Thought leaders in particulate matter…

Using precision measurement, science and environmental intelligence to answer complex environmental questions

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Every Grain Tells a Story:

The Elemental Chemistry of Marine Aerosols Modified by Urban Environments

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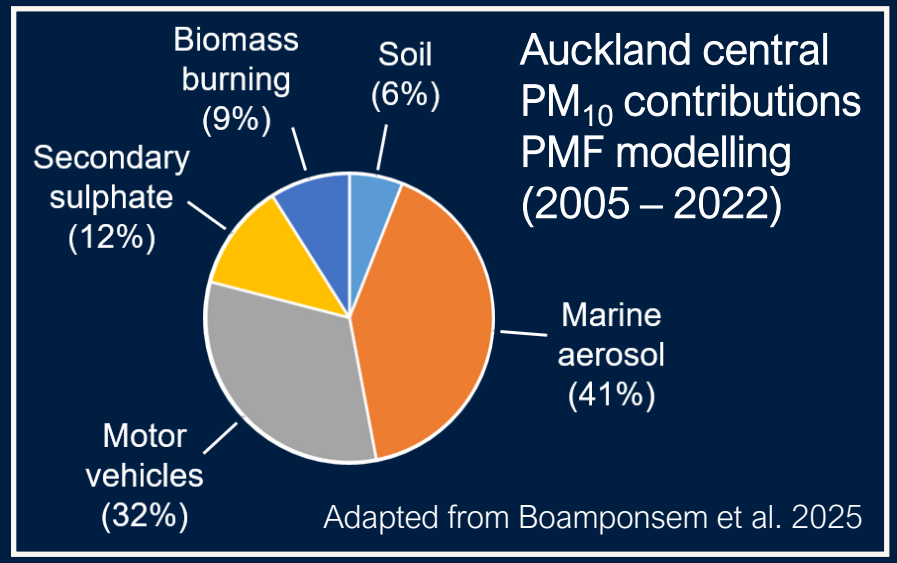
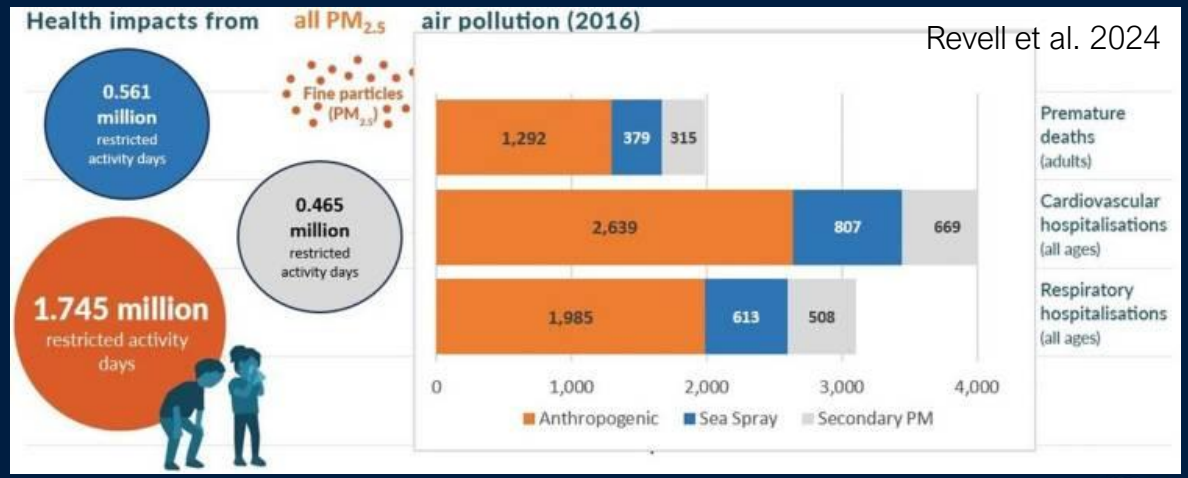
Background

- Marine aerosols are one of the largest contributors to PM fractions in coastal urban environments

- For heavily industrialised airsheds, contributions from marine aerosols often result in exceedances of the NES-AQ guidelines.
  - Historically, clause 16A of NES-AQ has been used to disregard exceedances relating to sea salt

- The underlying assumption is that marine aerosols are harmless
  - No epidemiological evidence linking *pure* sea salt to health outcomes
  - Do marine aerosols stay pure when travelling through urban environments?



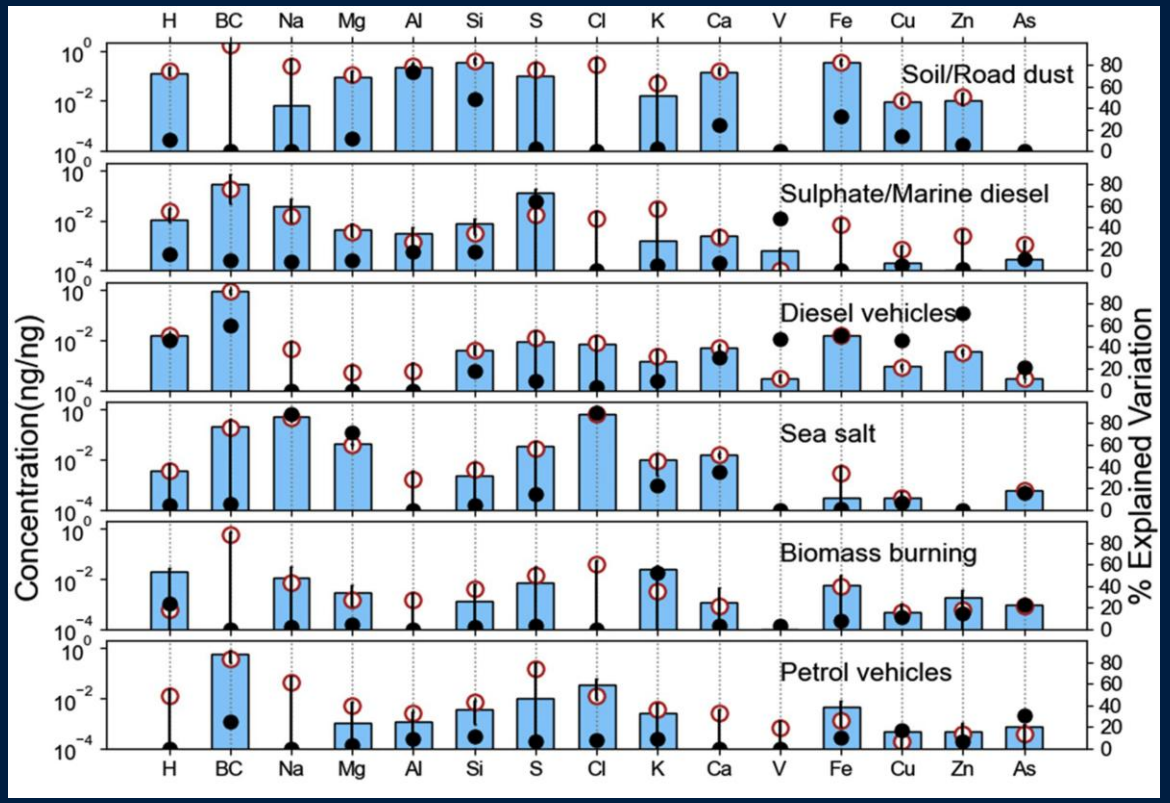


Background

- The chemistry of marine aerosols is known change with environmental aging
  - Sulphate/nitrate exchange
  - Internal mixing

- Information typically lost to conventional source apportionment using PMF
  - Estimation of particle populations from total gravimetric mass (chemical mass balance model)
  - Assumes each profile has a fixed composition
  - Difficulties dealing with subtle variance across similar classes

- Can single-particle level analysis provide insight into marine aerosol-anthropogenic pollution interactions?



