species (e.g. SO₄²⁻ and NO₃⁻) and basic species (e.g. NH₄⁺) are also transported over oceans from their continental origins and deposited into surface waters. Their deposition can alter the chemistry of surface seawater by changing the pH and impacting ocean biogeochemistry and biological productivity (Duce, Galloway and Liss, 2009; Ventura *et al.*, 2021). The study of anthropogenic aerosol transfer over the Arabian Sea indicates that deposited NH₄⁺, originating from agricultural activities and biomass burning in the Indo-Gangetic Plain and southern India, enhances the biological productivity of the Arabian Sea by providing a nitrogen source to phytoplankton in nitrogen-limited regions (Bikkina *et al.*, 2021). In the marine atmosphere, these aerosol sources are all expected to impact the formation, persistence, and dissipation of fog.

Since all atmospheric droplets nucleate on or grow from existing atmospheric aerosol, there is an expected intricate relationship between their characteristics; aerosol properties directly impact the life cycle of a fog layer through the growth of droplets, while the presence of fog droplets affects aerosol loading and chemistry (Gultepe *et al.*, 2007; Richter, MacMillan and Wainwright, 2021). Fog droplets have competing effects on aerosol concentration in the atmosphere (Lillis *et al.*, 1999). Primarily, aerosol reduction occurs through scavenging mechanisms like nucleation where aerosols are activated and grow into fog droplets or impaction through collection of aerosols by droplets via collision-coalescence processes (referred to as *collection* henceforth), followed by loss through precipitation or deposition (Noone, 1992; Gilardoni *et al.*, 2014; Wainwright, Chang and Richter, 2021). However, aerosol mass loading can also increase by the uptake of gaseous species into fog droplets, resulting in formation of secondary aerosol mass via aqueous processing (Kaul *et al.*, 2011; Ervens *et al.*, 2013). These aerosols are then released into the atmosphere following droplet evaporation, alongside repartitioning of gases from the aqueous phase throughout the process. The relative significance of these processes

depends on the environmental parameters influencing fog formation, including meteorological conditions, aerosol composition, gas-phase chemical composition, and the duration of the fog episode. As a consequence, aerosol-fog interactions fundamentally underpin the processes required to forecast fog formation, duration, and subsequent occurrences on the same aerosol. This is particularly important for sea fog which reduces visibility and disrupts aviation and marine transportation (Thuman and Robinson, 1954; Koraćin *et al.*, 2014). There remains a need for comprehensive studies on these processes to improve safety through forecasting for marine activities and transportation (Yue *et al.*, 2012). Previous studies have focused on aerosol-fog interaction on land, with fewer studies in the marine environment (Sasakawa, Ooki and Uematsu, 2003; Aikawa *et al.*, 2007; Pant, Deshpande and Kamra, 2010; Boutle *et al.*, 2018; Tsai *et al.*, 2021; Zhao *et al.*, 2022). Sea fog usually forms when warm marine air advects over a cold ocean current, leading to advection warm fog like that found near the Grand Banks of Newfoundland (Taylor, 1917; Gultepe *et al.*, 2007; Fernando *et al.*, 2024), which is the focus region for this study. Conversely, advection cold fog occurs when cooler air moves over warmer ocean surfaces, resulting in saturation and fog formation. Lastly, fog may form through cloud base lowering over the open ocean, occurring within a shallow cloudy marine boundary layer (MBL) and characterized by a strong inversion and adequate moisture in the subcloud layer (Peak and Tag, 1989). The Grand Banks and Sable Island regions in the Northwest Atlantic Ocean rank as the second-largest marine fog area globally, where all these fog types might occur, particularly during June, July, and August, which account for approximately 45% of occurrences from 1950 to 2007 (Koracin and Dorman, 2017). During this period, there has also been an increasing overall trend in fog incidence of ~12.8% (or 0.22% per year) in this region. This trend correlates with an ongoing increase in sea surface temperature of 0.9 °C over the same 57 years of observations. Zhao *et al.* (2022) recently reported that sea salt ions like Na^+ , Mg^{2+} , Cl^- , and sea salt sulfate (ss-SO_4^{2-}) were more likely to be present in fog and their precursor aerosol, and suggested they were acting as CCN over the Arctic Ocean. The results from another sea fog study over the Northwestern North Pacific indicated a decrease in the number concentration of coarse mode aerosols during fog events, while fine mode aerosols remained unchanged. Coarse particles such as sea salt and NaNO_3 preferentially acted as CCN compared to fine particles (e.g., H_2SO_4 , $(\text{NH}_4)\text{HSO}_4$, and $(\text{NH}_4)_2\text{SO}_4$) (Sasakawa, Ooki and Uematsu, 2003). Knowledge gaps remain regarding the formation of fog droplets from coarse mode aerosols, such as sea salt, despite their frequent lower number

concentration than those of fog droplets. It is unclear how these aerosols grow and sustain a larger droplet population through nucleation and subsequent microphysical processes, and which aerosols persist throughout and/or sustain fog droplet populations during long marine fog events (> 24 hours). Additionally, missing information on the size-resolved aerosol composition across many fog episodes limits models to being informed by bulk particulate matter (PM_{2.5} or PM₁₀) measurements from a limited number of marine fog events in prior studies (Liu *et al.*, 2020; Wainwright and Richter, 2021; Wainwright, Chang and Richter, 2021; Kecorius *et al.*, 2023)

During the Fog and turbulence interactions in the marine atmosphere (Fatima) project, we explored the initiation and persistence of marine fog events in the Grand Banks and Sable Island regions of the Northwest Atlantic Ocean by measuring size-resolved aerosol chemical composition. In this work we measured the chemical composition of 10 nm to 100 µm aerosols during multiple transient and sustained marine fog episodes to better understand changes in chemical composition of aerosol due to the onset of fog conditions; identified fog types based on measured aerosol chemical composition and meteorological conditions; assessed which aerosol chemical components are transferred into fog droplets and the corresponding impact of the presence of fog on aerosol chemical mass loading; and conducted a case study examining the microphysical chemistry of aerosols during an intense sustained fog event near Sable Island. An interpretation of chemical transformations, fog water chemistry, and detailed aerosol chemistry is beyond the scope of this work and will be the focus of a future manuscript.

3.2 Method

3.2.1 R/V Atlantic condor cruise and observation region

The principal data collection for this study occurred in July 2022 during a scientific cruise in the Northwest Atlantic Ocean off the coast of Eastern Canada. During the Fatima field campaign fog samples were collected aboard the Atlantic Condor, a supply ship refitted for research. This cruise was divided into two fog investigation phases: one in the Grand Banks region and the other near Sable Island (Figure 3-1). From July 3 to 17, the initial Grand Banks phase was undertaken with the Atlantic Condor departing from Halifax, Nova Scotia and arriving in St. John's, Newfoundland and Labrador. In this period, measurements primarily focused on collecting fog near the Hibernia offshore oil platform. Following a short resupply in St. John's, the second phase of the cruise

occurred from July 19 to August 1 in the Sable Island region, with the Atlantic Condor returning to port in Halifax, and included a transect southwards into the warmer waters of the Gulf Stream.

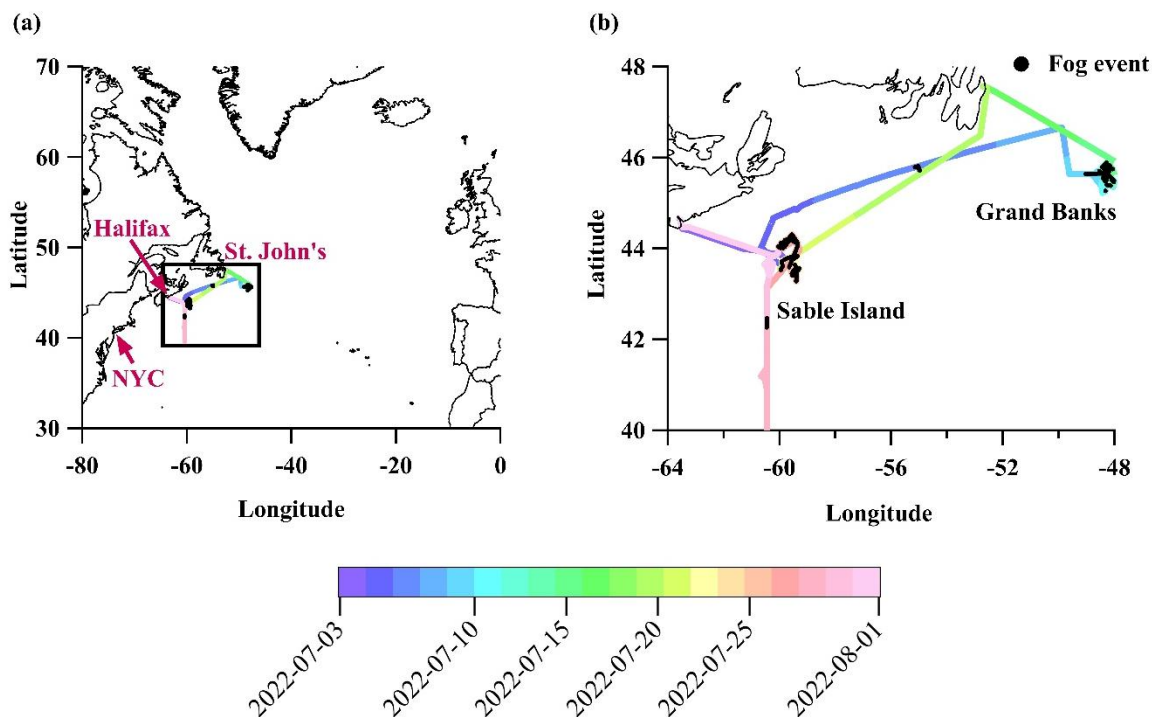


Figure 3-1: Atlantic Condor traversed (a) the coastal waters of North America in the Northwest Atlantic Ocean, off the coast of Eastern Canada, in July 2022 during Fatima, with (b) the ship track traversing from Halifax to St. John's and returning to Halifax, encountering fog for sampling (black dots) in the Grand Banks and Sable Island regions.

3.2.2 Meteorology and radiosonde measurement of atmospheric conditions

Meteorological parameters were collected using a set of sensors installed on various parts of the Atlantic Condor superstructure. Visibility (km) was measured using the FD70 Visibility Sensor, which was installed on the deck above the pilot house of the ship (sample height ~18 m above the mean water line). Co-located with visibility was a fog droplet monitor (FM-120, Droplet Measurement Technologies), which sampled droplet number concentration across a size range of 2 to 50 μm ; sea surface temperature (SST, $^{\circ}\text{C}$) was measured radiometrically using the Remote Ocean Sensing Radiometer (ROSR, Remote Measurements & Research Co.). From the ship's bow mast, air temperature (T_{air} , $^{\circ}\text{C}$), relative humidity (RH, %), wind speed/direction (WS, m s^{-1} /WD, $^{\circ}$ from north as 0°), and rain rate (mm hr^{-1}) were recorded with a Vaisala WXT 520 weather station

(~18 m above the mean water level). To supplement a gap in the bow mast time series, wind speed and direction from an ultrasonic three-dimensional anemometer (IRGASON, Campbell Scientific) deployed as part of the deck-mounted cloud aerosol measurements system (D-CAMS) installed on the ship crow's nest was used (approximately 27 m above the mean water level). Detailed information on the measurement systems deployed on the Atlantic Condor can be found in Fernando *et al.* (2025). A time series of visibility and these meteorological parameters spanning the duration of the campaign is provided in Appendix B (Figure B-1).

Meteorological vertical profiles of temperature, RH, wind speed, wind direction, and pressure were also acquired through 66 radiosonde launches during fog events from the aft deck of the Atlantic Condor. The measurements were carried out using the Vaisala DigiCora system and RS41-SGP rawinsondes. A more complete description of the Atlantic Condor radiosonde profiling system can be found at Ortiz-Suslow *et al.* (2025). The vertical atmospheric profiles provide a measurement of atmospheric stability or stratification within fog events and throughout the MBL.

Synoptic conditions during the campaign were characterized using HYSPLIT back trajectories (air-mass origin) and Global Forecast System sea-level pressure fields (GFS, MSLP) for wind direction and pressure; summaries for each fog type are provided in Table B-3 (GFS, NOAA; Stein *et al.*, 2015).

3.2.3 Chemical and aerosol instruments

Size-resolved aerosol samples were collected using a Micro Orifice Uniform Deposit Impactor (MOUDI, model 100-NR, MSP Corp., Shoreview, MN, USA) and a nano-Micro Orifice Uniform Deposit Impactor (nanoMOUDI II, model 122-R, MSP Corp., Shoreview, MN, USA), positioned within a stainless steel weatherproof enclosure mounted to the railing on the deck above pilothouse (~ 10 m a.s.l.). The vessel was consistently angled into the headwind and remained mobile during all sampling periods; the scientific operations were planned to maintain a headwind orientation at all times. All aerosol sampling inlets were mounted forward and across the bridge deck from the ship exhaust to prevent self-sampling, with a communication procedure within the ship and science teams in place to stop sampling and avoid contamination. Size-resolved chemical analysis was performed on MOUDI impaction plate extracts to quantify major anion and cation components using an ion chromatograph with conductivity detector (IC-CD; Thermo Scientific ICS-6000), also

fitted with an autosampler (AS-DV) for continuous analysis throughout the cruise. A scanning mobility particle sizer (SMPS, TSI Inc, Differential-Mobility Analyzer 3082, Electrostatic Classifier 3081, Condensation Particle Counter 3772) had an inlet placed close to the MOUDI enclosure to continuously measure dry aerosol number. The SMPS, operated with sheath flow rate of 5 L min⁻¹ and sample flow rate of 1.05 ± 0.05 L min⁻¹, measured aerosols that passed through a silica gel dryer to reduce water content. Dry aerosol size-resolved number distributions were then collected by the SMPS which used a 0.071 cm impactor at the inlet, excluding particles larger than 507 nm. Overall, this SMPS configuration allowed for the counting of dry aerosol number with diameters ranging from 10.6 to 496 nm, resulting in size-resolved number concentrations. Detailed information on instrument setup and QA/QC can be found in Giacosa *et al.* (2026).

3.2.3.1 Size-resolved aerosol composition

Size-resolved aerosol samples were collected both from droplets (<100 µm) and interstitial hydrated aerosol using the MOUDI during fog events and only ambient aerosol with the nanoMOUDI between fog events. Although the MOUDI is a time-integrated sampler and lacks high time resolution, it captures representative spatial and temporal characteristics within each sampling period. Both instruments sampled through a total suspended particulate inlet with rain cap at a flow rate of 30 L min⁻¹. The MOUDI uses nine inertial impaction stages to capture particle fractions with aerodynamic diameters centered at 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10, and 18 µm, operated as in our prior work for the collection of marine aerosol samples (Chisholm *et al.*, 2021). The nanoMOUDI covers the same aerodynamic cut stages as the MOUDI but includes five extra impaction stages for aerodynamic diameters smaller than 0.1 µm (0.100, 0.056, 0.032, 0.018, and 0.010 µm). A total of fifteen samples were collected during fog events as well as fourteen ambient samples, with durations spanning from 197 to 2490 min (3 to 42 hours). Fog intervals were characterized by an FD70 visibility less than 1 km and concurrent increases in the FM-120 droplet number concentration and liquid water content. Aerosol and meteorological conditions were likely spatially and temporally heterogeneous within fog events such that each MOUDI sample reflects a time-averaged measurement over its sampling period. The cessation of a fog event could correspond to either dissipation or advection relative to the planned transit of the Atlantic Condor. The rotary vane oil pump for the nanoMOUDI was fitted with an exhaust filter and mounted on the deck outside the weatherproof enclosure, due to its size and heat dissipation

requirements, with the vacuum and power lines passing through weather-tight fittings installed into the side of the enclosure. A description of MOUDI sampler performance for marine aerosol collection is detailed in Section B2 of Appendix B, followed by our validation of the chemical size distributions by comparison between MOUDI and nanoMOUDI throughout the campaign, with a side-by-side sample collected under ambient conditions on July 26 near the end of the campaign.

Aerosols were collected by impaction on 47 mm and 84 mm clean aluminum foil, where the latter were only used for the additional stages in the nanoMOUDI. Foils were cleaned by soaking and rinsing six times in ultra-pure deionized water (DIW; resistivity of 18.2 M Ω ·cm; Milli-Q Direct 8) followed by combustion at 500 °C for one hour. Three aluminum foils were used as field blanks every time a sample was collected by either instrument. Samples were stored at -20 °C in the on-board lab until extraction, with only half of the samples being extracted and analyzed in the field lab on board the Atlantic Condor. The foils were extracted by rolling them inside pre-cleaned 15 mL polypropylene (PP) falcon tubes. The samples were extracted in 15 mL of DIW by sonication for one hour at room temperature and then centrifuged at 6000 rpm for 20 minutes to settle any aluminum debris. An aliquot of the supernatant was transferred into a 5 mL IC autosampler vial for analysis. The IC-CD has a dual pump module, allowing two separations to take place simultaneously, yielding an analysis of major cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) and anions (CH₃SO₃⁻ = MSA⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, SO₄²⁻), using H⁺ and OH⁻ competing ions respectively, at a flow rate of 1 mL min⁻¹ and a column temperature of 30 °C for 35 minutes following our established methods (Place *et al.*, 2018; Salehpoor and VandenBoer, 2023) with minor modifications (Appendix B; Section B3). Post-campaign, the remaining samples were stored in a cooler, transferred to a refrigerator at 4 °C in the lab, and subsequently extracted and analyzed for major cations and anions. Additionally, all aerosol extracts were reanalyzed for quantification of alkylamines such as dimethylamine (DMAH⁺) and diethylamine (DEAH⁺) as the suppressors are not robust enough to use continuously in the field lab installed on the Atlantic Condor for this campaign. The analysis utilized an MSA (1-8 mM) gradient method at 55 °C with stepped-legacy external water suppression mode, as in our prior work (Salehpoor and VandenBoer, 2023). A few aerosol extract samples were also analyzed to identify organic acids using ion chromatography coupled with an ISQEC single quadrupole mass spectrometer (IC-MS; Thermo Scientific ICS-6000 DC). The samples were first preconcentrated on an anion concentrator column (TAC-ULP1, P/N: 061400), then passed through an AG24 guard column (2 x 50 mm, P/N: 064151), and

separated on an AS24 analytical column (2 × 250 mm, P/N: 064153) using a NaOH gradient (10–60 mM) at flow rate of 0.35 mL min⁻¹. The eluent was passed through an ADRS 600 suppressor (2mm, P/N: 088667) before entering the mass spectrometer, which operated in negative electrospray ionization (ESI⁻) mode. Additional method details can be found in Joudan *et al.* (2024).

3.2.4 Data analysis

Quality assurance and quality control (QA/QC) were conducted on all IC-CD determinations, including standard calibration curves, with assessment of method precision and accuracy to ensure reliable and accurate ion concentration measurements (Appendix B; Section B3). The IC-CD data results were obtained using Chromeleon™ v7.2.10 software. All size-resolved aerosol samples were corrected by subtraction for ions detected in field blanks to mitigate systematic error. The concentrations of ions in sea salt aerosols (e.g., Cl⁻, Na⁺, Mg²⁺, Ca²⁺, ss-SO₄²⁻, K⁺, and NO₃⁻) and non-sea salt aerosols, including processed-S (e.g., nss-SO₄²⁻ and MSA⁻), and reduced-N (e.g., NH₄⁺, DMAH⁺, and DEAH⁺) were calculated as mass (μg m⁻³) and equivalent ionic loadings (neq m⁻³). Concentration of nss-SO₄²⁻ was determined using E3-1 (Itahashi *et al.*, 2018):

$$\text{nss-SO}_4^{2-} = [\text{SO}_4^{2-}] - (0.06028 \times [\text{Na}^+]) \quad (\text{E3-1})$$

where the value of 0.06028 represents the molar ratio of SO₄²⁻/Na⁺ in seawater. Mass loading refers to the concentration of ions by mass in the air and equivalent ionic loading represents the concentration of ion charge balance per mole of chemical in the air. The calculations for ion mass loading and equivalent loading were performed using a combination of Excel (O365, Microsoft Corp.) and Igor Pro (v8, Wavemetrics).

The aerosols were classified into fine and coarse modes for comparison against expected bulk aerosol composition. To validate the ion measurements in the coarse mode, the molar ratio of sea salt ions, i.e., Σ (Cl⁻, SO₄²⁻, NO₃⁻) to Σ (Na⁺, Mg²⁺, Ca²⁺, K⁺) was compared with the expected ionic composition of seawater, which was also used to determine non-sea salt component loadings (Appendix B; Section B3). In the fine mode, the ratio of Σ_{base} (NH₄⁺, DMAH⁺, DEAH⁺) to Σ_{acid} (processed-S: nss-SO₄²⁻, MSA⁻; and NO₃⁻) was analyzed to assess acid-base neutralization and additional gas-particle partitioning processes (Appendix B; Section B3). Therefore, the fine mode comprised the sum of the mass or equivalent loadings from the MOUDI and nanoMOUDI stages between 0.18 and 0.56 μm, and the coarse mode included stages from 1.0 to 18 μm. The dry

residual diameters for wet aerosols collected by the MOUDI were calculated for comparison to the SMPS measurements using the total mass loading from MOUDI ($\mu\text{g m}^{-3}$) and the number concentrations from the fog droplet monitor (cm^{-3}) to estimate particle mass (m_p , μg) using E3-2.

$$m_p = \frac{m_{total}}{N_d} \quad (\text{E3-2})$$

Then, the density of each ion was used to calculate a representative particle density (ρ_p , $\mu\text{g m}^{-3}$) and E3-3, which was used to derive a corresponding particle volume (V_p , m^3).

$$V_p = \frac{m_p}{\rho_p} \quad (\text{E3-3})$$

The residual particle diameter was calculated using E3-4, assuming spherical particles, from this volume.

$$D_p = \left(\frac{6V_p}{\pi} \right)^{1/3} \quad (\text{E3-4})$$

The calculation of residual diameters follows QA/QC protocols detailed in SI; Section S3, including verification of MOUDI ion concentration measurement and validation of FM-120 droplet number concentrations (Giacosa *et al.*, 2026). Calculating residual diameters enables the comparison of aerosol mass loadings (MOUDI) with corresponding number concentrations (SMPS), providing insight into whether fine and/or coarse mode aerosol are activated into fog droplets.

3.3 Results and Discussion

3.3.1 Chemical composition of marine size-resolved aerosol during ambient and fog conditions

The chemical composition of aerosols observed under ambient conditions and bordering fifteen fog events over the whole campaign (July 4 to August 1, 2022) is presented in Figure 3-2, with the average equivalent ionic loadings provided in the SI; Figure S4. In this analysis a general picture of how fog formation alters the chemical composition of aerosols in both coarse and fine modes across all measurement locations is presented. The trends and quantities presented herein are reliable based on the IC quality control results which found that the analytical precision of the method was $\pm 12\%$ and $\pm 10\%$ for cations and anions, respectively in both the analyses from the Atlantic Condor field lab and the remaining analyses conducted in our analytical lab (Appendix B; Section B3). The accuracy of analytical determinations of all ions was $>90\%$ in both settings. These performance metrics align with those we have previously reported for our IC analyses

including those on MOUDI samples, such that the size-resolved aerosol measurements in the current work are reliable for further interpretation (Place *et al.*, 2017, 2018; Salehpoor and VandenBoer, 2023).

To further validate the ion measurements in size-resolved aerosols under ambient and fog conditions (Appendix B; Section B3), the coarse mode molar ratio of sea salt ions Σ (Cl^- , SO_4^{2-} , NO_3^-) to Σ (Na^+ , Mg^{2+} , Ca^{2+} , K^+) was calculated. Although this ratio is approximately one in bulk seawater, the ratio below one is reasonable to expect in MBL aerosols subjected to chemical reactions such as Cl^- displacement by acidic species and gas-particle partitioning (Section B3). The average charge balance ratio of sea salt aerosol (Σ^-/Σ^+) was 0.77 ± 0.12 for ambient aerosols and 0.51 ± 0.27 for fog aerosols, indicating an excess of cations from the measured ionic species (Figure B-3a). This imbalance may be due to chloride depletion in coarse mode sea salt aerosols. The mass ratio of Cl^-/Na^+ , relative to the bulk seawater ratio ($\text{Cl}^-/\text{Na}^+ = 1.79$), indicated an average Cl^- depletion of $25 \pm 14\%$ in ambient aerosols and $43 \pm 22\%$ in fog aerosols. We observed increased MSA^- levels during fog events, consistent with fog having enhanced acid displacement through aqueous-phase reactions, resulting in chloride depletion and contributing to the lower (Σ^-/Σ^+) ratio. Ion chromatography coupled with mass spectrometry (IC-MS) analysis was conducted on two coarse mode aerosol samples, one each from ambient and fog conditions, which identified a diverse suite of organic acids present in both (Joudan *et al.*, 2024). Organic acids were detected at levels above their corresponding blanks included lactic, acetic, citric, propanoic, butanoic, formic, pyruvic, succinic, and oxalic acids. These findings are consistent with the lower ratio of sea salt aerosol ($\Sigma^-/\Sigma^+ < 1$) originating from inorganic and organic acid processing of marine sea salt Cl^- by displacement. This process is likely responsible for the cationic excess observed in this region when assessing ionic balance of sea salt ions using only major ions in coarse mode aerosol analysis by IC (Laskin *et al.*, 2012; Angle, Nowak and Grassian, 2022).

In the fine mode, the summed molar ratio of the base cations NH_4^+ , DMAH^+ , and DEAH^+ (Σ_{base}) to acids like processed-S as nss-SO_4^{2-} , and MSA^- and NO_3^- (Σ_{acid}) was analyzed to assess the extent of acid-base neutralization. The calculated mean molar ratio of ($\Sigma_{\text{base}}/\Sigma_{\text{acid}}$) was 0.99 ± 0.34 (ranging from 0.32 to 1.57) in ambient samples and 1.10 ± 0.48 (ranging from 0.58 to 2.33) in fog samples (Figure B-3b). These results suggest that ambient aerosols were more typically neutralized than fog aerosols, as the additional aerosol water content in fog appears to facilitate

the uptake of basic species and probably also the organic acids detected by IC-MS, which we are currently unable to quantify (Pye *et al.*, 2020; Tilgner *et al.*, 2021).

Based on these quality control results and the measured ion composition of aerosol in both coarse and fine modes under ambient and fog conditions, the variations in chemical composition were further investigated to determine the changes instigated by the presence of fog. Coarse mode sea salt aerosols are more likely to take up water to grow into fog droplets due to their larger size and hygroscopic properties (Lewis and Schwartz, 2004), leading to further growth and/or removal from the atmosphere by collection, gravitational settling, and precipitation. Fine mode aerosols, in contrast, have a larger surface area due to their smaller size for the same mass and are expected to take up some water which might enhance aqueous-phase reactions and gas-particle partitioning under fog conditions. Although fine mode aerosols have a lower probability of growing into droplets, their higher number concentrations imply that even a small fraction becoming droplets might be sufficient to sustain fog droplet populations. Consequently, comparing the chemical composition of both coarse and fine mode aerosols under ambient and fog conditions is essential for a comprehensive understanding of their potential roles in formation and persistence.

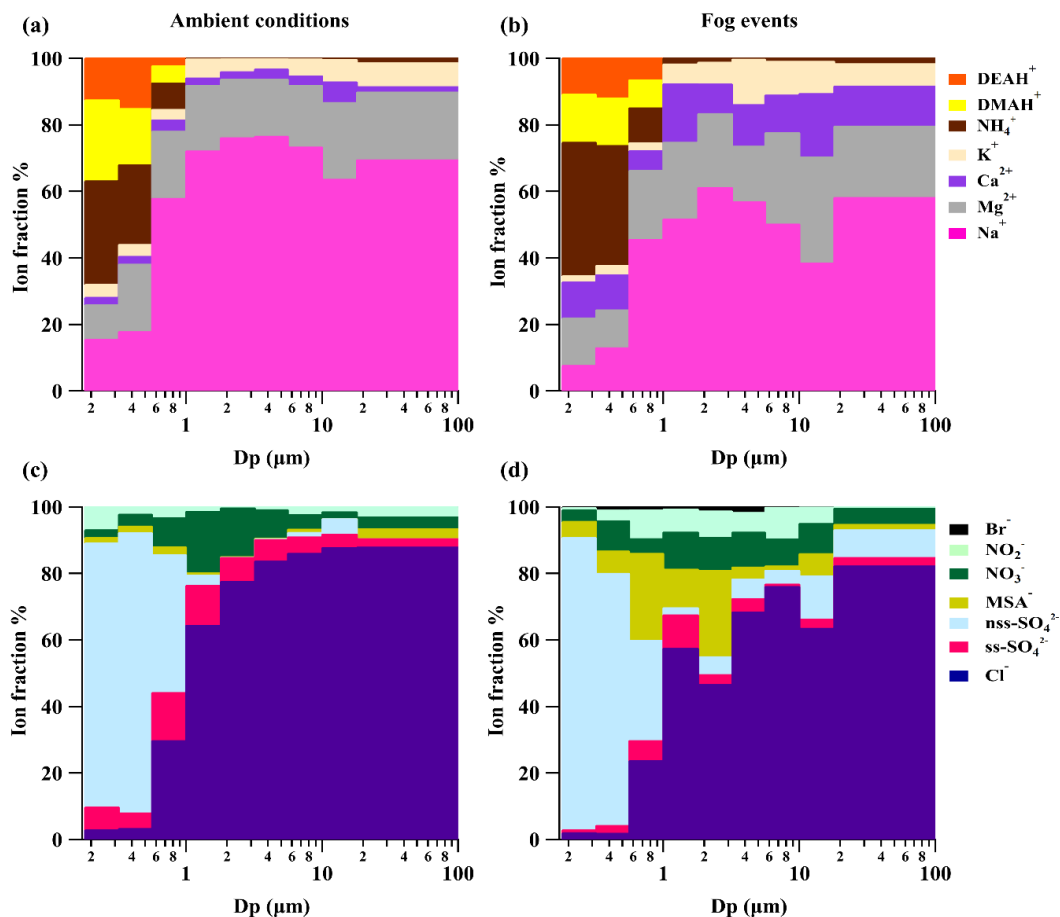


Figure 3-2: Average size distributions of equivalent ionic loading (neq m^{-3}) of aerosols expressed as percentage contributions of the total measured over the entire Fatima campaign. The top row represents the major cations, while the bottom row depicts the anions under ambient conditions ((a) and (c)) and fog events ((b) and (d)).

3.3.1.1 Coarse mode chemical composition

In the coarse mode, the size distribution analysis of cations (Figure 3-2a-b; Figure B-4a) and anions (Figure 3-2c-d; Figure B-4b) demonstrated that Na^+ and Cl^- dominated the equivalent ionic loading during ambient and fog periods, consistent with their origins from sea spray generated by wave breaking processes in a marine environment where production can continue even in the presence of fog (Lewis and Schwartz, 2004). The average mass loadings of coarse mode sea salt ions during ambient and fog conditions are summarized in Table 3-1. In ambient conditions, the order of average mass loading is $\text{Cl}^- > \text{Na}^+ > \text{ss-SO}_4^{2-} > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+}$, but in fog conditions these changed to $\text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} \geq \text{Ca}^{2+} > \text{ss-SO}_4^{2-} \geq \text{NO}_3^-$. The total coarse mode sea salt mass loadings averaged $6.23 \pm 4.27 \mu\text{g m}^{-3}$ in ambient marine air and $1.30 \pm 1.75 \mu\text{g m}^{-3}$ during fog

events. Notably, extreme coarse mode sea salt aerosol mass loadings were observed in one ambient sample and during two fog events (discussed further in Section 3.2.3), which were excluded as outliers from the average calculations presented here (Table 3-1). Saliba *et al.* (2019) reported sea salt mass loadings in the North Atlantic Ocean ranging from 3 to 8 $\mu\text{g m}^{-3}$ during NAAMES campaign. Also, Bates *et al.* (2001) measured marine supermicron sea salt aerosol mass concentrations ranging from 4.6 to 19 $\mu\text{g m}^{-3}$ during the Aerosols99 cruise in the Atlantic Ocean. The mass loadings of ambient sea salt aerosols observed in this study are consistent with those reported in North Atlantic Ocean; however, lower concentration ranges are associated with the influence of fog. Unlike previous studies, since this work collected aerosol samples under persistent fog conditions, which acts as a sink for sea salt aerosols, this enhances the scavenging and deposition of the coarse mode aerosol that have grown into droplets. Last, variation in the ambient aerosol mass loading within this study and between those previously conducted are expected to originate largely due to wind speed differences changing the rate of generation of coarse mode sea salt aerosols.

The variation in the chemical composition of coarse mode sea salt ions between ambient and the fifteen Fatima campaign fog events were assessed by comparing the average equivalent ionic loadings, excluding the extreme events. The percentage change in average equivalent ionic loading during fog events compared to ambient conditions is indicated as follows: Cl^- (-78% $\pm$ 22%), Na^+ (-73% $\pm$ 23%), Mg^{2+} (-71% $\pm$ 21%), SO_4^{2-} (-81% $\pm$ 16%), K^+ (-34% $\pm$ 15%), and NO_3^- (-58% $\pm$ 32%). This means that the presence of fog resulted in a decrease in the equivalent ionic loadings of sea salt ions, likely due to their growth into fog droplets larger than 100 μm , which are not captured by MOUDI and/or were deposited continuously during the sampling period. During the fog events, Ca^{2+} was the only sea salt ion to exhibit an increase in coarse mode, with a +27% $\pm$ 15% rise in equivalent loading. The enrichment of Ca^{2+} in sea salt aerosols is attributed to its complexation with organic molecules. Enrichment of Ca^{2+} has been reported in supermicron aerosols, with a trend of greater enrichment observed as particle size decreases (Salter *et al.*, 2016; Sultana, Collins and Prather, 2017). Jayarathne *et al.* (2016) conducted a mesocosm wave flume experiment to investigate the enrichment of saccharides and cations in sea spray aerosols during phytoplankton blooms. Their results demonstrated significant enrichments of divalent cations like Ca^{2+} associated with saccharides in both $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ sea spray aerosol fractions. The higher Ca^{2+} enrichment in coarse mode aerosols during fog events compared to ambient aerosols is likely

due to the decreased solubility of the saccharide–Ca²⁺ complex, preventing transfer into the fog droplets and their subsequent deposition. Thus, such biologically sourced Ca²⁺ associated with saccharides would be less likely to grow into a fog droplet due to its lower hygroscopicity, resulting in the Ca²⁺ enhancements we observed. Such primary aerosol components would be expected widely across the biologically productive regions of the Grand Banks and Sable Island (Matulová *et al.*, 2014; Mukherjee, Reinfelder and Gao, 2020). In contrast, the more hygroscopic inorganic Ca²⁺ salts, such as CaCl₂ and CaSO₄, would be expected to hydrate and grow readily into fog droplets (Cochran *et al.*, 2017), consistent with the decrease seen in both of those ions.

3.3.1.2 Fine mode chemical composition

In the fine mode, sea salt ions showed average mass loadings ranging from 0.01 to 0.1 µg m⁻³ under ambient conditions and from 0.01 to 0.06 µg m⁻³ during fog events (Table 3-1), which aligns with previously reported submicron sea salt mass loadings of 0.08 to 0.39 µg m⁻³ in the Atlantic Ocean (Bates *et al.* 2001). The chemical composition of fine mode aerosols was compared between ambient and fog conditions by examining the total average equivalent ionic loadings of sea salt aerosols, processed-S species (nss-SO₄²⁻ and MSA⁻), and reduced-N species (NH₄⁺, DMAH⁺, and DEAH⁺) (Figure B4c-d). The total average equivalent ionic loading of fine mode sea salt aerosols was 9.82 ± 1.60 neq m⁻³ in ambient air and remained relatively unchanged under fog conditions with an equivalent loading of 10.13 ± 1.18 neq m⁻³, indicating that these aerosols were not greatly affected by the presence of fog. In contrast, the total average equivalent ionic loading of processed-S species increased from 5.50 ± 2.46 neq m⁻³ under ambient conditions to 8.27 ± 2.64 neq m⁻³ during fog events (+33% ± 18%). Similarly, reduced-N species increased from 4.78 ± 1.15 neq m⁻³ in ambient conditions to 8.74 ± 2.34 neq m⁻³ during fog events (+45% ± 20%). These results suggest that fog droplets potentially facilitate aqueous-phase reactions and/or gas-particle partitioning, consistent with prior reports for these two compound classes (Ge *et al.*, 2012; Bergman *et al.*, 2015; Liu *et al.*, 2022). Further interpretation of these chemical processes is beyond the scope of this manuscript and will be considered in detail alongside other chemical components and changes in a future publication.

3.3.1.3 Comparison of fine and coarse mode aerosol composition

Overall, fog clearly impacts the chemical composition of marine aerosols, as shown by a reduction in coarse mode sea salt ions, likely due to their growth into fog droplets followed by subsequent removal through collection, gravitational settling, and precipitation. Fine mode aerosols, with their smaller size and higher surface area-to-volume ratio, will also take up water under fog conditions, which appears to enhance aqueous-phase reactions and/or gas-particle partitioning, leading to an increase in the relative and absolute abundances of processed-S and reduced-N species. This comparison of coarse and fine mode aerosols under ambient and fog conditions demonstrates that fog processing alters marine aerosol chemistry as a function of size through both physical and chemical processes.

Table 3-1: The average ion mass loading of sea salt aerosol in fine mode (PM_{0.1-1}) and coarse mode (PM₁₋₁₀₀) during ambient and fog periods during the Fatima campaign. Total MOUDI fog sampling times by fog type were: type I, 109 h (n = 8); type II, 20 h (n = 2); type III, 53 h (n = 5; see Table B-3).

	Na⁺ ($\mu\text{g m}^{-3}$)		Mg²⁺ ($\mu\text{g m}^{-3}$)		Ca²⁺ ($\mu\text{g m}^{-3}$)		K⁺ ($\mu\text{g m}^{-3}$)		Cl⁻ ($\mu\text{g m}^{-3}$)		ss-SO₄²⁻ ($\mu\text{g m}^{-3}$)		NO₃⁻ ($\mu\text{g m}^{-3}$)	
	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse
<i>Ambient periods (n=14)*</i>														
Average	0.10	2.16	0.03	0.26	0.005	0.06	0.02	0.17	0.05	3.00	0.02	0.30	0.02	0.28
SD	0.09	1.50	0.02	0.18	0.01	0.08	0.02	0.14	0.08	2.24	0.02	0.23	0.01	0.19
Min	0.01	0.33	0.004	0.06	0.006	0.002	0.003	0.04	0.001	0.24	0.002	0.04	0.001	0.05
Max	0.31	4.73	0.09	0.65	0.04	0.26	0.06	0.57	0.25	7.06	0.07	0.71	0.05	0.70
<i>Fog periods (n=15)**</i>														
Average	0.07	0.44	0.03	0.08	0.06	0.08	0.02	0.09	0.04	0.51	0.01	0.05	0.02	0.05
SD	0.07	0.59	0.04	0.09	0.07	0.09	0.01	0.12	0.07	0.84	0.01	0.1	0.03	0.05
Min	0.006	0.03	0.002	0.003	0.01	0.005	0.004	0.007	0.001	0.03	0.002	0.004	0.001	0.001
Max	0.24	2.12	0.14	0.27	0.20	0.33	0.05	0.43	0.25	3.05	0.06	0.38	0.10	0.16

* An ambient event from July 19-21, 2022 (Table B-3) with a total coarse mode sea salt aerosol mass loading of $72 \mu\text{g m}^{-3}$ was identified as an outlier using the Grubbs test.

** Two fog events from July 12-13, 2022, and July 27, 2022 (Table B-3) with total coarse mode sea salt aerosol mass loadings of $35 \mu\text{g m}^{-3}$ and $99 \mu\text{g m}^{-3}$ were identified as outliers using the Grubbs test.

3.3.2 Fog characterization by aerosol chemical composition and physical properties

During the campaign, there were fifteen size-resolved aerosol samples collected during fog events. These samples were classified into three types based on their overall ion mass distribution as a function of particle diameter (see Table B-3; Figure 3-3; B-5; B-6). Co-located observations of wind speed and direction, air and sea surface temperature, precipitation, and fog duration from the Atlantic Condor, along with vertical temperature, humidity, and wind speed profiles from radiosondes launched from the aft deck of the Condor (see Figure 3-4; 3-5; B-7; B-8), were recorded during our chemical measurements of these fog types. These supporting variables were considered to further interpret the drivers of aerosol chemical composition and change during fog events, as past aerosol-fog measurements are highly limited in their number, let alone supported by such an extensive set of meteorological and microphysical measurements. A description of each fog type and their characteristics follows. Synoptic conditions were assigned to each fog type to characterize the ambient factors such as air mass, wind direction, and pressure associated with each chemical fog type we identified (Table B-3).

3.3.2.1 Type I fog chemical characteristics and physical controls

Type I fog was characterized by coarse mode sea salt mass loadings that were typically below $1 \mu\text{g m}^{-3}$, with an average of $0.48 \pm 0.46 \mu\text{g m}^{-3}$ ($n = 8$), notably lower compared to the other fog types (e.g., type I event on July 21-22, 2022; Figure 3-3a and d). In contrast, the hydrated interstitial fine mode aerosols exhibited higher average mass loadings of $1.13 \pm 0.75 \mu\text{g m}^{-3}$ (16% sea salt), with $+7\% \pm 24\%$ relative to fog type II and $+46\% \pm 17\%$ relative to fog type III. These fine mode aerosols were enriched in processed-S and reduced-N, and their mass loadings were higher than those observed in other fog types. During type I events, a distinct unimodal particle number distribution was observed with a peak concentration of approximately 1300 cm^{-3} near $0.15 \mu\text{m}$, and the average residual diameter was $0.31 \pm 0.09 \mu\text{m}$ (See Figure 3-6). During type I fog events, low to moderate wind speeds ($5 \pm 2 \text{ m s}^{-1}$) were generally observed, predominantly from the SW with occasional influence from the NE (Figure 3-4; B-8b; Table B-3). The average sea surface temperature was $15 \pm 4 \text{ }^{\circ}\text{C}$ ($10 - 22 \text{ }^{\circ}\text{C}$), with no precipitation recorded (Figure 3-4; B-1). Notably, type I fog events had the longest average fog duration ($814 \pm 468 \text{ mins}$) of the three groups (Figure B-8a). Type I also showed a broad air-sea temperature difference from -2 to $2.5 \text{ }^{\circ}\text{C}$

(Figure 3-4). Within the fog layer, wind speeds averaged $9 \pm 3 \text{ m s}^{-1}$, with a corresponding average fog layer depth of $274 \pm 182 \text{ m}$ (Figure 3-5).

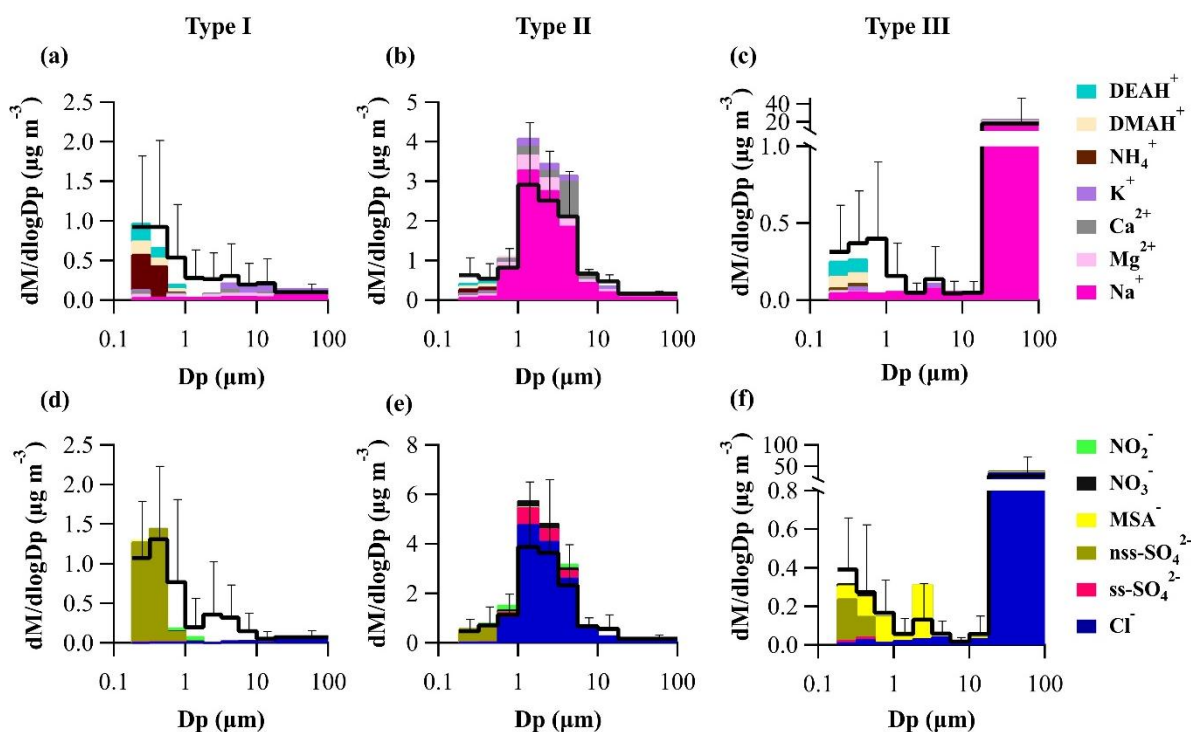


Figure 3-3: Ion mass distributions of measured ionic constituents from three size-resolved aerosol samples, as examples of the three fog types: type I (a and d, IOP #9, July 21-22), fog type II (b and e, IOP#11, July 25-26), and fog type III (c and f, IOP#4, July 12-13). Summed cations are shown as stacked contributions to the total in the upper row and likewise for the anions in the lower row. For each fog type, the mean total mass loading distribution (solid black line) is overlaid with the standard deviation (1σ ; shown on the upper side for clarity). All sample information and fog type classification can be found in Table B-3.

