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# A case study of aerosol trace element deposition to Moroccan coastal waters

Rachel Shelley\*, Géraldine Sarthou, Georges Tymen\*, Rémi Losno, Luis Tito de Morais, Ali Benhra, and Fatima Zohra Bouthir

\* rachel.shelley@univ-brest.fr; georges.tymen@univ-brest.fr

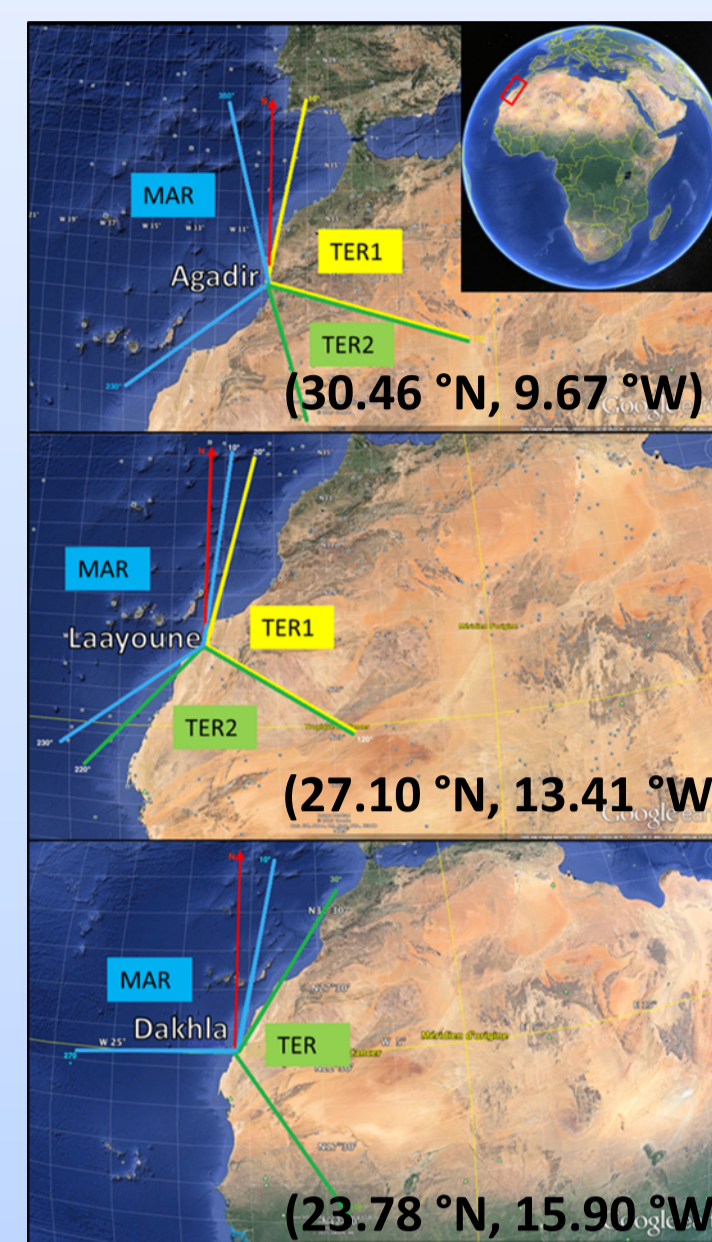
## Rationale

Aerosol deposition is an important source of trace elements (TEs) to the surface ocean. Proximity to the Sahara Desert/Sahel means that the North Atlantic receives some of the highest inputs of mineral dust globally (100-220 Tg yr<sup>-1</sup>; [1]; [2]). This input of TEs contributes to the greater efficiency of the Canary Current Upwelling System relative to its Pacific counterpart [3]; both of which support socio-economically important fisheries. However, mineral dust is just one component, human activities (e.g. fossil fuel burning, agricultural practices) also contribute to the atmospheric load.