Positive matrix factorization (PMF) analysis of Auckland air from ion beam analysis.

Adapted from Boamponsem et al. 2024

Sampling

- Particles collected on silicon carbide windows through impact sampling

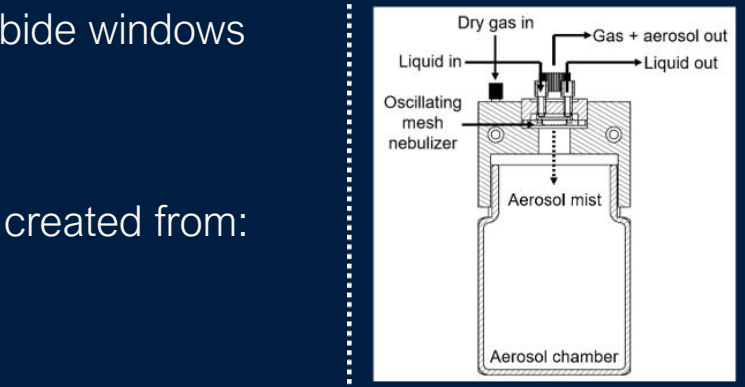
- Known reference-class samples created from:
  - Aerosolization
  - Controlled combustion
  - “Donut” sampling

- Ambient air samples collected using a FilterMote:
  - Urban air (Mt Eden, Auckland city)
  - Clean marine zone (West coast Auckland)

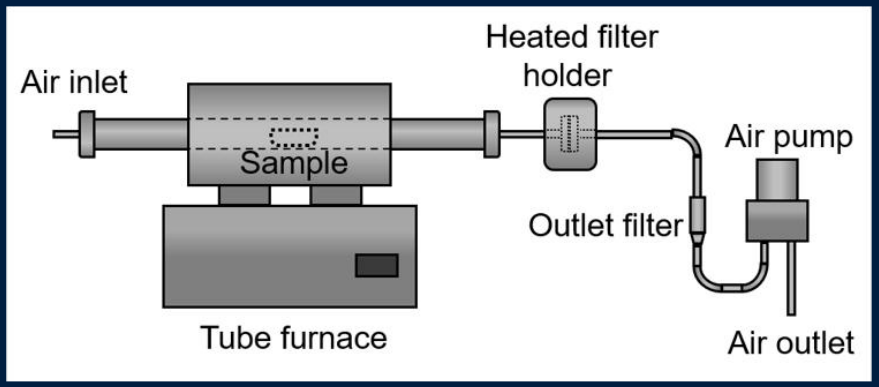
- X-ray fluorescence microscopy analysis was conducted on selected reference classes and ambient samples relevant to the marine aerosol problem

Reference sampling

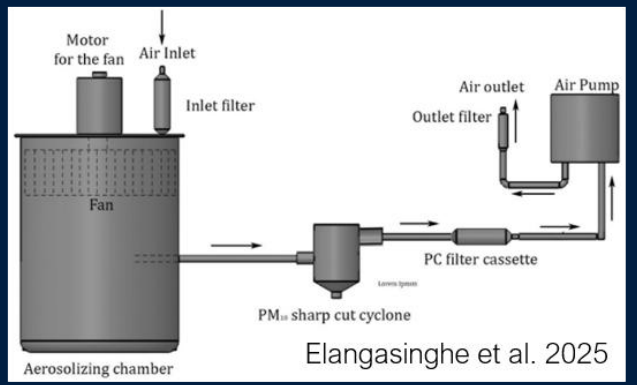
Aerosolization



Controlled combustion



“Donut” sampling



Elangasinghe et al. 2025

Ambient air sampling

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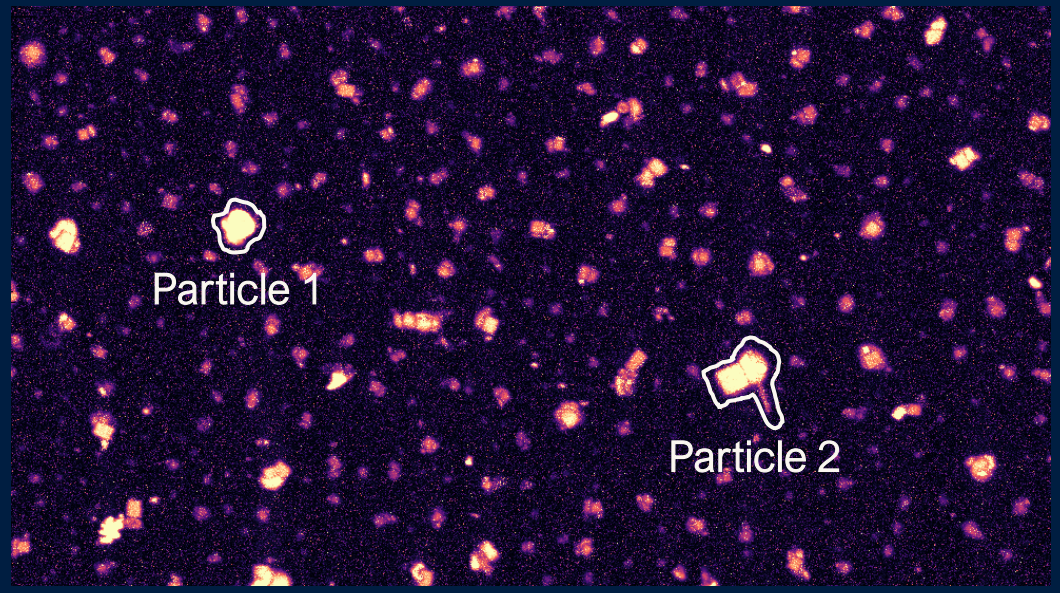
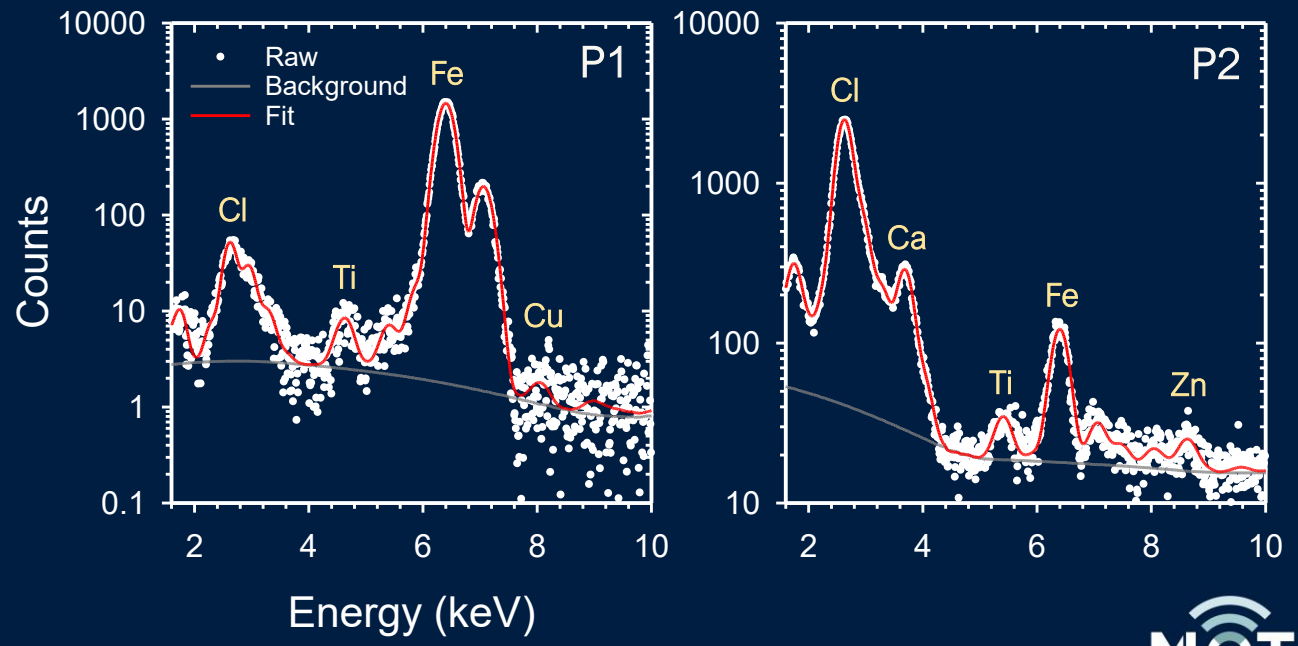
XFM in a Nutshell