The relatively depleted levels of sea salt aerosol in type I fog events are consistent with fog droplet growth from coarse mode sea salt into $\geq 20 \mu\text{m}$ droplets and subsequent removal via collection and gravitational settling since there was no drizzle and/or precipitation observed during type I fogs (Jensen and Nugent, 2017). The recorded wind speeds suggest that sea salt aerosol generation was facilitated continuously within the stable MBL, mainly through film and jet droplets (Wang *et al.*, 2017). However, sea salt aerosol did not show a strong positive linear relationship with wind speed in type I fogs (Figure B-7a). Similarly, across the broad range of sea surface temperatures sampled, sea salt aerosol did not display a strong positive association with sea surface temperature (Figure B-7b), suggesting that these source factors have a weaker

influence on sea salt aerosol mass loadings than sinks. Type I fogs had the longest average duration (814 ± 468 mins; Figure B-8a) and we know that both aerosol sources and sinks were active. Over time in these fogs, it appears that sink processes dominated the fate of coarse sea salt aerosol, leading to lower coarse mode sea salt mass loadings despite ongoing aerosol generation driven by substantial winds. The high mass loadings of processed-S and reduced-N species in fine mode aerosols are consistent with potential biological origins in this region (O'Dowd *et al.*, 2004). Elevated fine mode aerosol number concentrations in the type I events compared to type II and III, may be due to more influence by continental aerosol transport (Table B-3; Giacosa *et al.*, 2026) and this increased abundance of fine mode aerosols might lead to a greater number undergoing growth into fog droplets to sustain the long-duration events, while minimally impacting the mass loadings. Wind direction data indicated that winds from the NE were associated with these continental aerosols, while SW winds were more often associated lower numbers and therefore consistent with marine sources. Taken together, this suggests that there was a mixed influence of precursor aerosol populations on type I fog events (Figure B-8b). Analysis of air-sea surface temperature differences across fog types revealed a broad range from -2 to 2.5 °C for type I fog, indicating formation also through a combination of advection mechanisms: including both warm fog ($T_{\text{air}} > T_{\text{sea surface}}$) and cold fog ($T_{\text{air}} < T_{\text{sea surface}}$) (Figure 3-4). Further, the average residual diameter of $0.31 \pm 0.09 \mu\text{m}$ is consistent with the assertion that fine mode aerosols were effectively grown into fog droplets (Figure 3-6). These findings imply that type I fog droplets were initiated by growth of freshly emitted coarse mode aerosol and sustained by the fine mode throughout these events despite ongoing generation of sea salt aerosol, as the latter showed little presence in our chemical determinations.

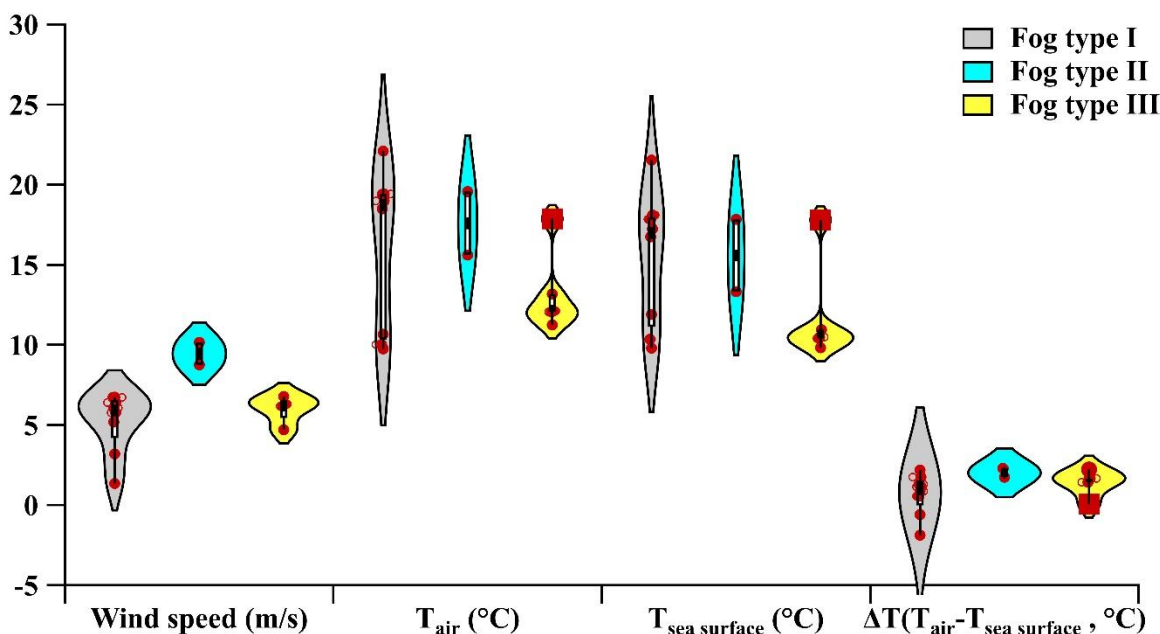


Figure 3-4: Meteorological parameters in the three chemically distinct fog types (I, II, and III; Figure 3-3, Table B-3), including wind speed (m s^{-1}), air and sea surface temperature ($^{\circ}\text{C}$), and temperature difference (ΔT) between air and the sea surface. Wind speed and air temperature were measured approximately 18 m above water level. Data points are shown as red circles, outliers as red squares, and the width of the violins represents the frequency distribution of each measurement population.

Last, wind speeds were measured by radiosonde during fog events (Figure 3-5) providing insights into how wind-driven turbulence influenced fog layer depth, stability, and aerosol vertical mixing within the MBL. The observed low to moderate wind speeds, combined with relatively shallow fog layer depths, reflect weaker vertical mixing and more stable fog conditions, supporting the extended duration characteristics of type I fog compared to the other types.

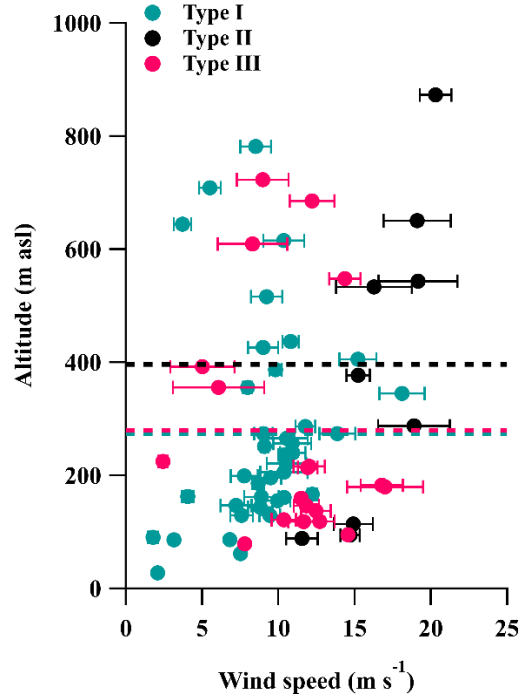


Figure 3-5: Wind speed (m s^{-1}) within and above the marine fog layer. The average depth of the fog layer in each of the three distinct fog types (I, II, and III) was determined by potential temperature and relative humidity from radiosonde profiles taken during all fog episodes in the Fatima campaign. The average fog layer depth is indicated by the dashed horizontal line of the same colour as the fog type. Note that the fog layer depths for types I and III are nearly identical. The mean MBL depths and their variance (1σ) across all events for fog types I, II, and III were 642 ± 276 m, 750 ± 398 m, and 683 ± 251 m, respectively.

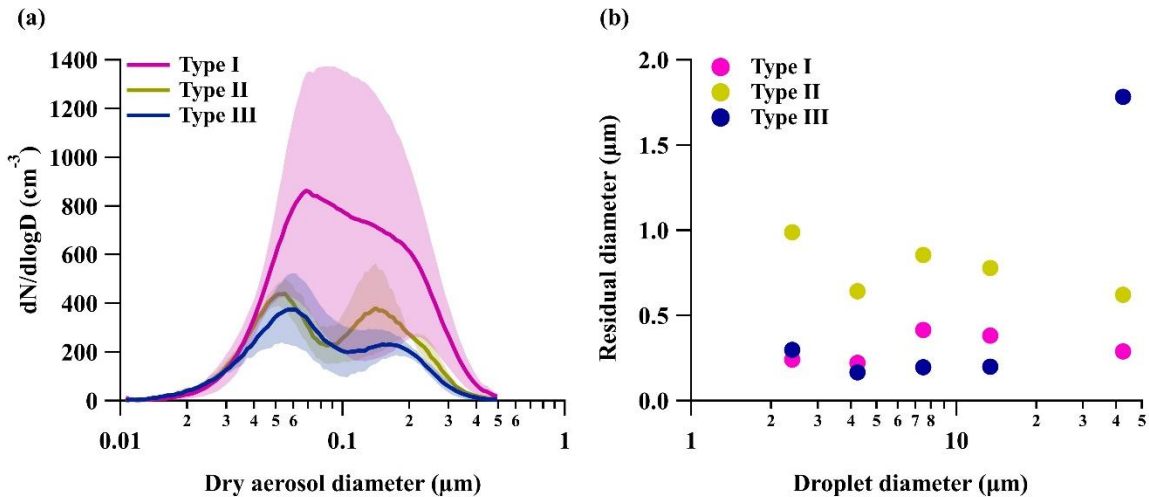


Figure 3-6: Comparison of (a) the average log-normalized number concentration (cm^{-3}) during the entire campaign for each fog type and (b) residual diameters (μm) of droplets from $1.8\text{--}100\ \mu\text{m}$ collected using the MOUDI for each fog type example. The calculated residual diameters are equivalent to a dry aerosol diameter but based solely on measured ionic composition and an assumed density (see E3-4).

3.3.2.2 Type II fog chemical characteristics and physical controls

Type II fog was characterized by elevated mass loadings of sea salt aerosols predominantly within the 1-10 μm range (e.g., type II event on July 25-26, 2022; Figure 3-3b and e), with an average mass loading of $4.55 \pm 2.54 \mu\text{g m}^{-3}$ ($n = 2$). The hydrated interstitial fine mode aerosols exhibited average mass loadings of $1.05 \pm 0.17 \mu\text{g m}^{-3}$, with 48% attributed to sea salt aerosols, (Section B3). Particle number concentrations for type II fog showed a bimodal distribution, with peaks at 400 cm^{-3} near $0.05 \mu\text{m}$ and 270 cm^{-3} near $0.20 \mu\text{m}$ (Figure 3-6a). The average residual diameter was $0.78 \pm 0.15 \mu\text{m}$ across all droplet diameters (Figure 3-6b). Type II fog events were associated with the highest wind speeds ($9 \pm 1 \text{ m s}^{-1}$) among the three fog types, predominantly from the SW and therefore marine aerosol sources (Figure B-8b; Table B-3). During these events, the average sea surface temperature was $16 \pm 3 \text{ }^{\circ}\text{C}$ ($13 - 18^{\circ}\text{C}$) (Figure 3-4). Brief precipitation events were observed, lasting only 120 s during the first event (July 7, 2022) and 40 s during the second event (July 26, 2022), compared to the fog durations of 197 min and 996 min, respectively (Figure B-8a). Type II fog exhibited normally distributed air-sea temperature differences, peaking at around $2 \text{ }^{\circ}\text{C}$ align with the formation of advection warm fog (Figure 3-4). Within the fog layer, wind speeds were notably high with an average of $17 \pm 3 \text{ m s}^{-1}$, corresponding to the deepest fog layer depths of $396 \pm 276 \text{ m}$ (Figure 3-5).

The observed sustained sea salt mass loading in the coarse mode indicates substantial ongoing primary sea salt aerosol production despite the presence of fog, which was not found in type I. Higher wind speeds appear to have enhanced aerosol production across all size ranges, particularly in the coarse mode, likely with contributions from spume drops with diameters $> 100 \mu\text{m}$ (Monahan *et al.*, 1983). The moderate sea surface temperature may have favored the formation of larger particles, further contributing to the elevated mass loading of sea salt aerosols. Type II fog periods having high wind speeds therefore corresponded to increased aerosol generation, driving coarse mode aerosol chemical composition during type II fog events. Although precipitation occurred, the very brief duration relative to the average fog episode lengths mean that collection and gravitational settling would remain the primary aerosol sink. The relatively lower mass loadings of processed-S and reduced-N in hydrated interstitial fine mode aerosols suggest less impact from local biological sources. These results suggests that type II fog was primarily sustained by the ongoing growth of coarse mode sea salt aerosols, which were readily available, with potential minor contributions from fine mode aerosols. The bimodal particle number

distribution supports this inference, suggesting the growth of some fine mode aerosols into the fog droplet (Figure 3-6a; Hoppel, Frick and Larson, 1986). The average residual diameter we calculated exceeded $0.5\ \mu\text{m}$, consistent with the primary droplet activation occurring on the coarse particles (Figure 3-6b). However, these residual diameters exceed the upper collection limit for SMPS, and we do not have direct observations. Overall, these results indicate that coarse mode sea salt aerosols were the dominant contributor to fog droplet activation and sustaining the fog events, with evidence of fine mode aerosol activation contributing as well. The increased wind speeds within the fog layer corresponded to deeper fog layer depths, suggesting a positive relationship between wind speed and fog layer height, with enhanced vertical mixing. Our findings indicate that in such deep fog layers, the strong source of sea salt aerosols appear sufficient to grow and sustain fog droplets over extended periods of time (Figure 3-5).

3.3.2.3 Type III fog chemical characteristics and physical controls

Type III fog was characterized by the highest mass loadings of sea salt aerosols in fog droplets between $10\text{-}100\ \mu\text{m}$ (e.g., type III event on July 12-13, 2022; Figure 3-3c and f), with an average mass loading of $27.23 \pm 42.45\ \mu\text{g m}^{-3}$ ($n = 5$), ranging from 0.68 to $98.71\ \mu\text{g m}^{-3}$ (Figure B-5; B-6). The two highest coarse mode and/or droplet sea salt aerosol mass loadings were observed during type III fog events. The upper range of these mass loadings was associated with an extreme event of sea salt aerosol production in fog on July 27, 2022 (Table 3-1), while the second highest sea salt aerosol mass loading ($34.93\ \mu\text{g m}^{-3}$), was recorded on July 12-13, 2022. Interstitial hydrated fine mode aerosols showed average mass loadings of $0.61 \pm 0.30\ \mu\text{g m}^{-3}$, with 26% attributed to sea salt (Section B3). Particle number concentrations for type III fog displayed a bimodal distribution, with peaks at $350\ \text{cm}^{-3}$ around $0.06\ \mu\text{m}$ and $219\ \text{cm}^{-3}$ around $0.15\ \mu\text{m}$ (Figure 3-6a). The calculated residual particle diameter was $0.22 \pm 0.06\ \mu\text{m}$ based on the composition found within the 2 to $18\ \mu\text{m}$ droplet diameter range collected by the MOUDI and $1.78\ \mu\text{m}$ for the $20\text{-}50\ \mu\text{m}$ range (Figure 3-6b). Type III fog occurred at moderate wind speeds ($6 \pm 1\ \text{m s}^{-1}$), predominantly originating from the SW, with occasional contributions from the NE and NW (Figure 3-4; B-8b; Table B-3). The average sea surface temperature during these events was $12 \pm 3\ ^\circ\text{C}$ ($10\text{--}18^\circ\text{C}$) (Figure 3-4). A brief precipitation episode lasting less than a minute was recorded during a single fog event on July 13, 2022. Type III fogs had an average duration of $634 \pm 104\ \text{min}$ (Figure B-8a). Air-sea temperature differences ranged from 0 to $2.5\ ^\circ\text{C}$ are associated with

advection warm fog (Figure 3-4). Wind speeds within the fog layer averaged $11 \pm 4 \text{ m s}^{-1}$ at a depth of $279 \pm 210 \text{ m}$ (Figure 3-5).

The high mass loadings of sea salt ions in fog droplets indicate effective growth of these particles into the fog. The precursor aerosol production was likely facilitated through film and jet droplets, with the higher sea surface temperatures promoting the formation of larger sea salt aerosols (Wang *et al.*, 2017; Hu *et al.*, 2024). An extreme sea salt aerosol event occurred during two out of five fog events, with the highest event observed under moderate wind speeds ($6.0 \pm 0.8 \text{ m s}^{-1}$) and elevated sea surface temperatures ($18 \pm 0.45 \text{ }^{\circ}\text{C}$). Based on regression analysis, sea salt aerosol showed a strong positive linear relationship with sea surface temperature but not with wind speed (Figure B-7e and f), suggesting that warmer ocean surface conditions were primarily associated with significantly enhanced aerosol mass production. The brief precipitation episodes provided only a temporary wet deposition sink, while collection and gravitational settling would remain the primary aerosol removal mechanisms during type III fog events. Despite the lower mass loadings of interstitial fine mode aerosols, their composition showed processed-S and reduced-N species consistent with biological sources which could contribute through both primary and secondary aerosol formation mechanisms (Figure 3-6a). The bimodal number concentration distributions indicate that fine mode aerosols were also grown into droplets during these events. Residual diameters were calculated to originate from both fine and coarse mode size ranges, which further supports the growth of both fine and coarse mode aerosols (Figure 3-6b). Overall, it appears that type III fog primarily formed through the growth of coarse mode sea salt aerosols, with additional contributions from the fine mode. During our 15 marine fog events, the synoptic conditions transitioned from low- to high-pressure systems and from clean marine to strong coastal influence, before returning to a low pressure regime (Table B-3). Type III occurred during low-pressure periods with either clean marine air or a mixture with coastal air. Type I tended to emerge under stable high pressure systems influenced by coastal air. Type II occurred in both regimes as there were only two observations of this: one was a clean marine low-pressure case and the second, a coastal high-pressure episode. Although the MOUDI is a time-integrated sampler, it effectively captures representative average spatial and temporal features during each sampling period, where higher time resolution methods may be capable of discerning even greater variability and chemical change. More chemical fog types may exist within those we are able to identify with the time-

integrated MOUDI and nanoMOUDI instruments and could be the focus of future studies with higher time resolution on aerosol and droplet chemical composition.

3.3.2.4 Spatial distribution of fog type events

In the Grand Banks region, there was a clear and sustained temporal transition from type I ($n = 3$) to type III ($n = 4$) fog events, which occurred from July 9-12 and July 13-16, respectively (Figure B-9). In the Sable Island region, temporal transitions between type I and type III fog events were more sporadic compared to the Grand Banks region, with type I ($n = 5$) occurring between July 21 to 25, including July 30th, and type III ($n = 1$) on July 26 (Figure B-6). Type II was limited to two occurrences separated widely in space and time, on July 7 near the Grand Banks and July 25-26 near Sable Island. The observed transitions between fog types suggest a temporal evolution of fog characteristics in these regions, seemingly driven by changing dynamics within the MBL conditions. As the MOUDI observations are temporally broad, this dataset – although rich – is still too limited to reach specific conclusions on the changes driving the observed chemical transitions based on the coupled ocean-atmosphere dynamics.

Meteorological parameters were nonetheless investigated to similarly broadly characterize the physical properties of the three chemically distinct fog types that relate to their chemical characteristics. Type I fog is characterized by depleted coarse mode sea salt mass loadings in the presence of low wind speeds and consistent with collection and gravitational settling losses over an extended fog duration. Fog droplets in type I appear to be sustained by the growth of freshly emitted coarse mode sea salt aerosols, but more so by fine mode aerosols. This fog type persists for extended durations under stable MBL conditions, with low to moderate wind speeds and reduced vertical mixing that translate to a shallow fog layer depth. Type II fog is characterized by sustained coarse mode sea salt aerosol production driven by high wind speeds, with collection and gravitational settling likely serving as the primary aerosol sink. Fog droplets in type II were likely sustained primarily by the growth of coarse mode sea salt aerosols, with additional contributions from fine mode aerosol. The enhanced vertical mixing resulting from high wind speeds leads to deeper fog layers but with shorter durations. Type III fog is characterized by the highest mass loadings of coarse mode sea salt ions in fog droplets, associated with moderate wind speeds and warm sea surface temperatures. Collection and gravitational settling would be the most likely primary removal processes based on theory but were not directly measured here. Fog droplets in

type III formed primarily through the growth of coarse mode sea salt aerosols, with additional contributions from fine mode aerosols. Moderate wind speeds and shallow to moderate fog layers provide stable MBL conditions with moderate fog durations in type III events. These observations indicate that the distribution of coarse mode sea salt mass loadings is driven by the interaction of source conditions, sink mechanisms, and that combined with sea surface conditions and meteorology they determine the overall fog persistence in the MBL.

3.3.3 Physical processing of aerosol during fog events

Understanding the physical processes of aerosol interacting with fog is critical for predicting fog formation in marine environments. Therefore, the study of aerosol-fog interactions is necessary to better comprehend the physical fog processes, as aerosols can act as CCN for fog droplet formation which can in turn impact an aerosol population. The presence of fog affects aerosol mass loadings via two competing processes. First, it can reduce aerosol mass loading via nucleation and impaction scavenging mechanisms, followed by subsequent precipitation or deposition. Conversely, the presence of fog may increase aerosol mass loading by collecting particles or accumulation of gases into droplets, which are then released back into the atmosphere after droplet evaporation. According to Köhler theory, sea salt aerosols can act as effective CCN due to their high hygroscopicity and the surface effects they generate to facilitate water vapor condensation (Köhler, 1936). The growth or activation of droplets by mass transfer of water vapour is influenced by the interaction between solute effect (Raoult's Law) and the curvature effect (Kelvin effect) (Orr, Hurd and Corbett, 1958; Pruppacher, Klett and Wang, 1998). Through the solute effect, hygroscopic and soluble salts like those that comprise sea salt, lower the vapor pressure of water over the droplet, facilitating condensation. Larger particles from sea spray also have lower curvature, which again reduces water vapor pressure. The combination of these effects makes sea salts highly effective as CCN. Thus, coarse mode sea salt aerosols should effectively act as CCN because of their high hygroscopicity and ability to maintain lower vapor pressure due to their dissolved salts and larger size, which facilitates water vapor condensation and the formation and growth of fog droplets.

Sea spray aerosols play an important role in aerosol-fog interactions and provide key indicators for understanding aerosol fog processing from a chemical perspective. In this study, fifteen fog events were analyzed, and nine distinct fog episodes with bordering ambient

observations were selected to study aerosol fog processing. These included only two from the initial leg of the campaign near the Grand Banks area, where fog events were more transient as the fog was fast moving and small in surface coverage, leading to the Atlantic Condor entering and leaving the fog layer(s) during a sample collection period. The seven episodes from the second leg near Sable Island had more prolonged fog and did not suffer this effect (Figure 3-1). Six episodes excluded from this analysis are due to the potential for some mixed pre-, during, and post-event ambient air being sampled due to transient fog conditions. The ionic mass loading specifically of sea salt aerosols, inclusive of Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , and ss-SO_4^{2-} , in addition to NO_3^- were measured before, during, and after fog occurrences, to demonstrate sea salt aerosol population changes due to aerosol-fog interaction processes (Figure 3-7). Within the nine isolated fog episodes, one in particular showed exceptionally high sea salt mass loading, approximately 50 times higher than the average mass loadings of the other fog events (Table 3-1; Section 3.3.1.3). In this case, mass loading increased during the fog, reaching levels much higher than before its formation and after its dissipation, opposite to the more general trend observed. As this was an outlier, we do not include it in the following analysis. Similarly, one ambient outlier was identified and also excluded (Table 3-1).

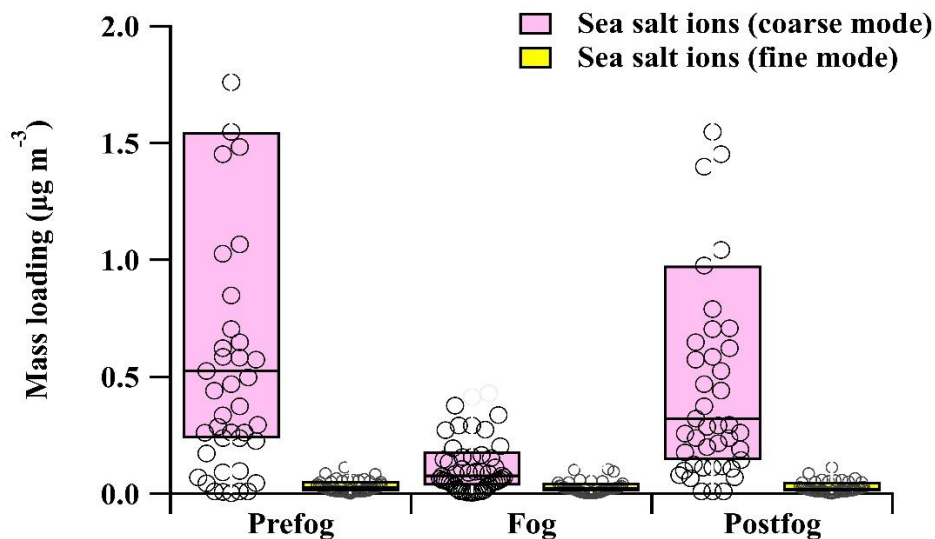


Figure 3-7: Ionic mass loading ($\mu\text{g m}^{-3}$) of sea salt aerosol in coarse (1-100 μm ; pink bars) and fine (0.1-1 μm ; yellow bars) modes before (prefog), during (fog), and after (postfog) fog occurrences. The horizontal distribution represents the frequency distribution within each measurement population. Note the small fine mode mass loadings are similar across all periods and the yellow shading may not be visible.

Generally, the ionic mass loading of coarse mode sea salt aerosols were highest in the ambient atmosphere prior to fog formation, decreasing from $7.95 \pm 4.20 \mu\text{g m}^{-3}$ to $1.64 \pm 2.17 \mu\text{g m}^{-3}$ during a fog episode, and began to recover after the fog dissipated to $6.86 \pm 4.30 \mu\text{g m}^{-3}$ on average. These findings with respect to coarse mode aerosols occurred while the mass loading of fine mode sea salt aerosols remained mostly unchanged at $0.32 \pm 0.01 \mu\text{g m}^{-3}$ throughout these periods. The average wind speed before, during, and after fog dissipation throughout these periods were $8.35 \pm 1.26 \text{ m s}^{-1}$, $6.47 \pm 2.00 \text{ m s}^{-1}$, and $7.60 \pm 2.02 \text{ m s}^{-1}$, respectively. Mass loadings were converted to column amounts by accounting for fog layer depth (FLD) or marine boundary layer (MBL), by taking their product, to compare values through the entire relevant mixed-layer for each sampling period (Appendix B; Section B6; Figure B-10), resulting in column masses ($\mu\text{g m}^{-2}$) in the mixed layer. The column mass trends of coarse mode aerosols before ($4105 \pm 2056 \mu\text{g m}^{-2}$), during ($410 \pm 485 \mu\text{g m}^{-2}$), and after fog dissipation ($3852 \pm 3303 \mu\text{g m}^{-2}$) are positively related at these wind speeds. A linear equation was determined from an orthogonal least distance regression that accounts for the variance in both measurements during all fog events and ambient conditions (pre- and post-fog) separately (Figure B-11). Both conditions show a positive relationship: fog ($R^2 = 0.741$, $y = (615 \pm 100 \mu\text{g s m}^{-3})x - (3.6 \times 10^3 \pm 7.6 \times 10^2 \mu\text{g m}^{-2})$) and ambient conditions ($R^2 = 0.678$, $y = (2045 \pm 657 \mu\text{g s m}^{-3})x - (1.3 \times 10^3 \pm 5.5 \times 10^3 \mu\text{g m}^{-2})$). It is clear from this that fog represents a sink pathway for sea salt in the mixed column and results in a decrease in the magnitude of the positive association compared to ambient conditions (Figure B-11). Additionally, the Pearson correlation ($r = 0.752$, $p < 0.001$) was calculated for all data types (pre, during, and after fog) still showed a statistically significant positive relationship between sea salt column mass and wind speed, as expected. This function suggests that fog ought to extensively scavenge coarse sea salt aerosol below winds of $\sim 6 \text{ m s}^{-1}$ based on the observations compiled across all of our fog events. We note that this relationship is driven usually by a single observation during any fog presence due to the necessity of time-integrated MOUDI sample collection, yet it yields new insight into fog-aerosol interactions previously unobserved. These results are consistent with the known marine sources of sea salt from wave breaking and bubble bursting (Kleefeld *et al.*, 2002; Gong, 2003; Smirnov *et al.*, 2003). These patterns also match the expected role of supermicron sea salt aerosols as effective CCN, due to their high hygroscopicity and reduced surface curvature (Sasakawa, Ooki and Uematsu, 2003; Lewis and Schwartz, 2004; Jung *et al.*, 2013; Väisänen *et al.*, 2016; Zhao *et al.*, 2022). Latham and Smith (1990) suggested that sea-salt aerosols larger than $0.5 \mu\text{m}$ can

effectively act as CCN, particularly in marine atmospheres, where wind speeds range from 5 to 10 m s⁻¹. Other studies have stated that Giant CCN (GCCN), correspond to sea salt coarse mode aerosols with a dry diameter > 0.5 µm, which can activate to form cloud droplets in marine environments (Feingold *et al.*, 1999; Jensen and Nugent, 2017). Due to their larger size, GCCN can activate into droplets at much lower supersaturations, playing a significant role in cloud microphysics and enhancing droplet growth (Richter, MacMillan and Wainwright, 2021). While the role of sea salt aerosols as cloud condensation nuclei have been well-studied, there have been few studies focusing on their role in fog formation in marine environments (Sasakawa and Uematsu, 2002; Sasakawa, Ooki and Uematsu, 2003; Zhao *et al.*, 2022). The results of this study underscore the significant role of coarse mode sea-salt aerosols in the growth and formation of marine fog droplets.

The observed decrease of coarse mode sea salt aerosols suggests they are scavenged in a supersaturated atmosphere into fog droplets (Figure 3-7). The decrease in mass loading of sea salt aerosols occurs as the resulting fog droplets grow larger than 100 µm, making them undetectable by MOUDI, and/or due to their collection and deposition from gravitational settling and/or precipitation. The ion mass loading scavenging ratio during fog was calculated using E3-5, representing collection and deposition scavenging by existing droplets. This resulted in average ratios of 81% ± 22% for Na⁺, 72% ± 25% for Mg²⁺, 39% ± 30% for Ca²⁺, 53% ± 25% for K⁺, 85% ± 21% for Cl⁻, 85% ± 20% for ss-SO₄²⁻, and 68% ± 35% for NO₃⁻ during these periods, primarily influenced by fog type I (Noone, 1992; Gilardoni *et al.*, 2014).

$$\text{Scavenging \%} = \left(1 - \frac{\text{mass loading during fog}}{\text{mass loading before fog}}\right) \times 100\% \quad (\text{E3-5})$$

This high scavenging ratio of coarse mode sea salt aerosols confirms the expected impact of fog in reducing their mass loading. Zhao *et al.* (2022) investigated the scavenging of sea salt ions during three fog events in the Arctic Ocean in 2017. Their study found higher scavenging ratios for coarse mode sea salt ions compared to fine mode ions during these fog events, consistent with our findings here. The scavenging ratios for coarse mode sea salt ion mass concentration in the Arctic Ocean were reported as Na⁺, Cl⁻, and ss-SO₄²⁻ > 80%, Mg²⁺, and Ca²⁺ > 60% in two fog episodes and ~30% in the third episode. They inferred that coarse mode sea salt aerosols likely act

as CCN and are subsequently removed, a process which our work shows to also be the case over more replicate measurements with greater chemical detail.

The interaction between aerosols and fog as a function of time is critical for a deeper understanding of the mechanisms controlling how aerosols grow into fog droplets and the subsequent impact of fog on aerosol mass loading. To provide better insight into the temporal evolution of such processes, we will examine a case study in the region of Sable Island, focusing on the aerosol-fog interactions through size-resolved chemical composition samples collected over a very long fog event.

3.3.4 Case study

A microphysical aerosol processing case study was selected from amongst our observations in a sustained fog event near Sable Island from July 23-25, 2022, including bordering ambient observations before and after the fog event, covering a 72-hour Intense Operational Periods (Super IOP #10; Fernando *et al.*, 2025). This case study allows us the best detail to explore the interplay between meteorology, turbulence, and aerosol mass loading from prior to fog formation, at two time points during the fog event, and after its dissipation. In doing so, we can explicitly consider source and sink terms for aerosol chemical composition in the context of prior reports from the literature. For example, the enhancement of the sea bubble-bursting process as a source with elevated wind speeds or collection and gravitational settling as a sink mechanism. Radiosonde profiles ($n = 13$) were used to determine the fog layer depth (FLD), in addition to the marine boundary layer (MBL) height, where the latter was measured as close as possible to ambient conditions (Figure 3-8B, Appendix B; Section B6; Figure B-10). Impacts of source and sink terms on aerosol mass loading within the fog was then possible to compare to ambient conditions. The size-resolved aerosol mass loadings are shown in Figure 3-8A, beginning with observations under ambient conditions on July 23 (a and e), followed by the development of persistent fog, sampled over two consecutive intervals spanning July 23-24 (b and f) and July 24-25 (c and g). Upon the dissipation of fog, ambient sampling resumed on July 25 (d and h).

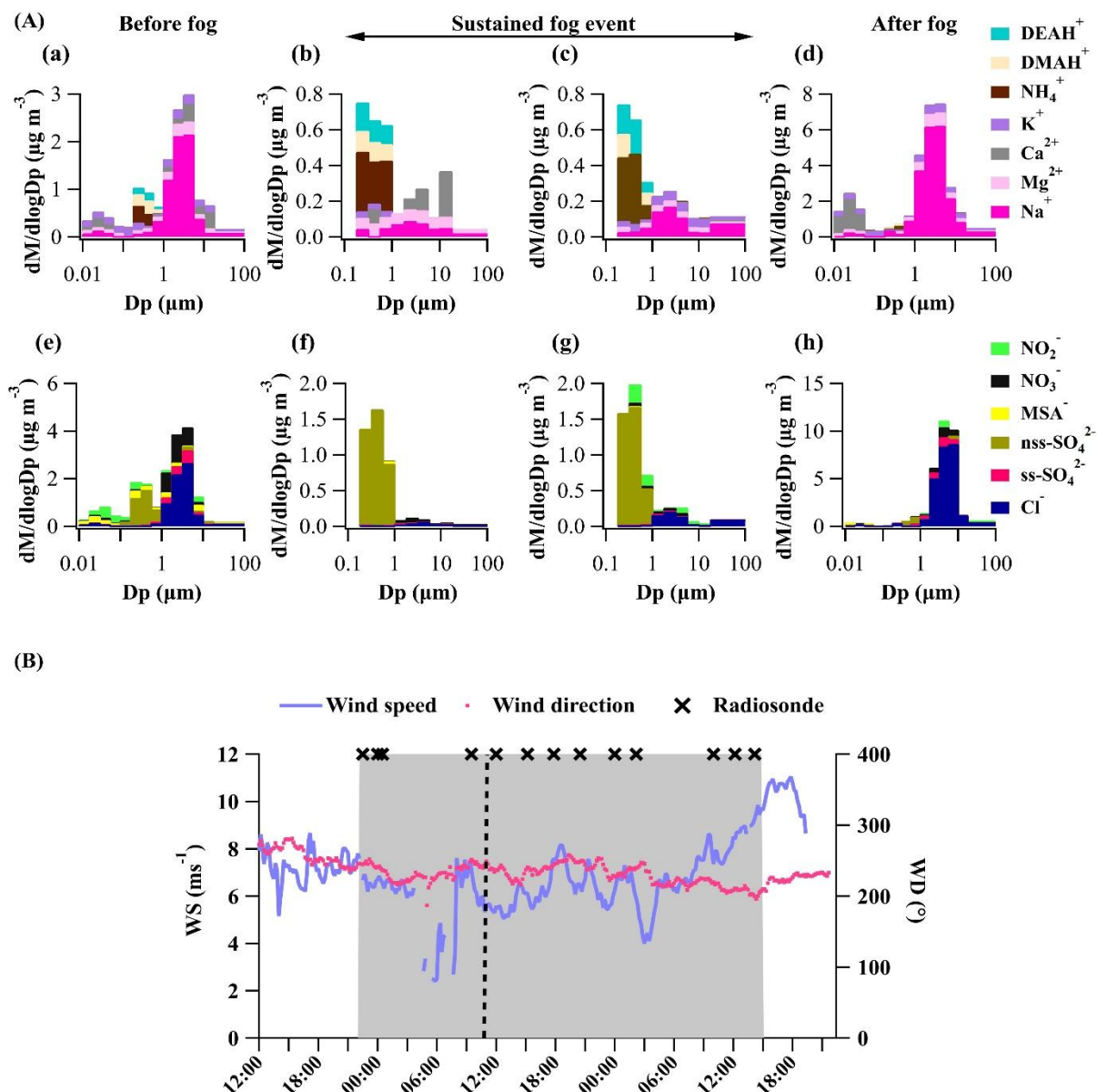


Figure 3-8: (A) Ion mass loading ($\mu\text{g m}^{-3}$) data from ambient and fog aerosol samples collected near Sable Island. The top row shows the ion mass loading of major cations, and the bottom row displays the ion mass loading of anions under different conditions: (a,e) ambient conditions before fog, (b-c,f,g) during fog persistence, and (d,h) after fog dissipation. (B) Wind speed/direction (WS/WD, $\text{m s}^{-1}/^\circ$, purple line/pink square), and radiosonde launches (black cross). No rain was recorded during these periods. Fog is present in the grey shaded region, with the first MOUDI fog sample collected to the left of the dashed line (i.e. b-f mass loading). Meteorological data presented correspond to 12:00 July 23 to 21:00 July 25, 2022 (local time).

At the onset of the fog event, the total column mass of sea salt aerosol components such as Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , ss-SO_4^{2-} , and NO_3^- decreased from $160 \mu\text{g m}^{-2}$ to a range of $26 \mu\text{g m}^{-2}$ to $37 \mu\text{g m}^{-2}$ in the size range of activated droplets ($10\text{-}100 \mu\text{m}$), as the MOUDI segregated the hydrated aerosols. This change is consistent with growth and droplet formation scavenging these aerosols, which were then lost through deposition processes (Table 3-2). Following the dissipation of fog, the sea salt column mass in the coarse mode, which overlaps with the droplet mode ($\geq 20 \mu\text{m}$), increased by approximately a factor of three, from $160 \mu\text{g m}^{-2}$ to $543 \mu\text{g m}^{-2}$ compared to the pre-fog period and more than a factor of ten compared to during the fog event. Before fog formation, the column mass of unactivated sea salt aerosols at smaller coarse mode sizes ($1\text{-}10 \mu\text{m}$) was $2207 \mu\text{g m}^{-2}$ when wind speeds were $7.26 \pm 0.71 \text{ m s}^{-1}$. These aerosol components then appear to have grown into fog droplets, reaching sizes larger than $100 \mu\text{m}$, and/or were subsequently lost through gravitational settling. Production of sea salt in the $1\text{-}10 \mu\text{m}$ MOUDI range continued throughout the fog even as wind speeds were sustained at 5.76 ± 1.46 and increased to $6.69 \pm 1.20 \text{ m s}^{-1}$ during the sampling periods (Figure 3-8B), and we observed unactivated sea salt column masses increase from 50 to $88 \mu\text{g m}^{-2}$, respectively, albeit still substantially lower than prior to the fog formation. Given the hygroscopicity of primary sea salt aerosol, the lower overall column masses are not surprising as these would be the first expected to undergo activation during fog events. As the fog dissipated, wind speeds in the ambient aerosol sampling period following the fog event reached $10.34 \pm 0.61 \text{ m s}^{-1}$, enhancing sea salt production and a higher column mass of $5700 \mu\text{g m}^{-2}$. Column masses of the sea salt components were influenced by both source and sink processes throughout the event. This fog processing case study suggests that similar scavenging mechanisms of supermicron sea salt aerosols into droplets beyond $10 \mu\text{m}$ in diameter are seen here as in prior studies (Feingold *et al.*, 1999; Jensen and Nugent, 2017; Richter, MacMillan and Wainwright, 2021), which is accompanied by their rapid and sustained reduction. The lower column masses during fog events suggests that sink mechanisms of scavenging and deposition of grown, collected, and/or activated droplets outweigh the source processes. Under ambient conditions, the source processes driven by wind speeds are more significant, and unactivated coarse mode sea salt aerosols are subject to a reduced sink term in the absence of their growing into fog droplets.

The mass loading of interstitial fine mode aerosol such as processed-S, and reduced-N increased during fog events compared to ambient conditions (Figure 3-4), suggesting that aqueous-

phase reactions and gas-phase partitioning were potentially taking place (Meng and Seinfeld, 1994; Ge *et al.*, 2012). After the dissipation of fog, the mass loading of interstitial fine mode aerosol ionic components decreased, likely reflecting the cessation of the chemical reactions and partitioning, deposition processes, and dilution of the fog-processed aerosol out of the 250 m fog layer into the 500 m deep marine boundary layer (Table 3-2). Kecorius *et al.* (2023) studied fog-aerosol processing during the Arctic summer, investigating fog growth mechanisms through fieldwork and modeling. Their work demonstrated that fog enhances aerosol growth through aqueous-phase reactions and gas-phase partitioning, leading to the formation of semi-volatile compounds (e.g., NH_4^+ , MSA^- , and NO_3^-) which repartitioned into the gas phase after fog dissipation. Their findings were derived from a limited dataset of three fog events with size-resolved aerosol samples ranging from 0.05 – 10 μm , but with only five size fractions. The current study shows similar results across our more extensive dataset of fifteen fog events, sampling aerosols between 0.01 – 100 μm across fourteen size fractions, providing deeper insights into the aqueous-phase chemistry occurring in fog.

Table 3-2: Column mass of sea salt aerosols ($\mu\text{g m}^{-2}$) measured by MOUDI, wind speed, and mixing height observed during ambient and fog conditions near Sable Island from July 23-25, 2022 (Super IOP #10).

Sampling Periods	Column mass ($\mu\text{g m}^{-2}$)			Wind speed (m s^{-1})	Mixing height (m)
	0.18-1 μm	1-10 μm	10-100 μm		
Ambient (before fog)	150	2207	160	7.26 $\pm$ 0.71	500
Fog Sample 1 (type I: 12h)	25	50	26	5.76 $\pm$ 1.46	201 $\pm$ 39
Fog Sample 2 (type I: 28h)	24	88	37	6.69 $\pm$ 1.20	259 $\pm$ 78
Ambient (after fog)	575	5700	543	10.34 $\pm$ 0.61	500

The number concentration of dry aerosol measured using SMPS from July 23-25, 2022 (Figure 3-9a), was compared with ion mass loading from MOUDI using the residual diameters that were calculated from the wet aerosol collected in the droplet range by the MOUDI (Figure 3-9b) and the Fog Droplet Monitor. Particle number concentrations provide information on the growth or activation of aerosols into droplets during fog events. Also, using ion mass loadings to derive residual diameters allows comparison with corresponding number concentrations to gain additional insight into which aerosol are growing into CCN. The result from the number

concentrations in this case study shows a unimodal distribution is present alongside both fog samples, indicative of the activation of fine mode aerosols. Average residual diameters were $0.18 \pm 0.05 \mu\text{m}$, and $0.20 \pm 0.04 \mu\text{m}$ for fog events from July 23-24 and July 24-25, respectively. Ion balancing yielded values of $0.30 \pm 0.10 \mu\text{m}$ and $0.30 \pm 0.06 \mu\text{m}$ for the same fog periods. The change in SMPS number concentrations between 0.20 to 0.40 μm throughout the fog event align with the changes in dry aerosol diameters determined to have activated into fog droplets via the MOUDI mass loading. The highest total number concentrations from 0.2-0.4 μm before the fog (sum of 224 cm^{-3}) decreased continuously during the two sampling intervals within the fog event (179 and then 142 cm^{-3}) and reached the lowest number concentration after the fog dissipated (77 cm^{-3}). The observed results indicate that, prior to the fog event, both fine aerosol number and mass loadings were higher than within the fog event. During fog formation, reductions in both number and mass loadings imply particle growth leading to fewer but larger particles and collision-coalescence aerosol scavenging, followed by deposition losses. Additionally, these sustained decreases indicate that the aerosols which underwent chemical processes within the aqueous phase were not returned to the atmospheric population post fog, despite our MOUDI observations showing that coarse sea spray aerosol generation was rapidly re-established (Figure 3-8A, d and h). Comprehensive analysis of ion mass loadings and aerosol number concentrations provide evidence that coarse mode sea salt aerosols and fine mode aerosols undergo growth into fog droplets and sustain fog events.