In the study region upwelling water also fuels high primary production via the supply of macro-nutrient-rich (N, P and Si) deep water. This deep water may also be enriched in TEs, such as those with water column distributions that mirror the macronutrients, e.g. Cd & P. A tangible concern for the fisheries off West Africa is the potential for toxic effects at all levels of the marine food web, due to inputs of Cd (and other potentially toxic TEs).

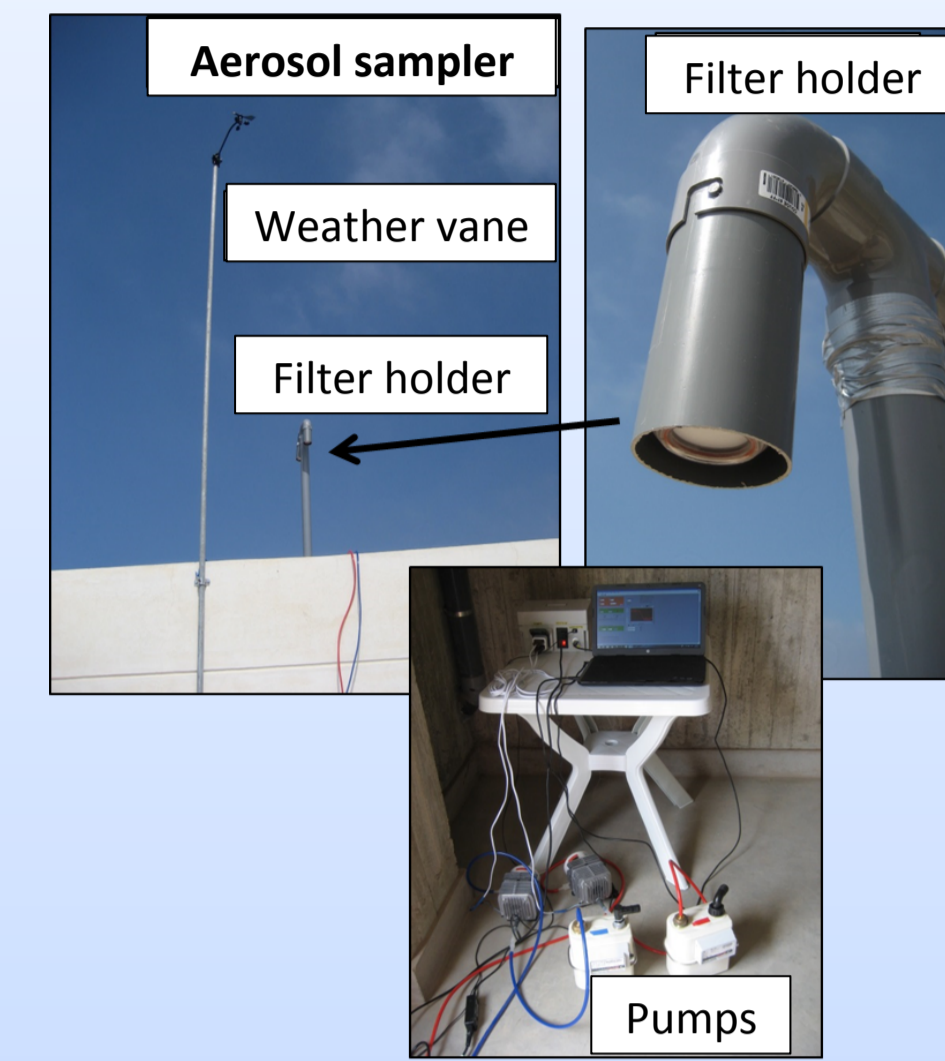
The aim of this project was to investigate the TE composition and relative levels of enrichment of aerosols delivered to the Atlantic coast of Morocco.