- Based on X-ray induced fluorescence (XRF) of elements within a sample
  - Each element has a characteristic fluorescence signature (number and position of peaks)

- In X-ray fluorescence microscopy (XFM), the X-ray beam is tightly focussed to a small spot size
  - 0.5 × 0.5 um pixel size achievable
  - Each pixel contains a full XRF spectrum for that beam position
  - Elemental composition is determined by peak fitting



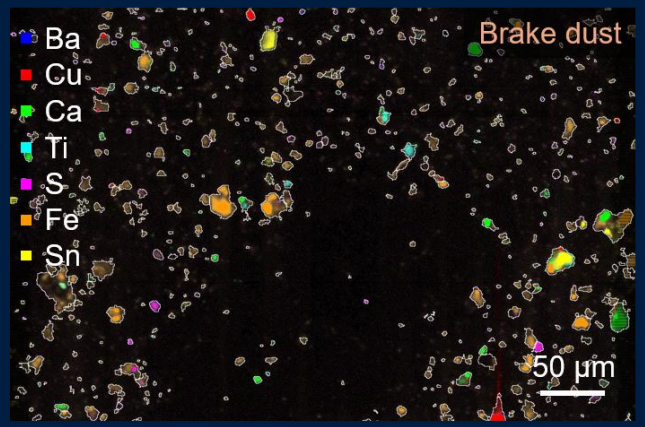


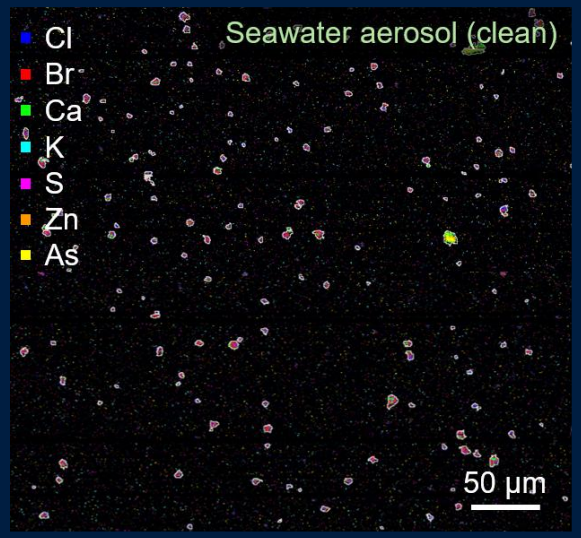
Elemental Maps: Reference Samples

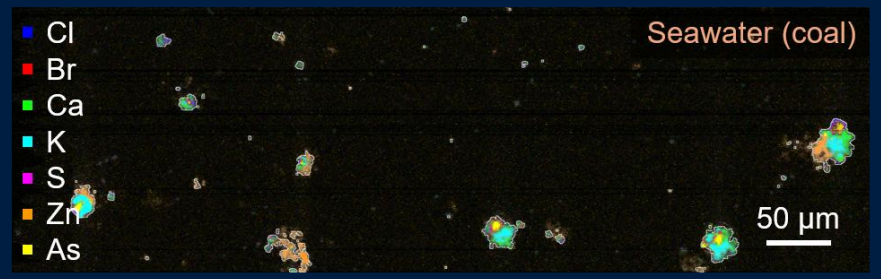
- Six total reference classes replicating expected real-world particles
  - Limitations with sample survivorship

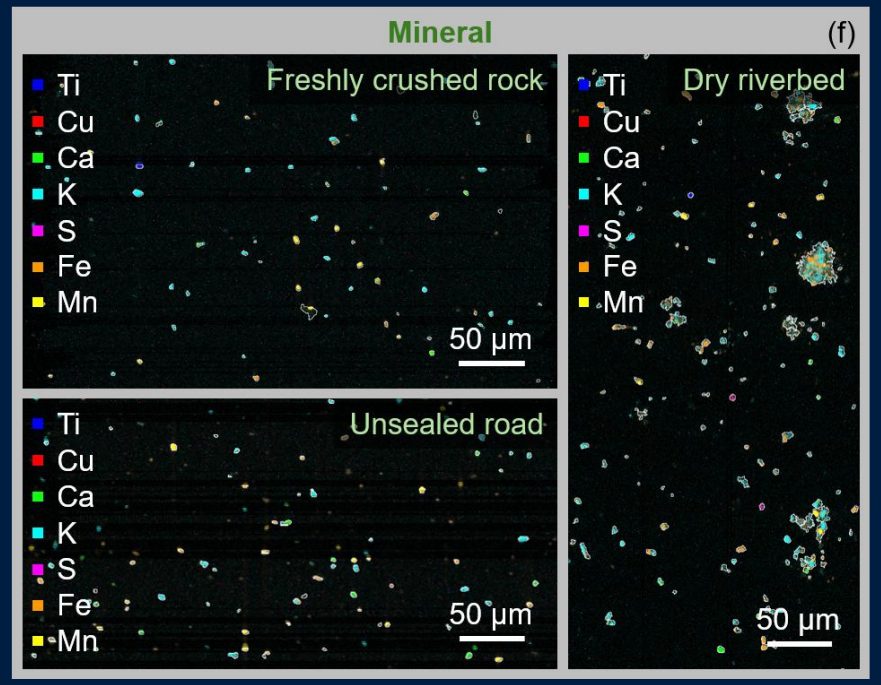
- "Biogenic" particles
  - Aerosolised seawater
  - Mineral dust

- "Anthropogenic" particles
  - TRWP (brake and tyre dust)
  - Soot from the combustion of a wood pallet
  - Aerosolised seawater passed through smoke from coal combustion