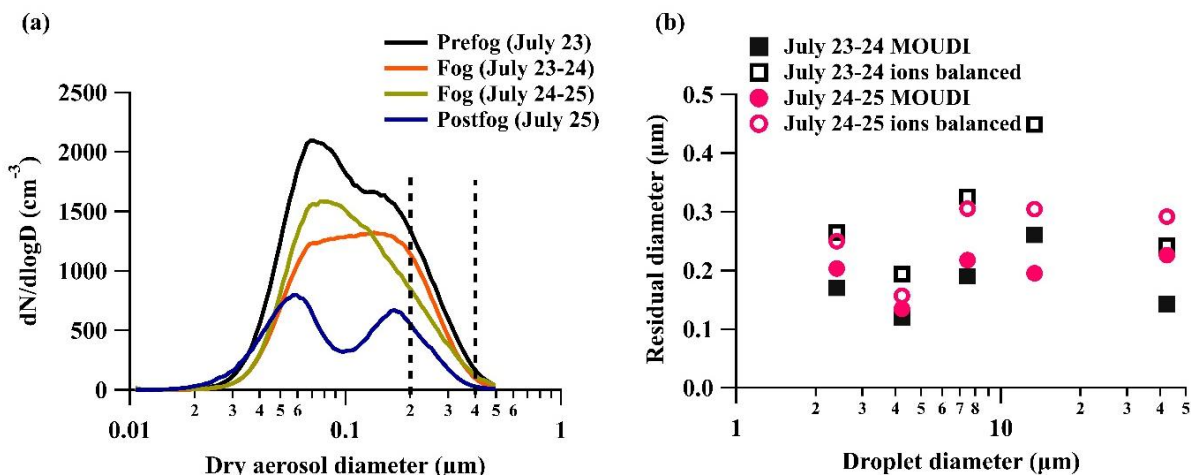


Figure 3-9: (a) Log-normalized number concentration of dry aerosols (cm^{-3}) measured using SMPS with 5-min scans averaged over fog event duration, and (b) residual ion diameters derived from 1.8–100 μm measured by the MOUDI and liquid water content determined from the Fog Droplet Monitor, from July 23–25, 2022 (Super IOP #10). MOUDI mass loadings were converted to dry residual diameters (Section 3.2.4, E3-4) and compared to the relevant changes in SMPS dry diameter number concentrations (vertical dashed lines in (a)) for the same integrated time periods throughout the fog event.

3.4 Conclusions

The primary motivation of this work was to generate an unprecedented amount of insight into the linkages between droplet microphysics and chemical composition of sized-resolved aerosols as indicated by their changes from ambient to fog conditions. A total of fifteen high-quality size-resolved fog aerosol samples were collected over durations ranging from 3 to 42 hours in the northwestern North Atlantic Ocean in the Grand Banks and Sable Island regions, with a high density of supporting meteorological and microphysical measurements. In the coarse mode, sea salt aerosols showed decreased in average equivalent ionic loading during fog events compared to ambient conditions: Cl^- ($-78\% \pm 22\%$), Na^+ ($-73\% \pm 23\%$), Mg^{2+} ($-71\% \pm 21\%$), SO_4^{2-} ($-81\% \pm 16\%$), K^+ ($-34\% \pm 15\%$), and NO_3^- ($-58\% \pm 32\%$). The total coarse mode sea salt mass loadings decreased from $6.23 \pm 4.27 \mu\text{g m}^{-3}$ in ambient marine air to $1.30 \pm 1.75 \mu\text{g m}^{-3}$ during fog events ($-79\% \pm 61\%$), likely due to their activation into fog droplets followed by growth and subsequent removal through gravitational settling and precipitation. In contrast, fine mode aerosols, including processed-S and reduced-N species increased during fog events. Therefore, fog processing alters marine aerosol chemistry as a function of size, driven by both physical and chemical processes.

Three distinct fog types were identified based on size-resolved ion mass distributions, aerosol microphysics (particle number concentrations), and meteorological parameters, providing insight into the drivers of aerosol chemical composition during fog events. Type I fog is characterized by depleted coarse mode sea salt aerosols, with fog droplets grown from freshly emitted coarse mode aerosols, but sustained by growth of fine mode aerosol. This fog type persists for extended durations (814 ± 468 mins) under stable MBL conditions, characterized by low to moderate wind speeds and reduced vertical mixing that translate to a shallow fog layer depth. Type II fog exhibits sustained production of coarse mode sea salt aerosols, with droplets primarily sustained by coarse mode aerosol activation and some evidence for additional contributions from fine mode aerosols. The fog is present despite high wind speeds and enhanced vertical mixing resulting which leads to deeper fog layers but with shorter durations, possibly because of increased generation of primary sea salt aerosol. Type III fog presents the highest mass loadings of coarse mode sea salt aerosols in fog droplets, with droplet formation primarily driven by coarse mode activation with additional contributions from fine mode aerosols. Moderate wind speeds and shallow fog layers provide stable MBL conditions with moderate fog durations (634 ± 104 mins) in type III events. These observations highlight that the distribution of coarse mode sea salt mass loadings is driven by the interaction of source conditions, sink mechanisms, and when combined with sea surface conditions and meteorology they determine the overall fog persistence in the MBL.

Aerosol physical processing underscores the reduction of coarse mode sea salt mass loadings during fog events. The total ionic mass loading of coarse mode sea salt aerosols was generally highest in the ambient atmosphere prior to fog formation, decreasing from $7.95 \pm 4.20 \mu\text{g m}^{-3}$ to $1.64 \pm 2.17 \mu\text{g m}^{-3}$ in the presence of fog, and recovering after the fog dissipated to $6.86 \pm 4.30 \mu\text{g m}^{-3}$ across all observations in this campaign. These findings align with the expected role of coarse mode sea salt aerosols as effective fog condensation nuclei. Also, the impact of fog on aerosol mass loadings was demonstrated by average aerosol scavenging ratios during fog events: 81% for Na^+ , 72% for Mg^{2+} , 39% for Ca^{2+} , 53% for K^+ , 85% for Cl^- , 85% for ss-SO_4^{2-} , and 68% for NO_3^- . The observed decreased in coarse mode sea salt aerosols suggests their scavenging occurs through nucleation or growth in a supersaturated atmosphere, forming fog droplets which are subsequently deposited and lost from the fog layer.

The study combines aerosol chemistry with microphysics, physical processes, and meteorological parameters to better understand fog–aerosol interactions across pre-fog, fog, and post-fog periods. By linking size-resolved aerosol chemical composition to aerosol microphysical properties, the results provide insights that can be incorporated into predictive models that previously focused only on microphysics, such as large eddy simulations which will be a component of our future work. We expect that these will enhance marine fog and visibility predictions and improve the current low fog-forecast accuracy for marine navigation in high-occurrence regions, such as Canada’s Grand Banks and Sable Island areas.

3.5 Acknowledgments

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CHAPTER FOUR - Marine fog aerosol and fog water chemistry over the Northwest Atlantic Ocean: Sources, processing, and implications (Fatima 2022)

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Abstract

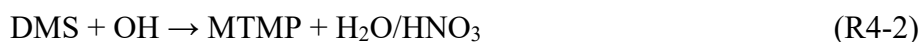
Marine fog plays a key role in modifying the physicochemical properties of fine mode aerosols in the marine boundary layer (MBL) by facilitating secondary aerosol formation and particle growth. During the Fog and Turbulence Interactions in the Marine Atmosphere (Fatima) 2022 campaign, the impact of fog on processed-S (nss-SO_4^{2-} and MSA^-) and reduced-N (NH_4^+ , DMAH^+ , and DEAH^+) species was examined over the Northwest Atlantic Ocean. During fog events, equivalent ionic loadings of processed-S and reduced-N increased, indicating enhanced aqueous-phase reactions and gas-to-particle partitioning. Fog water exhibited lower ionic loadings than fog aerosols, likely due to dilution. Elevated aerosol liquid water content (LWC) during fog events was identified as the primary driver of enhanced chemical processing, consistent with SO_2 oxidation, MSA and HPMTF uptake, and reduced-N partitioning. A statistically significant association between 8-day lagged chlorophyll-a concentrations and processed-S and reduced-N equivalent loadings suggests that marine biological activity influences aerosol composition after a delay of several days, consistent with the time required for phytoplankton decay, subsequent atmospheric oxidation, and gas-to-particle partitioning into aerosols. Fine mode aerosols were calculated to have elevated pH during fog events using the Extended Aerosol Inorganics Model (E-AIM), consistent with enhanced aqueous-phase uptake and increased equivalent ionic loadings of basic reduced-N species. Collectively, these findings demonstrate that fog serves as a critical interface linking marine biological processing, atmospheric transformations of volatile S and N gases, and secondary aerosol formation.

4.1 Introduction

Fog consists of numerous small liquid water droplets suspended in the air, which reduces horizontal visibility at the surface to less than one kilometer.¹ Reduced visibility conditions can affect air, maritime, and terrestrial transportation, increasing the risk of accidents and operational disruptions. Fog forms when the air becomes supersaturated ($RH > 100\%$), causing water vapor to condense onto pre-existing aerosols that act as cloud/fog condensation nuclei (CCN). Fog serves as a dynamic, multiphase reservoir in which gaseous species, interstitial (unactivated) aerosols, and droplets (activated aerosols) can coexist, enabling simultaneous processes such as scavenging, gas–particle partitioning, and aqueous-phase chemical reactions.²

In the marine environment, aerosols originate from both primary and secondary sources, and their chemical properties are mainly influenced by seawater composition and biological activity. Marine aerosols span a broad size range from nanometers to micrometers and are typically categorized into three modes based on their aerodynamic diameter: ultrafine ($0.01\text{--}0.1\ \mu\text{m}$), fine ($0.1\text{--}1\ \mu\text{m}$), and coarse ($1\text{--}100\ \mu\text{m}$).³ Primary marine aerosols originate from wave breaking driven by wind stress at the ocean surface, producing film, jet, and spume droplets.⁴ Film and jet droplets typically form at wind speeds $\sim 5\ \text{m s}^{-1}$, whereas spume droplets are generated at higher wind speeds ($>10\ \text{m s}^{-1}$).^{5,6} Film droplets primarily contribute to the fine mode and are enriched in surface organic matter, including polysaccharides, proteins, and phytoplankton-derived fragments, as well as inorganic sea salt ions.^{7,8} In contrast, jet droplets arise from bulk seawater and primarily contribute to the coarse mode. Secondary marine aerosols are mainly formed through the partitioning and/or oxidation of biologically emitted trace gases to particles. However, anthropogenic emissions transported from continental regions can also contribute to aerosol composition in the marine boundary layer (MBL). Marine phytoplankton are the primary biological source of dimethyl sulfide (DMS), which is produced through enzymatic cleavage of dimethylsulfoniopropionate (DMSP), a sulfur-containing cellular osmolyte synthesized by phytoplankton. Dimethyl sulfide represents the dominant natural source of reduced sulfur to the atmosphere, with global emissions ranging from $16\text{ to }28\ \text{Tg S a}^{-1}$.⁹ Once emitted through sea-to-air exchange, DMS is oxidized in the troposphere and has an atmospheric lifetime of approximately 1–2 days, reacting primarily with hydroxyl radicals (OH) during the day and nitrate radicals (NO_3) at night.^{10,11} Oxidation by OH occurs via two main pathways: (1) OH addition to

the sulfur atom, producing dimethyl sulfoxide (CH_3SOCH_3 , DMSO; R4-1), and (2) hydrogen abstraction by OH, forming the methylthiomethyl peroxy radical ($\text{CH}_3\text{SCH}_2\text{OO}\cdot$, MTMP; R4-2).



Dimethyl sulfoxide undergoes further oxidation to produce soluble products including dimethyl sulfone (DMSO_2), methane sulfinic acid (MSIA), methanesulfonic acid (MSA), and SO_2 . Sulfur dioxide can be oxidized in the gas phase to H_2SO_4 or dissolved into fog or cloud droplets, where aqueous-phase oxidation (e.g., with H_2O_2 and O_3) produces non-sea-salt sulfate (nss-SO_4^{2-}). In parallel, the MTMP formed via the hydrogen abstraction pathway can isomerize to hydroperoxymethyl thioformate (HPMTF), a relatively stable and water soluble intermediate.¹² Hydroperoxymethyl thioformate can be directly taken up into fog or cloud droplets and undergo aqueous-phase processing that yields SO_2 , or it can be oxidized in the gas phase to form SO_2 . These acidic products promote secondary aerosol formation within fog droplets through aqueous-phase reactions. These processes modify the chemical composition of aerosols within the droplets and, upon fog evaporation, enhance aerosol mass loading with potential implications for atmospheric radiative properties.

The ocean is also a source of reduced reactive nitrogen species (e.g., NH_3 and alkylamines (NR_3)) that contribute to marine aerosol growth. Ammonium in seawater is primarily produced through bacterial remineralization of organic matter and zooplankton excretion, with global oceanic emissions estimated at $7\text{--}13 \text{ Tg N a}^{-1}$.^{13,14} Short chain alkylamines (e.g., monomethylamine (MMA), dimethylamine (DMA), and trimethylamine (TMA)) are produced by microbial breakdown of quaternary ammonium compounds such as glycine betaine (GBT), trimethylamine N-oxide (TMAO), choline, and carnitine, with estimated emissions of $\sim 80 \text{ Gg N a}^{-1}$.^{15,16} These reduced nitrogen species are highly water soluble and readily partition into fog droplets, where they participate in acid-base reactions that promote secondary aerosol formation and particle growth. In the MBL, acidic sulfur species derived from marine biogenic processed-S (e.g., nss-SO_4^{2-} and MSA^-) can react with basic reduced-N species (e.g., NH_4^+ , DMAH^+ , and diethylamine (DEAH^+)) to form low-volatility salts (e.g., ammonium and alkylaminium sulfates), enhancing aerosol mass loading and influencing particle physicochemical properties. Facchini *et al.*¹⁷ (2008) reported that marine biogenically emitted alkylamines, such as DMAH^+ and DEAH^+ ,

contribute to secondary aerosol formation, similar to NH_4^+ , by reacting with SO_4^{2-} and MSA^- to form low-volatility alkylaluminium salts that accumulate in fine marine aerosols over the Ocean.

In addition to marine biogenic sources, anthropogenic aerosols can influence the chemistry of the aerosols in the MBL. Acidic species (e.g., SO_4^{2-} and NO_3^-) and basic species (e.g., NH_4^+) are transported over the ocean from continental regions and contribute to the chemical composition of marine aerosols. These anthropogenic inputs can influence new particle formation, aerosol growth, and their activation as cloud or fog condensation nuclei (CCN).^{18,19}

The chemical composition of marine fine mode aerosols reflects complex ocean–atmosphere interactions; however, their processing during fog events remains poorly understood, particularly over the Northwest Atlantic Ocean. Although marine biological activity and seawater composition are recognized drivers of aerosol chemistry, a significant knowledge gap persists regarding how fog affects multiphase chemical processes that alter fine mode aerosol composition in the MBL. During the Fog and Turbulence Interactions in the Marine Atmosphere (Fatima) 2022 project, we investigated the impact of marine fog on the chemical processing of fine mode aerosols over the Northwest Atlantic Ocean by quantifying changes in the equivalent ionic loadings of processed-S and reduced-N species in fine mode aerosols between ambient and fog conditions, as well as measuring these ionic loadings in fog waters, and then evaluating the influence of physical (LWC and T), biological (phytoplankton activity), and chemical (pH) factors for explanatory power over the observed equivalent ionic loadings of processed-S and reduced-N.

4.2 Method

Here, we briefly summarize the relevant measurements conducted during the Fatima 2022 campaign, including aerosol sampling and meteorological observations. Detailed descriptions of aerosol collection, extraction, quantitative analysis, QA/QC procedures, and meteorological measurements are presented in Chapter 3.²⁰

4.2.1 Sampling location and period

In this study, all data were collected during the Fatima field campaign in July 2022 aboard the Atlantic Condor in the Northwest Atlantic Ocean, off the eastern coast of Canada. The cruise was conducted in two phases. The first phase, from July 3 to 17, focused on fog sampling near the Grand Banks and the Hibernia offshore resource platform. The second phase, from July 19 to

August 1, was carried out near Sable Island and included a southward transect into the Gulf Stream region.

4.2.2 Instruments and data analysis

Size-resolved aerosol samples were collected using a Micro Orifice Uniform Deposit Impactor (MOUDI, model 100-NR, MSP Corp., Shoreview, MN, USA), and a nano-Micro Orifice Uniform Deposit Impactor (nanoMOUDI II, model 122-R, MSP Corp., Shoreview, MN, USA), both positioned within a stainless steel weatherproof enclosure mounted to the railing on the deck above pilothouse (~ 10 m a.s.l.). Fog water samples were collected using the Celtech Active Strand Cloudwater Collector (CASCC2), positioned on the left side of the same deck at a similar elevation. Liquid water content (LWC) was measured using a fog droplet monitor (FM-120, Droplet Measurement Technologies). Air temperature (T_{air} , °C) and relative humidity (RH, %) were recorded with a Vaisala WXT 520 weather station (~18 m a.s.l.). Vertical temperature profiles were obtained from 66 radiosonde launches during fog events from the aft deck of the Atlantic Condor. The measurements were carried out using the Vaisala DigiCora system and RS41-SGP rawindsondes.

All size-resolved aerosol and fog water samples were analyzed for major cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}), alkylamines (DMAH^+ and DEAH^+), and anions ($\text{CH}_3\text{SO}_3^- = \text{MSA}^-$, Cl^- , NO_2^- , Br^- , NO_3^- , and SO_4^{2-}) using an ion chromatograph with conductivity detector (IC-CD; Thermo Scientific ICS-6000).^{21,22} Aerosol extracts from coarse and fine modes during fog and ambient conditions ($n = 3$ for each), as well as fog water samples ($n = 3$), along with a field blank from each sampling time, were also analyzed to identify organic acids using ion chromatography coupled with an ISQEC single quadrupole mass spectrometer (IC-MS; Thermo Scientific ICS-6000 DC).^{23,24}

4.2.2.1 Size-resolved aerosol

Size-resolved aerosol samples were collected using a MOUDI during fog events and a nanoMOUDI under ambient conditions. Both instruments operated at a flow rate of 30 L min^{-1} through total suspended particulate inlets equipped with rain caps. The MOUDI utilized nine impaction stages to collect particles with aerodynamic diameters ranging from 0.18 to 18 μm , while the nanoMOUDI incorporated an additional five stages, capturing smaller particles from

0.01 to 0.10 μm . A total of fifteen fog aerosol samples and fourteen ambient aerosol samples were collected, with sampling durations ranging from 4 to 42 hours. Aerosols were collected by impaction on pre-cleaned aluminum foil, and field blanks were included for each sampling event. Samples were extracted in 15 mL of ultra-pure deionized water (DIW; resistivity: 18.2 $\text{M}\Omega\cdot\text{cm}$; Milli-Q Direct 8) and analyzed by IC-CD for major cations, anions, and alkylamines.

4.2.2.2 Fog water

Fog water samples were collected using CASCC2, which draws an air flow with suspended fog droplets at a rate of $5.8 \text{ m}^3 \text{ min}^{-1}$ and impacts them on six staggered Teflon strands, each with a diameter of 508 μm . A total of 31 samples were collected during the fog events from July 7 to 26, 2022. Prior to each sampling event, the fog collector was cleaned six times with DIW, followed by the collection of a 30 mL field blank. The field blank was generated by simulating fog, spraying DIW towards the CASCC2, and collecting the resulting water. The CASCC2 has a collection efficiency exceeding 80% for droplet sizes between 10 to 30 μm .²⁵ Immediately after sample collection, the pH of the bulk fog water was measured using a pH meter (Oakton PCTSTestrTM 50, WD-35634-35, Cole-Parmer, Vernon Hills, IL, USA) with a 5 mL subsample. The pH meters were calibrated with buffer solutions at pH values of 4, 7, and 10 four times before any measurements. Separate fog water aliquots were analyzed for major cations and anions using IC-CD, following the same method as for size-resolved aerosols (see above).

4.2.3 Chlorophyll-a concentration in marine surface water

Chlorophyll-a (Chl-a) concentration data were obtained from the NASA Ocean Biogeochemical Model (NOBM), acquired through the Moderate Resolution Imaging Spectroradiometer (MODIS) aboard NASA Aqua satellite.²⁶ An 8-day average with a 4-kilometer spatial resolution was used to estimate surface phytoplankton biomass. These data were used to generate a time-averaged map of Chl-a concentration for the study period from July 3 to August 1, 2022, which was overlaid with the Atlantic Condor ship track (Figure 4-1). This visualization highlights the spatial variability in Chl-a concentrations along the cruise path, particularly in the Grand Banks and Sable Island regions, where different biogeochemical gradients were observed.

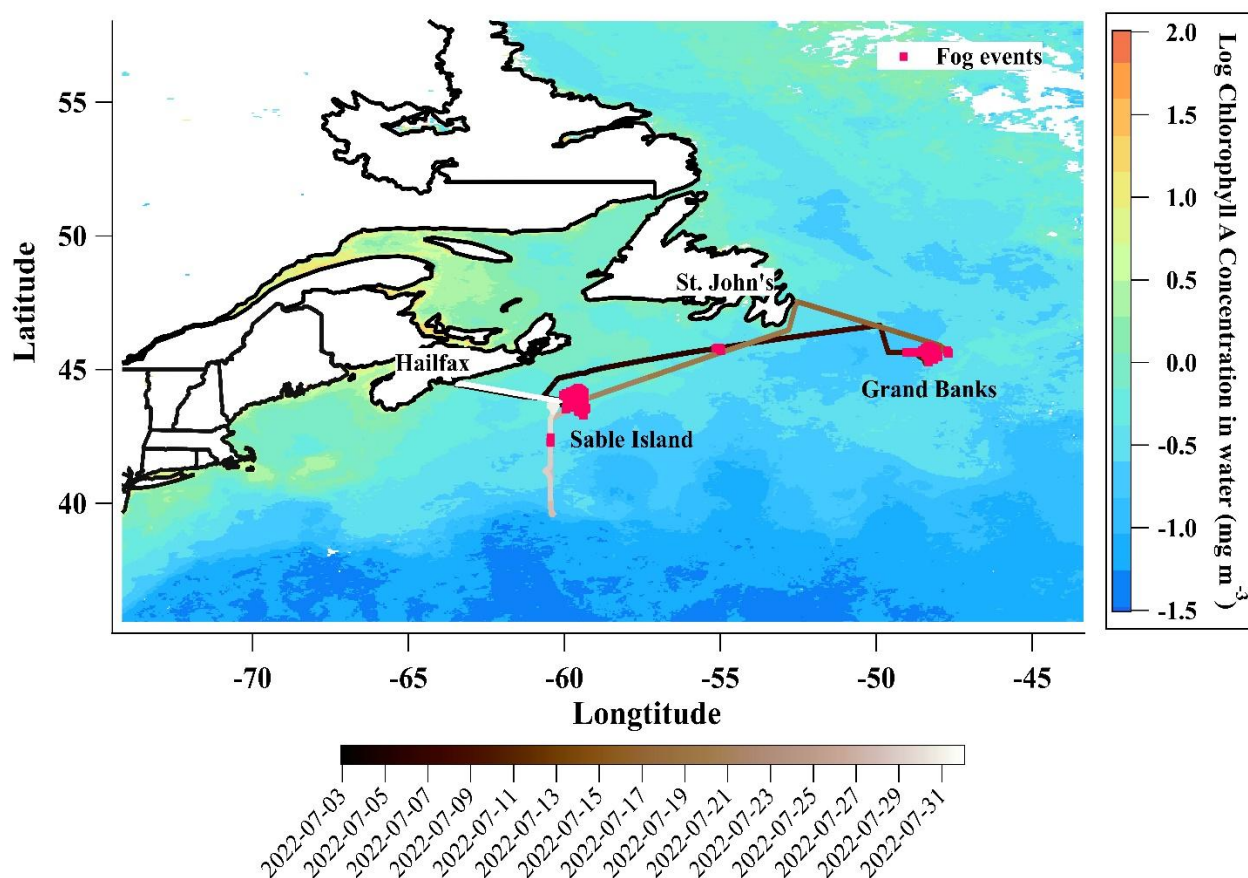


Figure 4-1: Time-averaged Chl-a concentrations derived from 8-day MODIS data aboard the NASA Aqua satellite, representing surface phytoplankton biomass at a spatial resolution of 4 km. The ship track of the Atlantic Condor shows the first phase from Halifax (departed July 3, 2022) to the Grand Banks and arrival in St. John's (July 17), followed by the second phase from St. John's (departed July 19) to the Sable Island region, with a final return to Halifax on August 1, 2022. Pink markers indicate sampling locations for fog aerosol and fog water during the campaign.

4.2.4 pH Calculation

Aerosol pH as a function of size and composition was calculated using the Extended Aerosol Inorganics Model version four (E-AIM IV), integrating the free gas-particle partitioning of semi-volatile species within the thermodynamic equilibrium of gas phase and aerosol liquid water. This comprehensive model accounts for the concentrations of a suite of ions, including the cations: Na^+ , Mg^{2+} , Ca^{2+} , K^+ , NH_4^+ , DMAH^+ , and DEAH^+ and anions: Cl^- , SO_4^{2-} , and NO_3^- . The concentration of $\text{NH}_3(\text{g})$ was measured using a modified version of our custom-built instrument for total gaseous reactive nitrogen ($\text{tN}_{\text{r,gas}}$), where only the combustion furnace for $\text{tN}_{\text{r,gas}}$ and an annular denuder for basic gas scrubbing ($\text{N}_{\text{r,scrubbed}}$) were operated, with the acid pathway not active.²⁷ Gas-phase basic

species ($N_{r,base}$) were quantified by subtracting $tN_{r,scrubbed}$ from $tN_{r,gas}$. This fraction represents the total pool of $N_{r,base}$ (e.g., NH_3 and amines) removed by the phosphorous acid-coated (H_3PO_3) denuder, with NH_3 expected to dominate due to its higher atmospheric abundance. Initially, the total amount of NH_3 and NH_4^+ was set to undergo free partitioning to establish a subsequent gas-particle equilibrium to constrain the possible aerosol pH range. The model includes consideration of environmental parameters such as temperature, and relative humidity (RH). The pH of size-resolved aerosols under both fog and ambient conditions was calculated using the mole fraction of protons (χ_{H^+}) and the corresponding activity coefficient (γ_{H^+}), which represents proton activity (a_{H^+}) (E4-1).²⁸

$$pH = -\log_{10} (a_{H^+}) = -\log_{10} [(\chi_{H^+})(\gamma_{H^+})(55.509)] \quad (E4-1)$$

It should be noted that excess cations are often observed in our samples, which means we measured an imbalance between the targeted and quantified cations and anions, and not satisfying the requirement of charge balance in this chemical system. This may result from the presence of carbonate or bicarbonate anions that we cannot quantified and/or unquantified organic acids. It is unreasonable, given such knowledge on other potential anions, to use OH^- to balance excess cations because it will yield unreasonably high pH values (>9) compared to a system where the unmeasured species with weaker impacts on pH in the real samples are considered. In order to fulfill the charge balance for E-AIM IV input requirement, our pH calculations employed three ion balance approaches: the first method included only Na^+ concentration as the balancing cation against measured anions. The second method extended the cations by adding Mg^{2+} , Ca^{2+} , and K^+ to the Na^+ concentration when additional cations are needed to achieve electroneutrality. The third method was applied when the total anion concentration was insufficient to balance measured cations. In this case, oxalate was introduced as a proxy for unmeasured organic acids to balance excess cations. This approach is reasonable and supported by previous measurements reporting oxalate as a ubiquitous, low-volatility secondary organic anion in remote marine aerosols, mainly formed through aqueous-phase cloud/fog processing.²⁹⁻³¹ Due to its stability in the particle phase and its significant contribution to organic acidity, oxalate has also been used in previous thermodynamic modeling studies as a proxy for unmeasured organic anions.³²⁻³⁵

4.3 Results and Discussion

4.3.1 Chemical composition of fine mode aerosol and fog water

The chemical composition of interstitial fine mode aerosols was characterized during fifteen fog events and fourteen ambient conditions in the Fatima campaign (July 4 to August 1, 2022), with concurrent fog water sampling. The combined analysis of fine mode aerosols and fog water chemistry provides a comprehensive assessment of multiphase chemical processing during fog events in the MBL. The primary objective was to quantitatively compare the equivalent ionic loadings of processed-S and reduced-N species under ambient and fog conditions to elucidate the influence of fog on fine mode aerosol composition through aqueous-phase processing.

4.3.1.1 Chemical composition of fine mode aerosol

The impact of fog on fine mode aerosol composition was examined by comparing their equivalent ionic loadings under ambient and fog conditions (Figure 4-2a). Under ambient conditions, fine mode aerosols had comparable quantities of processed-S (73 neq m^{-3}) and reduced-N (62 neq m^{-3}). Other major ions included Na^+ (61 neq m^{-3}), Mg^{2+} (31 neq m^{-3}), and Cl^- (29 neq m^{-3}). During fog events, processed-S (127 neq m^{-3}) and reduced-N (131 neq m^{-3}) increased by approximately a factor of two relative to ambient conditions. These results show that fog conditions enhanced the abundance of these components of secondary aerosols, either through aqueous-phase reactions and gas-to-particle partitioning.^{36,37} The potential drivers of this enhancement, including aerosol liquid water content (LWC), the marine biological sources, multiphase chemical processing, and aerosol chemical properties, are examined in the following sections.

The equivalent ionic loading of Ca^{2+} in fine mode aerosols also increased during fog events relative to ambient conditions, rising from 3 to 41 neq m^{-3} (Figure 4-2a). This enhancement likely reflects selective fog processing, in which more hygroscopic particles are preferentially activated into fog droplets, leaving less hygroscopic, organic-associated Ca^{2+} in the interstitial fine mode aerosol and leading to its relative enrichment during fog conditions.³⁸⁻⁴¹

The charge balance ratio (Σ^+/Σ^-) indicated an excess of cations relative to measured anions, with values of 1.51, 1.62, and 1.02 for ambient aerosols, fog aerosols, and fog water, respectively (Figure 4-2a). This suggests the presence of unmeasured anionic species, particularly in fog aerosols. Qualitative analysis of organic acids in fine mode aerosols identified lactic, acetic, citric, butanoic, formic, pyruvic, succinic, and oxalic acids. The relative ion abundance of these organic

acids was approximately three times higher in fog aerosols than in ambient aerosols and about two times higher than in fog water. Oxalic acid showed the highest relative ion signal in fog aerosols and fog water, consistent with its aqueous-phase formation during fog processing in the marine environment,^{29–31} whereas lactic acid had the highest relative ion abundance under ambient conditions. These findings suggest that organic acids may contribute to the missing anionic charge, which may explain the higher amounts of measured cations to anions observed during fog events.

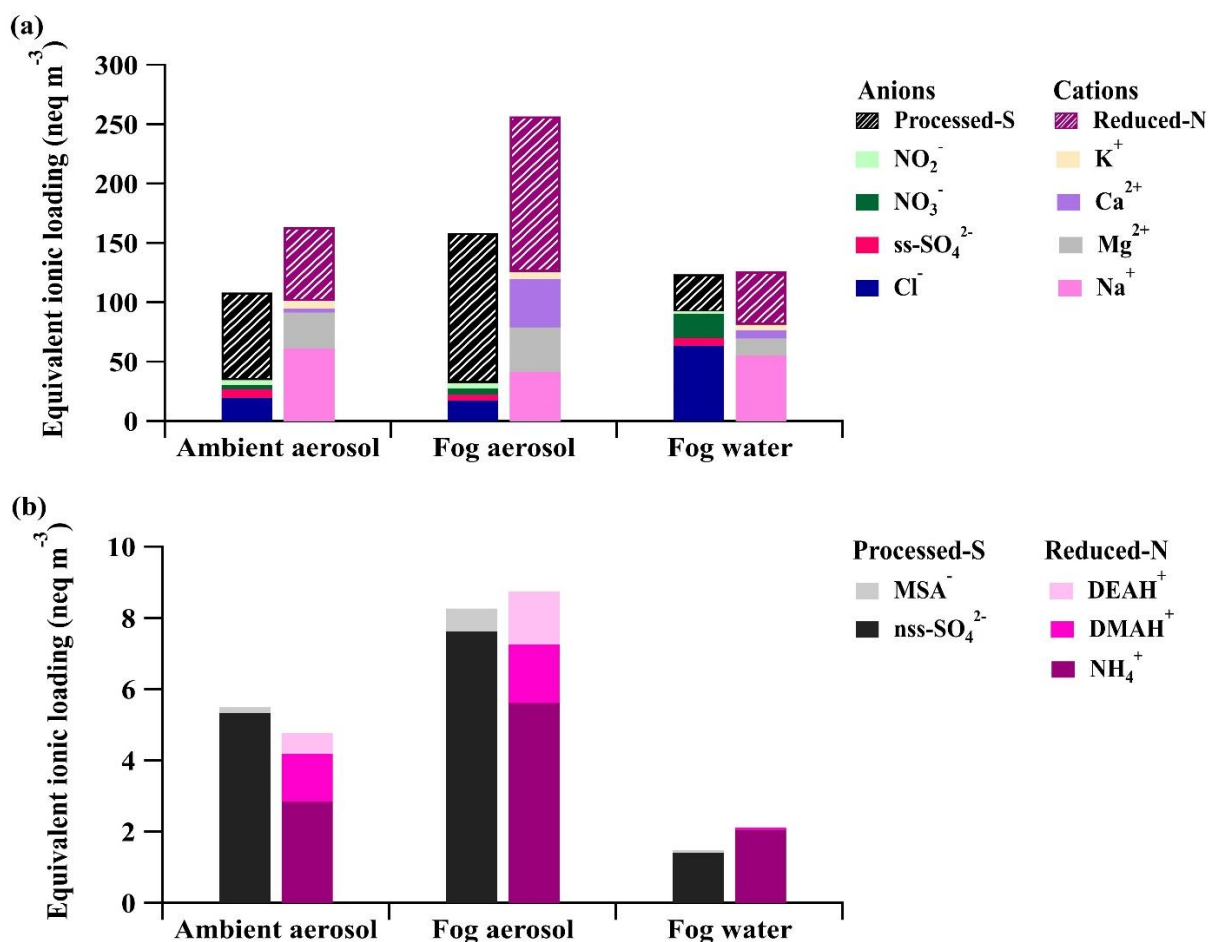


Figure 4-2: (a) Sum of total equivalent loadings (neq m^{-3}) of all the measured ions, and (b) mean equivalent ionic loadings (neq m^{-3}) of processed-S and reduced-N in fine-mode ($0.1\text{--}1\ \mu\text{m}$) ambient aerosols, fog aerosols, and fog water ($10\text{--}30\ \mu\text{m}$) collected over the entire Fatima campaign.

4.3.1.1.1 Processed-S and reduced-N

The average equivalent ionic loadings (neq m^{-3}) of processed-S and reduced-N were then compared between ambient and fog conditions (Figure 4-2b). Under ambient conditions, the equivalent ionic loadings for processed-S were $5.33 \pm 4.45 \text{ neq m}^{-3}$ and $0.17 \pm 0.40 \text{ neq m}^{-3}$ for nss-SO_4^{2-} and MSA^- , respectively. These increased under fog conditions to $7.62 \pm 7.57 \text{ neq m}^{-3}$ (factor of ~ 1.43) and $0.65 \pm 0.89 \text{ neq m}^{-3}$ (factor of ~ 3.82) for nss-SO_4^{2-} and MSA^- , respectively. The observed increases in nss-SO_4^{2-} and MSA^- during fog events are consistent with intensified multiphase processing of DMS oxidation intermediates under elevated LWC. Fog enhances aqueous-phase reactions and facilitates the efficient uptake of water-soluble precursors such as MSA and SO_2 , leading to the dissociation of MSA^- and oxidative formation of SO_4^{2-} .^{11,42–44} Fog also promotes the heterogeneous uptake of HPMTF, a key intermediate in DMS oxidation, which is a direct pathway to SO_4^{2-} formation.^{12,45–47}

A similar trend was observed for reduced-N species, where the average equivalent ionic loading of NH_4^+ increased from $2.84 \pm 3.48 \text{ neq m}^{-3}$ under ambient conditions to $5.62 \pm 5.53 \text{ neq m}^{-3}$ under fog conditions (factor of ~ 1.98). DMAH^+ increased from 1.35 ± 0.85 to $1.64 \pm 1.44 \text{ neq m}^{-3}$ (factor of ~ 1.21), and DEAH^+ from 0.58 ± 0.41 to $1.48 \pm 1.83 \text{ neq m}^{-3}$ (factor of ~ 2.55). This result confirms that fog also enhances the uptake of $\text{NH}_3/\text{NR}_{3(\text{g})}$ through increased partitioning into the aqueous phase, resulting in elevated equivalent ionic loadings of reduced-N species.^{48,49} Previous laboratory studies have shown that the oxidation of NH_3 , DMA, and DEA in the aqueous phase is relatively slow under acidic conditions, allowing these species to persist and accumulate after partitioning into the aqueous phase.⁵⁰ This behavior is consistent with increased production and neutralization of acidic species, such as nss-SO_4^{2-} , which can promote protonation and stabilize ammonium/alkylaminium salts in fine mode aerosols.

The average equivalent ionic loadings observed in the current study are consistent with previously reported values for fine mode aerosol mass loadings over the Atlantic Ocean (See Table C-1 of Appendix C). Mansour *et al.*⁵¹ reported mass loadings for nss-SO_4^{2-} , MSA^- , and NH_4^+ during summer 2015 at the Mace Head Research Station on the west coast of Ireland overlooking the northeast Atlantic Ocean, which are comparable to the current work. Facchini *et al.*⁵² (2008) quantified DMAH^+ and DEAH^+ in marine aerosol over the Atlantic Ocean during periods of high biological activity at both the Mace Head Research Station and onboard an oceanographic research vessel. The relatively higher mass loadings of DMAH^+ and DEAH^+ observed in ambient fine mode

aerosol during this study may reflect higher biological productivity and closer sampling proximity to it during the ocean-atmosphere transfer in the Grand Banks and Sable Island regions of the Atlantic Ocean. Quinn *et al.*⁵³ (2019) reported marine fine mode aerosol mass loadings during the NAAMES (1-4) and WACS-2 campaigns, based on seasonal variations over the North Atlantic Ocean. The sum of the mass loading of nss-SO_4^{2-} and NH_4^+ ranged from 0.09 to 0.59 $\mu\text{g m}^{-3}$, with the lowest values observed in November and the highest in May/June. In this study, the measured ambient fine mode aerosol mass loading of $\text{nss-SO}_4^{2-} + \text{NH}_4^+$ was $0.31 \pm 0.28 \mu\text{g m}^{-3}$, primarily collected in July, which aligns with their reported range and seasonality. Similarly, MSA^- mass loadings in this study ($0.02 \pm 0.04 \mu\text{g m}^{-3}$) were also consistent with the reported seasonal trend, aligning with reported summer ranges.

These results suggest the critical role of fog as a reactive multiphase medium that enhances the formation and partitioning of processed-S and reduced-N species, as evidenced by the increased equivalent ionic loadings of these compounds in fine mode aerosols under fog conditions.⁵⁴ Fog facilitates the dissolution of water-soluble gases such as MSA , SO_2 , and NH_3/NR_3 , as well as the uptake of HPMTF . These precursors undergo aqueous-phase reactions to form less volatile secondary products such as $((\text{NH}_4)_2\text{SO}_4)$, $(\text{NH}_4\text{CH}_3\text{SO}_3)$, and $((\text{CH}_3)_2\text{NH}_2)_2\text{SO}_4$. In addition, the elevated relative abundance of organic acids during fog suggests potential reactions between reduced-N species and organic acids in the aqueous phase, providing additional pathways for secondary salt formation (e.g., $(\text{NH}_4)_2\text{C}_2\text{O}_4$).

4.3.1.2 Chemical composition of fog water

Fog water samples showed a distinct total sum ionic distribution (Figure 4-2a), with elevated Cl^- (64 neq m^{-3}) and Na^+ (55 neq m^{-3}), consistent with efficient scavenging of sea-salt ions into the aqueous phase that we have reported in our prior work.²⁰ In contrast, the equivalent ionic loadings of processed-S (32 neq m^{-3}) and reduced-N (45 neq m^{-3}) were lower than those in fine mode aerosols during fog events. The average equivalent ionic loading of processed-S, primarily nss-SO_4^{2-} ($1.42 \pm 1.31 \text{ neq m}^{-3}$), and reduced-N, mainly NH_4^+ ($2.05 \pm 2.90 \text{ neq m}^{-3}$), was lower than those observed in fine mode ambient aerosol by approximately a factor of 2 and fog aerosol by nearly a factor of 4 (Figure 2-4b). This result suggests that the lower equivalent ionic loadings of processed-S and reduced-N in activated fog droplets are likely due to their reduced activation and the dilution effects of high LWC in fog droplets.^{55–57} The excess reduced-N relative to processed-

S may also reflect potential reactions between reduced-N species and organic acids identified in fog water.

Therefore, fog had contrasting impacts on the chemistry of interstitial fine mode aerosols compared to the resulting composition of fog water following aerosol activation. In fine mode aerosol, the presence of fog enhanced the equivalent ionic loadings of processed-S and reduced-N species through aqueous-phase reactions and gas-to-particle partitioning. Conversely, a dilution effect was observed in fog water samples, resulting in decreased equivalent ionic loading of these species. A comprehensive assessment of fog processing effects requires evaluating the physical (LWC and temperature), biological (phytoplankton activity), and chemical (pH) controls governing the equivalent ionic loadings of processed-S and reduced-N species in fine mode aerosols, as discussed in the following section(s).

4.3.2 Physical, biological, and chemical impacts on aerosol chemistry under fog and ambient conditions

The impact of fog on the equivalent ionic loadings of processed-S and reduced-N was investigated by examining potential source contributions, the physical processes governing phase partitioning and multiphase processing, and the resulting changes in aerosol and fog chemical properties. (Figure 4-3; Table C-2). Aerosol liquid water content (LWC), along with temperature profiles within the fog layer depth (FLD) and the MBL, are considered key physical factors influencing multiphase chemical processes. Sea surface Chl-a concentrations are used as a proxy for phytoplankton activity and a biological source of processed-S and reduced-N. These physical and biological parameters were analyzed for their effect on aerosol acid-base neutralization, reflected in aerosol pH variations. Statistical differences in physical (e.g., LWC, FLD and MBL temperature), biological (e.g., sea-surface Chl-a), and chemical factors (e.g., aerosol pH) between ambient and fog conditions were assessed using Student's t-tests (Table C-2).

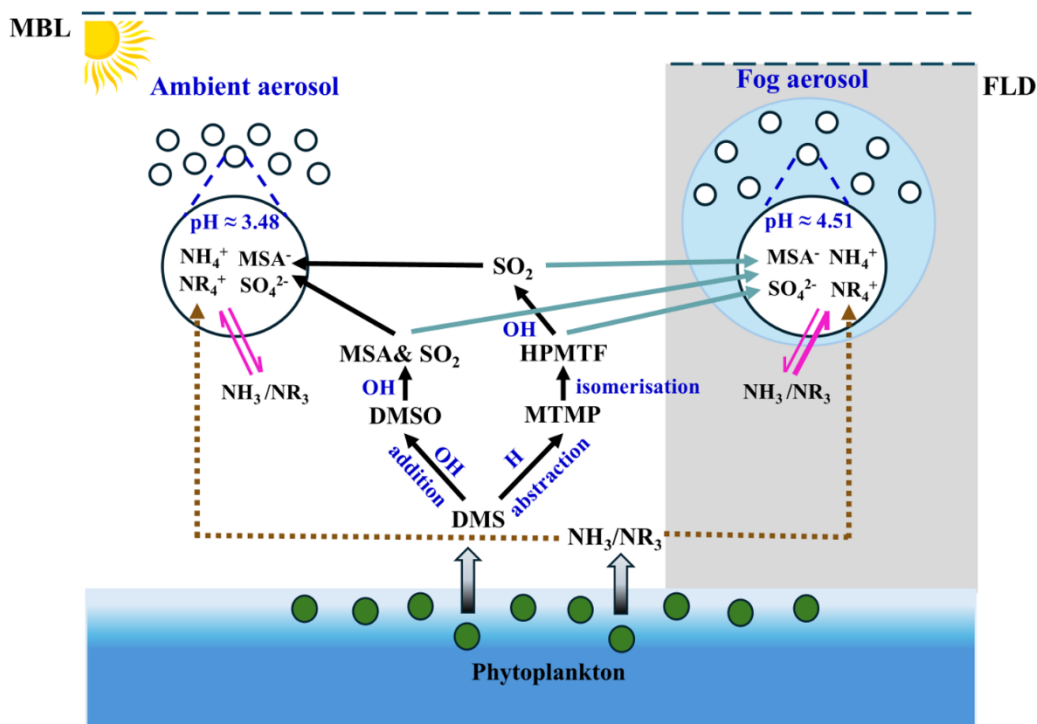


Figure 4-3: Impact of fog on aerosol chemical composition, illustrating the formation of processed-S and reduced-N from phytoplankton-derived precursors. DMS undergoes two primary oxidation pathways: OH-addition, leading to the formation of MSA and SO₂, and H-abstraction, producing intermediates such as HPMTF and SO₂. Under fog conditions, processed-S is further influenced by aqueous-phase oxidation via HPMTF pathway, potentially leading to higher equivalent ionic loading of SO₄²⁻ in fog aerosol samples. Increased gas-to-particle partitioning of reduced-N species during fog events contributes to an elevated aerosol pH. The fog layer depth (FLD) is highlighted in grey to distinguish it within the marine boundary layer (MBL).