## Methods



Sectors	AGADIR	LAAYOUNE	DAKHLA
MAR	230-350°	230-10°	270-10°
TER1	10-110°	20-120°	30-150°
TER2	110-170°	120-220°	

The red line points north (0°) for reference

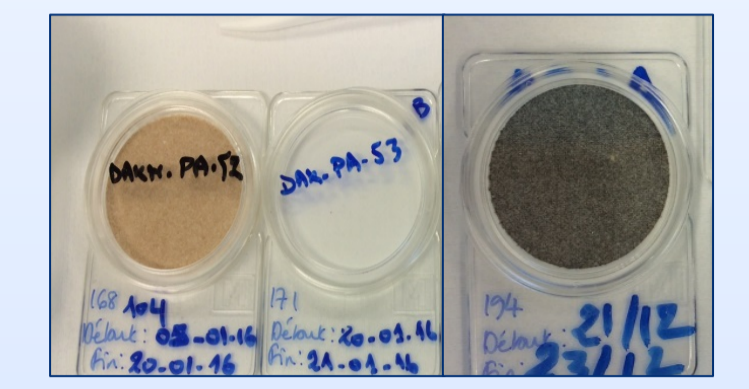


Three sampling sites 100-800 m from the coast, upwind of:

- Agadir
- Laayoune
- Dakhla

Aerosol samples were collected using a low-volume aerosol sampler manufactured in-house:

- two downward-facing, open face, polycarbonate filter holders (NILU) coupled to two pumps (NOVAIR NTV 0625) & two volumetric counters (Gallus 2000) operated in series, interfaced with a laptop
- wind speed (> 0.9 m s<sup>-1</sup>) & sector-controlled in order to minimise the sampling of local industrial emissions & sample aerosols delivered from specific sectors (see table)