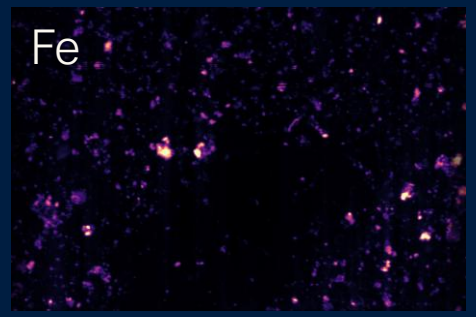


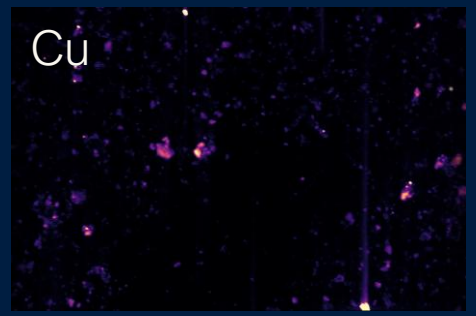




Statistical Analysis Pathway

- Individual heatmaps are element specific
  - Pixel intensity scales linearly with *relative* concentration
  - Maximum concentration may vary between images
- Particle recognition software (ImageJ) identifies unique particles
- Average pixel values per particle extracted from individual element heatmaps
- Elemental concentrations calculated and recorded for individual particles





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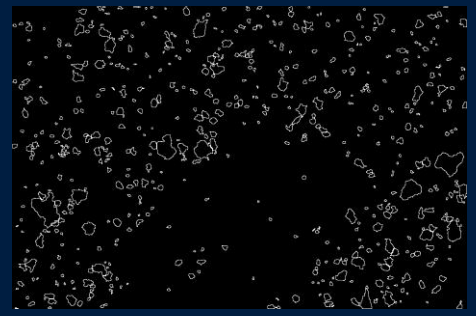
Concentration extraction

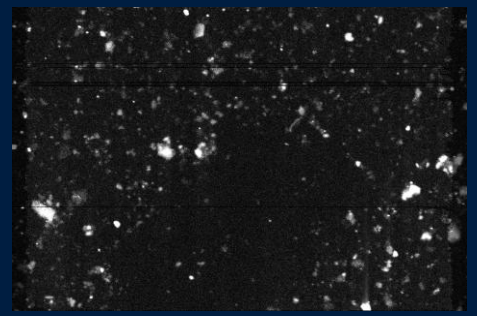
Ca	Ti	Cr	Mn	Fe	Cu	Zn
0	0	0	0	6021.694	288.607	0
6821.83	2254.089	0	1341.537	67886.52	607.0498	599.2393
25803.87	2309.203	0	1268.437	61211.26	1410.993	963.4094
7243.874	2054.792	0	624.3117	45921.29	1623.434	1345.243
13725.37	1502.262	0	492.2748	38331.02	1333.412	999.7219
8088.624	975.852	0	0	11841.44	551.9883	3568.879
25073.74	1567.214	0	0	33045.88	943.5377	585.7717
0	0	0	0	19533.79	583.4684	378.7284
6324.255	1131.877	0	0	21630.37	700.085	480.6367
0	0	0	620.2097	50396.44	1894.766	189.6369
0	2184.871	0	516.3835	35110.88	904.3984	509.8594
14580.28	1339.707	0	420.2195	35688.82	1119.503	778.0748
3973.309	19614.47	0	1660.871	82631.6	390.9562	333.9627
0	0	249.2141	382.4117	40476.07	1028.425	151.4914