4.3.2.1 Physical influences: LWC and temperature

Elevated equivalent ionic loadings of processed-S and reduced-N species during fog events can be attributed to enhanced aqueous-phase processing, driven by increased aerosol LWC and lower temperatures. In this study, the average aerosol LWC significantly increased from $0.004 \pm 0.008 \text{ g m}^{-3}$ under ambient conditions to $0.086 \pm 0.049 \text{ g m}^{-3}$ during fog events (P-value < 0.05; Table C-2). The elevated LWC promotes the aqueous-phase oxidation of DMS via the OH addition pathway, forming DMSO, and subsequently MSA and SO₂.^{44,58} These oxidation products partition into fog droplets, where they are further oxidized to stable species like MSA⁻ and SO₄²⁻ (Figure 4-3). Concurrently, the H abstraction pathway of DMS yields HPMTF, which is efficiently scavenged by fog droplets and subsequently oxidized to SO₄²⁻.^{59,60} These multiphase reactions are enhanced

in fog droplets due to higher LWC and the presence of aqueous-phase oxidants (e.g., H_2O_2),^{61,62} resulting in a greater conversion of DMS to non-volatile processed-S species. Additionally, reduced-N species such as NH_3 , DMA, and DEA, characterized by high basicity ($\text{pK}_a = 9.25\text{--}10.84$), polarity, and solubility, partition readily into the acidic aqueous phase of fog droplets, where they are protonated and retained as NH_4^+ , DMAH^+ , and DEAH^+ .⁶³ Ge *et al.*³⁶ (2012) investigated the impact of fog on submicron aerosol chemistry in Fresno, California, and emphasized the role of aqueous-phase chemistry in enhancing secondary organic aerosol (SOA) concentrations, of which amines may be considered a water-soluble fraction. Their field observations showed that during periods of high relative humidity (RH), such as fog events, water-rich particles more effectively uptake soluble gases like SO_2 and NH_3 , leading to increased formation of ammonium sulfate. Therefore, the high LWC of fog aerosols in this study constitutes an efficient sink for both processed-S and reduced-N species, resulting in the elevated equivalent ionic loadings observed during fog events.

Temperature influences both processed-S oxidation pathways and gas-to-particle partitioning of reduced-N species. The average air temperature within the MBL decreased from 18.59 ± 4.21 °C under ambient conditions to 16.45 ± 4.16 °C within the FLD during fog events (Table C-2). This difference was not statistically significant ($P\text{-value} = 0.180$), suggesting that temperature was not a primary controlling variable between fog and ambient periods. Lower temperatures can shift DMS oxidation toward the OH-addition pathway, which dominates at lower temperatures and generates highly soluble products such as MSA, while the slightly warmer ambient conditions favour the H-abstraction branch that mainly produces SO_2 (Figure 4-3).^{10,12,60} The observed ~ 2 °C decrease during fog events is consistent with enhanced MSA formation, suggesting that temperature likely has some effect on MSA enhancement relative to ambient aerosols (Section 4.3.1.1.1). Decreasing temperature also increases the effective Henry's law constants (M atm^{-1}) of reduced-N species and shifts acid-base equilibria toward protonated forms (NH_4^+ , DMAH^+ , and DEAH^+),⁶⁴ consistent with their relatively high enthalpies of dissociation (~ 50 kJ mol^{-1}).⁶⁵ Driessen and Murphy (2025) reported that gas-aqueous partitioning of low molecular weight amines is strongly temperature dependent.⁶⁶ They measured the large dissociation enthalpies of NH_3 (53 ± 3 kJ mol^{-1}) and methylamine (52 ± 3 kJ mol^{-1}), confirming that lower temperatures favour retention of protonated amines in the aqueous phase. Thus, even

small temperature reductions may enhance aqueous retention and reduce the volatilization of reduced-N species, as observed in this study.

4.3.2.2 Biological sources: Chl-a

Sea surface Chl-a was used as a proxy for phytoplankton biomass, the primary oceanic source of precursors to processed-S and reduced-N during bloom and decay phases. Mean Chl-a concentrations were calculated at four lag intervals (0, 8, 16, and 24 days) under ambient and fog conditions (Table C-2). These lag intervals represent the time between phytoplankton decay and the subsequent emission of precursor gases, which can partition into particles and undergo multiphase chemical reactions in aerosols and fog droplets to form processed-S and reduced-N species. Multiple linear regression analysis was performed to evaluate the relationship between biogenic activity and aerosol composition (Table C-3), with equivalent ionic loadings of processed-S and reduced-N as dependent variables and various lagged Chl-a concentrations as the independent predictor. The regression analysis was performed to assess whether phytoplankton decay, indicated by lagged Chl-a concentrations, influenced the equivalent ionic loadings of processed-S and reduced-N. It also examined if fog droplets enhanced these relationships through multiphase oxidation of sulfur precursors, leading to the formation of processed-S, with reduced-N subsequently impacted by partitioning and acid–base neutralization with acidic sulfur species.

Processed-S showed a positive association with 8-day lagged Chl-a, with a regression coefficient of 6.17 (P-value = 0.055) under ambient conditions and 6.59 (P-value = 0.018) under fog conditions (Table C-3). This relationship was marginally significant in the ambient regime and statistically significant during fog events (P-value < 0.05), suggesting a strengthened linkage between 8-day lagged Chl-a and processed-S formation under fog conditions. In contrast, associations between processed-S and Chl-a at 0, 16, and 24 lagged days were negative or not statistically significant under both regimes. Reduced-N followed a similar pattern, exhibiting a positive relationship with 8-day lagged Chl-a. The regression coefficient increased from 2.22 (P-value = 0.539) during ambient conditions to 5.267 (P-value = 0.086) during fog events. While not statistically significant in ambient conditions, the relationship approached significance under fog, suggesting that fog enhances the partitioning and retention of reduced-N in the particle phase through acid-base reactions with processed-S. Similar to processed-S, Reduced-N showed a negative or statistically non-significant relationship with Chl-a at 0-, 16-, and 24-day lag intervals.

The observed 8-day lag between Chl-a concentrations and the equivalent ionic loadings of processed-S reflects the timescale required for the biochemical processes of marine biological production into aerosol-phase composition.^{51,67,68} Following phytoplankton demise, DMS is produced in the surface ocean (with a lifetime of a few days), and about 10% of it is emitted into the atmosphere.¹¹ Once DMS is emitted, it undergoes oxidation in the atmosphere, producing sulfur-containing intermediates with specific lifetimes: DMSO (~ 0.5 days), MSA (~ 2.2 days), SO₂ (~ 1.4 days), and HPMTF (~ 2 days).^{69–72} As a result, the formation of MSA⁻ and SO₄²⁻ into the aerosol phase occurs over several days, consistent with the observed 8-day lag between Chl-a and processed-S equivalent ionic loadings. At the same time, reduced-N is emitted through biological degradation processes, including phytoplankton grazing and the breakdown of quaternary nitrogen osmolyte.¹³ However, these reduced-N species have much shorter atmospheric lifetimes and therefore reflect more localized emissions and rapid gas-to-particle partitioning rather than the longer processing timescales associated with sulfur chemistry. Consequently, the relationship between reduced-N and lagged Chl-a likely reflects the availability of biologically derived precursors combined with efficient partitioning and acid–base neutralization in aerosols influenced by processed-S formation.⁷³ Rinaldi *et al.*⁶⁸ (2013) identified an 8-day time lag in the correlation between Chl-a and the organic mass fraction of submicron sea spray aerosol (OMss) over the Atlantic Ocean at the Mace Head station from 2002 to 2009. They attributed this delay to the timescale required for biological processes to produce transferable organic material. They emphasized the importance of considering the temporal lags in source models of marine biogenic aerosol.

The average 8-day lagged Chl-a concentrations were $0.42 \pm 0.14 \text{ mg m}^{-3}$ under ambient conditions and $0.36 \pm 0.13 \text{ mg m}^{-3}$ during fog events (Table C-2). The elevated Chl-a under ambient conditions may be attributed to the higher sea surface temperatures that promote phytoplankton growth and reduce decay rates, averaging $16.55 \pm 4.96 \text{ }^{\circ}\text{C}$ compared to $14.27 \pm 3.98 \text{ }^{\circ}\text{C}$ during fog conditions.⁷⁴ However, the higher wind speed observed under ambient conditions ($6.97 \pm 1.93 \text{ m s}^{-1}$) likely reduces DMS emissions from the sea surface to the atmosphere by enhancing turbulent and vertical mixing, while the lower wind speed during fog events ($6.02 \pm 2.05 \text{ m s}^{-1}$) may facilitate more efficient DMS transfer to the atmosphere despite the lower Chl-a levels.⁷⁵ The combined influences of biological precursor availability and meteorological conditions may partly explain the higher equivalent ionic loadings of processed-S during fog conditions. Therefore, the observed

8-day lag between Chl-a concentrations and the equivalent ionic loadings of processed-S and reduced-N reflects the timescales required for the biochemical transformation of marine biological activity into aerosol-phase composition. The statistically significant association between 8-day lagged Chl-a and processed-S under fog conditions and the near-significant relationship with reduced-N suggests that fog conditions strengthen the coupling between marine biogenic precursor emissions and aerosol chemical composition by promoting multiphase chemical processing of sulfur precursors and enhanced formation of processed-S species, which consequently facilitates the partitioning and accumulation of reduced-N species in the aerosol phase.

4.3.2.3 Chemical implications: pH

The size-resolved aerosol pH was calculated using E-AIM IV, with the partitioning of acidic and basic gases into the aqueous phase. Meteorological parameters such as temperature and RH were averaged within the sampling periods of each nanoMOUDI and MOUDI for sampling ambient and fog aerosols, respectively. The average $\text{NH}_{3(g)}$ concentrations were 1.10 ± 1.30 ppbv in ambient and 1.09 ± 0.60 ppbv in fog periods, which were utilized in pH calculations.⁷⁶ The average pH of size-resolved aerosols (E-AIM IV) during ambient and fog events alongside fog water pH is presented in Figure 4-4.

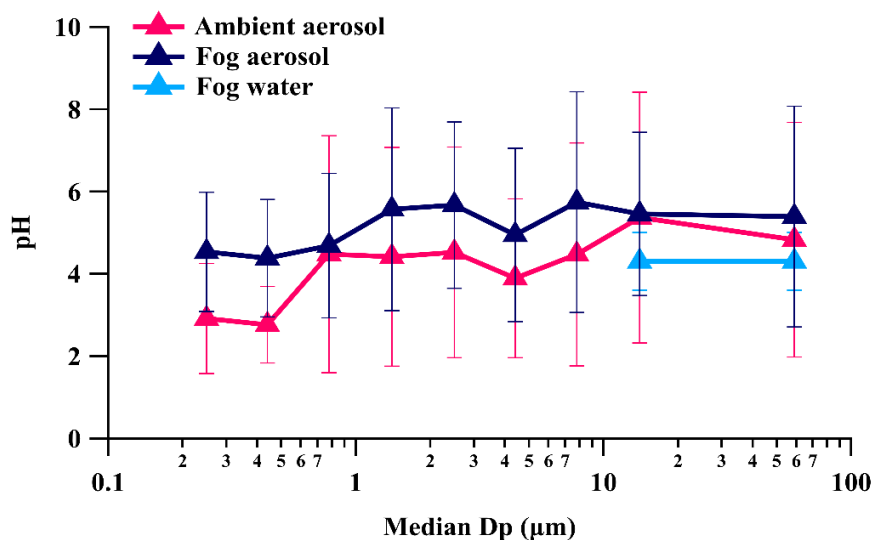


Figure 4-4: Comparison of pH values for ambient aerosol, fog aerosol, and fog water samples (integrated from 20-60 μm) during the entire Fatima campaign. Aerosol samples are categorized into fine mode (0.1-1 μm) and coarse mode (1-100 μm).

Fog events led to slightly higher aerosol pH in the coarse mode (5.46 ± 0.28) than what we measured as the fog water pH (4.33 ± 0.71). In comparison, the fine mode exhibited a pH of 4.53 ± 0.15 . In the absence of fog, the modeled coarse and fine mode pHs were more acidic at 4.58 ± 0.49 and 3.38 ± 0.95 , respectively, demonstrating that fog events may raise aerosol pH, most likely due to the uptake of strongly basic species facilitated by additional water and weaker organic acids. Fog inhibits $\text{NH}_3(\text{g})$ dilution by vertical mixing, promoting greater uptake into the particle phase.^{36,77,78} The elevated pH observed in fine mode aerosol during fog events is commensurate with the higher average equivalent ionic loading (neq m^{-3}) of basic species in fog aerosol samples (Figure 4-2b). There is a 1.8-fold increase in average equivalent ionic loading of our major measured basic species (reduced-N: NH_4^+ , DMAH^+ , and DEAH^+) during fog events, while the rise in acidic species (processed-S: nss-SO_4^{2-} and MSA^-) was comparatively lower, with an average ratio of 1.5 (Figure 4-2b). Qualitative analysis of organic acids further supports the observed pH trends in fine mode aerosols and fog water samples. The relative abundance of organic acids followed this order: fog fine mode aerosols (55%) > fog water (28%) > ambient fine mode aerosols (16%) > fog coarse mode aerosols (0.5%) > ambient coarse mode aerosols (0.4%). These findings suggest that fine mode aerosols during fog conditions contain the highest fraction of organic ions, consistent with increased multiphase processing and acid–base neutralization in the aerosol aqueous phase. The lower relative abundance in fog water likely reflects dilution due to larger droplet volumes, while reduced contributions under ambient fine mode conditions suggest weaker acid–base neutralization. The lowest organic acid abundance is expected in coarse mode aerosols, as these aerosols are dominated by inorganic sea-salt constituents, which are associated with higher pH and lower organic acid content.

The estimated aerosol pH range obtained from E-AIM (Figure 4-4) reflects the variability in predicted pH across the different aerosol size fractions, as pH was calculated for each size-resolved aerosol sample. This range is consistent with prior studies suggesting that fresh basic sea salt aerosols undergo rapid acidification in less than one hour after it crosses the ocean-air interface due to gas-phase partitioning and/or chemical reactions.^{79,80} This process leads to a decrease in pH within the range of 3 to 5.5, depending on the relative composition of acids and sea salt. Pszenny *et al.*⁸¹ inferred aerosol pH via phase partitioning measurements in the MBL, revealing pH ranges of submicron aerosols from 2.6 to 5.3 and supermicron aerosols from 4.5 to 5.4.

In both fog and ambient aerosols, the calculated mean pH exhibited size dependence, with fine mode aerosols having lower pH values compared to coarse mode aerosols. These differences can be attributed to the larger surface area of fine mode aerosols in contrast to the larger volume of coarse mode aerosols.^{38,82} Consequently, the increased surface area facilitates greater acid uptake in smaller particles compared to larger ones. As a result, coarse mode aerosols exhibit a higher buffering capacity with reduced accessibility to acidic species due to their smaller surface area, leading to a lesser acidification process compared to fine mode aerosols.

Additionally, differences in acidity may contribute to the formation mechanisms of these aerosols. Fine mode aerosols are primarily generated from film droplets, enriched with organic acids, while coarse mode aerosols are produced by jet droplets, having more similarity to bulk sea water.

4.4 Conclusions

Marine fog acts as an efficient multiphase chemical reactor, enhancing secondary aerosol formation in the MBL and increasing the equivalent ionic loadings of processed-S and reduced-N species in fine mode aerosols. Under ambient conditions, the average equivalent ionic loadings were $5.33 \pm 4.45 \text{ neq m}^{-3}$ for nss-SO_4^{2-} and $0.17 \pm 0.40 \text{ neq m}^{-3}$ for MSA^{-1} , increasing during fog to $7.62 \pm 7.57 \text{ neq m}^{-3}$ and $0.65 \pm 0.89 \text{ neq m}^{-3}$, respectively, consistent with enhanced aqueous-phase reactions and gas-to-particle partitioning. In contrast, fog water showed lower average ionic loadings due to dilution, with processed-S dominated by nss-SO_4^{2-} ($1.42 \pm 1.31 \text{ neq m}^{-3}$) and reduced-N primarily as NH_4^+ ($2.05 \pm 2.90 \text{ neq m}^{-3}$).

Elevated aerosol LWC is the primary driver of enhanced chemical reactions and gas-to-particle partitioning of processed-S and reduced-N by providing a sufficient aqueous medium for oxidation of SO_2 , uptake of MSA and HPMTF, and partitioning of reduced-N during fog events. A modest cooling of air temperature may have facilitated MSA enhancement and stabilized the protonated reduced-N in the aerosol aqueous phase.

An observed 8-day lag between Chl-a concentrations and the equivalent ionic loadings of processed-S and reduced-N species reflects the timescales required for the biochemical transformation of marine biological activity into aerosol-phase composition. The statistically significant association between 8-day lagged Chl-a and processed-S under fog conditions and the near-significant relationship with reduced-N suggests that fog conditions strengthen the coupling

between marine biogenic precursor emissions and aerosol chemical composition by promoting multiphase chemical processing of sulfur precursors and enhanced formation of processed-S species, which consequently facilitates the partitioning and accumulation of reduced-N species in the aerosol phase.

The elevated estimated pH (EAIM IV) of fine mode aerosols during fog events reflects the combined influence of physical drivers (enhanced LWC), a biologically sourced precursor, and in-droplet chemical reactions. Higher aerosol pH is consistent with increased equivalent ionic loadings of basic reduced-N species and enhanced aqueous uptake, facilitated by additional water during fog events. Concurrently, the highest relative ionic abundance of organic acids in fine mode aerosols suggests intensified acid–base neutralization within fog-processed aerosols.

These results show that marine fog influences aerosol physicochemical properties in the MBL through LWC-driven multiphase reactions and biologically influenced precursor supply, thereby affecting aerosol pH and acid–base chemistry. Therefore, fog is a critical interface connecting ocean productivity, atmospheric transformation, and the formation of secondary aerosols.

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CHAPTER FIVE - Controls on indoor ammonia in new Canadian homes during the first year of occupancy with reduced nitrogen case studies

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Abstract

Ammonia (NH_3) influences indoor air and surface chemistry. Its temporal dynamics and sources during early occupancy of new homes is not well characterized. As part of the New Home Air Quality Study (NHAQS), temporal changes in indoor reduced nitrogen, especially NH_3 , from pre-occupancy through 12 months was quantified in 48 new homes with non-smoking residents in the Ottawa-Gatineau area from 2019-2024. Passive samplers collected target analytes quantified by ion chromatography and liquid chromatography with mass spectrometry. Indoor NH_3 mixing ratios decreased from pre- to post-occupancy and remained relatively stable over 12 months following, consistent with reduced emissions from new materials and increased partitioning surface area upon occupancy. The NH_3 indoor-to-outdoor ratio indicated indoor sources dominated. Indoor NH_3 levels were higher in warmer months, likely due to temperature-driven repartitioning. A generalized linear mixed model identified glass cleaners and resident presence $\geq 18 \text{ h day}^{-1}$ as significant positive predictors of elevated NH_3 , while oven cleaner use decreased it. A case study found reduced nitrogen fate depends on surface chemistry, with potential pathways like carbonyl condensation, and amide and N-heteroaromatic formation shaping household-specific patterns. This work provides new insight on how homeowners may recognize and reduce NH_3 sources to improve indoor air quality.

5.1 Introduction

Ammonia (NH_3) and alkylamines (NR_3) are reduced nitrogen gaseous species with high volatility and often a sharp smell; even small sources can generate easily measured indoor concentrations.¹ Outdoor NH_3 mixing ratios typically range from parts-per-trillion by volume (pptv) to parts-per-billion by volume (ppbv) where it is primarily emitted by animal husbandry, ocean biota, biomass burning, industry, and automobiles.^{2–6} Ammonia mixing ratios vary by environment, typically <1 ppbv in remote marine and continental regions,^{7,8} ~0.01–1 ppbv over the open ocean,^{9,10} ~0.5–5 ppbv in coastal and rural environments,^{11,12} and ~5–20 ppbv in urban and agriculturally influenced regions,^{13–15} with mixing ratios exceeding 24 ppbv in intensive agricultural areas. Outdoor ambient NH_3 levels remain low due to rapid atmospheric dilution, dry and wet deposition, and gas-to-particle partitioning.¹⁶ Indoors, sources like humans and pets, tobacco smoke, cooking meat, ammonia-containing cleaners, and concrete curing agents or emissions from other building materials can elevate NH_3 mixing ratios to 10–70 ppbv.^{17–22} Ammonia and NR_3 act as the dominant alkaline buffers indoors, neutralizing acidic gases such as CO_2 and HNO_3 in air and surface-bound water, and promoting secondary aerosol formation through multiphase acid–base reactions.²³ Although these bases are present outdoors, their propensity to accumulate indoors due to limited ventilation and continuous emissions from occupants, consumer products, and their activities makes them important indoor air pollutants.

Ammonia and NR_3 are classified as hazardous air pollutants at high concentrations due to their irritant and toxic properties.²⁴ Even low-level exposure to NH_3 can cause sensory irritation; the odor threshold is approximately 1.5 ppm,¹ while ocular and respiratory irritation occur at around 30 ppm.²⁵ High exposure may lead to coughing, headaches, asthma, or other respiratory issues. Many indoor sources of NH_3 and NR_3 have been reported, but the temporal evolution of their indoor levels from pre- to post-occupancy in newly constructed homes and the extent to which specific building materials and daily occupant activities impact those levels remain scarcely quantified.

Aminium-based cleaning products in particular are known to cause occupational, and environmental health hazards due to inhalation, with components such as ethanolamine associated with occupational asthma.^{26,27} Hazardous fumes can also be generated when NH_3 -based cleaners are used, by releasing NH_3 directly, or as reaction products when mixed with other types of cleaning products or materials found on household surfaces.^{28–30} For example, mixing NH_3

cleaners with bleach (NaOCl) forms chloramines, volatile irritants that increase respiratory risks. Chloramines can also form during kitchen cleaning when chlorinating agents react with ammonium or aminium ions, or amino acids on surfaces.^{31–34} Ammonia and NR_3 can also have toxic and carcinogenic effects on human health by converting to nitrosamines on indoor surfaces in the presence of nitrous acid (HONO), and nitrite (NO_2^-), which are produced when combustion-generated $\text{HONO}_{(\text{g})}$ and nitrogen dioxide deposit on indoor surfaces and dissociate into water films. This chemistry can arise from common human activities that take place indoors such as cooking with a gas-stove, smoking, and burning candles.^{35–38} Nitrosamines are known to cause mutations and tumors in target organs by alkylating DNA. Therefore, the study of NH_3 and NR_3 as volatile basic species and precursors to well-documented hazardous reaction products in indoor environments is critical because they directly influence indoor air quality, yet their temporal dynamics and drivers are poorly understood, with the procession of chemistry from the building of a new home through continuous occupancy remaining an area of open inquiry.

People in North America spend more than 90% of their time indoors,³⁹ and the probability of inhaling indoor pollutant species is therefore 1000 times more likely to occur rather than outdoors.^{40,41} Ammonia and NR_3 have various indoor sources from both anthropogenic and biogenic processes. Humans produce NH_3 through bacterial deamination of amino acids inside cells.^{18,42} This NH_3 is transported to the liver, where it is converted into urea and excreted in urine. Some remaining bloodborne NH_3 is released through exhalation, sweat, and dermal diffusion, with skin emissions typically exceeding those of respiration.^{43,44} Both respiratory and skin emissions increase with higher metabolic activity, increased skin temperature, and a larger exposed skin surface area.¹⁷

Pets are a common feature of many home environments and pet waste can act as an indoor source of NH_3 and NR_3 , resulting from the microbial breakdown of urea and feces.^{18,45} Bacteria convert urea into NH_3 , leading to NH_3 emissions from litter boxes, soiled bedding, and uncleaned floors, which can increase indoor levels. At the same time, bacteria decompose and transform fecal nitrogenous compounds, releasing both NH_3 and volatile NR_3 .

Both secondhand and thirdhand tobacco smoke are known to contain hundreds of nitrogen-containing compounds, including NH_3 and NR_3 , making it a major source when this activity occurs indoors.^{19,46} Amine emissions from smoking are known to include both aliphatic NR_3 (e.g., methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, and butylamine) and

aromatic NR₃ (e.g., aniline, 1-naphthylamine, and 2-aminobiphenyl); where concentrations are consistently higher in smoking than in non-smoking homes, and both exceed outdoor levels.^{47–49} Similarly, cooking protein-rich foods (e.g., beef, pork, lamb, chicken, fish) releases NH₃, volatile NR₃, and basic N-heterocycles (e.g., pyrroles, pyridines, imidazoles) due to the thermal breakdown of amino acids, especially in poorly ventilated spaces, with emission levels influenced by the cooking method and temperature.^{20,50–52} Grilling and frying, particularly at temperatures above 150 °C (300 °F), generate higher NH₃, NR₃, and N-heterocycle emissions than lower temperature methods.

Household consumer products, including hair dyes, textiles, textile carpet tiles, skin moisturizers, and air fresheners can release NH₃ and NR₃ over time.^{29,53–56} Building materials can emit NH₃ and NR₃; some cement-based products release them during curing and decomposition.⁵⁷ For example, antifreeze additives in concrete can hydrolyze to release NH₃. Karlsson *et al.*²² demonstrated that casein-based self-leveling floor-topping putties undergo microbial decomposition in moist, high-pH environments, releasing triethylamine, pyrrolidine, di-isobutylamine, 2-ethylhexylamine, and n-octylamine at ppbv levels. This plethora of potential indoor sources of NH₃ and NR₃ dictate their indoor abundance and potential to form harmful reaction products.

The fate of indoor NH₃ and NR₃ depends on physicochemical and environmental processes involving air, water films, and solid surfaces.²³ When NH₃ is emitted, it initially partitions into thin water layers on surfaces because of its high solubility and basicity and forms NH₄⁺ according to its base dissociation coefficient until equilibrium between the gas and condensed phases is reached. Simultaneously, NH₃ may neutralize acidic species in particles (e.g., HNO₃ and H₂SO₄) to form ammonium salts (e.g., NH₄NO₃ and (NH₄)₂SO₄), contributing to indoor PM_{2.5} mass, although the abundance of these acids indoors has been shown to be low.⁵⁸ On indoor water films, NR₃ (1° and 2°) can react with carbonyls to form imines and enamines, which can further condense into amides and N-heterocycles, governing indoor N-speciation and potentially controlling part of the fate and final form of NH₃ and NR₃ in indoor environments.^{59–61} Sorption and desorption processes can also influence NH₃ and NR₃ levels; they can adsorb onto porous or acidic surfaces and be stored until higher temperature, or lower humidity or gaseous levels result in volatilization.⁴⁰ The microstructure of indoor materials (e.g., permeable or porous surfaces), ventilation, and air exchange rates are crucial in controlling these surface reservoirs.⁶² Low air

exchange rates extend surface retention, while high ventilation rates accelerate NH_3 removal. Due to these processes and the large surface area-to-volume ratio in indoor spaces, NH_3 and NR_3 tend to persist longer and undergo multiphase surface reactions with acids and carbonyls.⁶³

A characterization of temporal progression from pre-occupancy through the first year of occupancy of a new home has not been performed to date and would allow a first attribution of changes in reduced-N levels in relation to the addition of occupant-related surfaces and activities when paired with surveys. The result would be a more comprehensive assessment of indoor NH_3 , capturing the dominant drivers of indoor NH_3 and NR_3 levels, where pre-occupancy would reflect emission from building materials when surface reservoirs are at their lowest, and post-occupancy temporal observations insight on the influence of added furnishings that alter the surface area and materials within, all while occupants introduce the wide array of additional sources described above.

Accurate collection of gas-phase NH_3 and NR_3 indoors over long periods to pursue such observations has been challenging due to contamination, co-uptake of particulate NH_4^+ , strong surface reactivity, rapid wall losses in sampling inlets, and practical constraints in occupied spaces, such as the power, noise, and footprint of equipment.⁶⁴ Passive diffusive samplers mitigate these issues compared to active sampling: they are power-free, quiet, affordable, unobtrusive, avoid inlet wall loss, use diffusion barriers to limit particulate NH_4^+ uptake, and have rigorous protocols established for cleaning, preparation, exposure, and storage to minimize measurement bias.^{65–70} Therefore, indoor deployment of passive samplers is an attractive method for power-free, unattended, large-scale, and multi-site collection of NH_3 and NR_3 from pre-occupancy through the first year of occupancy in new homes. A few days of exposure can provide robust time-weighted average (TWA) concentrations with minimal disturbance across many homes, which can then be easily repeated across multiple sampling periods.

The objective of this study was to assess the controls on and evolution of indoor NH_3 in 48 newly constructed residences in Canada from 2019-2024 with non-smoking residents. We evaluated the NH_3 trends as they related to indoor air quality via sources and sinks in these homes. To do so, we collected NH_3 , NR_3 , and other reduced-N species using passive samplers and quantified our target molecules by ion chromatography with conductivity detection (IC-CD) following a new protocol for more accurate indoor measurements. Indoor levels of NH_3 were then quantified over the first year of occupancy in the newly constructed homes at seven timepoints to

track temporal and seasonal variability. Simultaneously, we determined the indoor-to-outdoor NH_3 concentration ratio to assess the relative contribution of indoor versus outdoor sources. We also explored indoor NH_3 emission pathways associated with building materials, occupant activities, consumer product use, and domestic appliances based on home characterizations and anonymized participant surveys. Lastly, five case studies were selected for a non-targeted analysis of reduced-N species by liquid chromatography coupled with electrospray ionization quadrupole time-of-flight tandem mass spectrometry (LC-ESI-QTOF-MS/MS) to consider the wider variety of related species present on indoor surfaces or resulting from indoor reactions.

5.2 Method

5.2.1 Study design

These measurements were conducted as part of Health Canada's New Homes Air Quality Study (NHAQS). The objectives of the NHAQS are to quantify concentrations of various air pollutants such as NH_3 , VOCs and SVOCs in new homes; to understand how these concentrations compare to existing health-based exposure limits; and to examine how these concentrations change during the first year of occupancy. The NHAQS was designed to capture several time points: two 24-hour periods immediately pre- and post-occupancy to minimize participant move-in constraints, as well as five 4-day time points (0, 3, 6, 9, 12 months post-occupancy) to improve temporal representativeness and reduced below detection limit occurrences. Supporting data was also collected over the first year of occupancy on other factors such as temperature, relative humidity, air exchange rate, building material emissions rates, occupant behaviours, and housing characteristics. Sampling took place from 2019 to 2024 in 48 homes within the Ottawa–Gatineau census metropolitan area in Ontario and Québec, Canada. This publication focuses on the NH_3 component of the study.

Ammonia was collected using Ogawa passive samplers (PS-154, Ogawa & Co. USA, Inc., Pompano Beach, Florida) with citric-acid coated reactive substrates (see Section D1 of the Appendix D). Indoor passive samplers were positioned 1.5 m above the floor in the primary living area to represent the breathing zone and were kept consistent across all sampling periods, while outdoor samplers were in backyards away from potential NH_3 sources (e.g., barbecues, vehicle exhaust, vents from indoors). Each sampling interval included four indoor reactive substrates (Section D1), collected using two separate Ogawa samplers, each containing two reactive pads.

Outdoor sampling consisted of one Ogawa sampler with two reactive substrates, and one field blank was collected using a single Ogawa sampler with one side exposed. During the COVID-19 pandemic period of this work, the number of field blanks increased to two due to our increased reliance on homeowners to deploy the samplers on our behalf as required by distancing requirements. This increased the need to track potential contamination and consider it in our determinations when necessary. Field blanks were exposed for a few seconds at the indoor sampling site while sampling substrates were put in place. Indoor temperature and relative humidity were recorded concurrently using HOBO[®] U12 Temp/RH/2 External Data Logger (U12-013, Onset Computer Corporation, Bourne, MA, USA) during the sampling times. Several deployments during the overall study were missed due to COVID-19 restrictions that prevented technicians or homeowners from installing the samplers.

Participants were homeowners over 18 years of age who moved into a newly built detached, semi-detached, or attached home after 1 April 2019, agreed to both pre- and post-occupancy air monitoring, completed a detailed questionnaire on housing characteristics and indoor activities, and did not smoke indoors.

5.2.2 Sample collection of NH_{3(g)}

The Ogawa passive sampler is a low-cost, compact, and reusable device to measure gas-phase NH₃ or NR₃ collected irreversibly by reaction onto a citric-acid coated filter via protonation and citrate salt formation (R5-1).



5.2.2.1 Deployment preparation

The entire assembly of the Ogawa device includes the sampler, support clip, brown gas-tight Nalgene container, and a weather shelter. Each sampler was disassembled and each part was cleaned prior to use by rinsing with ultra-pure milli-Q water (DIW; resistivity of 18.2 MΩ·cm) six times to remove any contamination and soaked overnight in a precleaned 1 L high-density polyethylene (HDPE) bottle filled with DIW. The bottle was shaken vertically and the water discarded and replaced six times to ensure soluble impurities were removed. The cleaned assemblies were shaken free of bulk water and then placed on top of and covered by Kimwipes

(S-12814, Kimberly-Clark Professional, Milton, ON, Canada) to dry in ambient room air for a few hours.

The Ogawa passive sampler contains six parts (Figure D-1). The body is comprised of two diffusion sampling chambers within one apparatus. Each sampler was assembled by placing a coated collection pad inside the chamber between two stainless screens using tweezers precleaned with DIW and dried with a Kimwipe. The sampler was then capped by inserting and pressing the end caps on each side to seat them as per the manufacturer's design. The assembled apparatus was inserted into a support clip and placed into a resealable gas tight plastic bag for protection and to prevent collection of the target gases during transport to the field sampling locations. The resulting bagged apparatus was placed into an airtight brown container and shipped to a holding facility in a cooler with a few ice packs, where it was then stored in a refrigerator until deployment.

5.2.2.2 Post-collection handling and extraction

All samplers received after deployment were first stored in a refrigerator and then transported in a cooler with ice packs. Once received, the samples were stored in a freezer (-20 °C) until the samples were extracted.

The stored samplers were brought slowly to room temperature before removing the filter pads for extraction. This prevented condensation of water vapour from room air on the apparatus, which can lead to analyte losses. All sample handling equipment was rinsed six times with DIW and dried with a Kimwipe prior to use. The recovered filter was inserted into a 15 mL polypropylene (PP) tube prefilled with 5 mL DIW using clean tweezers. Then the stainless screens which supported the reactive filter were also rinsed with 10 mL DIW into the PP tube to recover any trace analyte physically transferred to these parts of the passive sampler. The PP tube was mixed periodically by inversion for 1 hour at room temperature. The filter was then removed from the extraction solution using clean tweezers and the resulting extract was stored in the refrigerator at 4 °C until quantitative analysis by ion chromatography with conductivity detector (IC-CD) or liquid chromatography coupled with electrospray ionization quadrupole time-of-flight tandem mass spectrometry (LC-ESI-QTOF-MS/MS).

5.2.3 Analysis of NH₃ by Ogawa passive samplers coupled to IC-CD

5.2.3.1 IC-CD analysis

A total of 2307 NH₃ extracts from new homes were analyzed on a Thermo Scientific ICS-6000 IC-CD, employing three sequential cation separation methods: a gradient, and two isocratic methods. Approximately 300 samples were first analyzed by the gradient method with a methane sulfonic acid (MSA) eluent gradient of 1-8 mM and a flow rate of 1.25 mL/min at 55 °C, following sample delivery on an inline preconcentration column (35 min runtime) based on our prior work.⁷¹ This method was capable of separating inorganic cations and the 11 most abundant atmospheric NR₃. Since we were unable to detect any of the most abundant NR₃ in these initial pre-screening samples, the next 300 samples were analyzed using an isocratic eluent method with a MSA concentration of 8 mM and a flow rate of 1 mL/min at 30 °C, again with a preconcentration column (35 min runtime). This second method was chosen to extend analytical column and suppressor lifetimes. The remaining samples were analyzed isocratically with 6 mM MSA to retain peak resolution on an aging analytical column, and the preconcentration column was replaced with a loop (250 µL) to reduce run time to 20 mins per sample while keeping the target analytes separated from common matrix component and above the instrument detection limits.

5.2.3.2 Data Analysis

Collected amounts for field blank and sample extracts (ng) were calculated from a non-linear IC calibration fit,^{71,72} which yielded NH₃ mass (ng) per injection volume (mL). These values were then multiplied by the extract volume (mL) to obtain the total collected amounts. The gas-phase mixing ratio of NH₃ was determined by E5-1, which were provided by the NH₃ sampling protocol from Ogawa.⁷³

$$\chi = \frac{\alpha \times CA}{t} \quad (\text{E5-1})$$

Where χ is the calculated gas-phase NH₃ mixing ratio (ppbv), α is the mixing ratio conversion coefficient which is temperature dependent (ppbv min ng⁻¹) and was determined using the supporting measurements, CA is the collected amount of NH₃ (ng), and t is the collection time (min). Here, χ denotes the NH₃ gas-phase abundance, expressed as a mixing ratio, distinct from the concentration used in liquid- or particle-phase measurements.

All the sample amounts reported herein were corrected by subtraction of field blank amounts where they were above the detection limits of the method, and unusable (i.e. contaminated) field blanks were identified if an outlier was identified by applying Grubb's test to the full pool of blanks. In cases where a contaminated blank was identified, the background correction value was replaced by the average of the larger statistical pool of field blank samples collected across the entire project. Sample replicates were also screened for contamination using Grubb's test and any outliers identified were excluded (Section D1; sample outliers < 0.4%; blank outliers < 2% screened). If the concentration of a sample replicate fell below the calculated method limit of detection (LOD), it was substituted with a value of half of the LOD. The average method LOD was calculated as 3 times the standard deviation in the signal obtained from three sequential injections of a field blank. Four different method LODs have been calculated, corresponding to the four different large batches of samples we analyzed over the course of this study by the three different ion chromatographic methods. The LODs were calculated for both 24 h and 96 h sampling durations using E1 where CA is replaced with the LOD.

5.2.3.3 Quality Assurance and Quality Control of IC-CD

External calibrations of NH_4^+ were run (25 to 498 ng on column, $n = 5$) before and after each batch of samples, and two check standards (low = 37 ng and high = 374 ng) were analyzed before and after each lot of samples (~ 7 samples). Multiple injections of DIW (reagent blank) were injected before, between, and after the standards and samples to ensure there was no carryover of analytes or contaminants between analytical determinations. The accuracy of quantifying the NH_4^+ analyte was determined from replicate check standards ($n = 20$) and calculated by percent relative error (%RE) using the response of the calibrated instrument, which yielded a mean RE of $\leq 5\%$ for both check standards. The precision was determined using calibration replicates ($n = 5$), yielding a value of $\pm 8\%$. The precision and accuracy of NH_4^+ determined here are robust and consistent with our prior IC method performances for quantitative analysis.^{71,74,75}

5.2.4 Analysis of reduced-N species by Ogawa passive samplers coupled to LC-ESI-QTOF-MS/MS

A subset of passive sampler extracts ($n=5$), collected at pre-occupancy and 3, 9, and 12 months post-occupancy, were analyzed further to characterize reduced nitrogen species, including NR_3 ,

amides, imines, enamines, and nitrogen-containing ring structures. Analysis was performed using LC-ESI-QTOF in both TOF (MS-only) and QTOF (tandem MS) modes on an Agilent 1260 Infinity HPLC coupled to an Agilent 6550 QTOF mass spectrometer. Separation was performed on a reverse-phase column (Agilent Poroshell 120 SB-Aq, 2.1 x 50 mm, 2.7 μ m) using a methanol-DIW gradient. Citric acid-coated Ogawa substrates primarily capture gas-phase basic species, such as NH_3 and NR_3 , via acid-base reactions. Less basic reduced-N compounds (e.g., amides, imines, enamines, and N-heterocycles) may also be retained through protonation, but collection increasingly reflects surface deposition as basicity decreases. Amides and pyrrole-like N-heterocycles are effectively non-basic and are therefore expected to be collected predominantly by surface adsorption, whereas imines, enamines, and pyridine-like N-heterocycles retain sufficient basicity for partial protonation. Because passive sampling rates for NR_3 are not known, quantitative analysis is not possible. Instead, qualitative LC-MS/MS analysis of relative abundances was necessary to assess the presence and temporal trends of NR_3 . Detailed descriptions of the separation conditions, MS mode, data processing, and QA/QC procedures are provided in Ditto *et al.*^{76,77} Briefly, electrospray ionization was performed in positive mode under optimized source conditions for the detection of small molecules, with continuous reference mass calibration to ensure accuracy. Mass spectra from m/z 50–600 were extracted and filtered using quality criteria, including isotope height >1000 counts, compound height >5000 counts, and peak quality scores >70%. Molecular formulas were assigned within specified elemental ranges ($\text{C}_{3-60}\text{H}_{4-122}\text{O}_{0-20}\text{N}_{0-3}\text{S}_{0-1}$), and samples were blank corrected by calculating the abundance ratio of sample to blank. Samples with a ratio below 5:1 were excluded, while for ratios above 5:1, the blank abundance was subtracted from the sample. Tandem MS further analyzed selected reduced-N ions that passed QA/QC and blank correction; deconvoluted MS/MS spectra using Agilent Mass Hunter Qualitative Analysis were processed with SIRIUS and CSI:FingerID for structure prediction, followed by functional group identification using the APRL Substructure Search Program.^{78–81}

5.2.5 Statistical Analysis

The relationship between indoor NH_3 mixing ratios and various potential source and sink factors was examined using a Generalized Linear Mixed Model (GLMM; Section D2). This method was selected due to the complex correlation data with repeated measurements across 48 households over a year. The GLMM is well-suited to this dataset because it accounts for the hierarchical

structure of repeated measurements within homes and allows simultaneous evaluation of multiple fixed effects, such as sources and sinks, while modeling between-home variability with random effects. It provides a robust initial framework for identifying key predictors of indoor NH_3 in a heterogeneous residential setting. The dependent variable, NH_3 mixing ratio, showed a positively skewed and non-normal distribution; therefore, a Gamma distribution with a log link function was used in the GLMM. Predictor variables included continuous factors such as the number of occupants, pets, and reported durations of cooking, frying, grilling, baking, toasting, vacuuming, mopping, and window opening, as well as the square footage of concrete flooring (Table D-3). It also incorporated categorical variables indicating the presence or use of household products, such as gas stoves, candles, and cleaning products like bleach, disinfectants, and specific surface cleaners (e.g., tub, toilet, glass, multi-surface, metal, oven, floor, carpet, and upholstery; Table D-4). Random effects accounted for variability among the 48 homes, while repeated measurements within each household were modeled to address temporal correlation. This approach helps distinguish overall trends from household-specific variability, with an emphasis on understanding actual changes in NH_3 over time. An autoregressive covariance structure of order one (AR(1)) was applied to capture the temporal correlation of NH_3 measurements over time. Potential multicollinearity among predictors was assessed using tolerance and variance inflation factors (VIF) calculated from initial multiple linear regression analyses, because highly correlated predictors can inflate standard errors and destabilize coefficient estimates. Predictors with tolerance <0.1 and $\text{VIF} > 5$ were removed from the final model, as these statistically diagnostic thresholds indicate that a predictor overlaps too strongly with others to provide stable, interpretable estimates.⁸² All the statistical procedures were performed using IBM SPSS Statistics 29.0.1.0.

5.3 Results and Discussion

5.3.1 Temporal changes in indoor and outdoor NH_3

Indoor and outdoor NH_3 mixing ratios were measured during seven visits, from before occupancy to 12 months afterward (Figure 5-1). These distributions show the general temporal patterns across all study homes during the first year of occupancy and how the start of occupancy and occupant activities influence indoor levels compared to concurrent outdoor levels.