Examples of aerosol samples: left & middle = Dakhla, right = Agadir

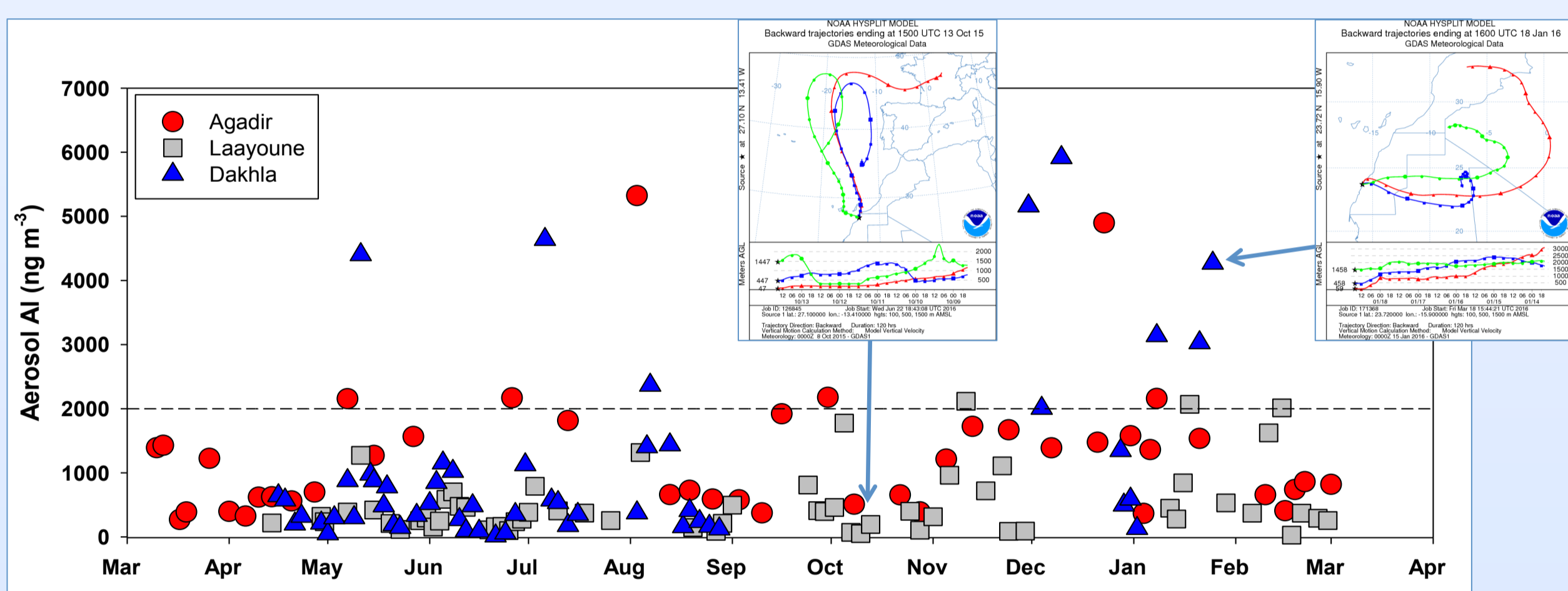
Sampling from March 2015-March 2016

- Agadir = 44 samples
- Laayoune = 66 samples
- Dakhla = 56 samples

Aerosol concentrations following:

- Sequential digests: (1) 5:1 HNO<sub>3</sub>: HF, (2) HNO<sub>3</sub> in capped, Teflon<sup>®</sup> vials at 130 °C
- Solutions re-dissolved in 0.48 M HNO<sub>3</sub> and analysed by ICP-MS (Thermo, Element 2)
- Positive Matrix Factorisation using EPA PMF v.5 for source apportionment