…

Statistical analysis

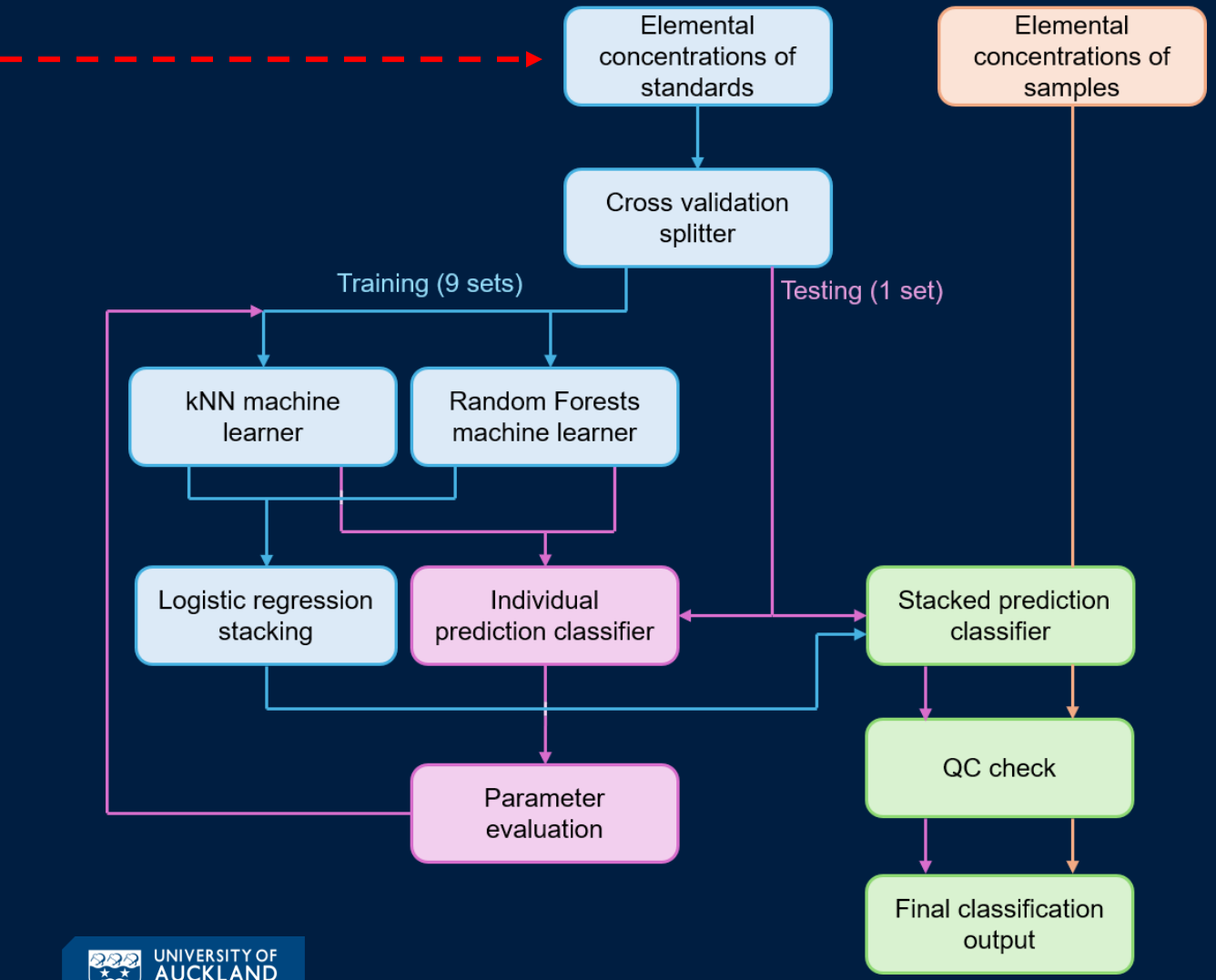


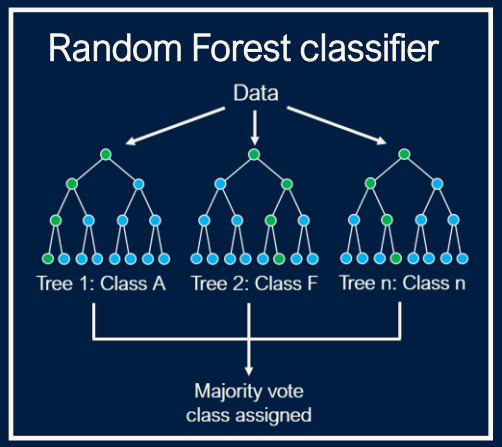
Particle ID

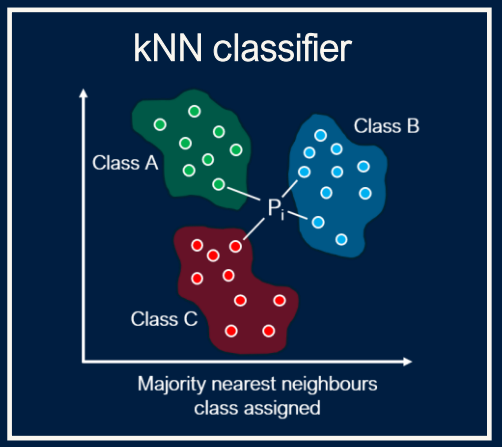


Greyscale compilation

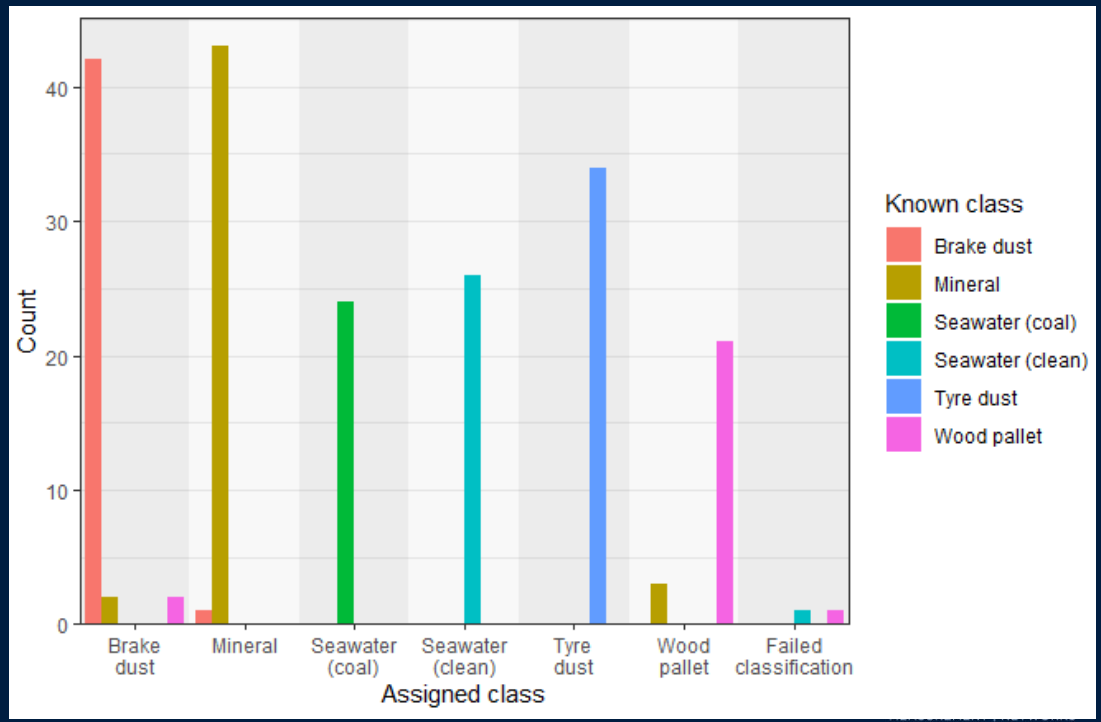
Particle Classification







Testing set stacked kNN-RF classification



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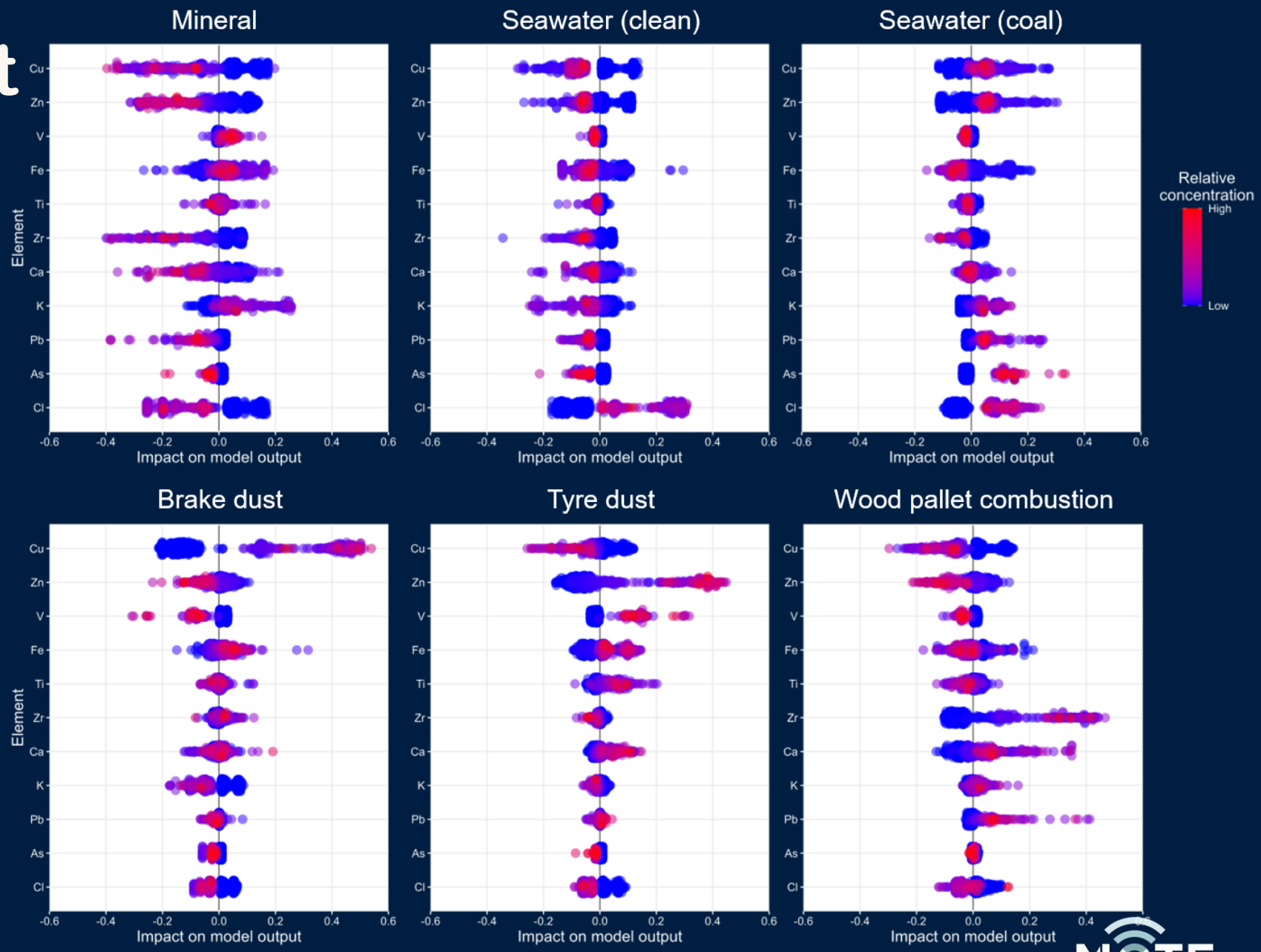
Random Forest SHAP values