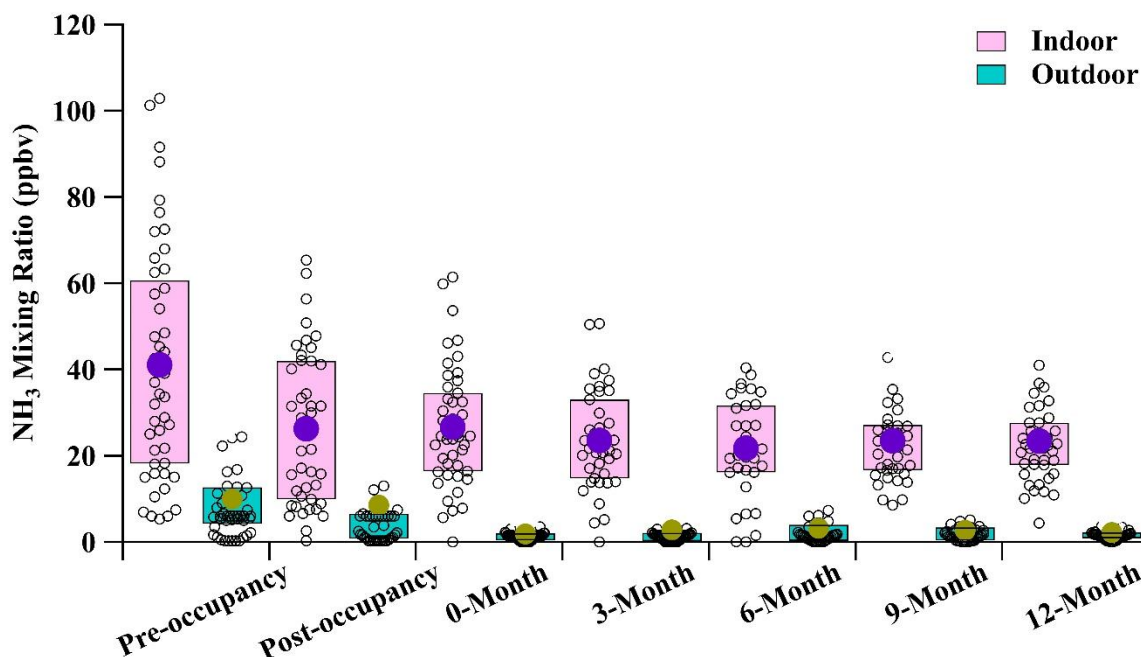


Figure 5-1: Changes in indoor and outdoor NH₃ mixing ratios (ppbv) over time in 48 newly built homes. For each sampling time point (24 h at pre- and post-occupancy, and 96 h at the 0-12 month visits), box plots show the mean (purple circles for indoor and brown for outdoor) and interquartile range (box limits), with the horizontal distribution of open circles indicating the frequency of a particular observational result.

Indoor NH₃ mixing ratios decreased from pre-occupancy to post-occupancy and then remained relatively stable through the 12-month observation period (Figure 5-1). The 0-month sampling started simultaneously with the post-occupancy visit, but extended the sampling duration from 24 to 96 h. The pre-occupancy mean ($\pm 1\sigma$) mixing ratio was 41 ± 27 ppbv ($n = 47$), decreasing to 26 ± 18 ppbv ($n = 42$) immediately after occupancy (post-occupancy). The overall average after occupancy, including post-occupancy, 0, 3, 6, 9, and 12 months, was 24 ± 2 ppbv ($n = 249$) after excluding 12 statistical outliers identified through Grubb's test. Statistical modeling using a GLMM confirmed a significant temporal effect on indoor NH₃ during pre-occupancy ($p = 0.001$; Table D-5) and at the 0-month timepoint ($p = 0.003$). Post hoc pairwise contrasts ($\alpha = 0.05$) revealed that pre-occupancy NH₃ mixing ratios were significantly different from all periods following occupancy (0, 3, 6, 9, and 12 months; all $p < 0.05$), confirming a pronounced reduction in indoor NH₃ (Figure D-2). During occupancy, NH₃ levels at 0 months were slightly higher than at the 9 and 12 month timepoints ($p < 0.05$), indicating a modest but statistically significant decrease over the occupancy period. Overall, these results demonstrate a statistically significant

decrease in indoor NH_3 from pre-occupancy to after occupancy, followed by stabilization at lower NH_3 levels by 9-12 months.

The highest NH_3 mixing ratios were observed prior to occupancy irrespective of the time of year that this activity took place, consistent with expected emissions from new building materials; however, variability likely reflects uncontrolled differences in the time between construction completion and pre-occupancy sampling. Once people moved in (post-occupancy/ 0-month), adding furnishings and increasing interior surface areas correlated with reduced NH_3 levels. This trend aligns with decreased emissions from new building materials and increased surface uptake and partitioning to indoor reservoirs (e.g., permeable and porous substrates),^{40,63} despite the addition of more human-related sources. By the 9- to 12-month period, NH_3 mixing ratios stabilized at ~ 23 ppbv, suggesting that NH_3 air-surface partitioning reached equilibrium as sources and sinks across this long time-period likely also reached a pseudo-steady state with repeated activities from occupants. The overall range of indoor NH_3 mixing ratios is consistent with previous studies in occupied residential indoor environments, which have reported levels ranging from approximately 15 to 75 ppbv.⁸³⁻⁸⁷ Most of these prior studies focused on NH_3 emissions from residential occupants, their activities, and in-home appliances during specific sampling periods. Ampollini *et al.*⁵⁰ reported a mean indoor NH_3 mixing ratio of 32 ppbv during the HOMEChem study conducted in an unoccupied test house which would have arisen from the materials therein, with levels increasing during experimental activities carried out by temporary occupants such as cooking (62 ppbv), cleaning (73 ppbv), and occupancy alone (52 ppbv). Since the surface-to-volume ratio remained unchanged, these increases in NH_3 levels are attributed mainly to activity-related emissions rather than changes in surface area. Additionally, only a few studies focus on NH_3 emissions from new building materials by controlling other indoor sources related to human occupancy.^{88,89} For example, Järnström *et al.*⁸⁸ measured NH_3 in 14 newly constructed residences along the Gulf of Finland, built with materials that had low NH_3 emissions, at 0 month (unoccupied), and at 6 and 12 months (occupied). They used closed-room sampling where windows and doors were shut and instructed residents to avoid using cleaners and fragrances, minimizing the influence of occupants on NH_3 emissions from building materials. Under these controlled conditions, NH_3 levels were approximately 60 ppbv across all three sampling periods, mainly reflecting emissions from specific new building materials with minimal impact from human activities. Our study provides a comprehensive indoor NH_3 measurement that

combines new-building material emissions with human occupancy and activities in genuine indoor environments for Canada. Pre-occupancy NH_3 levels were ~ 41 ppbv from new-material emissions and decreased to ~ 26 ppbv immediately after occupancy (post-occupancy/0-month), underscoring the effect of enhanced air-surface area upon occupancy.

Outdoor NH_3 mixing ratios, measured simultaneously with indoor samples for the same homes (Figure 5-1), decreased from pre-occupancy to 12 months and remained lower than indoor levels. The outdoor NH_3 mean ($\pm 1\sigma$) mixing ratios ranged from 1 ± 1 to 9 ± 8 ppbv (Figure 5-1). The reported outdoor NH_3 mixing ratios in previous studies in mixed rural-urban environments typically ranged from 0.5 pptv to 20 ppbv,⁹⁰⁻⁹² and the measured outdoor mixing ratios fell within these ranges, with elevated values during pre-occupancy (9 ± 8 ppbv) and immediately after occupancy (post-occupancy; 5 ± 5 ppbv). This may be due to increased outdoor sources during those times or indoor emissions influencing the results due to the proximity of samplers and potential building materials sources also be present on exterior surfaces (e.g. exposed concrete). Since indoor and outdoor NH_3 levels declined similarly over time, Pearson correlations (r) were calculated between paired indoor-outdoor measurements at each visit to see if outdoor levels were impacted by nearby new home emissions. This, along with the large I/O ratios (Figure 5-2), is indicative of substantial indoor-to-outdoor fluxes of NH_3 to the ambient atmosphere, which has been observed for a broad range of VOCs given high indoor concentrations, including in unoccupied homes.⁹³ The correlations (Table D-6) showed a positive relationship at pre-occupancy that was nearly significant ($r = 0.284$, $p = 0.053$) and a modest yet statistically significant correlation at 3 months ($r = 0.388$, $p = 0.013$). At all other sampling timepoints, correlations were small and not statistically significant. Therefore, this suggests that during pre-occupancy, material emissions from new homes influenced outdoor NH_3 levels near the home in a measurable way, but this was not the case post-occupancy.

The indoor-to-outdoor ratio is presented on a logarithmic scale, $\log_{10}(\text{I/O})$, to evaluate the dominance of indoor NH_3 sources during the first year of occupancy (Figure 5-2). This captures a wide range of I/O values influenced by very low outdoor mixing ratios: $\log_{10}(\text{I/O}) < 0$ corresponds to an $\text{I/O} < 1$ which indicates outdoor source dominance on indoor mixing ratios, while values greater than these thresholds indicate indoor source dominance. Only nine timepoints had $\log_{10}(\text{I/O}) < 0$, occurring pre-occupancy ($n = 3$), post-occupancy ($n = 4$), at 3 months ($n = 1$), and 6 months ($n = 1$); the remaining observations at other timepoints were all above zero ($n = 287$). The

potential correlation between indoor and outdoor NH_3 mixing ratios during pre-occupancy was examined by separating these data and presenting them as a separate stacked distribution above the after-occupancy data in the histogram (Figure 5-2). This approach shows that including pre-occupancy data does not change the overall interpretation of the I/O frequency distribution. When outdoor NH_3 levels are very low, the frequency distribution in Figure 5-2 is right-skewed, with a mode near one ($\text{I/O} \approx 10$), most values falling between 0 and 2 ($\text{I/O} \approx 1\text{--}100$), and a long tail extending to nearly 3–4 ($\text{I/O} \approx 10^3\text{--}10^4$) for some observations. Therefore, $\log_{10}(\text{I/O})$ was used to better represent indoor-to-outdoor NH_3 ratios by reducing skewness and making the distribution easier to visualize across several orders of magnitude. Overall, the histogram strongly suggests that indoor sources drive indoor NH_3 levels during the first year of occupancy, and likely at all times beyond, which aligns with previous studies showing that indoor NH_3 levels are often ten times or more higher than outdoor levels.^{23,84,94–96}

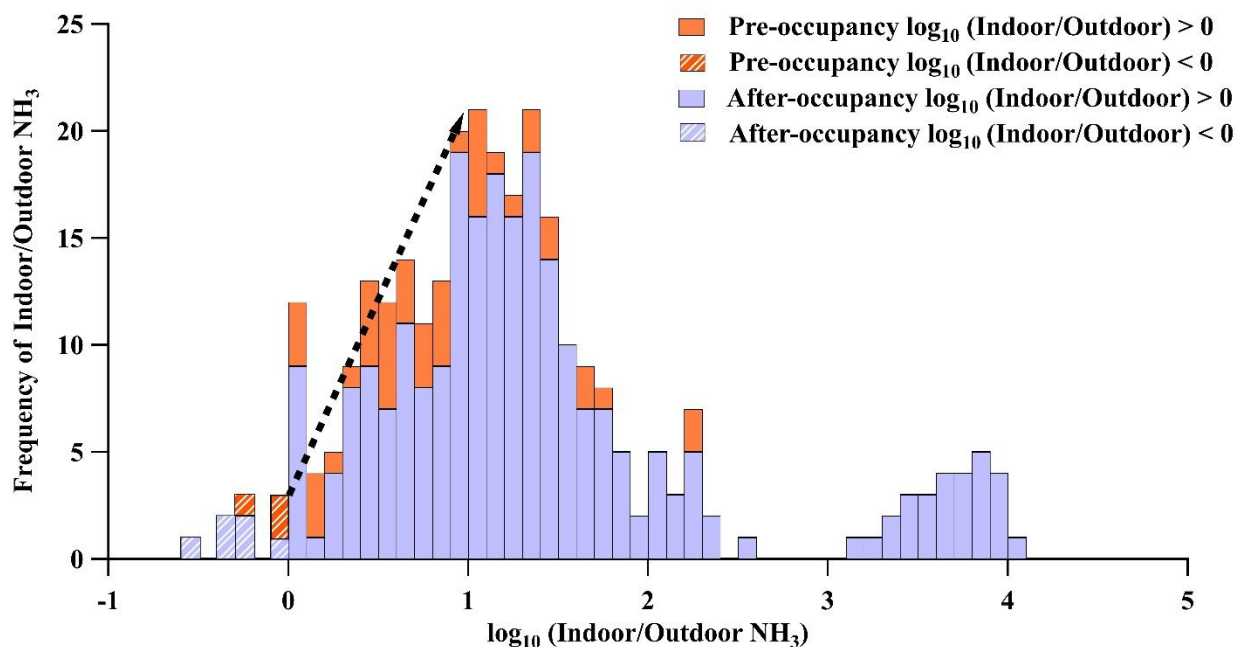


Figure 5-2: $\log_{10}$ Indoor-to-outdoor (I/O) ratio of NH_3 mixing ratios in 48 homes from pre-occupancy through 12 months. The histogram is separated into pre-occupancy and after-occupancy periods (post-occupancy, 0-, 3-, 6-, 9-, and 12-month) and displayed as stacked distributions. Values where $\log_{10}(\text{I/O}) < 0$ ($\text{I/O} < 1$) indicate outdoor-dominated conditions, while values where $\log_{10}(\text{I/O}) > 0$ ($\text{I/O} > 1$) indicate indoor-dominated conditions. The arrow shows a shift from outdoor- to one of two groups of indoor-dominated conditions.

Indoor NH₃ levels decreased from pre- to post-occupancy and then remained relatively stable over the next 12 months, consistent with predominantly indoor sources. Temperature can enhance NH₃ volatilization through increased vapor pressure and desorption, while relative humidity influences water-mediated air–surface partitioning. The following section examines how these key environmental factors impact the observed indoor NH₃ patterns, clarifying their influence on indoor NH₃ emissions and resulting concentrations.

5.3.2 Seasonal variation, temperature, and relative humidity impacts on indoor NH₃

Indoor NH₃ mixing ratios were classified into monthly intervals from pre-occupancy to 12 months post-occupancy to examine temporal trends and potential seasonal effects (Figure 5-3). Simultaneous measurements of indoor temperature (T, °C) and indoor relative humidity (RH, %) were collected to determine whether variations in indoor climate were associated with changes in indoor NH₃ levels (Section 5.2.1).

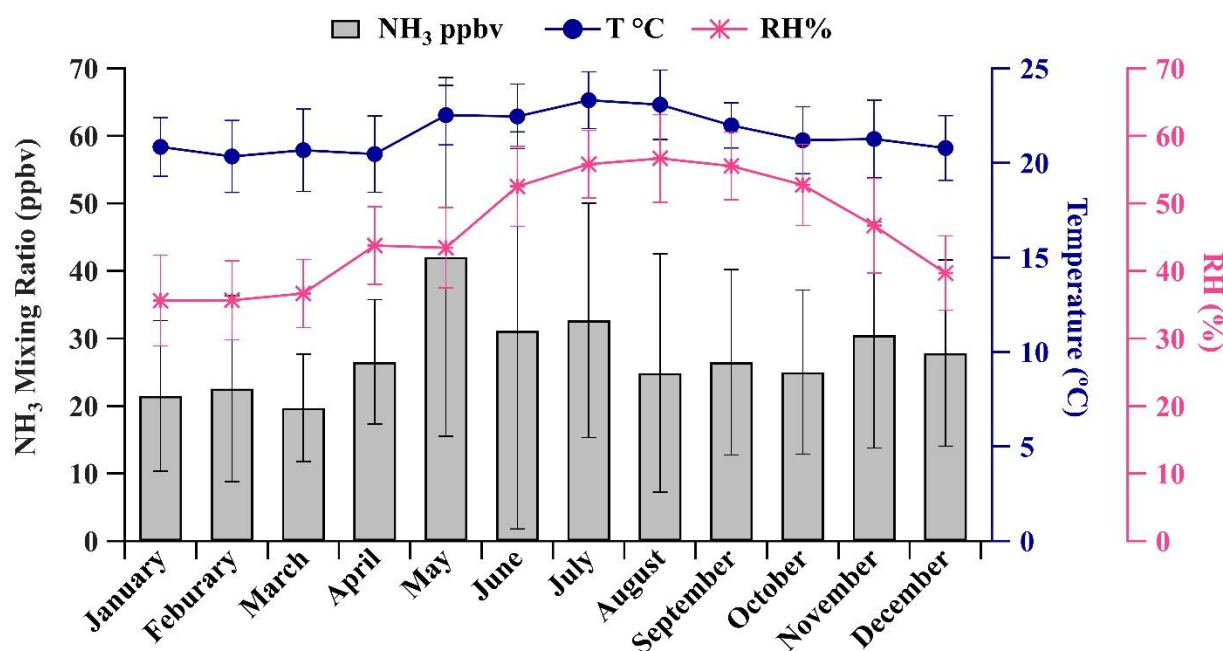


Figure 5-3: Monthly variation in average indoor NH₃ mixing ratios (ppbv), temperature (T, °C), and relative humidity (RH, %) in 48 newly built homes during the first year of occupancy.

During the warm season (May to September), indoor NH₃ mixing ratios averaged 31 ± 7 ppbv, with a notable peak in May (42 ± 27 ppbv) under high temperatures (23 ± 2 °C) and relatively low RH ($43 \pm 6\%$; Figure 5-3). In such hot and dry conditions, NH₄⁺ favors desorption and

volatilization from indoor surfaces, leading to higher gas-phase NH_3 indoors.⁵⁰ Despite similar or even higher temperatures from June through September ($22 \pm 1^\circ\text{C}$ to $23 \pm 2^\circ\text{C}$), NH_3 levels decreased to 31 ± 29 ppbv (-26%) in June, 33 ± 17 ppbv (-22%) in July, 25 ± 18 ppbv (-41%) in August, and 26 ± 14 ppbv (-37%) in September compared to May. Concurrently, indoor RH increased ($53 \pm 6\%$ to $57 \pm 7\%$). This inverse relationship suggests that rising RH offsets temperature-driven NH_3 volatilization by providing surface water for NH_3 uptake on to surfaces, resulting in lower indoor NH_3 levels during these warm months. This result aligns with Nazaroff and Weschler,²³ who showed that indoor T and RH affect water vapor levels that govern gas-surface partitioning. Higher T promotes volatilization, while higher RH thickens surface aqueous films, which increases the uptake and reaction of water-soluble gases, shifting partitioning toward surfaces and reducing the gas-phase concentrations. These findings also agree with the linear regression analysis (Table D-7), which shows that temperature was positively associated with indoor NH_3 , particularly in July ($r = 0.452$, $p = 0.027$). Generally, higher RH reduces this temperature dependency; in June, RH showed the strongest positive correlation with NH_3 ($r = 0.631$, $p = 0.016$). Despite a positive within-month correlation in June, higher RH was associated with lower NH_3 mixing ratios, consistent with increased water film-driven partitioning to surfaces predicted by Wang *et al.*⁹⁷ During the cold season (October-April) T and RH both decreased indoors and NH_3 levels expectedly decreased (mean 25 ± 4 ppbv), as the surface equilibria reversed in response. March recorded the lowest NH_3 levels (20 ± 8 ppbv) under relatively low T ($21 \pm 2^\circ\text{C}$) and RH ($37 \pm 5\%$). These results agree with a study of indoor NH_3 in 19 indoor spaces in Beijing conducted in 2011 and 2018, which identified seasonal patterns with higher levels (65-134 ppbv) during warm months (May-September) associated with higher T and RH, and lower levels (23-50 ppbv) in cold months (October-April) linked with lower T and RH.⁹⁸ In the Finnish indoor air quality study by Järnström *et al.*⁸⁸ the results showed NH_3 levels (mean 60 ppbv) followed a seasonal pattern, being higher in summer (ranging from 86 to 129 ppbv under RH >50%) and lower in winter (29 to 71 ppbv with RH <40%) across their 14 new residences.

The Van't Hoff equation (E5-2) was used to estimate the apparent vaporization enthalpy from the temperature dependence of NH_3 .⁹⁹

$$\ln(\text{NH}_3) = \left(-\frac{\Delta H}{R}\right)\left(\frac{1}{T}\right) + C \quad (\text{E5-2})$$

The apparent vaporization enthalpy (ΔH) values were derived from the slope of linear regressions of $\ln(\text{NH}_3)$ versus $1/T$ (slope = $-\Delta H/R$; Figure D-3). During the cold season, $\ln(\text{NH}_3)$ decreased

with increasing $1/T$, yielding a positive ΔH ($+34 \text{ kJ mol}^{-1}$), consistent with temperature-driven volatilization from indoor surfaces. In contrast, the warm season showed the opposite pattern ($\Delta H = -19 \text{ kJ mol}^{-1}$), indicating that NH_3 variability was not governed only by temperature. This suggests that non-thermodynamic processes, such as increased air exchange rates and ventilation, dominate under warm conditions.

Seasonal variations in indoor NH_3 mixing ratios, driven by changes in T and RH , highlight the dynamic behavior of NH_3 in indoor environments. These patterns emphasize the importance of understanding environmental factors that affect NH_3 trends in the gas phase. To expand on these findings, the next section examines indoor NH_3 sources and sinks in relation to observed changes in NH_3 levels during the first year of occupancy.

5.3.3 Source attribution of indoor NH_3 using a generalized linear mixed model

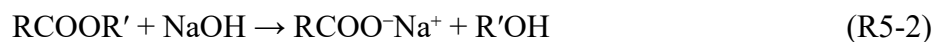
The GLMM (Section D2) was used to determine which predictors are associated with indoor NH_3 emissions to identify potential indoor sources and sinks (Tables D-3–D-5). Three predictors showed significant positive associations with higher indoor NH_3 levels: time points, use of glass cleaners, and the number of people who spend more than eighteen hours indoors (Table D-5). The relationship with time points was discussed in the previous section. Interpreting the modeled associations in terms of source and sink processes, glass cleaner use and the extended indoor presence of people were identified as potential indoor NH_3 source points. In contrast, different cleaners, including disinfectant, tub, toilet, multi-surface, metals, oven, and bleach, showed negative correlations with indoor NH_3 mixing ratios (Table D-5). However, only the use of oven cleaners was identified as a potentially substantive sink point and indicated a near-significant negative association with indoor NH_3 emissions ($\beta = -0.449$, $p = 0.084$).

The use of glass cleaner within the residence was positively correlated with elevated levels of NH_3 ($\beta = 0.233$, $p = 0.014$). It contributed to an approximate 8 ppbv increase in the indoor NH_3 mixing ratio relative to non-users (Section D-2: ED-2). Glass cleaner use was seen in 25% of sampling periods (Table D-4), and ammonia-based glass cleaners are common and popular household products. They contain ammonium hydroxide, which releases NH_3 during and after use, elevating indoor NH_3 levels proportionally to the frequency of their use and the extent to which ventilation measures are used during the cleaning process.^{100–102} In the study by Fedoruk *et al.*¹⁰³ cleaning a mirror with an ammonium hydroxide glass cleaner resulted in a peak NH_3 level of about

2.8 ppm, and spray-on window cleaners produced around 0.65 ppm, providing direct evidence of NH₃ emissions from glass-cleaning activities.

The number of people spending at least 18 hours per day indoors was positively correlated with indoor NH₃ mixing ratios; each additional individual was associated with approximately a 2 ppbv increase in NH₃ levels ($\beta = 0.055$ per individual, $p = 0.004$; Section D2: ED-2). On average, 2 ± 2 individuals per home spent ≥ 18 hours per day (Table D-3). Conversely, neither (i) the total number of residents, irrespective of the duration spent at home (merely headcount), nor (ii) the number of residents spending at least 6 hours per day at home showed significant associations with NH₃ levels (all $p > 0.05$). This pattern suggests that humans are a significant source of indoor NH₃ when they reside with an extended presence (≥ 18 hours per day) rather than mere occupancy with shorter durations. These findings are consistent with prior chamber experiments indicating that humans are a direct source of NH₃ emissions.¹⁷ However, the drivers within these homes do not have sufficient time resolution and controls to comment further on the observed trend.

The use of oven cleaners was negatively correlated with indoor NH₃ mixing ratios ($\beta = -0.449$, $p = 0.084$), resulting in an approximate reduction of 11 ppbv NH₃ (Section D2: ED-2). Oven cleaner use was reported in only 10 out of 246 sampling periods (4%; Table D-4). Therefore, this association should be interpreted with caution due to the low prevalence of use and the potential impact of the small number of observations. Oven cleaner use was recorded as a binary (yes/no) variable and may reflect broader cleaning activities involving wetting and rinsing that enhance NH₃ removal; however, this cannot be directly confirmed. Oven cleaners typically contain sodium hydroxide (NaOH), a strong base with a pH of ~ 13 . It saponifies triglyceride fats (R5-2), producing sodium fatty acid salts (soap) and glycerol.¹⁰⁴



Although direct partitioning of NH₃ onto a basic surface is unlikely, subsequent water cleaning and rinsing of oven cleaner increase surface wetness and can promote NH₃ loss by uptake to surfaces as NH₄⁺, often accompanied by increased ventilation. In practice, oven cleaning usually occurs alongside cleaning multiple surfaces, where additional wetting and rinsing further promote NH₃ removal. This aligns with the mostly negative correlations observed between NH₃ and various cleaners, such as disinfectant, tub, toilet, multi-surface, metals, and bleach products (Table D-5), implying that broader surface-cleaning activities may also facilitate NH₃ loss. The HOMEChem study showed rapid NH₃ reductions when surfaces were cleaned with vinegar (acetic acid),⁵⁰ and

another indoor study reported bleach washroom experiments in which sinks and bathtubs were scrubbed with water-dampened brushes and then rinsed with tap water after using bleach cleaner.¹⁰² Therefore, these findings suggest that common cleaning activities, such as acidic cleaning, rinsing, and frequent wetting of surfaces, promote indoor NH_3 surface uptake and influence acid–base surface chemistry, leading NH_3 to form stable NH_4^+ compounds on surfaces that act as indoor sinks. Additionally, ventilation further enhances NH_3 removal.

Identifying indoor NH_3 sources and sinks is essential for understanding the complex pathways that influence its behavior in indoor environments. Therefore, further analysis of additional reduced-N species was conducted in selected case studies to better understand these indoor reaction pathways.

5.3.4 Case studies on reduced-N species in the indoor environment

Five randomly selected homes with a complete indoor NH_3 mixing ratio timeseries at the four time points of pre-occupancy, 3, 9, and 12 months were analyzed by LC-QTOF-MS/MS ion quantification. This was used to identify and assign structures consistent with the presence of additional reduced-nitrogen species, including NR_3 , amides, imines, enamines, N-ring, and N-azoles that cannot be detected by IC-CD or would be below its detection limits. In all, the results revealed a diverse group of reduced nitrogen-containing organics with a range of molecular functionalities, including large relative amounts of amides and heterocyclic reduced nitrogen species (incl. azoles), as well as some amines. Here, we used the relative abundance of the ion signals from all detected reduced-N ions in a sample that passed QC/QA to assess the qualitative temporal trends in relative gas-phase composition, as well as the potential for surface indoor chemical reactions of NH_3 and NR_3 as loss pathways (Figure 5-4). Two homes (denoted as Homes A and B henceforth) were examined in greater detail (Figure 5-5).

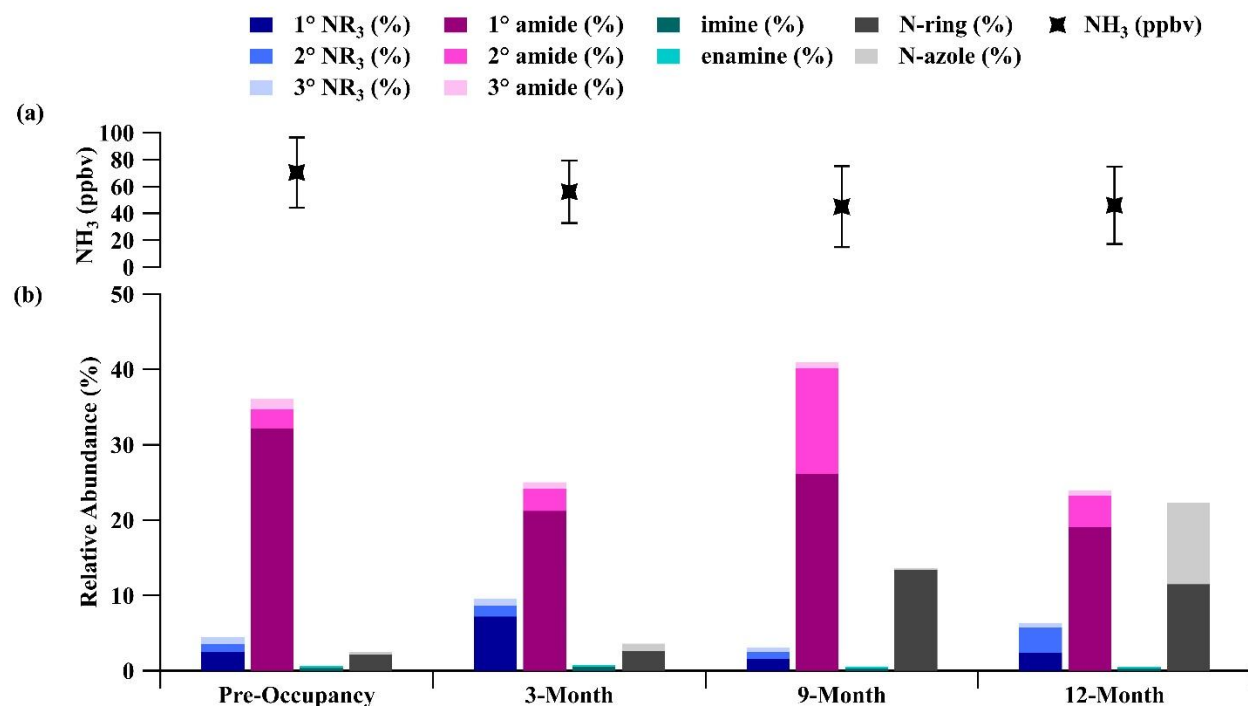


Figure 5-4: The mean (a) indoor NH_3 mixing ratio (ppbv), and (b) relative abundances (%) of reduced-N species, including NR_3 (1°, 2°, and 3°), amides (1°, 2°, and 3°), imines, enamines, N-rings, and N-azoles, across five homes at four time points (pre-occupancy, 3, 9, and 12 months).

Before occupancy, indoor NH_3 mixing ratios peaked at 70 ± 26 ppbv, while the average relative abundance of reduced-N species was low ($<5\%$), except for amides, which are likely emitted from new building materials such as wall paint (Figure 5-4).¹⁰⁵ After move-in, the significant increase in available surface area from items such as furniture, textiles, and belongings shifts the system from a gas-phase, NH_3 -dominated, regime to a surface-mediated one, as the increased surface area would also increase the absolute abundance of water film. By 3 months, we observed NH_3 declining to 56 ± 23 ppbv as it partitioned into surface water or adsorbed onto materials throughout homes in this study. Simultaneously, the relative ion abundances of amides decreased by a factor of ~ 1.5 , while heterocyclic N-ring compounds increased by nearly the same factor, suggesting potential acid–base partitioning and surface condensation pathways, emissions from other sources/activities during occupancy, or intrusion from outdoor air. On indoor water films, primary (1°) and secondary (2°) NR_3 can react with carbonyls (aldehydes/ketones) to form imines (R5-3; Schiff base) and enamines (R5-4), respectively.⁵⁹





Since indoor surfaces have lower water abundance compared to bulk water, an equilibrium within the surface film shifts toward the products (R3/R4) that may partially volatilize, with the fraction remaining able to undergo further reactions. This is followed by condensation, which can form secondary amides and promote intramolecular cyclization to N-heterocycles (e.g., N-rings such as pyrroles and N-azoles like imidazoles).^{60,61} Meanwhile, NH₃ and NR₃ (1° and 2°) can react with carboxylic acids, forming amides (1°, 2°, and 3°). However, the observed decrease in both NH₃ mixing ratio and amide relative ion abundance suggests that cyclization and/or loss predominated over amide accumulation, although our extraction methodology has not been validated to minimize amide losses during sample preparation. By 9 months, NH₃ (45 ± 30 ppbv) and NR₃ decreased, while amides and N-heterocycles increased relative to their 3-month levels. The elevated amide relative ion abundance likely reflects additional indoor sources (e.g., cooking),^{20,106} whereas the observed growth in N-ring and N-azole relative ion abundances suggests ongoing surface cyclization of imine/enamine intermediates. At 12 months, we observed that NH₃ has a relatively stable mixing ratio indoors at 46 ± 29 ppbv, but that N-azoles and N-rings show consistent slow, cumulative surface presence potentially reflecting chemistry of larger molecular weight and less volatile products that intensify as indoor surfaces are constantly exposed to elevated indoor NH₃ after occupancy. Overall, these temporal patterns of reduced-N species in the gas-phase suggest that there may be an important role of surface-mediated reactions originating from NH₃ and NR₃ that participate in defining the N-speciation on indoor surfaces and the fate of NH₃ and NR₃ following occupancy. The fate or impacts of these processes should be the subject of future investigation but is beyond the scope of this work. Such further work, could also leverage high resolution mass spectrometry measurements of surface extracts to determine the composition of condensed phase species for comparison.^{107,108}

The dynamics of these species across the measured homes will expectedly vary across the range of observed molecular functionalities with home conditions. Two homes were selected as case studies due to their contrasting indoor NH₃ mixing ratio trends (Figure 5-5). Home A initially had the highest pre-occupancy NH₃ levels at 103 ± 10 ppbv, which decreased to 21 ± 1 ppbv after 12 months, while Home B started with the lowest NH₃ levels at 21 ± 1 ppbv and increased to 101 ± 6 ppbv over the same period. They were sampled during similar seasons within the same region, making seasonal or outdoor sources unlikely drivers of the observed NH₃ trends. These opposite

NH₃ patterns were assessed to explore potential links with surface-mediated transformations of reduced-N species. The diagnostic ratio of ion counts for reduced-N species was analyzed to highlight potential surface-mediated pathways: NR₃ and carbonyl condensation to imines/enamines, followed by their conversion to amides and N-heteroaromatics (N-ring and N-azole), and linking these pathways to the temporal trends of indoor NH₃ as potential loss processes (Figure 5-5). Log₁₀ ion-count ratios of reduced-N species were used to compare qualitative QTOF-MS/MS signals across several orders of magnitude. This method highlights relative enrichment or depletion across the observed mix of gas-phase species, and specific molecular functionality pairs to explore potential chemical pathways (e.g., amide/NH₃).

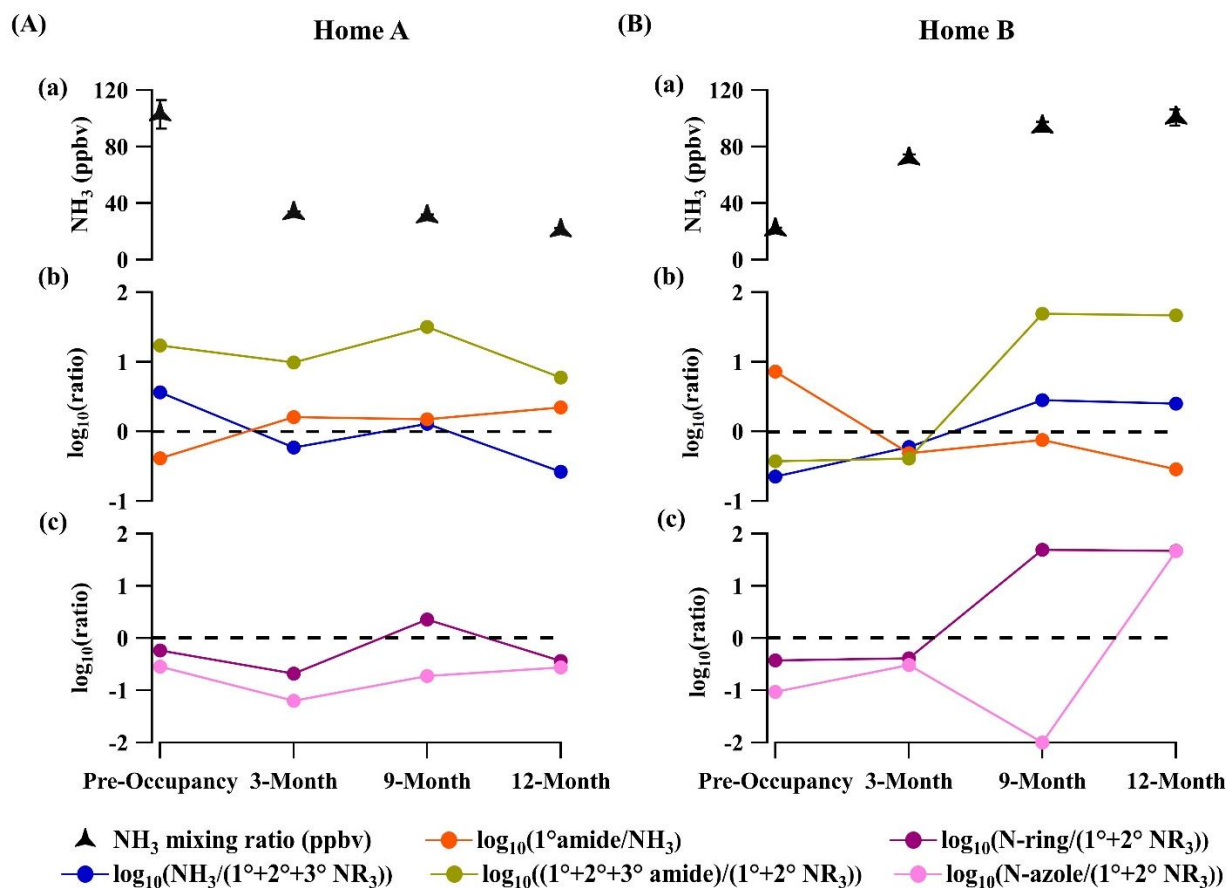


Figure 5-5: Temporal variation in indoor NH₃ mixing ratio (ppbv) and log₁₀ ion-count ratios of reduced-N species at four time points (pre-occupancy, 3, 9, 12 months) for (A) Home A and (B) Home B. Panels: (a) NH₃ mixing ratio (ppbv); (b) log₁₀ ratios: NH₃/(1°+2°+3° NR₃), 1° amide/NH₃, and (1°+2°+3° amides)/(1°+2° NR₃); and (c) log₁₀ ratios: N-ring/(1°+2° NR₃), and N-azole/(1°+2° NR₃). To enable comparison between NH₃ mixing ratio and reduced-N ion counts, all values were normalized for each house and species relative to the mean from that same house across the four time points.

In Home A, NH_3 mixing ratios decreased over time (Figure 5-5Aa), and $\log_{10}(\text{NH}_3/\Sigma \text{NR}_3)$ declined accordingly (Figure 5-5Ab). The decrease in NH_3 coincided with an increase in the $\log_{10}$ ratio of 1° amide/ NH_3 (Figure 5-5Ab), consistent with a strengthening of the shift from NH_3 to amide products. The ratio of amide to NR_3 decreased over time (Figure 5-5Ab), indicating an increase in NR_3 relative to amides. N-heterocycle formation (Figure 5-5Ac) appeared intermittently, suggesting a net shift toward NR_3 -influenced conditions. However, we note that at 9 months a decrease in ΣNR_3 caused transient increases in its ratios ($\text{NH}_3/\Sigma \text{NR}_3$, $(1^\circ+2^\circ+3^\circ \text{ amides})/(1^\circ+2^\circ \text{ NR}_3)$, and $\text{N-ring}/(1^\circ+2^\circ \text{ NR}_3)$).

In Home B, NH_3 mixing ratios increased from pre-occupancy to 12 months (Figure 5-5Ba). The $\log_{10}(\text{NH}_3/\Sigma \text{NR}_3)$ also rose over this period, indicating an NH_3 -dominated state (Figure 5-5Bb). Meanwhile, the ratio of 1° amide to NH_3 decreased, implying limited conversion of NH_3 into amide (Figure 5-5Bb), whereas the $(1^\circ+2^\circ+3^\circ \text{ amides})/(1^\circ+2^\circ \text{ NR}_3)$ ratio increased, suggesting conversion of amines to amides (Figure 5-5Bb). By 12 months, the ratios of N-ring and N-azole increased sharply, indicating surface cyclization (Fig. 5-5Cd) and possibly also impacts from direct cooking emissions (Figure D-4b).^{20,51,109} Overall, these results suggest that NH_3 remained relatively enhanced compared to NR_3 , with evidence for NR_3 conversion to amide and only intermittent conversion of NR_3 to N-heterocyclics rather than a sustained surface sink.

Reduced-N levels are specific to each household, driven by differences in sources, surface chemistry, indoor conditions and the relative dominance of pathways such as NR_3 -carbonyl condensation, amide formation, and N-heteroaromatic formation. Source points, such as cooking, supply precursors, affect pathway choice, such that we would expect reaction pathways within a given home to lead to unique abundance patterns. Overall, these observations highlight valuable new areas for future research on indoor air, and the study of chemical processes influencing the reactions and products of reduced nitrogen compounds in the gas and condensed phase in occupied homes.

5.3.5 Implications and future opportunities

Indoor NH_3 mixing ratios decreased from a pre-occupancy average of 41 ± 27 ppbv to 26 ± 18 ppbv post-occupancy, then remained relatively stable at 24 ± 2 ppbv over 12 months. Elevated pre-occupancy NH_3 aligns with expected emissions from new building materials; the subsequent

decline post-occupancy likely results from increased partitioning to an expanded indoor surface area after move-in, despite or alongside occupant activities increasing from new sources, or decreasing from sinks, respectively. Standardizing the interval between construction completion and pre-occupancy sampling would reduce variability associated with building material emissions in future studies. Outdoor NH_3 levels were significantly lower during the same period, ranging from 1 ± 1 to 9 ± 8 ppbv, and indoor-to-outdoor NH_3 ratios were mainly greater than one, indicating that indoor sources primarily drive indoor NH_3 levels during the first year of occupancy. Indoor NH_3 levels are higher during warmer months mainly due to temperature effects on volatilization/desorption from surfaces, despite concurrent increased RH. During these months, lower RH was associated with higher NH_3 levels, while higher RH reduced them by promoting surface partitioning. In contrast, colder seasons with lower T and RH showed overall lower NH_3 levels. The GLMM results show that indoor NH_3 mixing ratios are higher during pre-occupancy and early occupancy, then decrease to lower, stable levels by 9–12 months. The use of glass cleaners and resident presence ≥ 18 h day⁻¹ were significant positive predictors of NH_3 , indicating potential source points. In contrast, oven cleaner use was a nearly significant negative predictor, suggesting the product and associated human activities as a possible sink for NH_3 . Future work would benefit from more detailed, survey-based characterization of cleaning practices, including product types, frequency, timing, and co-occurring activities, to better understand the mechanisms underlying these associations. The temporal evolution of reduced-N species from pre-occupancy through the first year suggests an important role for surface-mediated reactions in determining indoor N-speciation and the fate of NH_3 and NR_3 after occupancy. Case studies further show that household-specific surface chemistry, driven by pathways like NR_3 –carbonyl condensation, amide formation, and N-heteroaromatic formation, influences observed patterns. These findings can help occupants identify and reduce controllable NH_3 sources to improve indoor air quality. They also highlight promising avenues for future research on indoor chemical processes that influence the reactions and products of reduced-nitrogen compounds in both gas and condensed phases. Extended passive sampler deployment could enhance detection and characterization of low-abundance reduced-N species, providing improved insight into the broader suite of indoor reduced-N compounds. Although the GLMM provides a robust framework for initial exploration of NH_3 drivers, future work could apply process-based indoor chemistry models to better represent emissions, deposition, and surface-mediated reactions.

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CHAPTER SIX – Conclusions and future directions

Author Contributions:

Leyla Salehpoor prepared the contents of this chapter, and Trevor C. VandenBoer provided editorial comments.

6.1 Conclusions

The primary goal of this thesis was to conduct a quantitative analysis of reduced nitrogen processing in marine aerosols during fog events and in the indoor air of new Canadian homes during the first year of occupancy. By integrating analytical method development, field observations, multiphase chemical analysis, and statistical modeling, this work advances understanding of how reduced nitrogen contributes to secondary aerosol formation and growth, fog-driven aqueous-phase chemistry, and surface-mediated chemical processes in indoor environments.

To achieve this, a robust ion chromatographic method was developed for the separation and quantification of NH_3 and the ten most abundant atmospheric NR_3 with high selectivity and separation efficiency (Chapter 2). The optimized IC method uses 4 μm packed columns and resin-based suppressors, alongside stabilizing NR_3 standards. Modern resin suppressors operating on a gradient elution program affected the linear response of this IC technique. Calibration statistical analyses found a loss of analytes in these cation-exchange devices. Suppressor operational longevity was optimized by using a stepped current and an external water supply, which improved precision, accuracy, and LODs compared to other suppression modes. When this new method was applied to real samples, amines were found ubiquitously in size-resolved marine aerosol samples; monpropylamine, isomonpropylamine, and monobutylamine were detected and quantified in these samples, which have not been reported before. The molar ratio of the sum of aminium to ammonium ranged from 0.02 to 0.2, showcasing the application of the developed method towards studying the diversity and importance of NR_3 in coastal marine particle composition. The new analytical method also found NH_3 present in a suite of new homes with a mean mixing ratio of 25 ± 15 ppbv; a common level reached between homes across the study during the first year of occupation which can then be transported outdoors.