## Results & Discussion

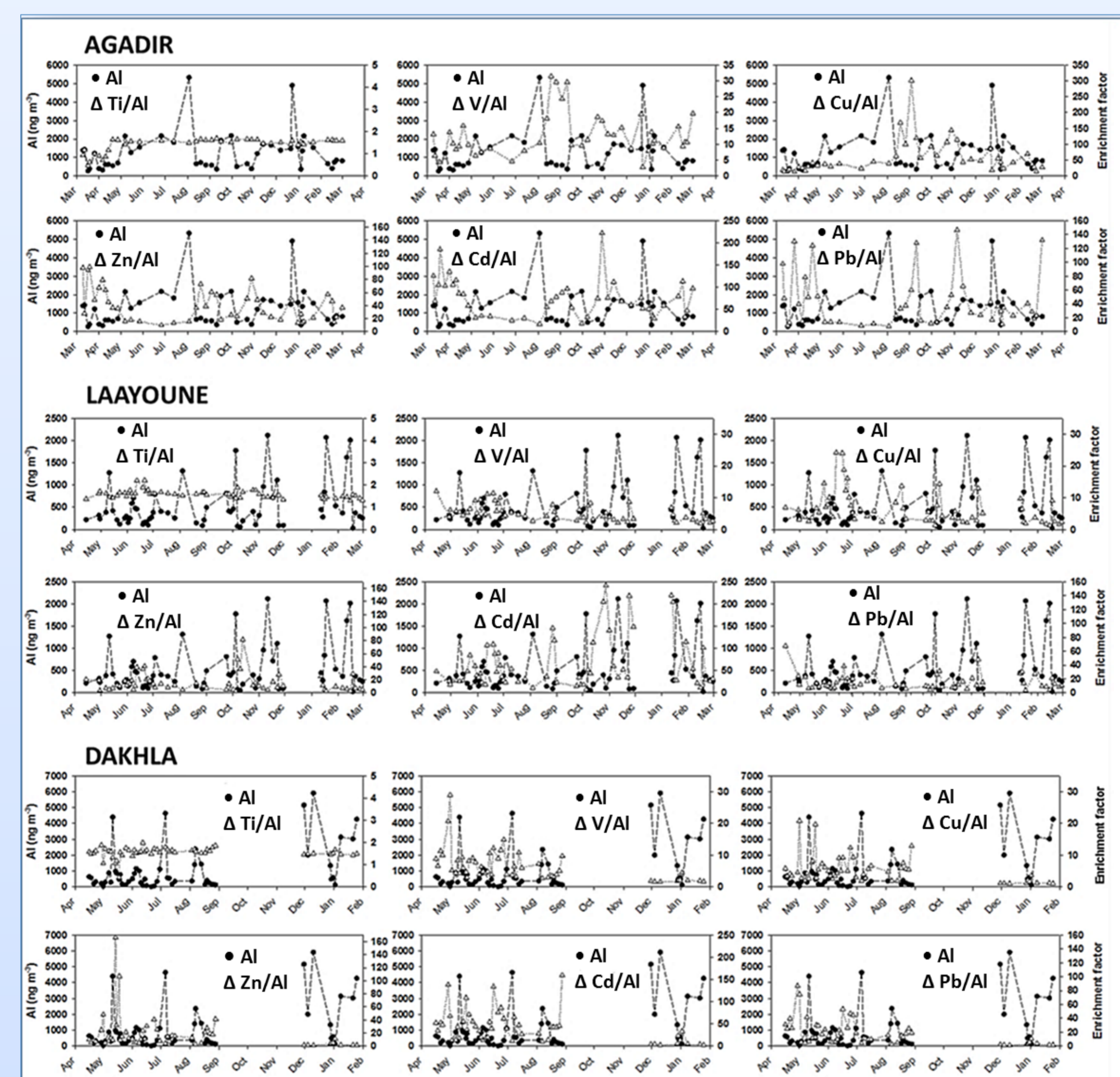
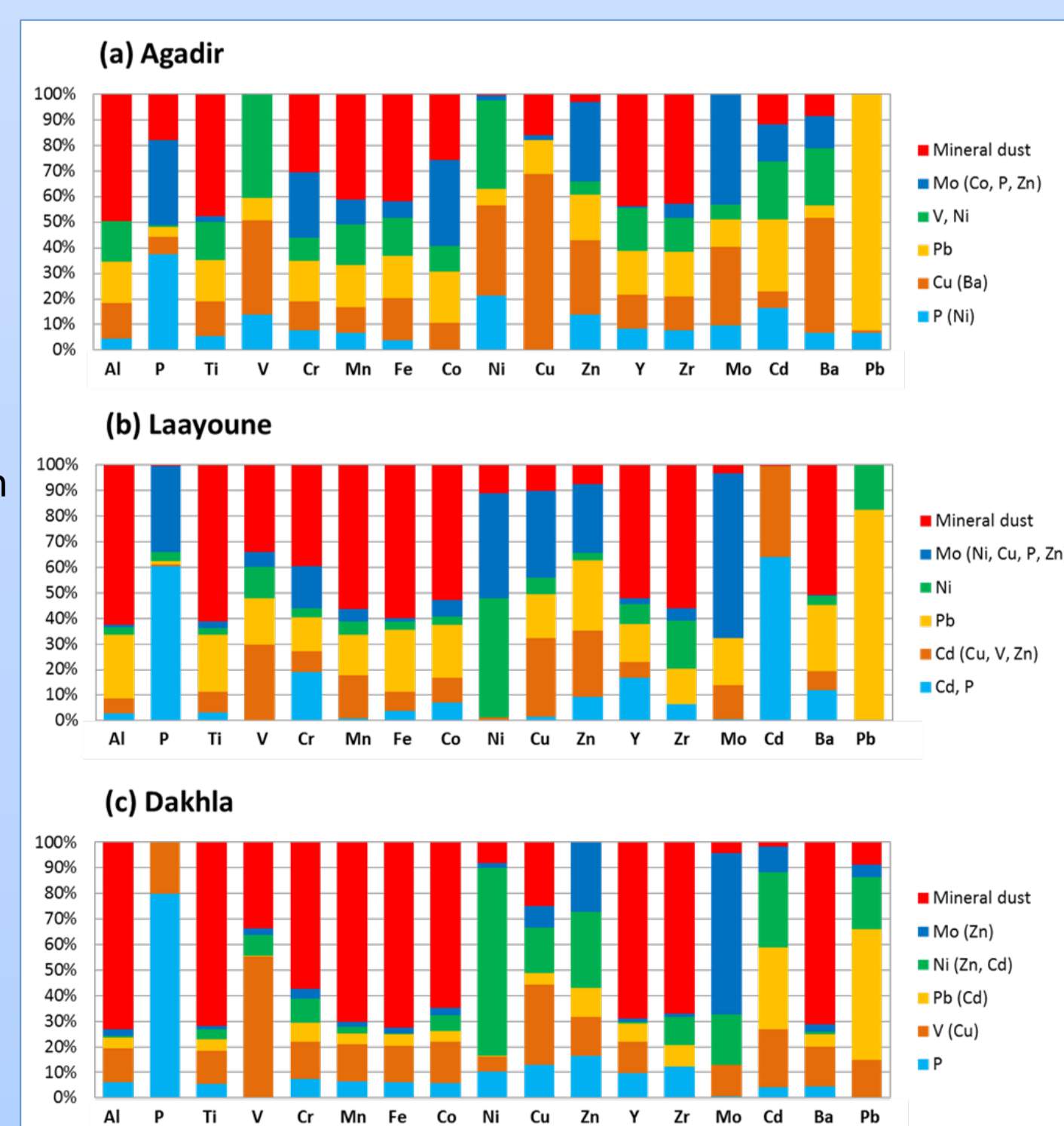