- Shapley additive explanations
  - Visual representation of machine learning model decision tree

- Different primary markers for non-tailpipe vehicle emissions:
  - Brake dust: Cu
  - Tyre dust: Zn

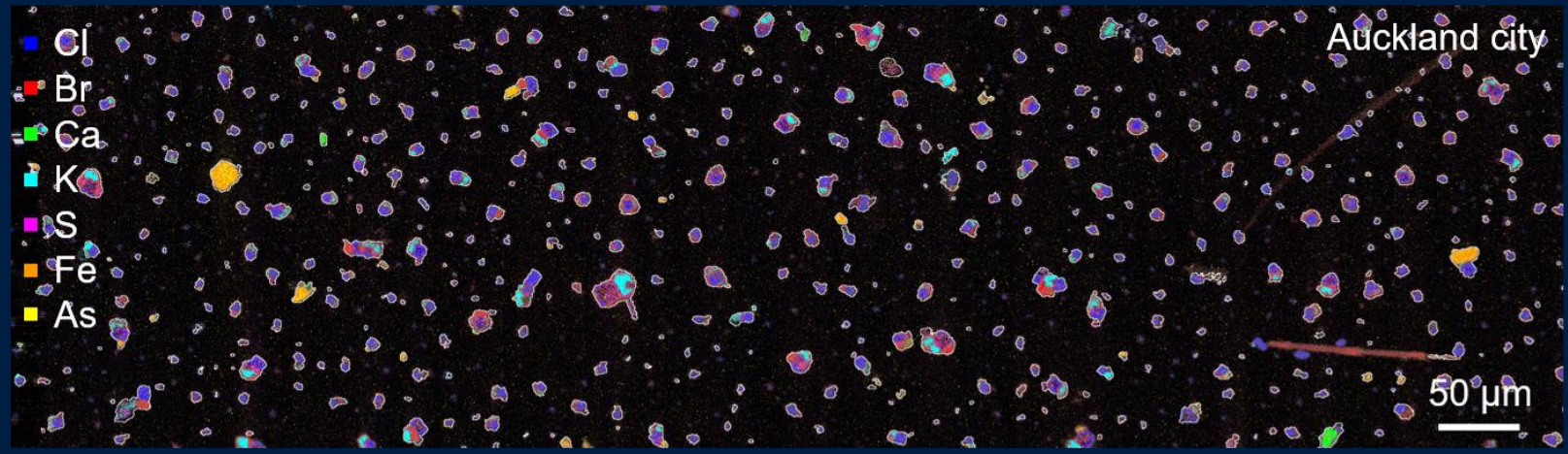
- Seawater primarily driven by Cl concentration
  - Elevated levels of Cu, Zn, K, Pb, and As after passing through coal burn

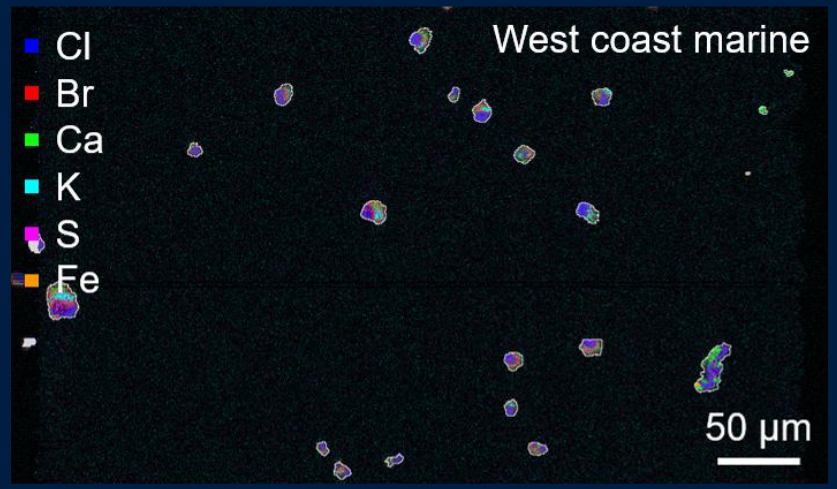


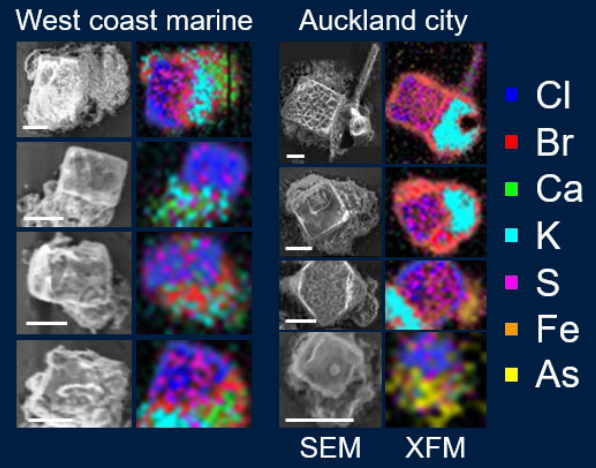
Elemental Maps: Ambient Air Samples

- XFM analysis and classification method applied to real world ambient air samples
  - Urban air from Mt Eden (Auckland city)
  - Clean marine air from Auckland west coast

- Cl containing particles (marine aerosols) dominate both samples
- Larger variety in trace elements for urban air
- Some particles show trace metal signatures in conjunction with Cl particles