Building on this analytical framework, the microphysical chemistry of fog-aerosol interactions over the Northwest Atlantic Ocean during Fatima 2022 was quantitatively assessed (Chapter 3). A comprehensive study of aerosol chemistry, microphysics, physical processing, and meteorological parameters was conducted to investigate fog-aerosol interactions over the Northwest Atlantic Ocean during the fog and turbulence interactions in the marine atmosphere (Fatima) 2022. Chemical analysis of size-resolved aerosols and fog droplets revealed a reduction in coarse mode sea salt ions (e.g., Cl^- , Na^+ , Mg^{2+} , ss-SO_4^{2-} , K^+ , and NO_3^-) compared to ambient

conditions, attributed to their growth into fog droplets. In contrast, fine mode aerosol processed-S and reduced-N increased during fog events. Three distinct fog types were identified based on size-resolved ion mass distributions, combined with particle number concentrations and meteorological parameters, to provide insight into the drivers of aerosol chemical composition during each chemically distinct fog type. Type I fog was the most common, characterized by depleted coarse mode sea salt aerosols, with fog droplets initially formed from freshly emitted coarse mode aerosols and most likely sustained by growth of fine mode aerosols. Type II fog was least common, sustained by ongoing production of coarse mode sea salt aerosols due to elevated winds, and supplemented by fine mode aerosol contributions. Type III fog had highest mass loadings of sea salt ions at fog droplet sizes, with droplet formation primarily driven by coarse mode growth with minor contributions from fine mode aerosol. Reduction of coarse sea salt mass loadings during more than a dozen fog events confirms their expected role as effective fog condensation nuclei and the physical impact of fog processing in reducing their atmospheric mass loading. This dataset shows these aerosols are scavenged (~70%) in a supersaturated atmosphere to form droplets. This is the most extensive marine fog dataset to date to study fog-aerosol interactions from a chemical perspective, with the potential to improve marine fog forecasting models to provide safer marine transportation.

Beyond physical processing, the chemical processing of fine mode aerosols by marine fog over the Northwest Atlantic Ocean during Fatima 2022 was quantitatively evaluated (Chapter four). Marine fog functioned as an efficient multiphase chemical reactor, enhancing secondary aerosol formation within the MBL. Fine mode aerosols exhibited increased equivalent ionic loadings of processed-S and reduced-N during fog events, whereas fog water displayed lower ionic loadings due to dilution relative to the more concentrated fine mode particles. Elevated aerosol LWC was identified as the primary driver of enhanced aqueous-phase oxidation of SO₂, uptake of MSA and HPMTF, and partitioning of reduced-N. Using surface Chl-a concentrations as a proxy for marine biological sources of processed-S and reduced-N, an 8-day lag was observed between Chl-a and the equivalent ionic loadings of these species. This lag reflects the timescales required for the biochemical transformation of marine biological activity into aerosol-phase composition. The statistically significant association between 8-day lagged Chl-a and processed-S under fog conditions and the near-significant relationship with reduced-N suggests that fog conditions strengthen the coupling between marine biogenic precursor emissions and aerosol chemical

composition by promoting multiphase chemical processing of sulfur precursors and enhanced formation of processed-S species, which consequently facilitates the partitioning and accumulation of reduced-N species in the aerosol phase. Elevated estimated aerosol pH (EAIM IV), together with the highest relative ionic abundance of organic acids in fine mode aerosols, suggests intensified acid–base neutralization within fog-processed aerosols. Collectively, these findings demonstrate that marine fog represents a critical interface linking marine biological processing, atmospheric transformation, and secondary aerosol formation.

Extending the quantitative investigation to indoor environments, the controlling factors governing indoor ammonia in newly constructed Canadian homes during the first year of occupancy were systematically evaluated, including reduced nitrogen case studies (Chapter 5). Ammonia influences indoor air and surface chemistry. Its temporal dynamics and sources during early occupancy of new homes is not well characterized. As part of the New Home Air Quality Study (NHAQS), temporal changes in indoor reduced nitrogen, especially NH_3 , from pre-occupancy through 12 months was quantified in 48 new homes with non-smoking residents in the Ottawa-Gatineau area from 2019-2024. Passive samplers collected target analytes quantified by ion chromatography and liquid chromatography with mass spectrometry. Indoor NH_3 mixing ratios decreased from pre- to post-occupancy and remained relatively stable over 12 months following, consistent with reduced emissions from new materials and increased partitioning surface area upon occupancy. The NH_3 indoor-to-outdoor ratio indicated indoor sources dominated. Indoor NH_3 levels were higher in warmer months, likely due to temperature-driven repartitioning. A generalized linear mixed model identified glass cleaners and resident presence $\geq 18 \text{ h day}^{-1}$ as significant positive predictors of elevated NH_3 , while oven cleaner use decreased it. A case study found reduced nitrogen fate depends on surface chemistry, with potential pathways like carbonyl condensation, and amide and N-heteroaromatic formation shaping household-specific patterns. This work provides new insight on how homeowners may recognize and reduce NH_3 sources to improve indoor air quality.

Overall, this thesis shows that the processing of reduced nitrogen in marine aerosols and indoor air is primarily governed by sources, multiphase chemistry, liquid water availability, and sink mechanisms in both environments. These results emphasize the need for quantitative analysis of reduced nitrogen across diverse environments to better understand its role in secondary aerosol formation and growth, acid–base chemistry, atmospheric transformation, climate impact, and air

quality. Climate warming is expected to influence fog occurrence and persistence through coupled changes in air–sea temperature gradients, atmospheric water vapour, marine biological activity (e.g., the phytoplankton lifecycle supplying aerosol precursors), and large-scale ocean circulation (e.g., thermohaline circulation). Observations from the northwest Atlantic Ocean suggest that these changes can modify fog-aerosol interactions and reduced-N processing. Enhanced responses are anticipated in regions with emerging anthropogenic influence, particularly increased human shipping activity associated with remote Arctic mines accessible only by sea, where evolving emissions and atmospheric conditions may further influence fog formation and multiphase chemistry.

6.2 Future directions

This thesis identifies several key avenues for advancing the quantitative analysis of reduced-N processing in marine aerosols and indoor air. A critical next step is to further improve quantitative analytical methods for alkylamine analysis. Although the optimized ion chromatographic approach improved separation efficiency and selectivity, as well as method precision, accuracy, and detection limits, suppressor-induced analyte loss remains an important limitation. Future work should focus on developing improved suppression strategies or alternative detection methods that minimize analyte loss and improve calibration robustness. Strengthening analytical reliability is essential for more accurate analysis of alkylamine contributions to reduced-N processing in both aerosol and gas phases.

This thesis combines aerosol chemistry with microphysics, physical processes, and meteorological parameters to better understand fog–aerosol interactions across pre-fog, fog, and post-fog periods. By linking size-resolved aerosol chemical composition to aerosol microphysical properties, the results provide insights that can be incorporated into predictive models that previously focused only on microphysics, such as large eddy simulations which will be a component of our future work. We expect that these will enhance marine fog and visibility predictions and improve the current low fog-forecast accuracy for marine navigation in high-occurrence regions, such as Canada’s Grand Banks and Sable Island areas.

Finally, the indoor component of this work highlights the need for further research into the chemical processes governing the reactions and products of reduced-N compounds in the gas and condensed phases of occupied homes. Future research should especially examine gas–surface

interactions and heterogeneous reactions, influenced by factors such as surface material composition, porosity, and sorptive capacity. Investigating how building materials, coatings, furnishings, and porous substrates influence the uptake, retention, and transformation of reduced nitrogen will enhance our understanding of indoor air chemistry and reduce indoor exposure. This effort would be strengthened by standardizing the interval between construction completion and pre-occupancy sampling to better constrain variability in early indoor emissions from building materials, and by incorporating more detailed, survey-based characterization of cleaning practices, including product types, frequency, timing, and co-occurring activities, to better resolve source and sink mechanisms. Extended passive sampler deployment may further improve detection of low-abundance reduced-N species and expand characterization of indoor composition. In addition, while the GLMM provides a robust framework for identifying NH_3 drivers, integrating process-based indoor chemistry models would better represent emissions, deposition, and surface-mediated reactions.

Together, these directions extend the quantitative analysis, predictive modeling, and indoor air chemistry assessment developed in this thesis, enabling a more comprehensive understanding of reduced-N processing from ocean–atmosphere systems to indoor environments.

Appendices

Appendix A: Supporting information for Chapter Two

Suppressor and calibration standard limitations in cation chromatography of ammonium and 10 alkylamines in atmospheric samples

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A1. Chromeleon data file of the final optimized cation separation method

The final optimized ion chromatographic method was developed using the script editor in Chromeleon to separate and quantify ten alkylamines and six inorganic cations. The highest selectivity and separation efficiency were achieved using 4 μm packed columns and resin-based suppressors. In this method, the MSA gradient was from 1-8 mM with a flow rate of 1.25 mL min^{-1} at $55\text{ }^{\circ}\text{C}$, a total run time of 35 mins. Analytes were passed through a suppressor in stepped-legacy external water mode with a current of 4-30 mA before detection in the conductivity detector (Figure A-1).

```
{Initial Time}      Instrument Setup
DC.Compartment_TC.AcquireExclusiveAccess
DC.Column_TC.AcquireExclusiveAccess
DC.Suppressor1.PowerMode          Legacy
Sampler.DelayVolume              125 [ $\mu\text{L}$ ]
Sampler.FlushFactor              1
Sampler.DeliverSpeed              1.0 [ $\text{mL/min}$ ]
Pump_1.Degasser                  Off
DC.Suppressor1.OtherEluent        0.0 [ $\text{mN}$ ]
Pump_1.Pressure.UpperLimit        4500 [ $\text{psi}$ ]
Pump_1.%A.Equate                  "%A Water"
Pump_1.Pressure.LowerLimit        300 [ $\text{psi}$ ]
Pump_1.%B.Equate                  "%B 100 mM NaOH"
Pump_1.%C.Equate                  "%C 20 mM MSA"
Pump_1.%D.Equate                  "%D Water"
DC.Column_TC.Mode                 On
DC.Column_TC.TemperatureSet       55.00 [ $^{\circ}\text{C}$ ]
DC.Compartment_TC.Mode           On
DC.Compartment_TC.TemperatureSet  15.00 [ $^{\circ}\text{C}$ ]
DC.Suppressor1.Type CDRS_4mm
DC.Suppressor1.H2SO4              0.0 [ $\text{mM}$ ]
DC.Suppressor1.MSA                1.0 [ $\text{mM}$ ]
DC.Suppressor1.RecommendedCurrent 4 [ $\text{mA}$ ]
DC.Suppressor1.CurrentSet         4 [ $\text{mA}$ ]
CDet1.Rise_Time                   0.50 [ $\text{s}$ ]
CDet1.Data_Collection_Rate       10.0 [ $\text{Hz}$ ]
CDet1.CellHeater.Mode            On
CDet1.CellHeater.TemperatureSet  35.00 [ $^{\circ}\text{C}$ ]
CDet1.Temperature_Compensation    1.7 [ $\text{\%/}^{\circ}\text{C}$ ]
Sampler.InjectPosition
Sampler.DeliverSample             Volume=Bleed
Sampler.DeliverRinse             400,
Position=Rinse
Sampler.LoadPosition
Sampler.DeliverSample
Sampler.EndSamplePrep
0.000 Inject
Wait Sampler.CycleTimeState,
Run=Hold,
Timeout=Infinite
Sampler.Inject
0.000 Start Run
Pump_1.Degasser                  On
Pump_1.Pump_1_Pressure.AcqOn
CDet1.CD_1.AcqOn
CDet1.CD_1_Total.AcqOn
CDet1.Autozero
0.000 Run                        Duration = 35.000 [ $\text{min}$ ]
```

	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	5.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	5
5.000	Sampler.BeginOverlap	
18.000	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	5.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	5
	DC.Suppressor1.CurrentSet	15 [mA]
20.000	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	5.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	7
	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	20.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	7
	DC.Suppressor1.CurrentSet	30 [mA]
25.000	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	40.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	7
30.000	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	40.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	5
	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	5.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	5
	DC.Suppressor1.CurrentSet	30 [mA]
34.000	Pump_1.Flow	1.250 [ml/min]
	Pump_1.%B.Value	0.0 [%]
	Pump_1.%C.Value	5.0 [%]
	Pump_1.%D.Value	0.0 [%]
	Pump_1.Curve	5
	DC.Suppressor1.CurrentSet	4 [mA]
35.000	Stop Run	
	Pump_1.Pump_1_Pressure.Acq	Off
	CDet1.CD_1_Acq	Off
	CDet1.CD_1_Total.Acq	Off
35.000	Post Run	
	DC.Column_TC.ReleaseExclusiveAccess	Duration = 0.000 [min]
	DC.Compartment_TC.ReleaseExclusiveAccess	
End		

Figure A-1: Chromeleon method data file at optimum gradient method with mobile phase flow rate of 1.25 mL min⁻¹ at 55 °C and suppressor stepped-legacy mode.

A2. Statistical approaches to evaluate the significance of the y-intercept

There are three different statistical approaches to evaluate the significance of the y-intercept value (Table A-1 and A-2).^{1,2} The first approach considers the null hypothesis by equating the y-intercept to zero ($H_0: b = 0$) at the 95% confidence interval and this hypothesis is evaluated based on the Student's test statistic or p -value. The null hypothesis is accepted when the t -statistic $<$ t -critical value or p -value $>$ 0.05. This statistically proves that the y-intercept is not significantly different from zero and a calibration curve can be forced through the origin. Next, the confidence interval (CI) of the y-intercept can be calculated by using equation EA-1.

$$CI = b \pm t \times SE_b \quad (EA-1)$$

where b is the y-intercept, t is the Student's t -value (degree of freedom = $n - 2$), and SE_b is the standard error of the y-intercept. If the obtained value spans zero, the y-intercept is not significantly different from zero. Finally, by comparing the b with SE_b : if $b > SE_b$ then the intercept value is significant but if $b \leq SE_b$ then the intercept is insignificant, and a calibration curve can be statistically justified to be forced through the origin.

Table A-1: Three different statistical approaches to check significance of intercept value of inorganic cation standards.

Cation	t-statistic 95% CI	t-critical (LC–UC)*	P-value	CI of b	b $\pm$ SE _b
Li ⁺	-1.728	-0.125–0.029	0.159	-0.125–0.029	-0.048 $\pm$ 0.028
Na ⁺	-1.611	-0.135–0.036	0.182	-0.135–0.036	-0.050 $\pm$ 0.031
K ⁺	-1.938	-0.280–0.050	0.125	-0.280–0.050	-0.115 $\pm$ 0.059

*LC and UC stand for lower critical and upper critical values in t-critical.

Table A-2: Results of statistical approaches to accept or reject the significance of intercept value of inorganic cation standards.

Cation	t-statistic $<$ t-critical	P-value $>$ 0.05	Zero includes in CI of b	b $\leq$ SE _b
Li ⁺	✓	✓	✓	X
Na ⁺	✓	✓	✓	X
K ⁺	✓	✓	✓	X
	H ₀ : b = 0	H ₀ : b = 0	H ₀ : b = 0	H ₁ : b $\neq$ 0

A3. The impact of temperature on the separation of inorganic cations and alkylamines

The effect of elevated temperature on the analytical column across the range of 45 °C to 55 °C resulted in enhanced selectivity, chromatographic peak shape, and separation efficiency when separating ten alkylamines and four inorganic cations in dynamic recycled water mode (Figure A-2).

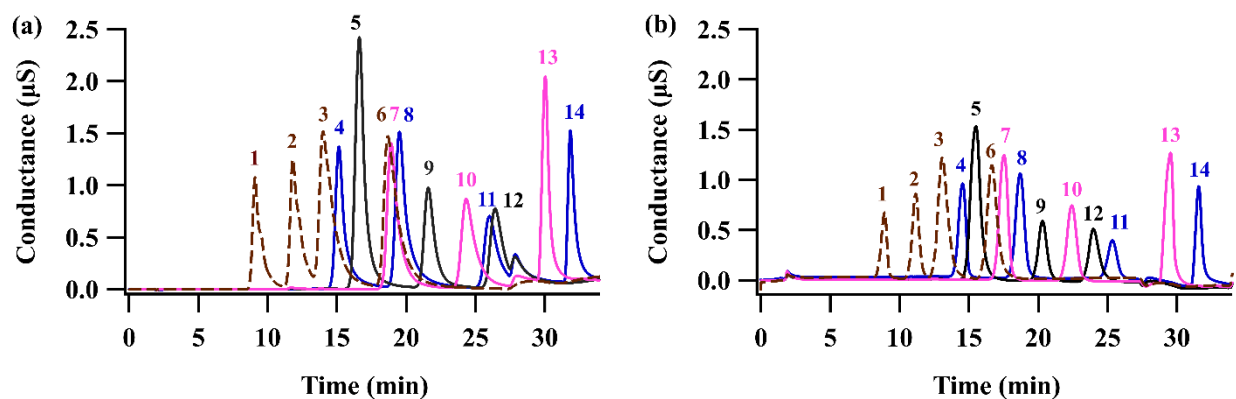


Figure A-2: Separation of inorganic cations and three amine mixtures with an MSA gradient from 1- 8 mM and flow rate of 1.25 mL min⁻¹ at (a) 45 °C and (b) 55 °C. Analytes were passed through a suppressor in dynamic recycled water mode before detection. Inorganic cations and three amine mixtures are coloured separately: dashed trace (inorganic cations), blue solid trace (MEtAH⁺, DMAH⁺, DEAH⁺, TEAH⁺), black solid trace (MMAH⁺, iMPAH⁺, TMAH⁺), and pink solid trace (MEAH⁺, MPAH⁺, MBAH⁺). The identity, numeric order of elution, and mass of each cation separated are: Li⁺ (1, 74 ng), Na⁺ (2, 296 ng), NH₄⁺ (3, 374 ng), MEtAH⁺ (4, 991 ng), MMAH⁺ (5, 358 ng), K⁺ (6, 743 ng), MEAH⁺ (7, 567 ng), DMAH⁺ (8, 356 ng), iMPAH⁺ (9, 684 ng), MPAH⁺ (10, 712 ng), DEAH⁺ (11, 703 ng), TMAH⁺ (12, 326 ng), MBAH⁺ (13, 736 ng), and TEAH⁺ (14, 718 ng).

A4. Stability of amine standards over time

Instrumental sensitivities of amines prepared in DIW and MSA were measured over 90 days with three different suppressor modes: dynamic recycle, stepped-legacy recycle, and stepped-legacy external water (Figure A-3). The decay rate of amines (day^{-1}) was measured by plotting natural logarithm of the normalized amine sensitivities relative to K^+ versus their age in days in both DIW and MSA to investigate the effect of volatilization on the amine loss mechanism. Figure A-4 illustrates the decay rate of iMPA at different suppressor modes. Also, relative effective volatilities of amines ($K_{\text{eff}} = K_a/K_H$) were calculated (Table A-3) to compare to the losses measured in both matrices over 90 days.

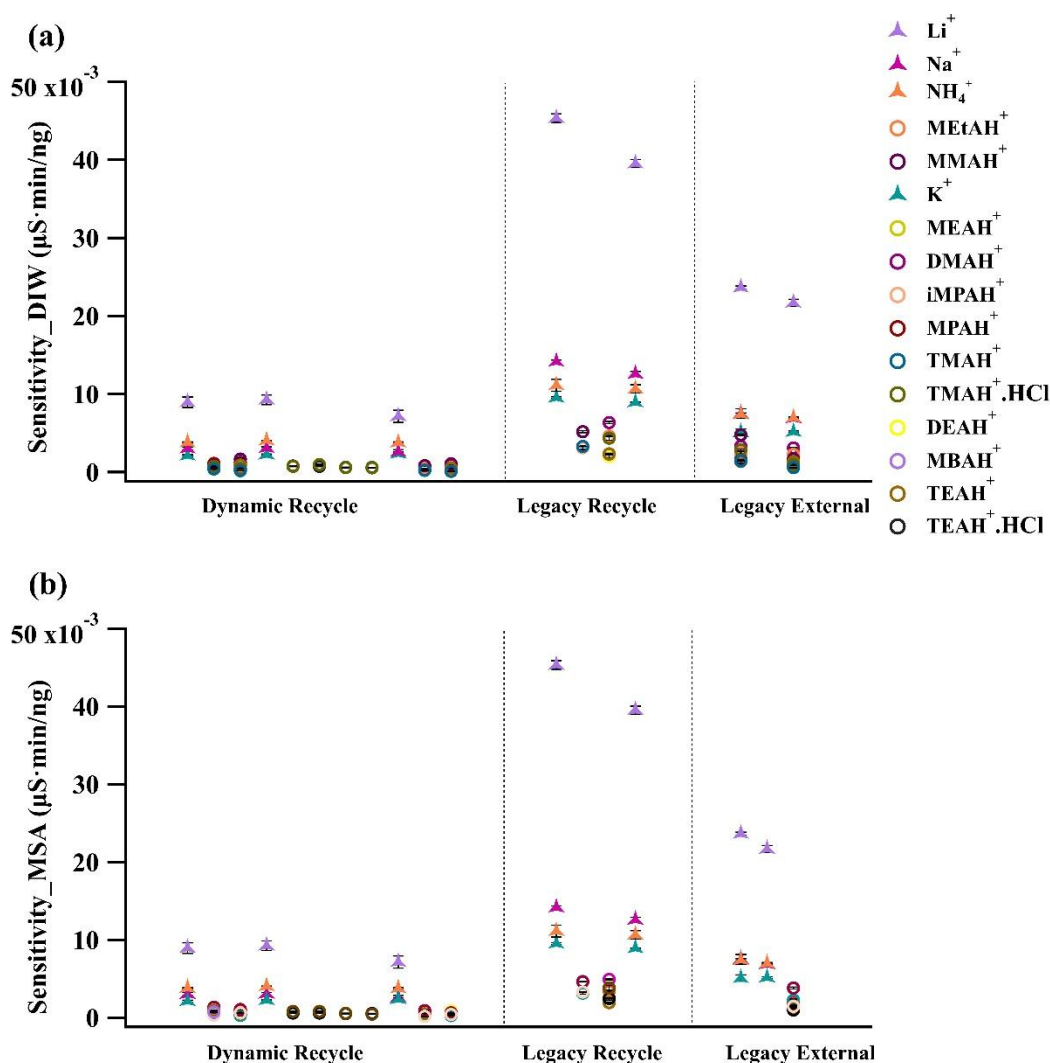


Figure A-3: Sensitivities of inorganic cations and alkylamines at different suppressor setups: dynamic recycle, stepped-legacy recycle, and stepped-legacy external water in (a) DIW and (b) MSA solutions.

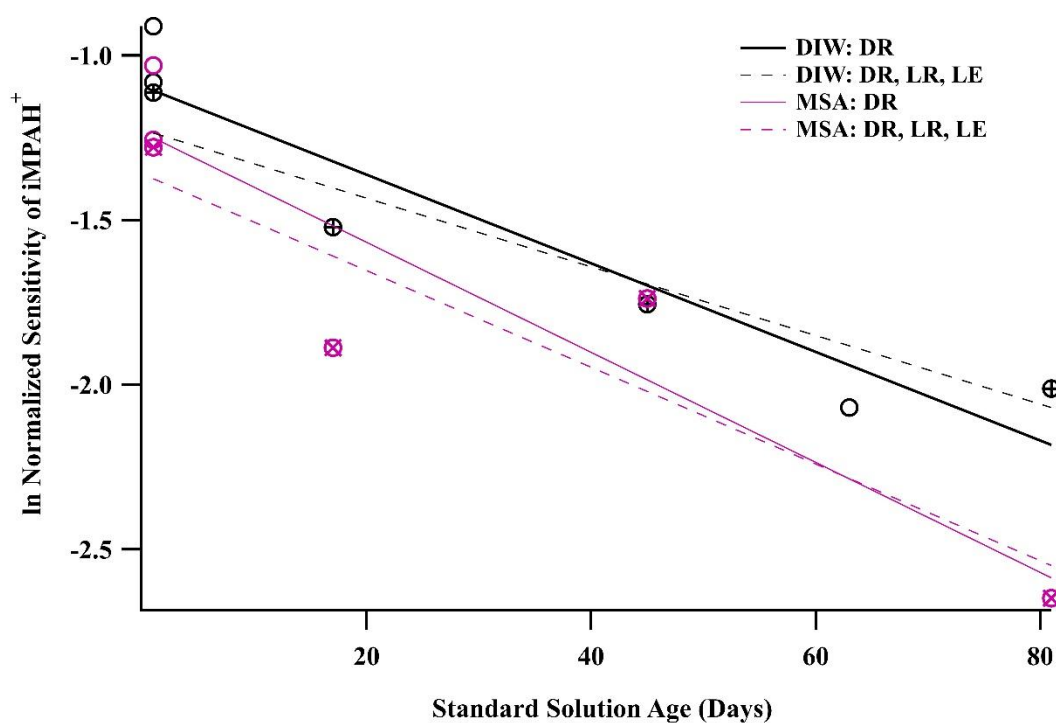


Figure A-4: The experimental loss rate of iMPAH⁺ was determined by the slope of natural logarithm of normalized iMPAH⁺ sensitivities with K⁺ versus its age in day. The decay rate in DIW and MSA was 0.010 ± 0.002 (Day⁻¹; $r^2 = 0.917$) and 0.015 ± 0.005 (Day⁻¹; $r^2 = 0.819$), respectively, with suppressor in dynamic recycle mode. The decay rate with suppressor in three different modes: dynamic recycle (DR), stepped-legacy recycle (LR), and stepped-legacy external (LE) was measured 0.013 ± 0.002 (Day⁻¹; $r^2 = 0.903$) in DIW and 0.016 ± 0.003 (Day⁻¹; $r^2 = 0.855$) in MSA.

Table A-3: Weak acid ionization constant (K_a), pK_a , Henry's law constant (K_H), and the ratio of K_a -to- K_H of alkylamines at 298 K.

Amine	Formula	MW (g/mol)	pK_a	K_a	K_H (M atm ⁻¹)	K_a/K_H (atm M ⁻¹)
MEtA	HOC ₂ H ₄ NH ₂	61.1	9.50	3.2×10^{-10}	6.1×10^6	5.2×10^{-17}
MMA	CH ₃ NH ₂	31.1	10.66	2.2×10^{-11}	1.2×10^2	1.8×10^{-13}
MEA	C ₂ H ₅ NH ₂	45.1	10.65	2.2×10^{-11}	8.0×10^1	2.8×10^{-13}
DMA	(CH ₃) ₂ NH	45.1	10.73	1.9×10^{-11}	6.1×10^1	3.1×10^{-13}
iMPA	C ₃ H ₉ N	59.1	10.63	2.3×10^{-11}	2.2×10^1	1.1×10^{-12}
MPA	C ₃ H ₇ NH ₂	59.1	10.54	2.9×10^{-11}	4.9×10^1	5.9×10^{-13}
TMA	(CH ₃) ₃ N	59.1	9.80	1.6×10^{-10}	3.8	4.2×10^{-11}
DEA	(C ₂ H ₅) ₂ NH	73.1	10.84	1.5×10^{-11}	1.8×10^1	8.0×10^{-13}
MBA	C ₄ H ₉ NH ₂	73.1	10.60	2.5×10^{-11}	2.9×10^1	8.6×10^{-13}
TEA	(C ₂ H ₅) ₃ N	101.2	10.75	1.8×10^{-11}	8.7	2.0×10^{-12}

A5. Calibration approaches of cation standards

The accuracy of linear calibration curves of inorganic cations was assessed using the R^2 values of calibration standards and RE% of both calibration standards and check standards compared to their known concentrations as an evaluation of accuracy. Figure A-5 shows three different types of regression lines with corresponding RE%: (a,b) forced through (0,0), (c,d) not forced through origin but included (0,0) in the regression, and (e,f) not forced through the origin and not including (0,0). Metrics describing the performance of the optimized method for quantifying our full suite of cations are provided in Table A-4.

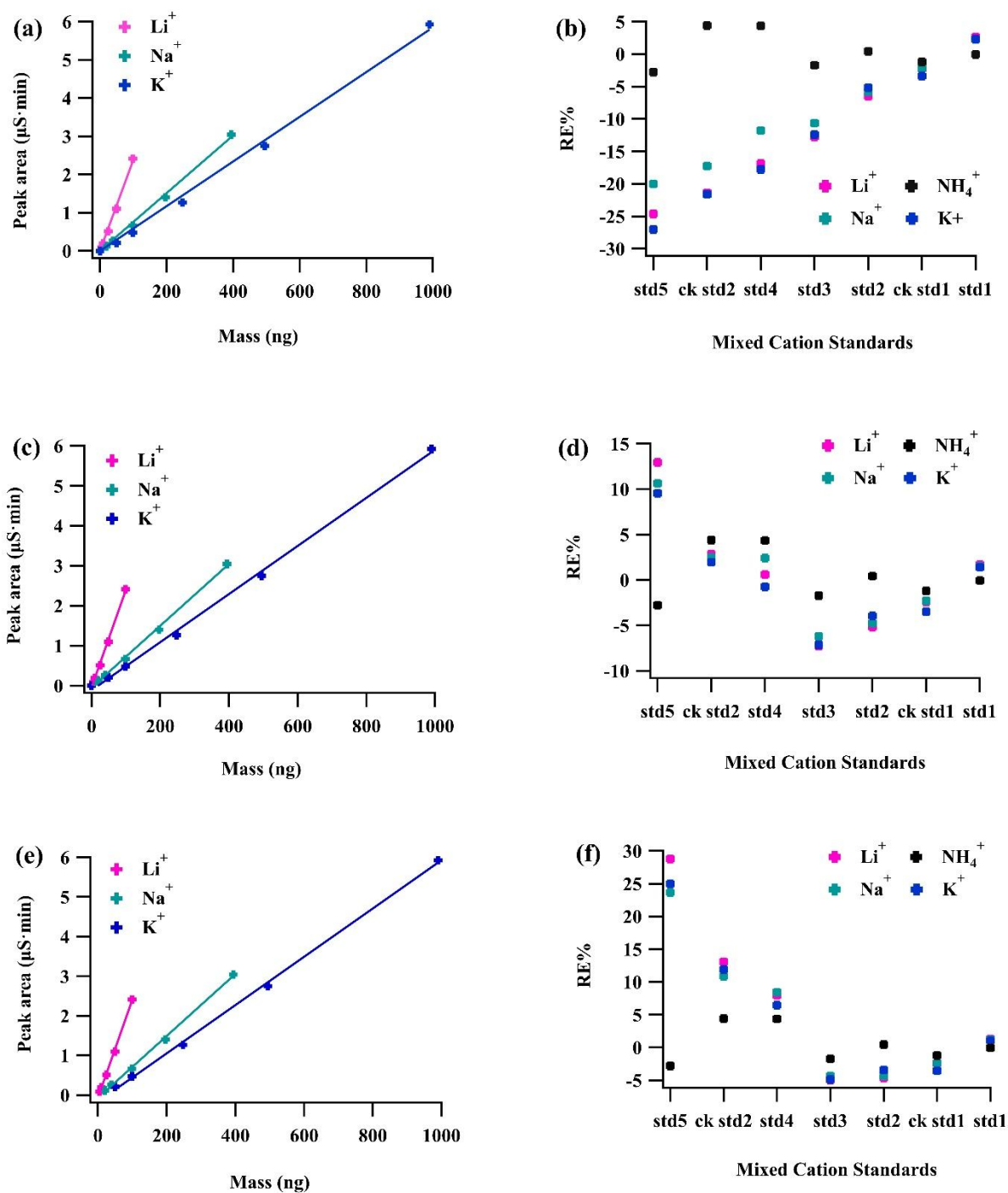


Figure A-5: Three different calibration curves of inorganic cations and RE % from both calibration standards (std) and check standards (ck std): (a) regression lines and (b) RE% by forcing to zero; (c) regression lines and (d) RE% not forcing to zero and including (0,0); (e) regression lines and (f) RE% not forcing to zero and excluding (0,0).

Table A-4: Calibration standards and reagent blanks of inorganic cations and alkylamines were used to analyze sensitivity (n = 5 inorganic cation, n = 3 amines), precision (n = 5 inorganic cation, n = 3 amines), accuracy (n = 5), and an average of LODs with ranges (n = 3). The suppressor was operated in stepped-legacy external water mode.

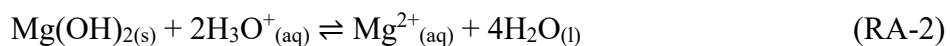
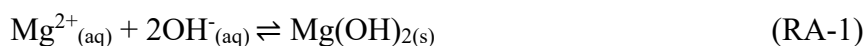
Cation	Sensitivity ($\mu\text{S}\cdot\text{min mol}^{-1}$)	Precision¹ (%)	Accuracy² (%)	Average LOD (nmol)	LOD range (nmol)
Li ⁺	1.61E08	7	97-98	0.20 ± 0.01	0.19–0.21
Na ⁺	1.73E08	6	97-98	0.29 ± 0.20	0.13–0.51
NH ₄ ⁺	1.32E08	4	95-99	0.17 ± 0.12	0.09–0.31
MEtAH ⁺	1.60E08	7	82	0.13 ± 0.01	0.11–0.14
MMAH ⁺	1.52E08	8	91	0.17 ± 0.01	0.16–0.18
MEAH ⁺	1.48E08	13	87	0.21 ± 0.003	0.21
K ⁺	2.17E08	8	97-98	0.17 ± 0.05	0.13–0.22
DMAH ⁺	1.65E08	6	90	0.17 ± 0.02	0.15–0.19
iMPAH ⁺	1.20E08	11	87	0.35 ± 0.06	0.36–0.30
MPAH ⁺	1.55E08	8	83	0.22 ± 0.03	0.20–0.25
DEAH ⁺	1.39E08	7	88	0.45 ± 0.02	0.43–0.47
TMAH ⁺	1.07E08	11	85	0.43 ± 0.06	0.36–0.43
TMAH ⁺ .HCl	1.68E08	4	86	0.27 ± 0.04	0.23–0.32
MBAH ⁺	1.55E08	11	80	0.13 ± 0.02	0.12–0.15
TEAH ⁺	1.47E08	4	94	3.41 ± 0.32	3.11–3.74
TEAH ⁺ .HCl	1.60E08	4	94	1.68 ± 0.16	1.54–1.85

¹ Precision was calculated using %RSD of the slope from replicate linear calibration curves for both inorganic cations and alkylamines.

² Accuracy was determined by calculating the %RE of the check standards selected from the upper and lower ranges (inorganic cations) and midpoints (alkylamines) of the calibration standards (Sections 2.2.4.2. and 2.2.4.3).

A6. Methods to optimize suppressor functionality

Suppressor cleaning with MSA (500 mM) and NaOH (200 mM) were each performed at a flow rate of 1.25 mL min⁻¹ for 12 mins according to the manufacturer's instructions. The acid wash was intended here to dissolve Mg(OH)_{2(s)} and Ca(OH)_{2(s)} (RA-1; Ca²⁺ has the same salt formation equilibria) which were hypothesized to have been generated in the resin bed due to an excess of OH⁻ in the electrolytic channel when operating in recycled water mode, particularly where the applied current from the dynamic approach may have been over-suppressing the column effluent compared that required for the eluent strength (RA-2). The suppressor was then reconditioned using NaOH to resume normal operation.



However, this acid and base treatment procedure did not recover sensitivity nor detection of Mg²⁺ and Ca²⁺ analytes once they were observed to start declining (Figure A-6). The suppressor was then changed from dynamic to stepped-legacy mode with the same recycled water supply, to reduce the possibility of prolonged over-suppression of the eluent compared to dynamic mode, particularly at the low initial 1 mM MSA concentrations which our optimized method holds for an extended period at the start of each run. The very low eluent strength conditions provide the needed selectivity to separate the target analytes. Using a new suppressor in stepped-legacy mode was used with the current changed to match the eluent programming, taking into account the solvent delay for the increased OH⁻ concentration to reach the suppressor. There was an improvement in analyte sensitivities, a reduction in the extent of loss for monovalent cations, and it was possible to detect Mg²⁺ and Ca²⁺ ions in ~ 100 samples. However, losses of alkylamines in the suppressor were persistent along with fatal damage to the suppressor after 2 months of operation. With the improved performance, the suppressor had the option to be cleaned with oxalic acid to restore suppression capability. In this cleanup procedure, the suppressor was flushed out with oxalic acid as an alternative to dissolve Mg(OH)_{2(s)} and Ca(OH)_{2(s)} that may have formed in the resin and remove them more effectively as MgC₂O₄ and CaC₂O₄. Unfortunately, the oxalic acid wash was found to only temporarily improve suppressor function, with the loss of Mg²⁺ and Ca²⁺ peaks reoccurred after running ~ 80 additional samples. Finally, the suppressor was switched to external water to prevent the degree to which intrusion and accumulation of column stationary phase

material and/or $\text{Mg}(\text{OH})_{2(s)}$ and $\text{Ca}(\text{OH})_{2(s)}$ were possible on the regenerant side of the electrolytic suppressor compartments (Figure 2-1).

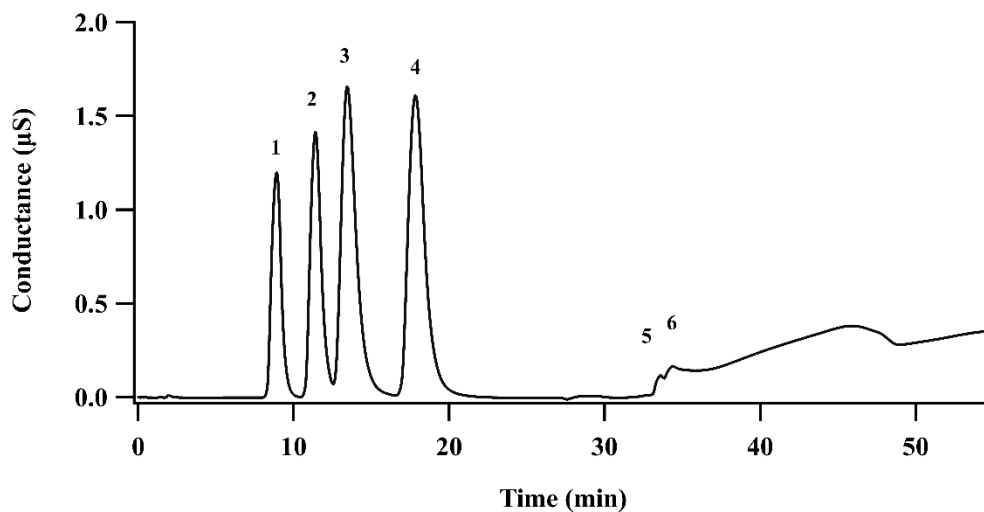


Figure A-6: Chromatogram of inorganic cations: Li^+ (1), Na^+ (2), NH_4^+ (3), K^+ (4), Mg^{2+} (5), and Ca^{2+} (6) to demonstrate the loss of Mg^{2+} and Ca^{2+} ions due to suppressor failure.

A7. Review of quantitative IC methods for inorganic cations

Over the past decade, ion chromatographic methods have been developed using H_3O^+ gradient methods to separate and quantify inorganic cations (Figure A-7). Various cation-exchange columns and suppressors were utilized in these methods, such as CS12A (8.5 μm) and CSRS 300, CS17 (7 μm) and CSRS 300, CS19 (5.5 μm) and CERS 500, and CS19 (4 μm) and CDRS 600.

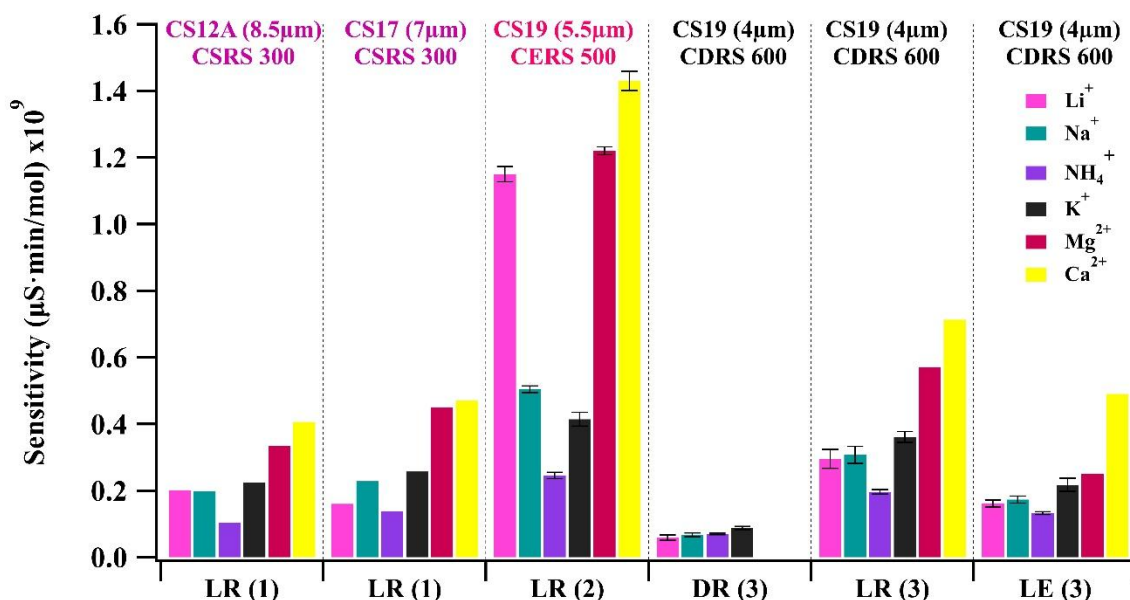


Figure A-7: Sensitivity of inorganic cations by using different cation-exchange columns and suppressors over a decade. The analytes separation and suppression performed by CS12A and CS17 columns, and CSRS 300 in legacy recycle (LR) mode by VandenBoer *et al.* (1);³ CS19 (5.5 μm), and CERS 500 in LR mode by Place *et al.* (2);⁴ and CS19 (4 μm), and CDRS 600 in dynamic recycle (DR), stepped-legacy recycle (LR), and stepped-legacy external (LE) modes in present work (3).

A8. Size-resolved coastal aerosol sample from the marine atmosphere

During the Coastal Fog campaign, nine rounds of aerosol sampling were conducted along the coast of Eastern Canada from September 13 to 24, 2018. Size-resolved atmospheric aerosol samples were collected over the open ocean, the Gulf of the St. Lawrence, and urban harbours. Figure A-8 shows the ship track from St. John's, Newfoundland and Labrador to Halifax, Nova Scotia, including indicators for the two sampling sites of the marine and harbour air samples discussed in the main manuscript.

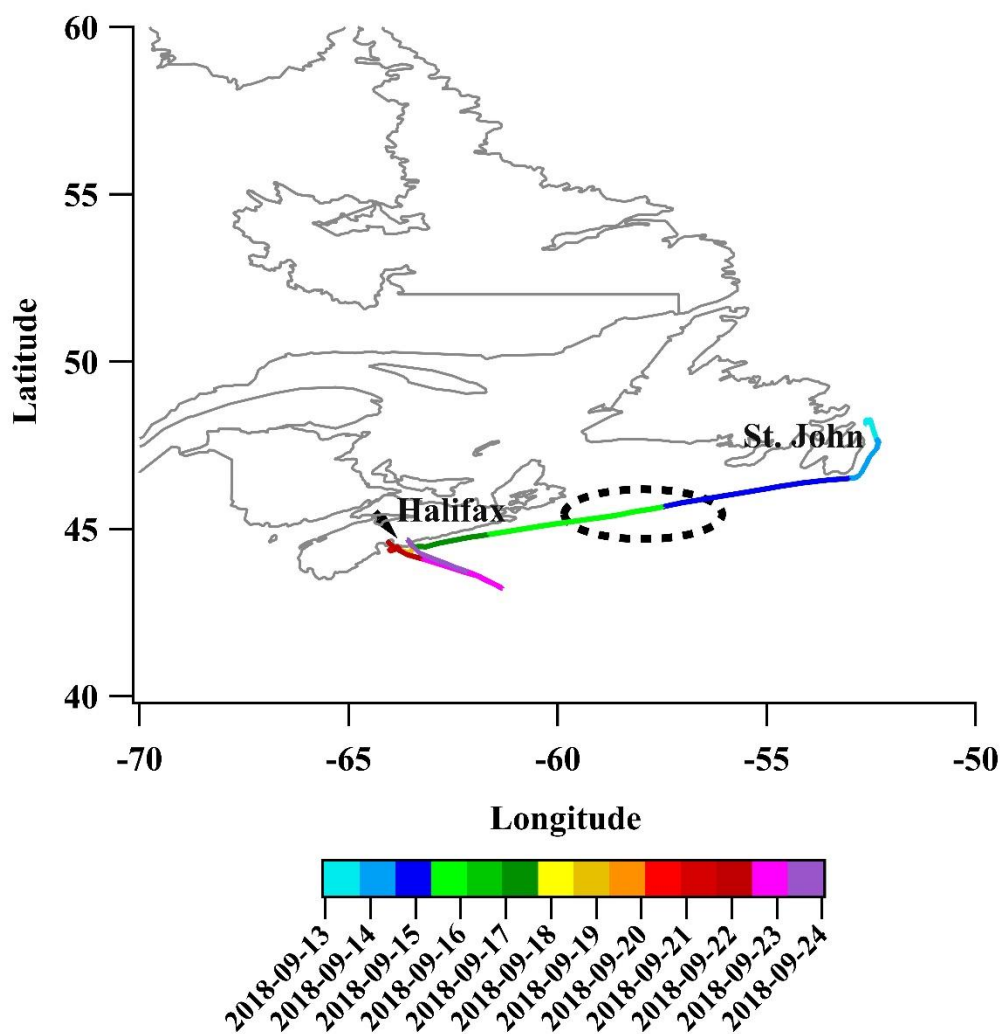


Figure A-8: Coastal FOG ship track from St. John to Halifax along the coast of Eastern Canada from September 13 to 24, 2018. Two MOUDI samples were collected from marine air from 15/09/2018 to 16/09/2018 (dashed black circle), and Halifax harbour air from 18/09/2018 to 19/09/2018 (black arrow) on the Atlantic coast of Nova Scotia, Canada.