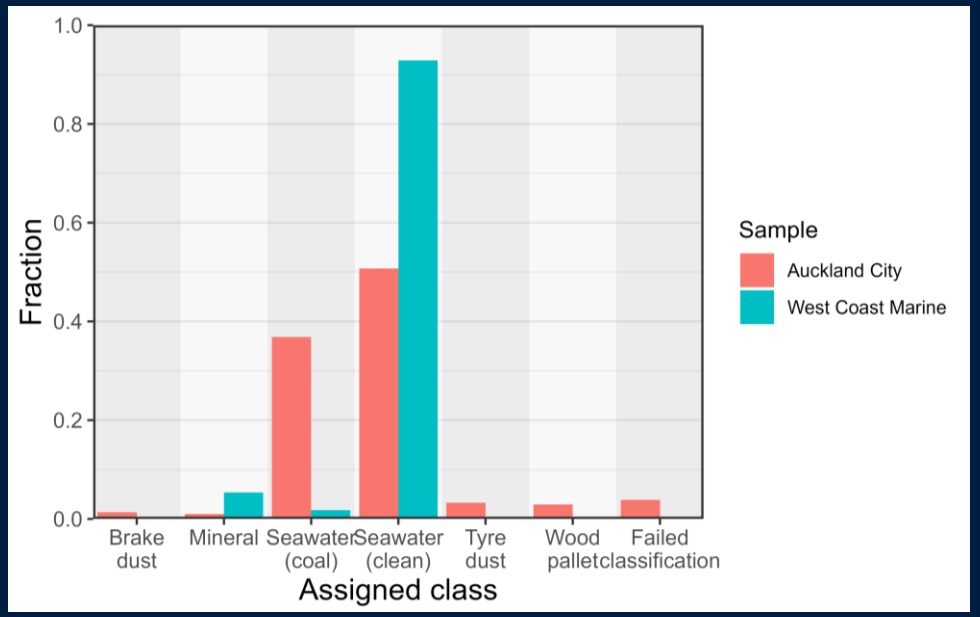


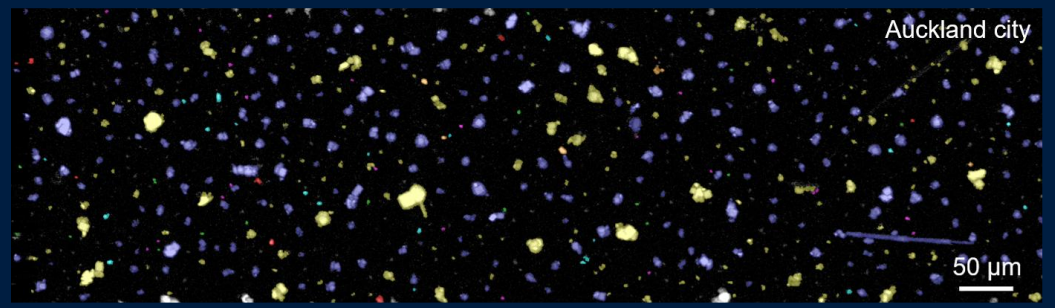


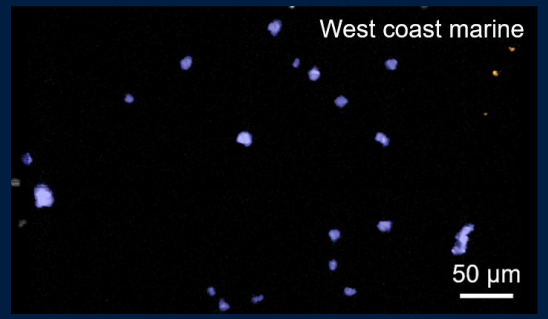
Particle Classification

- Ambient air elemental data fed through reference-trained stacked kNN-RF classifier
- Seawater-related particles dominant fraction for both coastal urban (Auckland city) and clean marine (west coast) air
- Higher levels of vehicle and combustion related particles in urban sample
- Coastal urban air shows a significant increase in seawater-coal-like particles compared to clean air
  - Marine aerosols with trace metals included
  - Carriers of anthropogenic pollutants

Stacked kNN-RF classification







- Brake dust
- Mineral
- Seawater (coal)
- Seawater (clean)
- Tyre dust
- Wood pallet
- Failed classification

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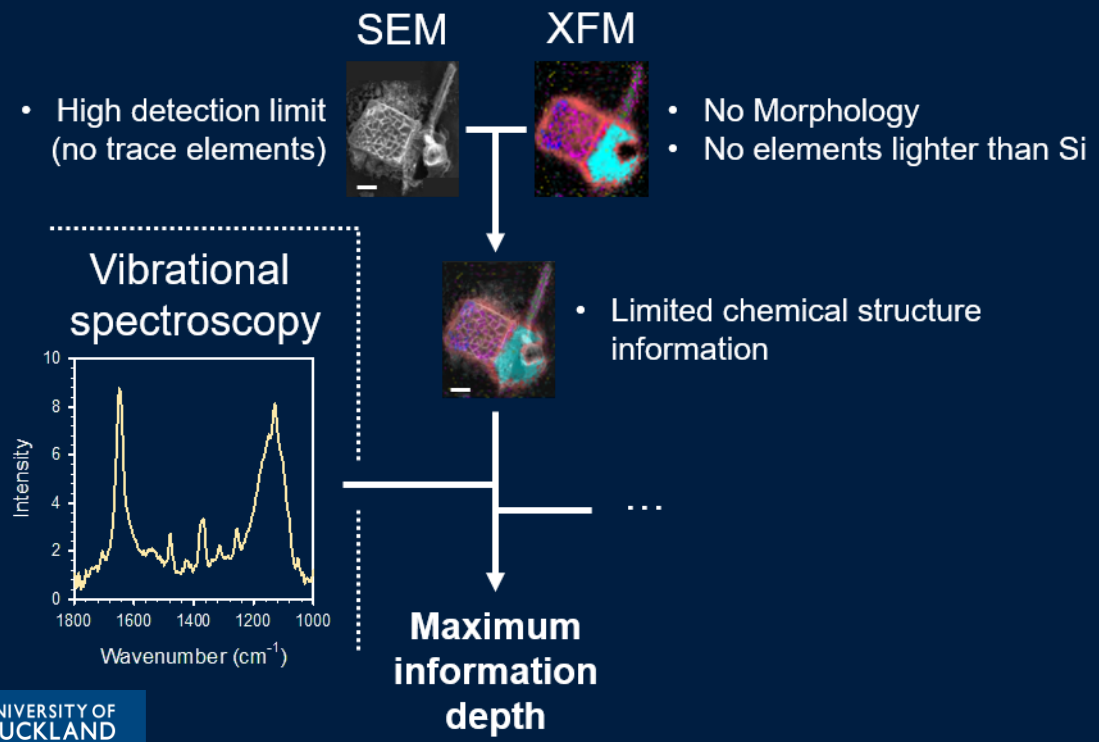
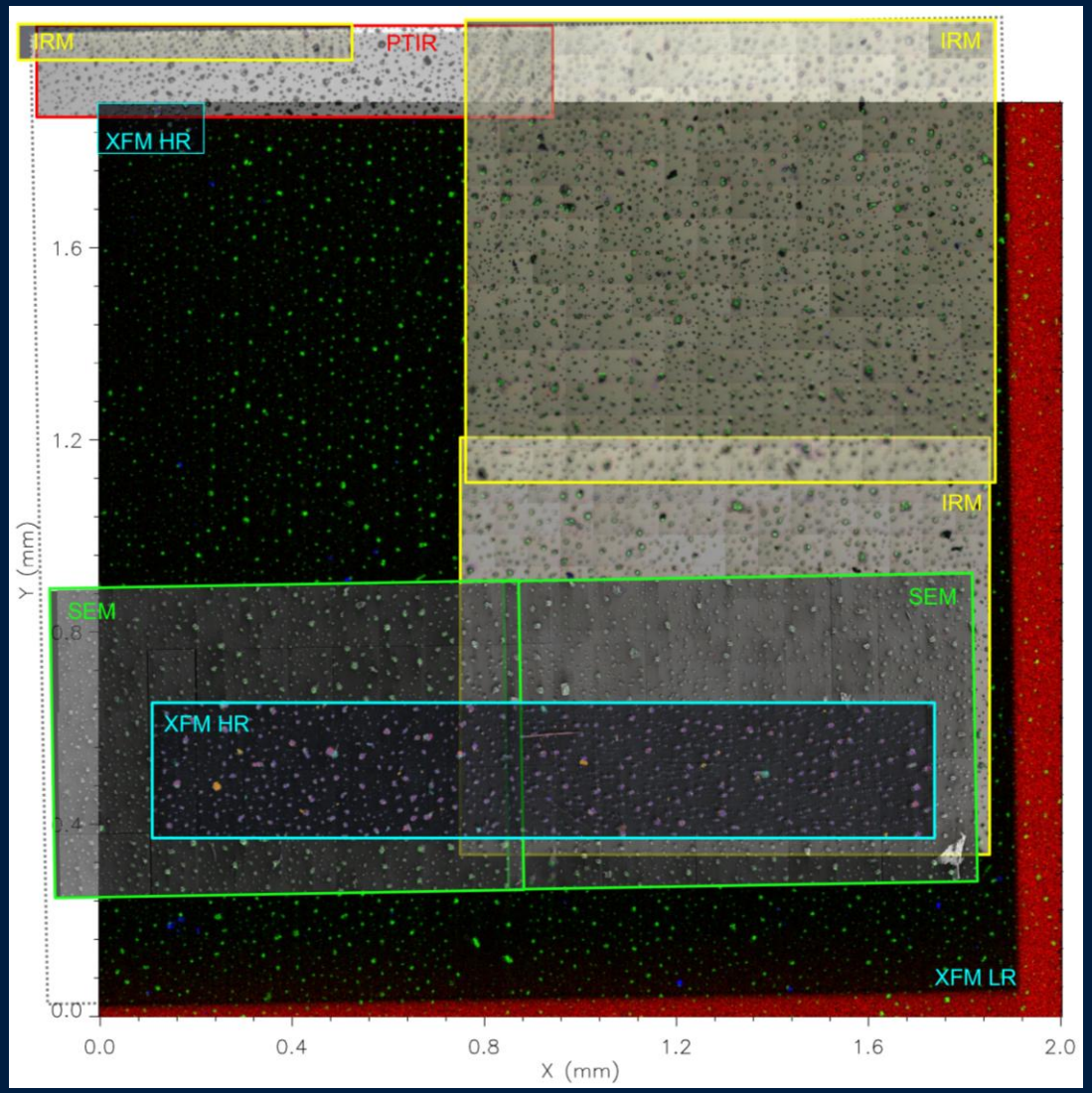
Multimodal Analysis

- Limited information from individual techniques
- Shift to multimodal models – combining information from multiple techniques





Overlay of data collection areas from individual characterisation techniques for the Auckland city sample

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Summary

Key questions:

- Do marine aerosols stay pure when travelling through urban environments?
- Can single-particle level analysis answer this?

- XFM has been used to explore associations between trace metal contaminants and marine aerosol particles
- Compelling evidence that marine aerosols collect chemical signatures of anthropogenic pollution from urban environments

- Do we need more research around the health impacts of marine aerosols exposed to urban environments?

This case study highlights the potential of XFM single-particle level analysis for separately chemically similar particle classes

Do you have a complex particle problem?

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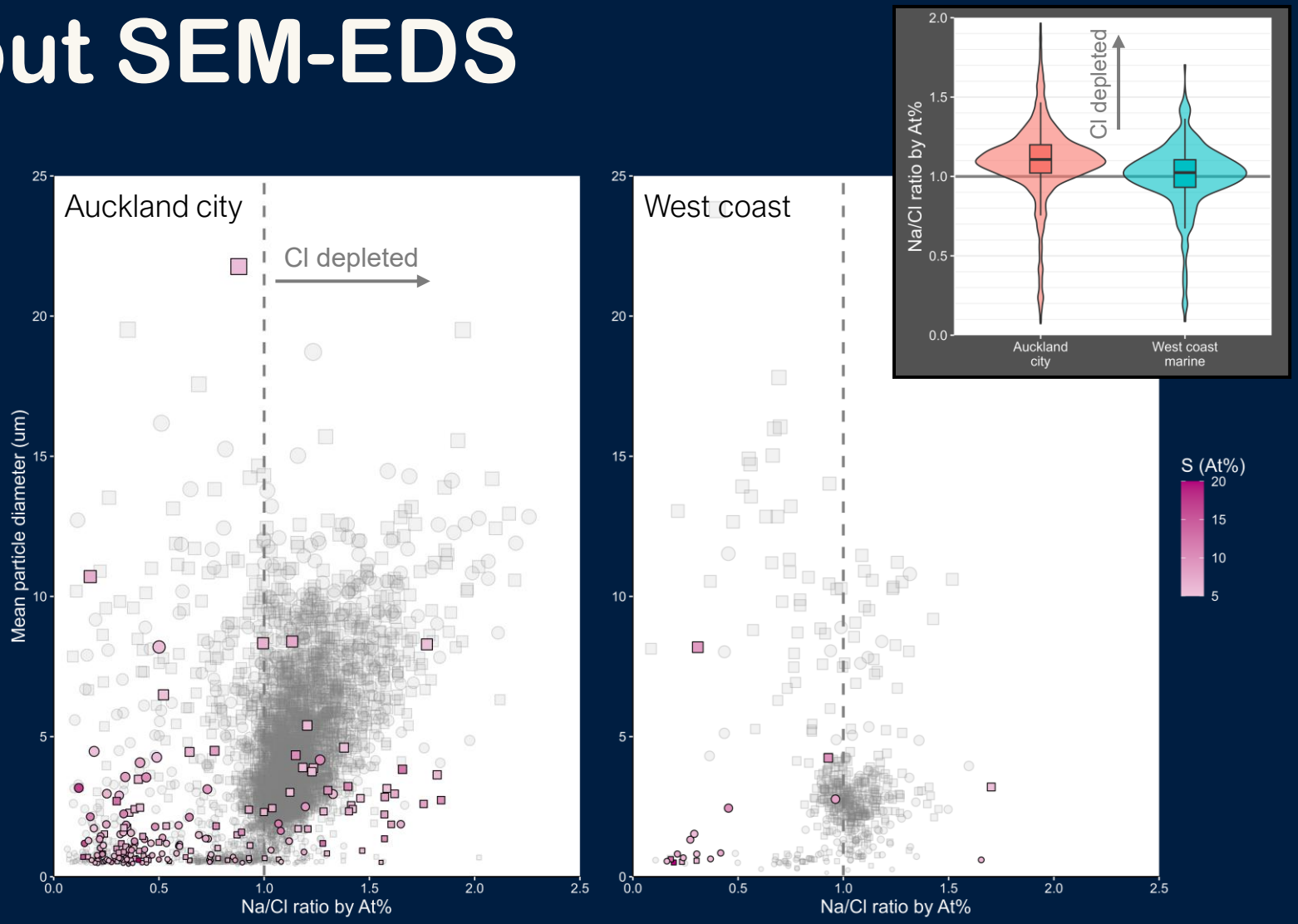
High-throughput SEM-EDS

- The ambient air samples were also examined by semi-automated high-throughput SEM-EDS
- Particles containing both Na and Cl were selected for analysis
  - The ideal At% ratio for pure NaCl is 1:1
  - Values greater than 1 indicate particles with reduced Cl
- NaCl particles from Auckland city show greater levels of Cl depletion
  - Possibly due to sulphate modification



SEM-EDS summary plots showing the Na/Cl ratio versus mean particle diameter for the ambient air samples. Squares represent particles with cubic-like morphologies