A9. Upper limits on alkylamine mixing ratios in new home air quality samples

The upper limits of detectable amine mixing ratios were calculated for samples where these were below the detection limit in the NHAQS samples (Table A-5). Mixing ratio equivalents (ppbv) were calculated using equation EA-2 by using the determined detection limits from our method.

$$\text{Mixing Ratio} = \frac{(2\alpha)(\text{LOD})}{\text{Sampling time}} \quad (\text{EA-2})$$

Where 2α (ppbv min ng⁻¹) represents the diffusion coefficient of the NH₃ sampling rate, and instrumental LOD (ng) was obtained from those determined for the stepped-legacy external water mode. Sampling times (min) used were representative of typical sampling durations for this study and many others.⁵⁻⁷ The α values for alkylamines have not been reported and may differ from those of NH₃, but serve as an initial estimate that we expect to be within a factor of 5 of their true values, based on the relative difference in their gas phase diffusion coefficients, and assuming the same collection efficiency on the citric acid Ogawa reactive pads used.

Table A-5: The upper limits of detectable amine mixing ratios were measured in NHAQS, and instrumental LODS were calculated using an optimized method. The diffusion coefficient of NH₃ sampling rate was used at 21 °C ($2\alpha = 87$), and mixing ratios were determined for two different sampling periods: 1 day (1425 min) and 5 days (5772 min).

Amine	LOD (ng)	Mixing ratio 1day (ppbv)	Mixing ratio 5 days (ppbv)
MEtA	7.99	0.49	0.12
MMA	5.49	0.34	0.08
MEA	9.74	0.59	0.15
DMA	7.90	0.48	0.12
iMPA	21.32	1.30	0.32
MPA	13.39	0.82	0.20
DEA	33.73	2.06	0.51
TMA	16.52	1.01	0.25
MBA	9.70	0.59	0.15
TEA	171.95	10.50	2.59

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Appendix B: Supporting information for Chapter Three

Microphysical chemistry of fog-aerosol interactions over the Northwest Atlantic Ocean during Fatima 2022

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B1. Meteorological measurements

Meteorological parameters, including visibility (km, FD70), relative humidity (RH, %, WXT520), air temperature (T_{air} , °C, WXT520), sea surface temperature (SST, °C, ROSR), rain rate (mm hr⁻¹, WXT520) and wind speed and direction (WS, m s⁻¹/WD, ° from north as 0°, WXT520 and D-CAMS) were recorded during the campaign (Figure B-1).

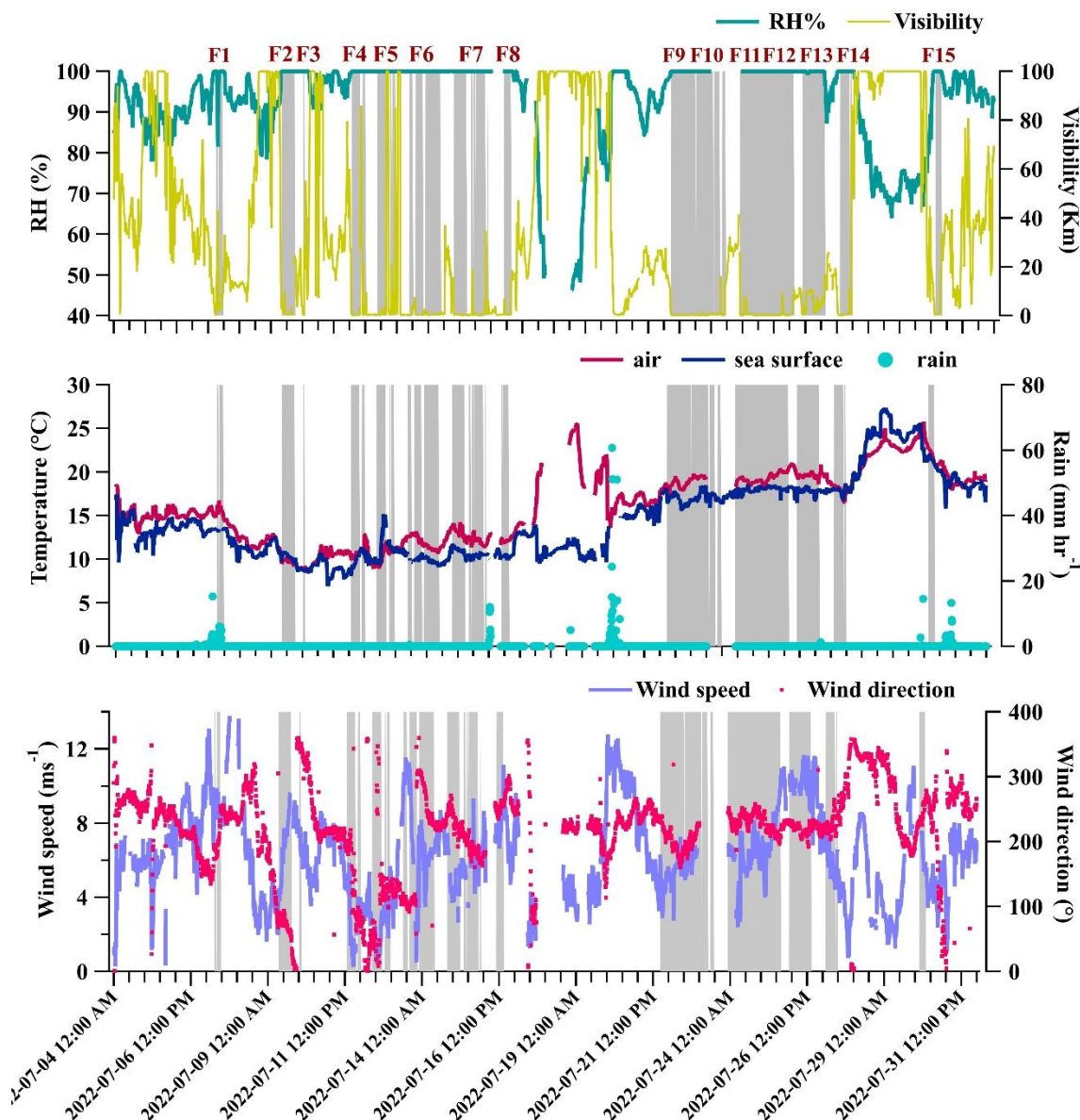


Figure B-1: Time series of meteorological parameters (RH, visibility, air and sea surface temperature, rain, and wind speed and direction) recorded over the Northwest Atlantic Ocean from July 4 to August 1, 2022, in UTC. Shaded areas indicate periods of fog during which MOUDI aerosol samples were collected, with corresponding fog events labeled (Table B-3).

B2. Validation of equivalence between nanoMOUDI and MOUDI aerosol samplers: A comparative study

Size-resolved aerosols were collected using Micro-Orifice Uniform Deposit Impactors (MOUDI and nanoMOUDI), which are well-established, commercially validated instruments known for their effective particle-size separation (Marple, Rubow and Behm, 1991). They use approximately 2,000 micro-orifice nozzles with diameters as small as 50 μm (MSP Corp., Shoreview, MN, USA). The large nozzle array reduces jet velocity and pressure drop, keeping the stage Reynolds numbers within the laminar range (500–2420), thereby reducing particle bounce and re-entrainment while enhancing collection efficiency. We confirmed this performance in the field as part of an active QA/QC strategy, where immediately after aerosol collection, the samples were extracted and analyzed on the board the Atlantic Condor by IC-CD to ensure there was no evidence of impact-induced droplet shattering by assessing the chemical distribution of NaCl as fingerprints of sea salt. Enrichment of NaCl was not detected in any of our lower stages, confirming that droplets did not shatter or escape their impaction stages or bleed into the fine particle stages below, thus confirming that bounce, shattering, or coalescence losses did not impact the samples (Figure 3-3). We note that marine conditions with high RH have been previously reported to minimize expectations of particle bounce as this increases capillary adhesion between particles and impaction substrates (Stein *et al.*, 1994; Bateman, Belassein and Martin, 2014). Thus, the design features and quality controls we performed support that the MOUDI size distributions reported here accurately represent hydrated aerosol and droplet collection in the marine environment and are then valid for further intercomparison to cross-validate them with one another.

The comparability between nanoMOUDI (ambient sampling) and MOUDI (fog sampling) was assessed through concurrent ambient aerosol sampling conducted for 624 minutes on July 26, 2022, during the Fatima Campaign. The ion mass loading obtained from both instruments is depicted in Figure B-2, revealing a notable similarity. The equivalent ionic loadings for each pair of ions were compared, with uncertainties derived from the accuracy of the IC method (Table B-1). The variances of each pair were used to calculate the F value, which in all cases resulted in a value lower than F-critical (19), at a 95% confidence interval, indicating no significant differences between the two measurements. Student's test statistic (paired t-test) was performed to assess differences in equivalent ionic loading between the means of the two instruments (Table B-2). The null hypothesis (H_0) stated no significant differences existed at a 95% confidence interval between

nanoMOUDI and MOUDI. The results indicate acceptance of H_0 , supported by t-statistic $(1.09) < t\text{-critical } (2.12)$ or a P-value $(0.29) > 0.05$. Thus, no significant differences were statistically observed at a 95% confidence interval between nanoMOUDI and MOUDI, on an ion-by-ion basis or in total, indicating that our subsequent evaluation of chemical composition changes between the ambient and fog aerosol samples collected by these instruments are justified.

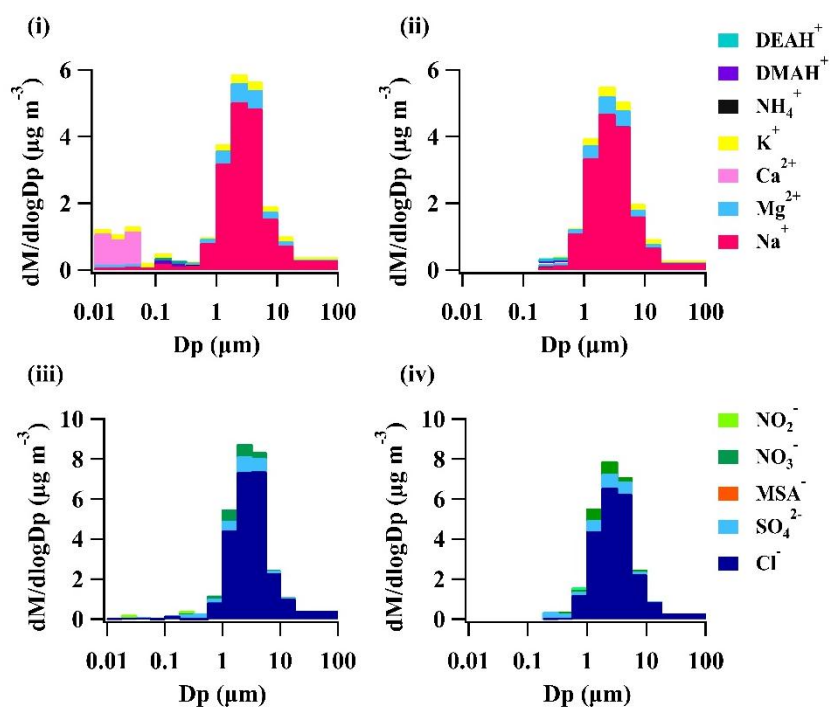


Figure B-2: Ion mass loading of ambient air on July 26, 2022, aboard the Atlantic Condor during the Fatima campaign, comparing nanoMOUDI (i) cations and (iii) anions with MOUDI (ii) cations and (iv) anions.

Table B-1: Summary of variance in equivalent ionic loading of coarse (C) and fine (F) mode aerosols, collected by both nanoMOUDI and MOUDI .

Ion	NanoMOUDI (neq m ⁻³)	MOUDI (neq m ⁻³)	Variance NanoMOUDI (neq m ⁻³) ²	Variance MOUDI (neq m ⁻³) ²	F-calculated
Na ⁺ (C)	167 $\pm$ 10	157 $\pm$ 9	100	81	1.23
Mg ²⁺ (C)	38.47 $\pm$ 1.15	35.92 $\pm$ 1.08	1.32	1.17	1.13
K ⁺ (C)	7.32 $\pm$ 0.07	7.63 $\pm$ 0.08	4.9x10 ⁻³	6.4x10 ⁻³	0.77
Na ⁺ (F)	10.13 $\pm$ 0.61	13.11 $\pm$ 0.79	0.37	0.62	0.60
Mg ²⁺ (F)	4.10 $\pm$ 0.12	5.60 $\pm$ 0.17	0.04	0.03	0.50
K ⁺ (F)	0.39 $\pm$ 0.004	0.39 $\pm$ 0.004	1.6x10 ⁻⁵	1.6x10 ⁻⁵	1
NH ₄ ⁺ (F)	0.36 $\pm$ 0.007	0.38 $\pm$ 0.008	4.9x10 ⁻⁵	6.4x10 ⁻⁵	0.77
DMAH ⁺ (F)	0.89 $\pm$ 0.06	0.75 $\pm$ 0.05	3.6x10 ⁻³	2.5x10 ⁻³	1.44
DEAH ⁺ (F)	0.57 $\pm$ 0.05	0.58 $\pm$ 0.05	2.5x10 ⁻³	2.5x10 ⁻³	1
Cl ⁻ (C)	158 $\pm$ 1.58	141 $\pm$ 1.41	2.50	1.99	1.26
NO ₂ ⁻ (C)	0.04 $\pm$ 0.0005	0.04 $\pm$ 0.0005	2.5x10 ⁻⁷	2.5x10 ⁻⁷	1
NO ₃ ⁻ (C)	6.02 $\pm$ 0.42	6.05 $\pm$ 0.42	0.18	0.18	1
SO ₄ ²⁻ (C)	10.92 $\pm$ 0.87	10.52 $\pm$ 0.84	0.76	0.71	1.07
Cl ⁻ (F)	5.43 $\pm$ 0.05	8.14 $\pm$ 0.08	2.5x10 ⁻³	0.0064	0.39
NO ₂ ⁻ (F)	0.62 $\pm$ 0.007	0.62 $\pm$ 0.007	4.9x10 ⁻⁵	4.9x10 ⁻⁵	1
NO ₃ ⁻ (F)	0.80 $\pm$ 0.06	0.76 $\pm$ 0.05	3.6x10 ⁻³	2.5x10 ⁻³	1.44
SO ₄ ²⁻ (F)	3.14 $\pm$ 0.25	3.42 $\pm$ 0.27	0.06	0.07	0.86
SUM	414 $\pm$ 10	392 $\pm$ 9	100	81	1.23

Table B-2: T-test results for null hypothesis acceptance between nanoMOUDI and MOUDI.

Source of Variation	df	t-statistic	t-critical	P-value
nanoMOUDI and MOUDI	16	1.09	2.12	0.29

B3. Ion chromatography analysis: Quality assurance and quality control (QA/QC), sea salt and non-sea salt components

Simultaneous analysis of major cations and anions was performed with minor modifications of our previously established methods (Place *et al.*, 2017; Place *et al.*, 2018; Salehpour and VandenBoer, 2023). The cation channel employed an isocratic method with a 4 mM MSA concentration and a CDRS 600 suppressor (4mm, P/N: 088668) operated at a current setting of 12 mA in legacy external water mode. Two columns were used for the cation isocratic method: a CG19-4 μ m guard column (4 x 50 mm, P/N: 078840) and a CS19-4 μ m analytical column (4 x 250 mm, P/N: 078837). The anion channel utilized the hydroxide (OH^-) gradient method, with an initial concentration of 10 mM OH^- maintained for 12 minutes. The concentration was then increased to 60 mM over the next 8 minutes and held constant for 5 minutes until 25 minutes. Finally, the OH^- concentration was decreased to 10 mM and maintained for the remaining 10 minutes to re-equilibrate the column as the next sample was prepared by the autosampler for injection and analysis. Two columns were used for the anion gradient method: an AG23 guard column (4 x 50 mm, P/N: 064147) and an AS23 analytical column (4 x 250 mm, P/N: 064149). An ADRS 600 suppressor (P/N: 088666) was operated in dynamic mode with a constant voltage setpoint of 3.9 V. Each sample injection consisted of 500 μ L aqueous sample, 250 μ L loaded into each channel using an injection loop installed into sample delivery valve. The analytes were quantified using a conductivity detector (DS6 heated conducting cell at 35 $^{\circ}\text{C}$).

Quality assurance and quality control (QA/QC) were conducted by preparing calibration standards, with the calculation of method precision and accuracy both in the field lab and university lab to ensure consistent and reliable results across different environments. Approximately half of the collected MOUDI samples were analyzed on the board using IC-CD, with the remaining samples analyzed post-campaign in the university lab. A total of five calibration standards were prepared for inorganic cations and anions in ultra-pure deionized water. Three sets of analytical standards were prepared on the ship at the start (July 5, 2022), mid-point (July 18, 2022), and end of the Fatima campaign (July 31, 2022). Two sets of analytical standards were prepared and analyzed for the analyses conducted in the university lab after the campaign, before and after running the remaining samples. Calibration ranges for cations were as follows: Li^+ (5 to 99 ng), Na^+ (20 to 394 ng), NH_4^+ (25 to 498 ng), K^+ (50 to 990 ng), Mg^{2+} (25 to 502 ng), and Ca^{2+} (49 to 988 ng). Anion ranges included: F^- (22 to 345 ng), MSA^- (2 to 25 ng), Cl^- (109 to 1725 ng), NO_2^-

(109 to 1725 ng), Br⁻ (109 to 1725 ng), NO₃⁻ (109 to 1725 ng), SO₄²⁻ (109 to 1725 ng) and PO₄³⁻ (219 to 3450 ng). The method precision of the inorganic cations and anions calibration standards was determined by calculating the standard deviation (σ) in the slope (sensitivity) of the linear calibration curves, with analyses conducted both in the field lab (n = 3) and university lab (n = 2). The precision for cations was $\pm 6\%$ on the ship, and $\pm 12\%$ in the university lab, with the decreased overall precision in the university lab originating from known issues with Mg²⁺ and Ca²⁺, as the cation suppressor lost sensitivity over time (Place *et al.*, 2017; Salehpoor and VandenBoer, 2023). The precision for anions was $\pm 10\%$ in the field lab, and $\pm 7\%$ university lab. The accuracy of inorganic cations was measured by preparing two check standards within the calibration range, positioned between the two highest and two lowest standards. These check standards were used to calculate the percentage relative error (%RE) of the measured concentrations compared to the known concentration (n = 10). A similar approach was used for anions, but only one check standard was prepared with a concentration in the middle of the calibration range (n = 10). The accuracy of all ions ranged from 90% to 99% for both field and university lab analysis. The precision and accuracy of cations and anions are consistent with the prior IC analysis from our group (Place *et al.*, 2018; Salehpoor and VandenBoer, 2023).

Ion quality control was conducted to validate the ion measurements in marine aerosols, accounting for both inorganic and organic compounds in seawater. Sea salt aerosols (SSA), including NaCl, KCl, MgCl₂, CaCl₂, Na₂SO₄, K₂SO₄, MgSO₄, and CaSO₄, are generated through the sea bubbles bursting due to wind action on the ocean surface. The coarse mode molar ratio of sea salt anions Σ (Cl⁻, SO₄²⁻, NO₃⁻) to cations Σ (Na⁺, Mg²⁺, Ca²⁺, K⁺) was presumed to be lower than that of bulk seawater, which has a ratio of approximately one (Lewis and Schwartz, 2004). These proportions comprising Cl⁻ (0.546 meq), Na⁺ (0.469 meq), Mg²⁺ (0.106 meq), SO₄²⁻ (0.056 meq), Ca²⁺ (0.02 meq), and K⁺ (0.01 meq) per kilogram of bulk seawater (kg-sw)⁻¹. A lower ratio of (Σ^-/Σ^+) is reasonable to expect in MBL aerosols subjected to chemical reactions and gas-particle partitioning. Thus, NO₃⁻ was included in the molar ratios because it can replace Cl⁻ in sea salt aerosols (e.g., NaCl) through acid displacement reaction as HNO₃ is produced photochemical from nitrogen oxides in the troposphere, and it should therefore be accounted for in the quality control of coarse mode sea salt aerosols potentially mixed with polluted continental air mass outflow. The remaining ions that do not originate from sea salt aerosols were classified as non-sea salt species, including anions (processed-S: nss-SO₄²⁻ and MSA⁻) and cations (reduced-N: NH₄⁺, DMAH⁺, and

DEAH⁺). The relative contribution of each group (sea salt versus non-sea salt) was determined by its fraction of the total equivalent ionic or mass loading, relative to the combined total of sea salt and non-sea salt loadings. The charge balance ratio of sea salt aerosol (Σ^-/Σ^+) was calculated for both ambient and fog aerosols (Figure B-3a). The charge balance ratio below one was observed in all the samples, with a more pronounced reduction in fog aerosols. These findings suggest the displacement of Cl⁻ by inorganic and organic acids (see main manuscript: Section 3.3.1). In the fine mode, the molar ratio of Σ_{base} (NH₄⁺, DMAH⁺, DEAH⁺) to Σ_{acid} (processed-S: nss-SO₄²⁻, MSA⁻; and NO₃⁻) was calculated for both ambient and fog aerosols (Figure B-3a). The fog aerosol samples indicated higher ratios of ($\Sigma_{\text{base}}/\Sigma_{\text{acid}}$) compared to ambient samples, suggesting that fog aerosols, likely take up additional base due to enhanced water content and the uptake of unquantified species like organic acids.

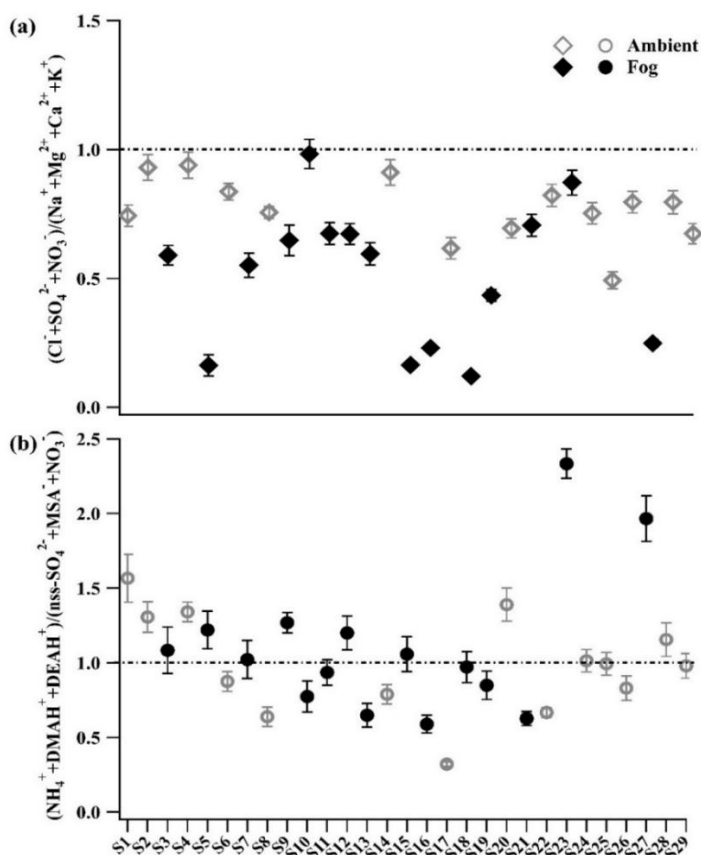


Figure B-3: Molar ratios of (a) anions Σ (Cl⁻, SO₄²⁻, NO₃⁻) to cations Σ (Na⁺, Mg²⁺, Ca²⁺, K⁺) in coarse mode sea salt aerosols, and (b) Σ_{base} (NH₄⁺, DMAH⁺, DEAH⁺) to Σ_{acid} (processed-S: nss-SO₄²⁻, MSA⁻; and NO₃⁻) in fine mode aerosols during ambient and fog conditions in Fatima campaign. The uncertainty in each molar ratio ($\pm 1\sigma$) was calculated through error propagation, accounting for the IC accuracy of each ion and the uncertainties in the extraction volumes of each MOUDI impaction substrate.

B4. Impact of fog on chemical composition of size-resolved aerosols

The impact of fog presence on the ion composition of coarse and fine mode aerosols was assessed by comparing the average equivalent ionic loadings (neq m^{-3}) of aerosols in ambient conditions ($n = 14$) and fog events ($n = 15$), excluding the extreme conditions (Figure B-4; Section 3.3.1.3: Table 3-1). In coarse mode sea salt aerosols (Figure B-4a-b), the equivalent ionic loading decreased under the fog conditions. In contrast, fine mode aerosols (Figure B-4c-d) showed an increase in processed-S (nss-SO_4^{2-} and MSA^-) species and reduced-N (NH_4^+ , DMAH^+ , and DEAH^+) species during fog conditions. This comparison of coarse and fine mode aerosols under ambient and fog conditions indicates the different impact of fog on marine aerosol chemistry, driven by size-dependent physical and chemical processes, which is discussed in detail in the main manuscript (see Section 3.3.1).

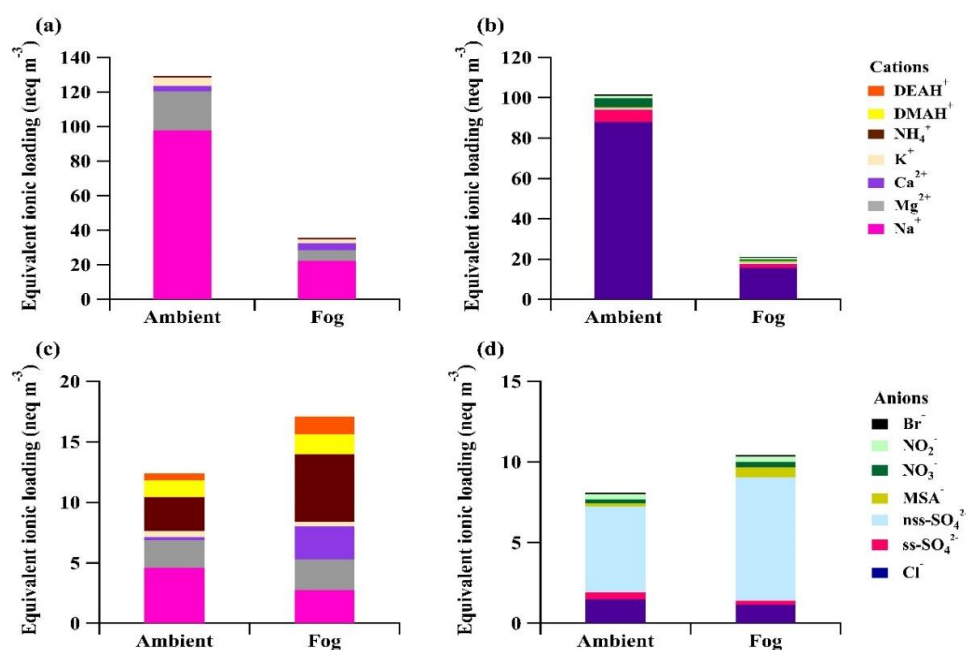
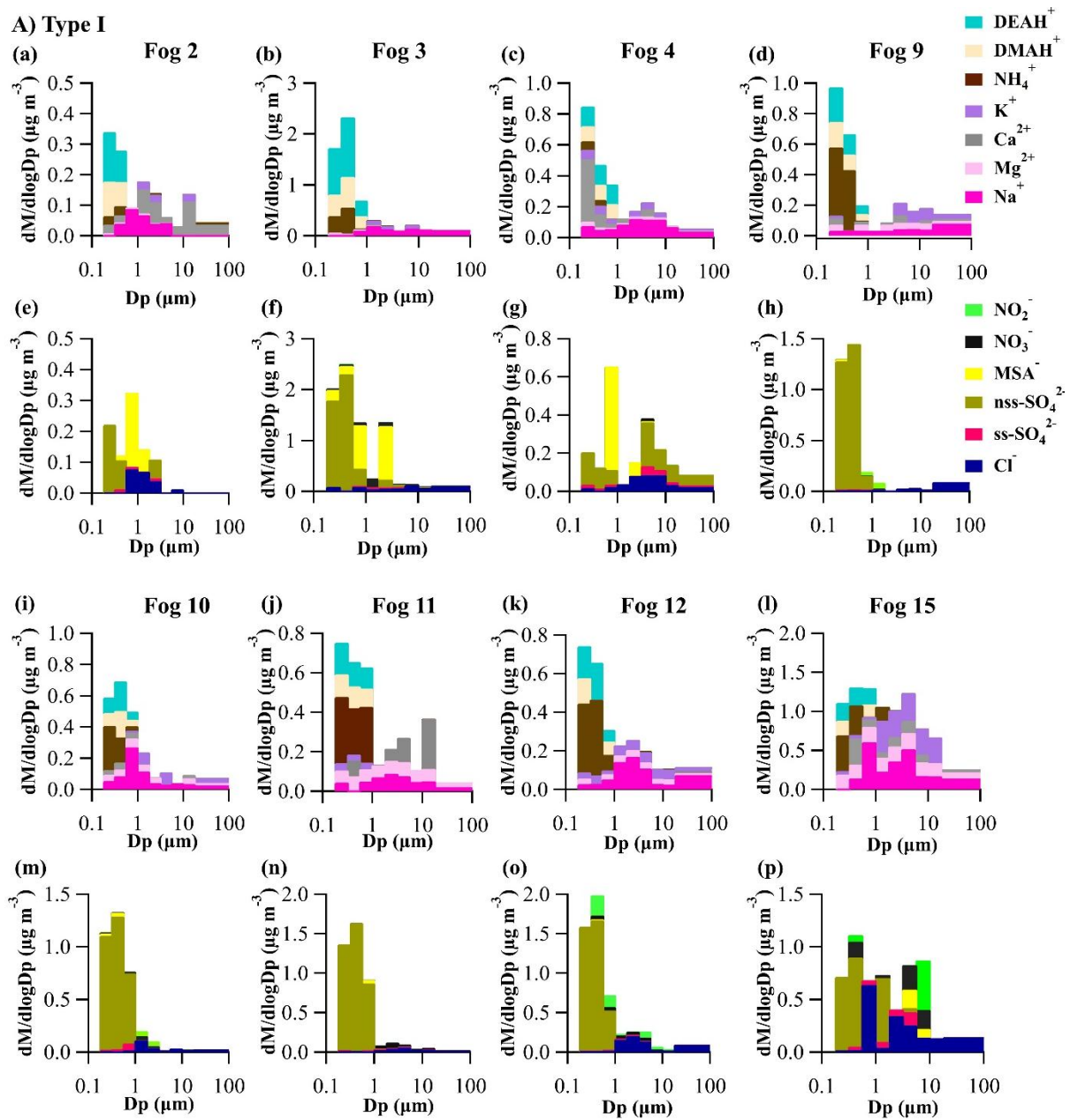


Figure B-4: Average equivalent ionic loading (neq m^{-3}) of aerosols categorized into coarse mode (1-100 μm) for (a) cations and (b) anions, and fine mode (0.1-1 μm) for (c) cations and (d) anions observed in the entire Fatima campaign.

B5. Fog type events

Three fog types were classified based on their ion mass distributions as a function of particle diameters: type I, characterized by a depleted sea salt coarse mode; type II, showing a sustained sea salt coarse mode; and type III, exhibiting the highest mass loadings of sea salt coarse mode aerosols in fog droplets (Figure B-5 and B-6). These fog aerosol samples were collected over durations ranging from 3 to 42 hours in the Northwest Atlantic Ocean during the Fatima campaign from July 7 to 30, 2022 (Table B-3 and Figure B-8a). The coarse mode sea salt ion mass loadings versus meteorological parameters showed differences for each fog type (Figure B-7), and wind direction (Figure B-8b) indicated that type I fog dominantly originated from the SW, with some contributions from NE. Type II fog was dominantly associated with winds from the SW, while type III fog was also dominated by SW winds, with additional contributions from SE and NW. Spatial distribution patterns (Figure B-9) indicated the occurrence of these fog types over Sable Island and Grand Banks.



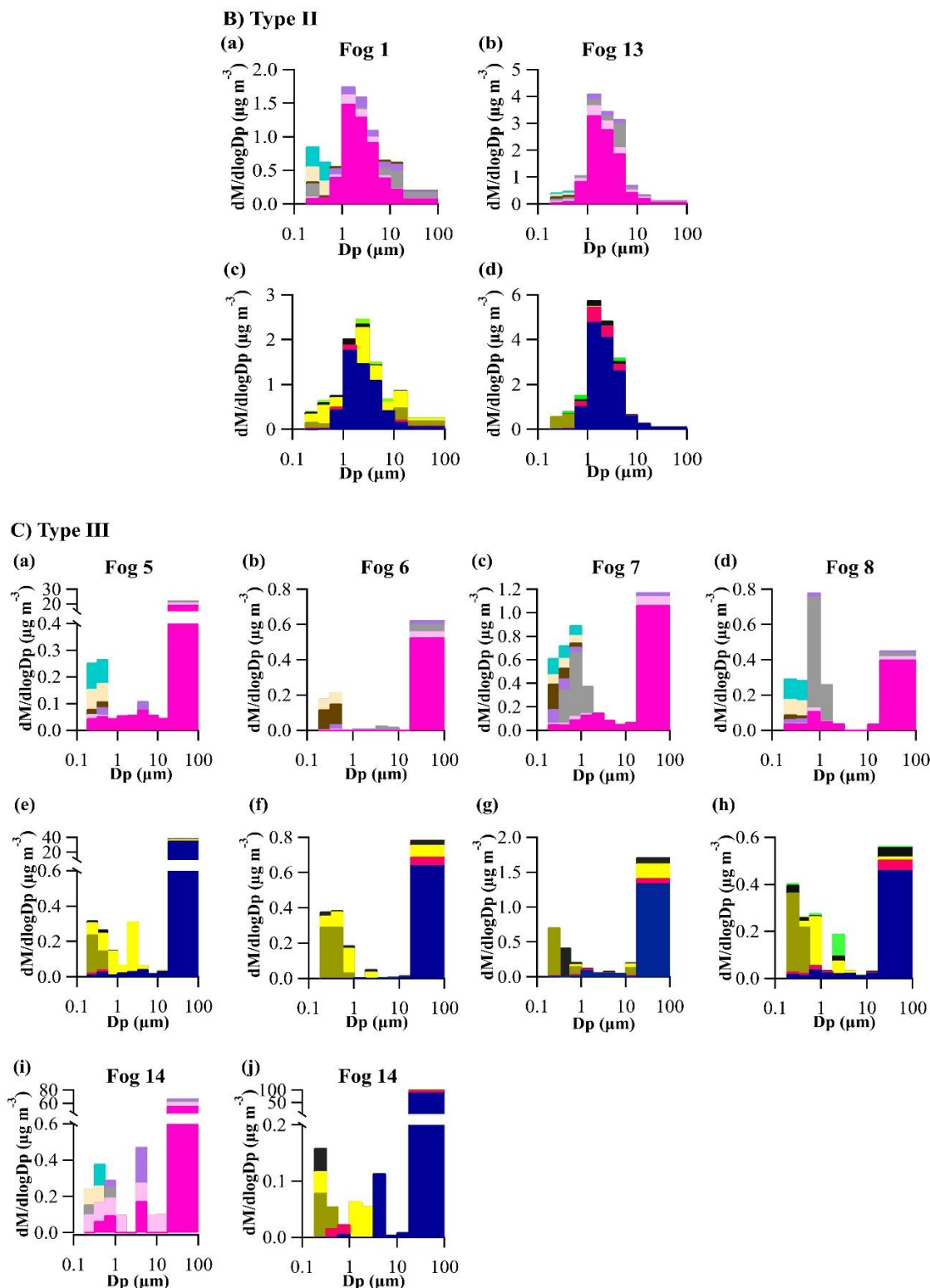


Figure B-5: Ion mass distributions of measured ionic constituents from all fog events across three fog types. (A) Type I: fog 2 (a and e), fog 3 (b and f), fog 4 (c and g), fog 9 (d and h), fog 10 (i and m), fog 11 (j and n), fog 12 (k and o), and fog 15 (l and p). (B) Type II: fog 1 (a and c), and fog 13 (b and d). (C) Type III: fog 5 (a and e), fog 6 (b and f), fog 7 (c and g), fog 8 (d and h), and fog 14

(i and j). Summed cations are shown as stacked contributions to the total in the upper row, and likewise for the anions in the lower row, except for fog 14, where cations and anions are displayed side by side. All sample information and fog type classifications can be found in Table B-3.

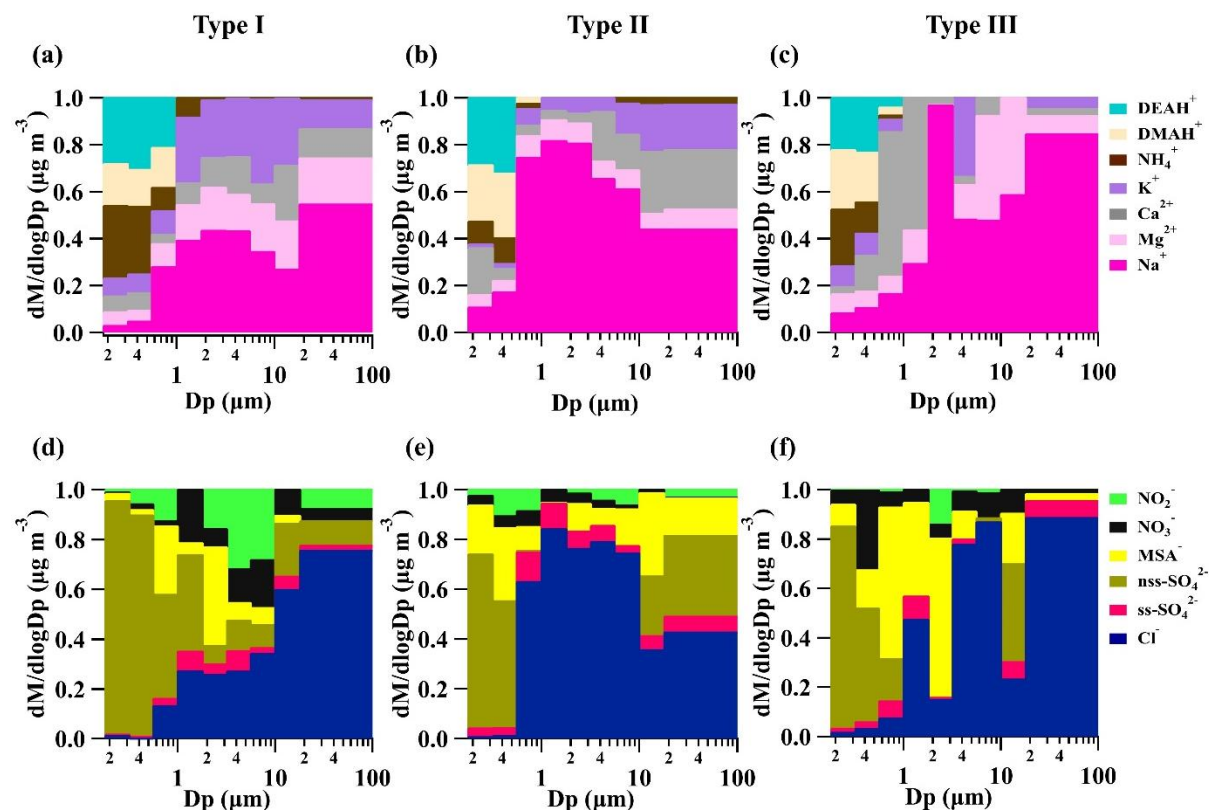


Figure B-6: Normalized average ion mass distributions of measured ionic constituents from three fog types: type I (a and d), fog type II (b and e), and fog type III (c and f). Normalized average cations are shown as stacked contributions to the total in the upper row and likewise for the anions in the lower row.

Table B-3: Classification of fog types and fog aerosol sampling times over the Northwest Atlantic Ocean during the Fatima campaign (July 7 to 30, 2022) using ion mass distribution analysis. Synoptic conditions for each fog type are summarized from, air-mass origin identified using HYSPLIT back trajectories, surface wind direction, and sea level pressure fields.

Surface wind direction, and sea level pressure holds:								
Fog Type	Set Number	Collection Time UTC				Synoptic condition		
						Air mass	Wind Direction	Pressure
I	2	July 9, 08:15 – 17:52				Coastal (NW)	SW	Low
	3	July 10, 00:38 – 01:20	July 11, 13:23 – 19:49	July 11, 21:56 – 22:17	July 11, 22:32–July 12, 00:48	Coastal/Clean marine (W/SW/S)	SW/S	Low
	4	July 12, 09:08 – 16:02				Clean marine (S)	SW	High
	9	July 21, 17:30 – July 22, 11:54				Coastal (SW)	SW	High
	10	July 22, 12:22 – July 23 01:18	July 23, 02:18 – July 23, 6:14	July 23, 8:25 – 10:42		Coastal (SW)	SW	High
	11	July 23, 22:13 – July 24, 10:20				Coastal (SW)	SW	High
	12	July 24, 10:43 – July 25, 14:50				Coastal (SW)	SW	High
	15	July 30, 03:18 – 07:37				Coastal (W)	SW	Low
II	1	July 7, 06:21 – 07:00	July 7, 08:07 – 10:45			Clean marine (S)	SW	Low
	13	July 25, 21:51 – July 26, 14:27				Coastal (SW)	SW	High
III	5	July 12, 19:08 – 19:58	July 12, 20:42 – 22:37	July 13, 09:34 – 11:50	July 13, 14:17 – 19:47	Clean marine (S)	SE/SW	High/Low
	6	July 13, 21:49 – July 14, 09:08				Clean marine/Coastal (S/SW)	SW	Low
	7	July 14, 19:42 – July 15, 04:47	July 15, 08:40 – 09:40	July 15, 10:54 – 11:53		Coastal (SW)	SW	Low
	8	July 15, 12:24 – 19:24	July 15, 21:07 – 21:23	July 16, 09:58 – 10:22	July 16, 10:27 – 15:03	Clean marine/Coastal (S/SW)	W	Low
	14	July 27, 02:21 – July 27, 09:26	July 27, 10:28 – 11:05			Coastal (W)	SW	Low

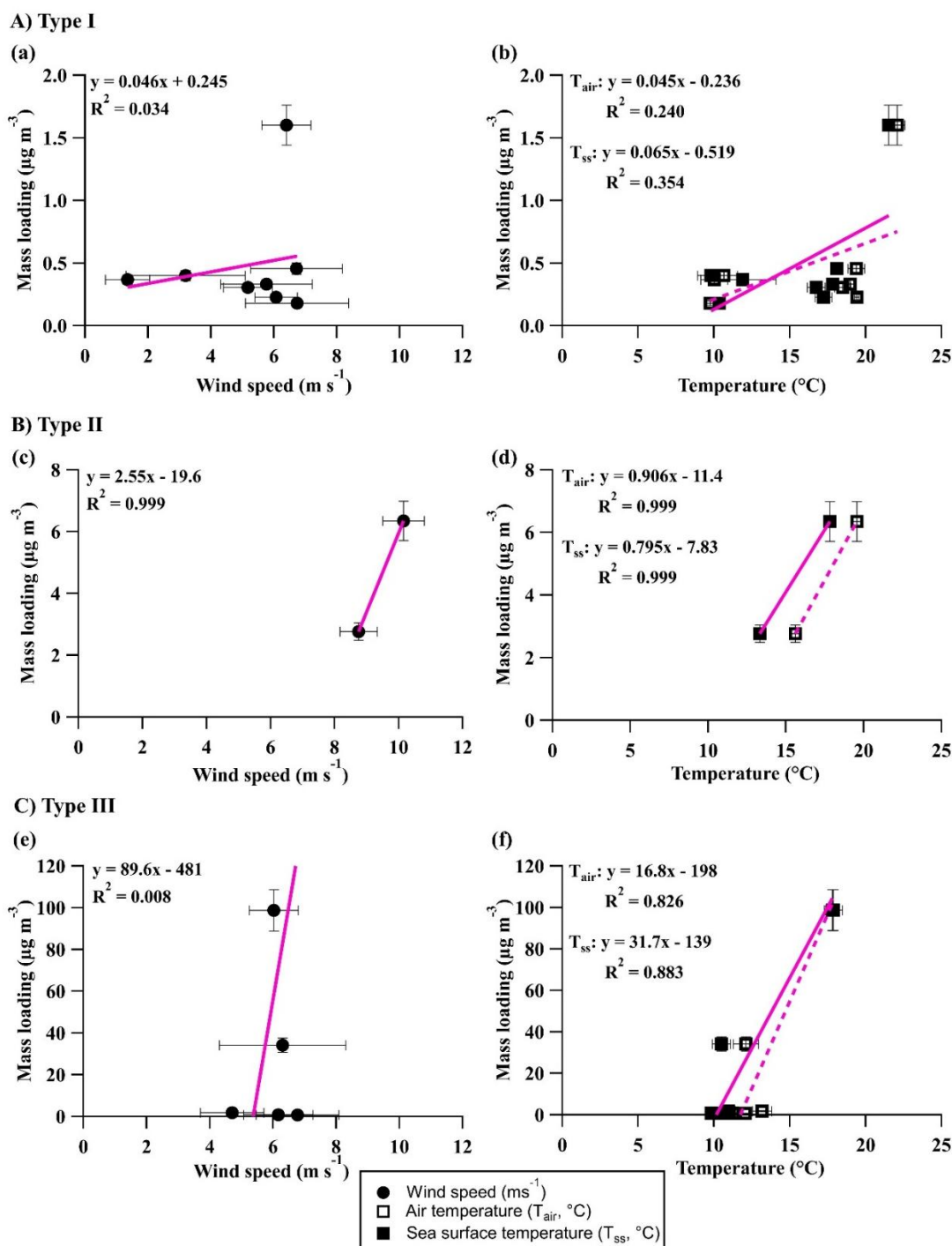


Figure B-7: Coarse mode sea salt ion mass loadings ($\mu g m^{-3}$) versus meteorological parameters by fog type: (A) type I: panels a and b, (B) type II: panels c and d, and (C) type III: panels e and f. Within each pair, the first panel shows mass loading versus wind speed ($m s^{-1}$), and the second shows mass loading versus temperatures (T_{air} and T_{ss} ; °C). The three fog types are shown separately due to their markedly different mass loadings. Curves were fitted using orthogonal least distance regression to account for uncertainties along both axes, and the correlation coefficient (R^2) from the depicted linear regression is reported.

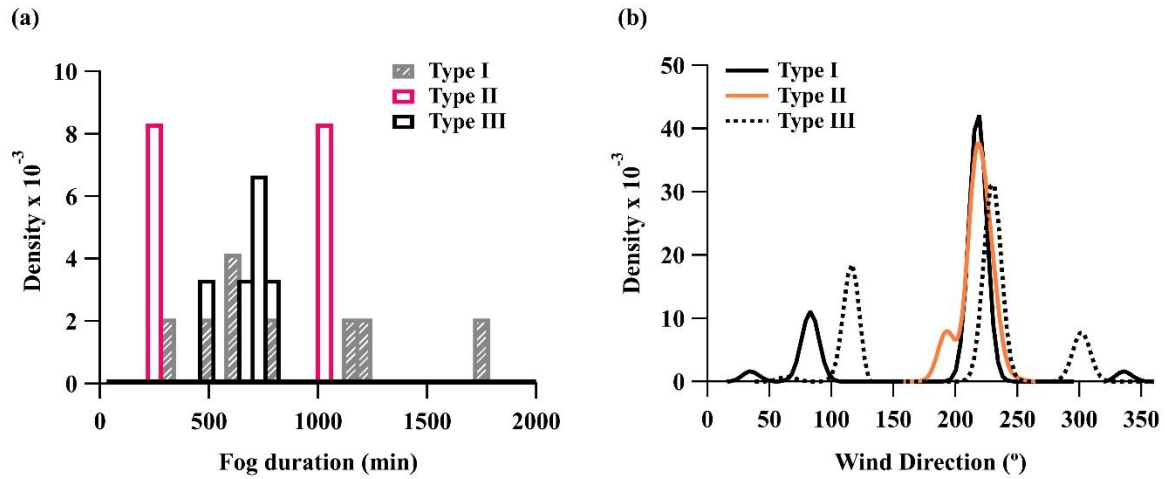


Figure B-8: (a) Probability density of fog duration (min) (b) kernel density of wind direction ($^{\circ}$) in three distinct fog types (I, II, and III), recorded during fog events in the Fatima campaign.

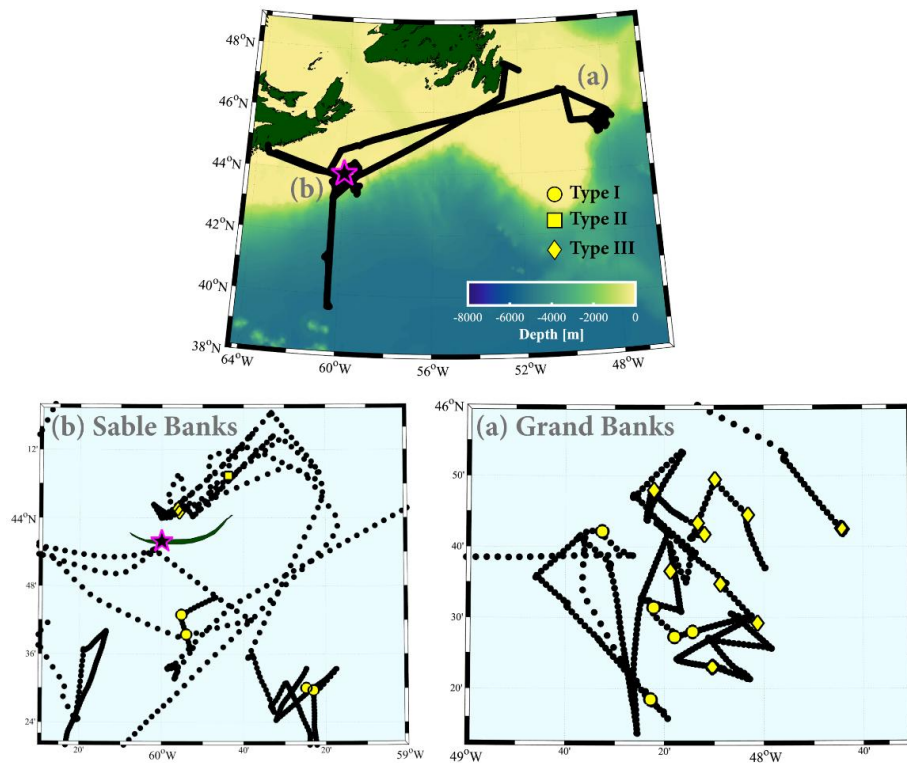


Figure B-9: The spatial distribution of three different fog types (I – circles, II – squares, III – diamonds) during the Fatima cruise, with detailed views of (a) the Grand Banks and (b) the Sable Island (pink star) areas. The symbols representing different fog sampling times, as detailed in Table B-3, are shown intermittently along the ship track (black dots) to emphasize the spatial and temporal transition between fog types.

B6. Column mass calculation (Super IOP #10)

Column mass ($\mu\text{g m}^{-2}$) of coarse mode sea salt aerosols was calculated under both ambient and fog conditions to compare values through the entire relevant mixed-layer for each sampling period, assuming sea salt is well-mixed within the marine boundary and fog layers especially from the sampling height of the MOUDI (Hoppel, Frick and Fitzgerald, 2002; Lewis and Schwartz, 2004; Boutle *et al.*, 2018). Much closer to the surface, we know a negative concentration gradient in the largest aerosols and droplets to be present from the C-CAMS observational platform (Ortiz-Suslow *et al.*, 2025), which would have a trivial impact on our observations and assumptions here. Column mass ($\mu\text{g m}^{-2}$) was determined by multiplying mass loadings ($\mu\text{g m}^{-3}$) by the marine boundary layer (MBL) depth (m) for ambient aerosols and fog layer depth (FLD, m) for fog aerosols. The MBL depth was identified based on the presence of a temperature inversion, whereas the FLD was determined by the occurrence of both a temperature inversion and relative humidity $\sim 100\%$ (Figure B-10). Column mass calculations utilized the averaged FLDs obtained from multiple radiosondes launches. In the absence of radiosonde measurements during ambient conditions, the MBL at the onset of fog was used for before fog conditions, while the MBL from the final radiosonde measurement during the dissipation of fog event was utilized for the after-fog conditions. The relationship between column mass ($\mu\text{g m}^{-2}$) and wind speed (m s^{-1}) was calculated during ambient and fog conditions using orthogonal least distance regression that accounts for the variance in both measurements (Figure B-11).

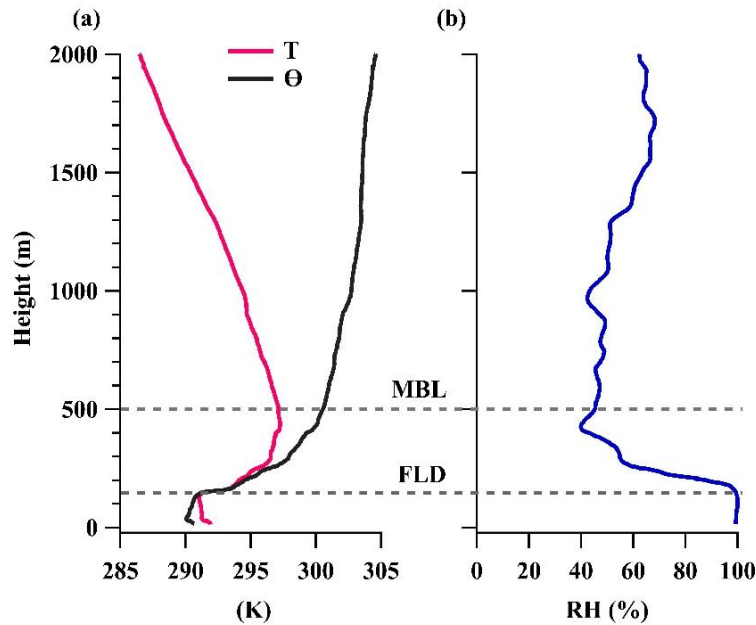


Figure B-10: Radiosonde profile showing (a) temperature (K), potential temperature (θ , K), and (b) RH (%) used to identify the fog layer depth (FLD) and marine boundary layer (MBL) heights during a fog event on July 23, 2022, at 22:28 UTC.

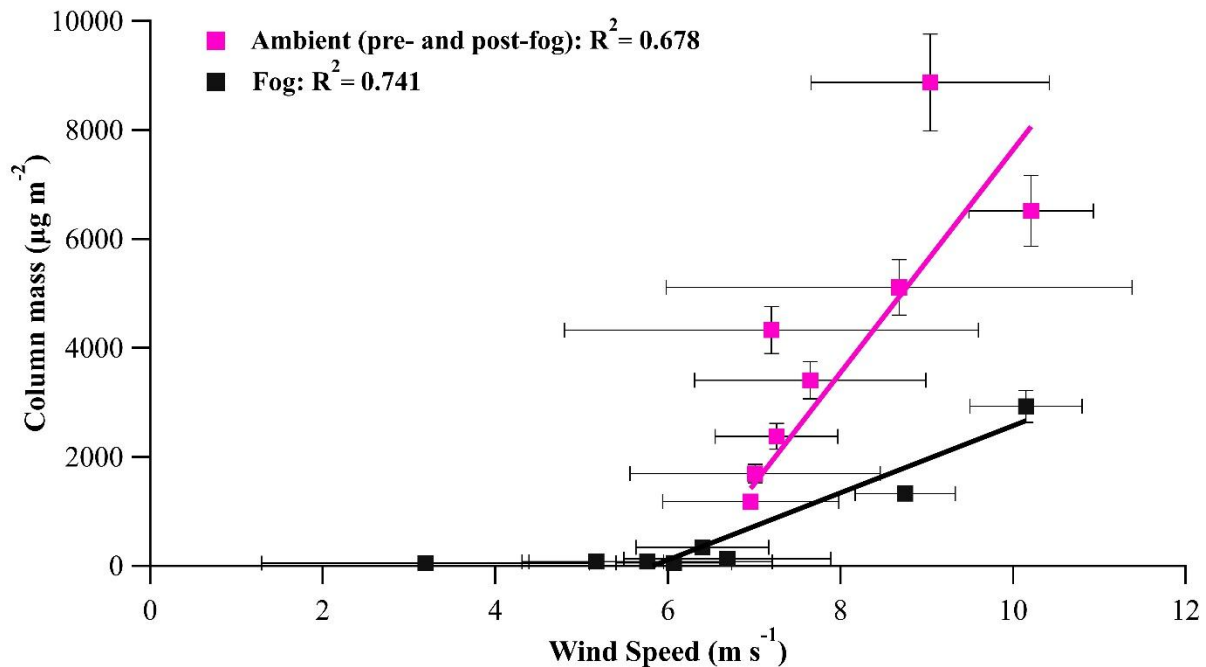


Figure B-11: Coarse mode sea salt column mass ($\mu\text{g m}^{-2}$) as a function of wind speeds (m s^{-1}) for ambient conditions (before and after fog) and during fog events. The linear trends were fitted using orthogonal least distance regression to account for uncertainties along both axes. The R^2 values were obtained using least-squares regression.

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Appendix C: Supporting information for Chapter Four

C1. Equivalent ionic and mass loadings of processed-S and reduced-N in fine mode aerosols and fog water samples

The average equivalent ionic loadings (neq m^{-3}) and corresponding mass loadings ($\mu\text{g m}^{-3}$) of processed-S and reduced-N species were compared for fine mode aerosols under ambient and fog conditions, along with fog water samples collected during the Fatima campaign. The results show that fog enhanced the equivalent ionic/mass loadings of processed-S and reduced-N in fine mode aerosols, while indicating a dilution effect in fog water samples. The measured values were consistent with those previously reported over the Atlantic Ocean (Table C-1).

Table C-1: Average equivalent ionic loadings (neq m^{-3}) and mass loadings ($\mu\text{g m}^{-3}$) of processed-S and reduced-N in fine mode aerosols ($0.1\text{--}1\ \mu\text{m}$) under ambient and fog conditions, as well as fog water droplets ($10\text{--}30\ \mu\text{m}$) collected during the Fatima campaign. Mass loadings from this study are also compared with values reported in previous studies over the Atlantic Ocean.

	nss-SO ₄ ²⁻		MSA ⁻		NH ₄ ⁺		DMAH ⁺		DEAH ⁺		References
	neq m ⁻³	$\mu\text{g m}^{-3}$	neq m ⁻³	$\mu\text{g m}^{-3}$	neq m ⁻³	$\mu\text{g m}^{-3}$	neq m ⁻³	$\mu\text{g m}^{-3}$	neq m ⁻³	$\mu\text{g m}^{-3}$	
Ambient aerosol	5.33 ± 4.45	0.26 ± 0.21	0.17 ± 0.40	0.02 ± 0.04	2.84 ± 3.48	0.05 ± 0.06	1.35 ± 0.85	0.06 ± 0.04	0.58 ± 0.41	0.04 ± 0.03	This study
Fog aerosol	7.62 ± 7.57	0.37 ± 0.36	0.65 ± 0.89	0.06 ± 0.09	5.62 ± 5.53	0.10 ± 0.09	1.64 ± 1.44	0.07 ± 0.07	1.48 ± 1.83	0.11 ± 0.14	This study
Fog water	1.42 ± 1.31	0.07 ± 0.06	4.40x10 ⁻³ $\pm 3.30\text{x}10^{-3}$	4.27x10 ⁻⁴ $\pm 3.17\text{x}10^{-4}$	2.05 ± 2.90	0.04 ± 0.05	---	---	---	---	This study
Ambient aerosol	---	0.25 ± 0.18	---	0.02 ± 0.02	---	0.03 ± 0.02	---	---	---	---	Mansour et al.(2020) ¹
Ambient aerosol	---	---	---	---	---	---	---	0.002- ^{*1} 0.024		0.004- ^{*1} 0.032	Facchini et al. (2008) ²
	---	---	---	---	---	---	---	0.004- ^{*2} 0.013		0.007- ^{*2} 0.024	
Ambient aerosol	---	0.09- ^{*3} 0.59	---	0.006- ^{*4} 0.06							Quinn et al. (2019) ³

^{*1}Mass loading range of amines measured at the coastal site of Mace Head Research Station.

^{*2}Mass loading range of amines measured aboard the oceanographic research vessel *Celtic Explorer*.

^{*3}Mass loading range of nss-SO₄²⁻+NH₄⁺ measured from November to September.

^{*4}Mass loading range of MSA⁻ measured from March to September.

C2. Physical, biological, and chemical measurements during ambient and fog conditions

Comprehensive physical, biological, and chemical measurements were conducted during the Fatima campaign to characterize ambient and fog conditions. Physical parameters included aerosol liquid water content (LWC, g m^{-3}), air temperature (T_{air} , $^{\circ}\text{C}$), sea surface temperature (T_{ss} , $^{\circ}\text{C}$), and wind speed (WS, ms^{-1}). Phytoplankton biomass was inferred using sea surface chlorophyll-a (Chl-a, mg m^{-3}) as a biological proxy. Chemical variables included aerosol pH, total reactive nitrogen (tN_r , ppbv), and ammonia ($\text{NH}_{3(\text{g})}$, ppbv; Table C-2). The Student's t-test revealed significant differences in LWC between ambient and fog events ($P\text{-value} < 0.05$), and a near-significant difference in pH ($P\text{-value} = 0.055$).

Table C-2: Comparison of mean physical, biological, and chemical parameters between ambient and fog conditions using independent Student's t-tests.

parameter	Ambient (mean, n = 14)	Fog (mean, n = 15)	P-value (2-tailed)	Significant
LWC (g m ⁻³)	0.004 ±0.008	0.086 ±0.049	0.001	Yes
Air temperature (T _{air} , °C)	18.586* ±4.205	16.446** ±4.158	0.180	No
Sea surface temperature (T _{ss} , °C)	16.553 ±4.961	14.273 ±3.983	0.182	No
Wind Speed (WS, m s ⁻¹)	6.973 ±1.926	6.019 ±2.047	0.208	No
Chl-a (0 lag day, mg m ⁻³)	0.421 ±0.144	0.355 ±0.139	0.216	No
Chl-a (8 lag day, mg m ⁻³)	0.420 ±0.143	0.357 ±0.130	0.226	No
Chl-a (16 lag day, mg m ⁻³)	0.412 ±0.115	0.412 ±0.061	0.998	No
Chl-a (24 lag day, mg m ⁻³)	0.424 ±0.113	0.419 ±0.069	0.887	No
pH	3.484 ±1.301	4.508 ±1.434	0.055	Nearly significant
tN _r (ppbv)	17.296 ±18.022	10.707 ±6.937	0.246	No
NH ₃ (ppbv)	1.101 ±1.127	1.088 ±0.598	0.970	No

*Mean air temperature in the marine boundary layer (MBL) during ambient conditions measured by radiosondes.

**Mean air temperature in the fog layer depth (FLD) during fog events measured by radiosondes.

C3. Multiple linear regression analysis

Multiple linear regression analysis was performed to explore the relationship between Chl-a concentrations at different lag intervals (0, 8, 16, and 24 days) and the equivalent ionic loadings of processed-S and reduced-N under ambient and fog conditions (Table C-3). This analysis aimed to identify the timescale associated with the biochemical transformation of phytoplankton-derived precursors in seawater into aerosol phase processed-S and reduced-N species. The results indicated the strongest positive associations by the highest standardized regression coefficients (B) at an 8-day lag for both processed-S and reduced-N, with enhanced association observed under fog conditions. Associations were considered significant at P-value < 0.05. For processed-S, the relationship was marginally significant under ambient conditions (P-value = 0.055), and statistically significant during fog events (P-value = 0.018). For reduced-N, the association was not significant under ambient conditions (P-value = 0.539) but approached significance under fog conditions (P-value = 0.086).

Table C-3: Multiple linear regression analysis of equivalent ionic loadings of processed-S and reduced-N (dependent variables) with lagged chlorophyll-a concentrations (independent variables) under ambient and fog conditions during the Fatima campaign.

Dependent variable	Independent variable	<i>Ambient periods</i>		<i>Fog periods</i>	
		Standardized coefficient (B)	P-value (significant)	Standardized coefficient (B)	P-value (significant)
Processed-S	Chl-a (0 day)	-5.552	0.041	-5.276	0.025
	Chl-a (8 day)	6.168	0.055	6.594	0.018
	Chl-a (16 day)	1.783	0.202	-0.109	0.788
	Chl-a (24 day)	-2.298	0.190	-1.213	0.061
Reduced-N	Chl-a (0 day)	-2.199	0.466	-4.237	0.104
	Chl-a (8 day)	2.218	0.539	5.267	0.086
	Chl-a (16 day)	-0.064	0.969	-0.262	0.588
	Chl-a (24 day)	0.173	0.933	-0.949	0.193

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Appendix D: Supporting information for Chapter Five

Controls on indoor ammonia in new Canadian homes during the first year of occupancy with reduced nitrogen case studies

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D1. Statistical analysis of the number of reactive substrates required for accurate NH₃ measurement with Ogawa passive samplers

Passive samplers collect gases by molecular diffusion onto a coated surface without the need for pumps. They are particularly useful indoors because they are quiet, power-free, unobtrusive, and can operate for long periods in occupied spaces without disturbing residents.¹ Parallel replicate deployments have been found to yield robust time-weighted average (TWA) concentrations, with no back diffusion over deployed exposure periods due to reactive uptake on the sampling substrates.² Sampling primarily occurs through molecular diffusion (ED-1), which follows by Fick's first law.³

$$m = \left(\frac{D \cdot A}{L} \right) (C_e - C_0) t \quad (\text{ED-1})$$

Where m is the mass (g) of analyte collected, D is its diffusion coefficient in air ($\text{cm}^2 \text{s}^{-1}$), A is the cross-sectional area of the sampler (cm^2), C_e is the external concentration of analyte (g cm^{-3}), C_0 is the concentration of analyte at the sorbent interface (typically zero), t is the sampling time (s), and L is the length of the diffusion path (cm).

A pilot study was conducted within NHAQS using one Ogawa sampler with two reactive substrates (Figure D-1) and two Ogawa samplers with four substrates. A total of ten samplers were deployed for 24-hour ($n = 6$) and 96-hour ($n = 4$) periods in indoor environments that included different conditions, such as construction, construction with welding, unoccupied, and occupied homes (Table D-1). We expect the replicates to follow a normal distribution around the mean mixing ratio of NH₃ present in the atmosphere during these sampling periods, with random error from the methodology driving its variance. In each condition, a field blank sampler was exposed for 30 seconds in the exact same location as the samples, and all indoor samples were blank corrected by subtraction of the blank signal if it was above the instrument LOD. The goal was to identify the number of reactive substrates required for accurate indoor NH₃ measurement (Table D-1). The percentage relative standard deviation (RSD%) from two reactive substrates was compared with four substrates (sample and duplicates), and the results showed that the RSD% generally decreased as the number of substrates increased to four. Additionally, the increased number of replicates also enables a Grubb's test to be applied to any four replicate sample substrates at both 95% and 90% confidence intervals (CI), and removing identified outliers during any sampling periods expectedly improved the overall method precision.

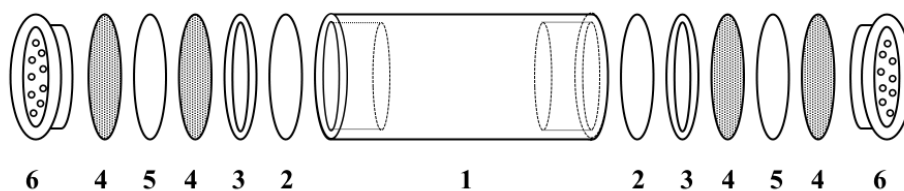


Figure D-1: Schematic of the Ogawa passive sampler assembly. Key components: (1) chambers of sampler body; (2) solid pad; (3) pad retaining ring; (4) stainless screen; (5) coated collection filter pad; (6) diffuser end cap (Adapted from Ogawa & Co.⁴).

The error in indoor NH_3 mixing ratios was compared across measurements using two substrates, four substrates, four substrates with Grubb's test at 95% CI, and four substrates with Grubb's test at 90% CI to identify the number of substrates and statistical CI that provided the highest accuracy (Table D-2). Measurements with two substrates exhibited high variability, with large errors (>40%) occurring in approximately 40% of samples and a few extreme outliers exceeding 100%. Increasing the number of replicate substrates from two to four reduced occurrences of extreme relative errors and applying Grubb's test within the quadruplicate samples further improved precision by increasing the proportion of low error outcomes (i.e. $\text{RSD} < 10\%$). In particular, using four substrates with outlier removal at 90% CI resulted in 75% of average measurement variances from replicate samples being below a 10% relative error from the mean. Based on these findings, all indoor NH_3 mixing ratios in the NHAQS study were collected with four reactive substrates, and outliers were identified and discarded at the 90% CI. The percentage of outliers identified was 0.4% for replicate samples and 2% for field blanks, the populations of which we all expect to return normal distributions due to the presence of a constant amount of gaseous analyte, or its absolute absence, respectively.

Table D-1: Mean and relative standard deviation (RSD%) of indoor NH₃ mixing ratios, measured in a pilot study within NHAQS using the Ogawa sampler.

Sample #	Condition	Sample type	Sampling time (h)	NH ₃ (ppbv) substrate 1	NH ₃ (ppbv) substrate 2	Mean ± STD substrate 1&2	Mean ± STD sample & duplicate (S & D)	RSD% substrate 1 & 2	RSD% (S & D)	RSD% G-test CI = 95%* (S & D)	RSD% G-test CI = 90%** (S & D)
1	construction	sample	24	0.97	1.88	1.42 ± 0.64	1.61 ± 0.43	45.06	26.93	4.53	4.53
2		duplicate	24	1.73	1.88	1.80 ± 0.10		5.61			
3	Construction + welding	sample	96	2.23	1.58	1.91 ± 0.64	---	24.07	---	---	---
4	unoccupied	sample	24	0.002	0.19	0.10 ± 0.14	0.20 ± 0.14	139.14	70.97	---	---
5		duplicate	24	0.29	0.31	0.30 ± 0.02		5.18			
6		sample	96	1.24	0.65	0.95 ± 0.42	0.04 ± 0.27	43.88	25.65	---	6.81
7		duplicate	96	1.08	1.19	1.14 ± 0.07		6.53			
8	occupied	sample	24	1.28	1.36	1.32 ± 0.06	1.38 ± 0.08	4.30	5.84	---	---
9		duplicate	24	1.46	1.42	1.44 ± 0.03		2.08			
10		sample	96	0.52	0.28	0.40 ± 0.17	---	42.98	---	---	---

* Critical values for Grubb's Test (G-test) at 95% confidence interval for outlier rejection in 4 substrates (sample & duplicate): 1.46. If G-calculated > G-table, the outlier can be rejected with 95% CI.

** Critical values for the G-test with a 90% confidence interval for rejecting outliers for 4 substrates: 1.42. If G-calculated > G-table, the outlier can be rejected with 90% confidence CI.

Table D-2: Comparison of relative error or relative standard deviation variances (Errors) in indoor NH₃ mixing ratios obtained with two and four substrate replicates at different CIs when applying the Grubb's outlier test followed by removal of outliers and recalculation of the sample variance in a pilot study within NHAQS using Ogawa samplers.

Errors	2-substrates % (CI=100%)	4-substrates % (CI=100%)	4-substrates % (CI=95%)	4-substartes % (CI=90%)
< 10%	50	25	50	75
< 30%	60	75	75	75
> 40%	40	25	25	25
> 100%	10	---	---	---

D2. Generalized linear mixed model (GLMM)

Indoor NH₃ (ppbv) was measured in 48 newly built homes from pre-occupancy through 12 months (n = 246 observations); 8 were excluded due to missing data in the survey. Also, post-occupancy was not included in the survey; instead, 0-month data was used as these technically began at the same point in time but were conducted for integrated intervals of 24 and 96 hr. The data were analyzed using a generalized linear mixed model (Gamma distribution, log link). Fixed effects consisting of 24 predictors, including both continuous variables (see Table D-3) and categorical variables (see Table D-4), were obtained from detailed questionnaires on housing characteristics and indoor activities completed for each sampling period. The GLMM extends generalized linear models by incorporating fixed effects (predictors) and random effects to account for non-independence resulting from correlation among repeated measurements within the same home over the first year of occupancy. In this study, fixed effects represent potential NH₃ sources and sinks, while a random intercept for each home accounts for within-home correlation and between-home variability, enabling estimation of overall relationships across homes. A first-order autoregressive [AR(1)] residual structure was used for correlation within homes across visits. The Gamma-log model was selected because NH₃ was not normally distributed, as shown by the Shapiro-Wilk test ($W = 0.648$, $p < 0.05$), indicating that NH₃ has a right-skewed distribution. Before running the GLMM, two highly redundant variables were removed through a collinearity test (swept/dusted/vacuum and wet mop; VIF = 62 and 257, respectively; tolerance = 0.016 and 0.004).

Predictor effects on indoor NH₃ were assessed using F-tests for fixed effects (F) and the corresponding fixed-effect coefficients (β) with 95% confidence intervals (Table D-5). The F-test shows how a predictor improves model fit. The coefficient β shows both the direction and magnitude: $\beta > 0$ indicates a positive association with an increase in NH₃ mixing ratio, while $\beta < 0$ indicates a negative association with a decrease in NH₃ mixing ratio. Statistical significance was set at $p < 0.05$. GLMM results (Table D-5) suggest that the time points at pre-occupancy ($\beta = 0.584$, $p = 0.001$) and 0 months ($\beta = 0.250$, $p = 0.003$; with 12 months as the reference), use of glass cleaner ($\beta = 0.233$, $p = 0.014$), and the number of people spending more than 18 hours indoors ($\beta = 0.055$, $p = 0.004$) are positively and significantly associated with higher indoor NH₃ mixing ratios. These two predictors, the use of glass cleaners and the number of people spending more than 18 hours indoors, were identified as the potential indoor NH₃ source points. Different types

of cleaners showed negative correlations with indoor NH₃ mixing ratios, but only oven cleaner indicated a near-significant negative association ($\beta = -0.449$, $p = 0.084$), suggesting its potential role as an indoor NH₃ sink compared to other cleaners. Changes in NH₃ mixing ratios were estimated based on source and sink effects, with the natural log coefficient (β) from the model being back-transformed using ED-2.

$$\Delta\text{NH}_3 = \text{average NH}_3 \times (e^{\beta}-1) \quad (\text{ED-2})$$

Post hoc pairwise tests ($\alpha = 0.05$) across various time points, from pre-occupancy to 12 months post-occupancy, revealed that the pre-occupancy indoor NH₃ mixing ratio was significantly higher compared to all post-occupancy visits. Also, the NH₃ measured at the 0-month visits were only significantly different from those measured at the 9 and 12 month timepoints (Figure D-2).

Table D-3: Descriptive statistics for continuous variables (n = 246) over the first year of occupancy in 48 houses.

Continuous variable	Mean	Std	Median	Min	Max	Categorical breakdown
Concrete (ft ²)*	66	59	60	0	319	---
People (#)	3	2	3	0	7	1 person: 52 (21%) 2-3 people: 113 (46%) ≥4 people: 81 (33%)
People (#) > 6 hrs	2	2	2	0	10	---
People (#) > 18 hrs	2	2	1	0	8	---
Pet (#)	0.44	0.69	0	0	3	0 pet: 163 (66%) 1 pet: 63 (26%) ≥2 pets: 20 (8%)
Cooking (min)	125	139	82	0	900	---
Sauté, frying, grilling (min)	38	61	10	0	540	---
Baking (min)	50	72	20	0	360	---
Toasting (min)	18	21	11	0	100	---
Window Open (hr)	99	137	55	0	780	---

*Total indoor concrete area

Table D-4: Frequency statistics for categorical variables (n = 246) over the first year of occupancy in 48 houses.

Categorical variable	Category	Frequency (n)	Percent (%)
Gas-stove	Yes	97	40
	No	149	60
Candles	Yes	35	15
	No	211	85
Glass cleaner	Yes	60	25
	No	186	75
Disinfect cleaner	Yes	80	33
	No	166	67
Tub cleaner	Yes	53	22
	No	193	78
Toilet cleaner	Yes	68	28
	No	178	72
Multi-surface cleaner	Yes	114	46
	No	132	54
Metals cleaner	Yes	8	4
	No	238	96
Oven cleaner	Yes	10	4
	No	236	96
Floor cleaner	Yes	49	20
	No	197	80
Carpet cleaner	Yes	8	4
	No	238	96
Upholstery cleaner	Yes	5	2
	No	241	98
Bleach	Yes	34	14
	No	212	86

Table D-5: Generalized linear mixed model (GLMM) for indoor NH₃ mixing ratio (dependent variable) over the first year of occupancy: fixed effects (F-test) and fixed-effect coefficient (β) with 95% confidence intervals (CI; $\alpha = 0.05$). Statistically significant results ($p < 0.05$) are highlighted in bold.

Predictor	Fixed factor F	Fixed coefficient β	p-value (95% CI)
Time points (pre-occupancy)_	3.034	0.584	0.001
Time points (0-month)	3.034	0.250	0.003
Time points (3-month)	3.034	0.106	0.237
Time points (6-month)	3.034	0.153	0.243
Time points (9-month)	3.034	0.016	0.805
Time points (12-month)*	3.034	0.000	-----
Concrete (ft ²)	0.398	-0.001	0.529
Gass-stove	0.581	0.130	0.447
Candles	0.085	0.050	0.772
Glass cleaner	6.175	0.233	0.014
Disinfect cleaner	0.055	-0.023	0.815
Tub cleaner	0.042	-0.022	0.839
Toilet cleaner	0.455	-0.075	0.501
Multi-surface cleaner	0.275	-0.047	0.601
Metals cleaner	1.697	-0.222	0.194
Oven cleaner	3.009	-0.449	0.084
Floor cleaner	1.473	0.156	0.226
Carpet cleaner	0.088	0.045	0.766
Upholstery cleaner	0.298	0.095	0.585
Bleach	0.286	-0.054	0.594
People (#)	0.687	-0.030	0.408
People (#) > 6 hrs	0.617	0.018	0.433
People (#) > 18 hrs	8.408	0.055	0.004
Pet (#)	1.014	0.099	0.315
Cooking (min)	0.256	0.001	0.613
Sauté, frying, grilling (min)	1.763	0.001	0.186
Baking (min)	0.114	0.001	0.736
Toasting(min)	1.086	-0.003	0.298
Window Open (hr)	0.191	0.001	0.529

*The 12-month timepoint is the reference category (coefficient fixed at 0), coefficients for all other time points indicate differences relative to 12 months.

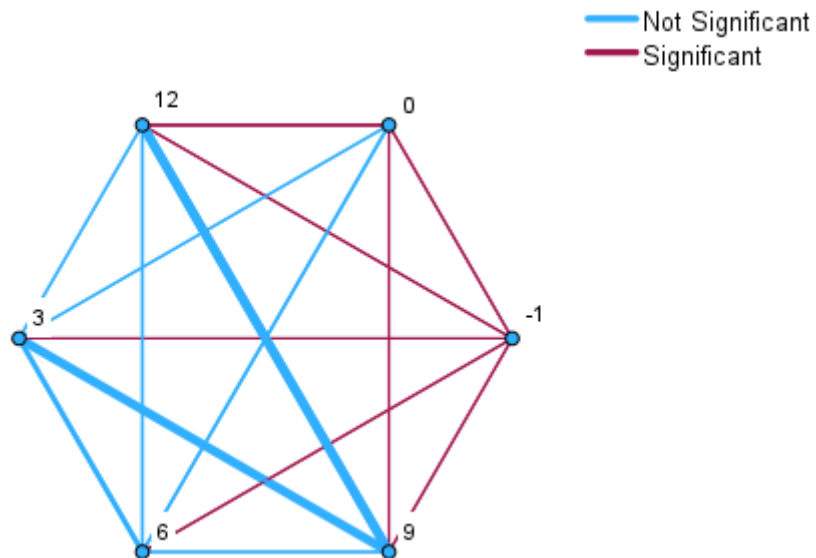


Figure D2: Pairwise post-hoc comparisons of indoor NH₃ mixing ratios at different time points: pre-occupancy (-1), 0-month (0), 3-month (3), 6-month (6), 9-month (9), and 12-month (12). Connecting lines indicate significant differences at $\alpha = 0.05$.

D3. Relationship between indoor and outdoor NH₃ mixing ratios

Pearson correlations were calculated on paired indoor-outdoor NH₃ mixing ratios measurements at each time point from pre-occupancy through 12 months. As summarized in Table D-6, a significant positive correlation was found at 3 months ($r = 0.388$, $p = 0.013$). At pre-occupancy, the correlation was positive but marginally significant ($r = 0.284$, $p = 0.053$).

Table D-6: Pearson correlation coefficients (r) between paired indoor and outdoor NH₃ mixing ratios by timepoints, from pre-occupancy through 12 months, in 48 newly constructed homes. Statistically significant results ($p < 0.05$) are shown in bold.

Indoor and Outdoor	r	p -value (two tails) CI 95%	n
Pre-occupancy	0.284	0.053	47
Post-occupancy	0.113	0.461	45
0-month	0.136	0.362	47
3-month	0.388	0.013	40
6-month	0.249	0.143	36
9-month	0.121	0.469	38
12-month	0.053	0.738	43

D4. Monthly variation in indoor NH₃ relative to temperature and relative humidity

Linear regression analysis was performed to assess the monthly variation of indoor NH₃ levels in relation to indoor T and RH from pre-occupancy to 12 months in 48 newly built homes. The Pearson correlation coefficient (*r*) with a two-tailed *p*-value ($\alpha = 0.05$), along with variance inflation factors (VIFs), are summarized in Table D-7. Significant positive correlations were only observed during warm season months: NH₃-RH in June (*r* = 0.631, *p* = 0.016) and NH₃-T in July (*r* = 0.452, *p* = 0.027). May showed a positive but marginally significant NH₃-RH relationship (*r* = 0.371, *p* = 0.057). The VIFs for T and RH were < 5 across all months, indicating no problematic collinearity between these two variables.

The apparent enthalpy of vaporization (ΔH) for NH₃ was derived from a linear regression of $\ln(\text{NH}_3)$ versus $1/T$ (Figure D-3), with slope $-\Delta H/R$. The warm season slope (2237K) yielded $\Delta H = -19 \text{ kJ mol}^{-1}$, while the cold season slope (-4041 K) yielded $\Delta H = +34 \text{ kJ mol}^{-1}$.

Table D-7: Monthly variability in linear regression results showing Pearson correlations (*r*) between indoor NH₃ mixing ratios and predictor variables (T and RH%) over the first year of occupancy in 48 houses. Statistically significant results (*p*<0.05) are shown in bold.

	NH ₃ -T <i>r</i> (<i>p</i> -value)	NH ₃ -RH% <i>r</i> (<i>p</i> -value)	VIF	n
January	-0.208 (0.494)	0.415 (0.159)	1.011	14
February	0.192 (0.294)	0.126 (0.491)	1.026	33
March	-0.016 (0.955)	0.192 (0.510)	1.003	15
April	-0.083 (0.845)	-0.403 (0.322)	1.011	9
May	0.250 (0.208)	0.371 (0.057)	1.007	27
June	0.036 (0.902)	0.631 (0.016)	1.102	15
July	0.452 (0.027)	0.107 (0.620)	1.008	25
August	-0.290 (0.066)	-0.079 (0.625)	1.164	42
September	-0.169 (0.408)	0.100 (0.626)	1.030	27
October	0.116 (0.591)	0.263 (0.214)	1.194	25
November	0.116 (0.547)	0.247 (0.197)	1.188	30
December	0.142 (0.432)	-0.124 (0.492)	1.000	34

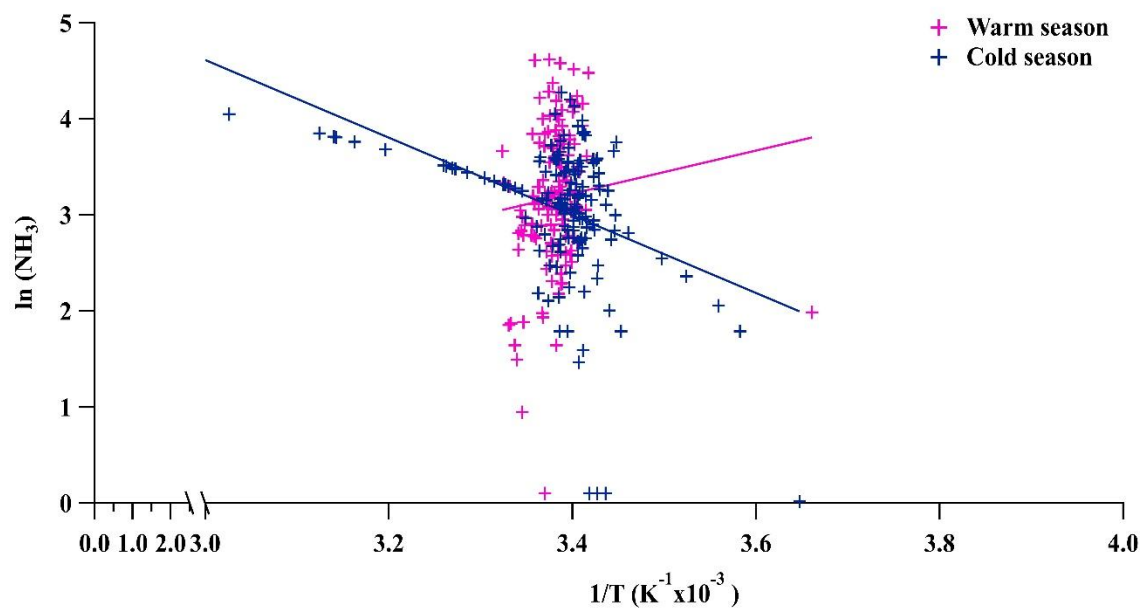


Figure D-3: Apparent enthalpy of vaporization (ΔH) of NH_3 , derived from linear regression of $\ln(\text{NH}_3)$ versus $1/T$ for the warm and cold seasons in 48 houses during the first year of occupancy.

D5. Variation in N-heteroaromatic ion counts depending on cooking method and time

N-heteroaromatic ion counts (N-ring, N-azole) were analyzed based on cooking methods: stovetop versus high-heat (sauté, fry, grill on the stove, or stand-alone devices) and cooking duration from pre-occupancy to 12 months in Home A and Home B, based on occupant activity questionnaires (Figure D-4). This evaluation aimed to identify cooking as a potential source of N-heteroaromatics. Pre-occupancy levels were low in both homes, consistent with the absence of cooking. In Home A, only N-ring increased with cooking time at 9 months (Figure D-4a). In Home B, N-ring was elevated at 9 and 12 months, and N-azole increased at 12 months (Figure D-4b). The highest ion signals of N-ring in both homes occurred when cooking duration was ≥ 80 min; no increases were seen at 3 months in Home B when cooking time was ~ 60 min. Peak N-ring intensities were higher in Home B than in Home A, coincident with longer high-heat durations. Overall, the patterns suggest that prolonged high-heat cooking likely contributes to N-heteroaromatic (N-ring) formation, while non-cooking sources (e.g., biomass burning) may also contribute.^{5,6} N-azole levels showed intermittent increases, suggesting additional pathways (e.g., ozonolysis of imine/enamine intermediates in humid surface films).⁷

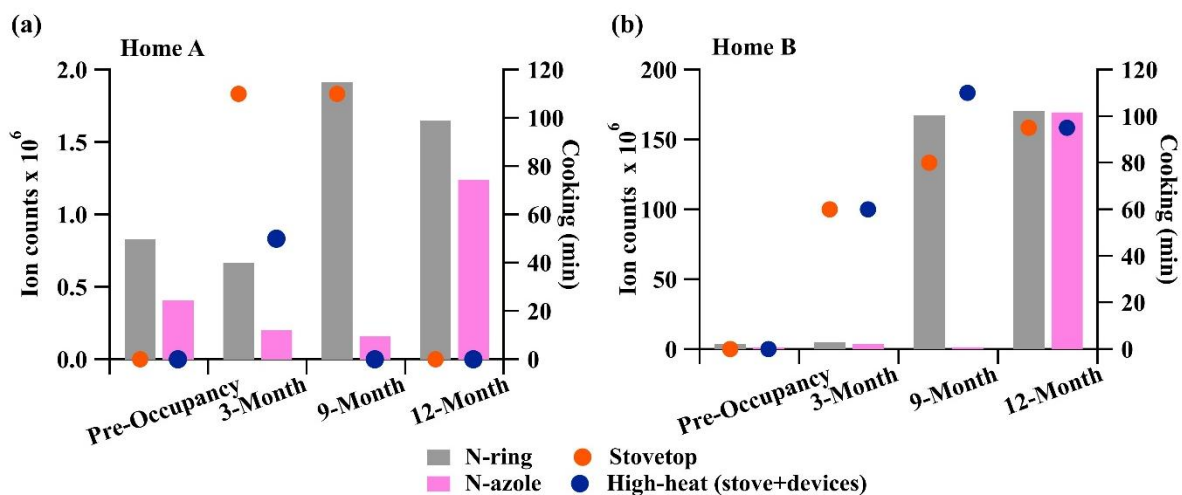


Figure D-4: Ion counts of N-ring and N-azole across pre-occupancy, 3, 9, and 12 months for (a) home A and (b) home B (left y-axis). On the right y-axis, cooking durations by method are shown: stovetop and high-heat (sauté/fry/grill) on stove plus stand-alone devices (min).

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