(1) Aerosol Al concentrations, March 2015-2016. 90% of data falls below the dashed line (2000 ng Al m<sup>-3</sup>). Concentrations of ~ 100-2000 ng Al m<sup>-3</sup> could be considered as an effective background concentration

- ❖ No strong seasonal pattern in aerosol Al concentration, but tendency towards higher frequency of dust events from Dec-Feb
- ❖ 8% Al abundance [4] used to estimate total dust mass for the year of study
  - ❖ 3400-67000 ng m<sup>-3</sup> (Agadir)
  - ❖ 350-26000 ng m<sup>-3</sup> (Laayoune)
  - ❖ 205-74000 ng m<sup>-3</sup> (Dakhla)
- ❖ Maximum Al concentrations in this study are an order of magnitude lower than observed on islands downwind of the Saharan plume, e.g. Gran Canaria = 26200 ng m<sup>-3</sup> [5] & Sal, Cape Verde = 26487 ng m<sup>-3</sup> [6]
- ❖ Despite large interannual variability in dust supply [7], this result was unanticipated. Possibilities that could account for the difference:
  - ❖ A 'low dust' year
  - ❖ Dust loadings could be higher offshore as the dust is transported in the Saharan Air Layer (SAL) at altitudes of 1500-6000 m in boreal summer. However, the SAL is at lower altitudes in boreal winter, so this hypothesis seems unlikely
  - ❖ We used low volume samplers (~ 1 m<sup>3</sup> air filtered h<sup>-1</sup>), [5] & [6] used high volume samplers (~ 1 m<sup>3</sup> min<sup>-1</sup>). Low volume samplers require longer sampling durations in order to collect sufficient material on the filters. This would manifest as a reduction in the concentration of Al per air volume filtered per time unit, due to the longer run times
  - ❖ We were sampling from specific sectors

### (2) PMF output: factor fingerprint of aerosol sources

- Used for aerosol source apportionment
- Mineral dust
- = red, other factors do not necessarily represent the same source, but an attempt has been made to colour-code them based on similar groupings of elements
- Smallest contribution from mineral dust in Agadir, greatest in Dakhla
- Some TEs have little to no mineral dust source:
  - Agadir: V, Ni, Zn, Mo, Pb
  - Laayoune: P, Mo, Cd, Pb
  - Dakhla: P, Ni, Mo, Cd, Pb
- P is an interesting case. We tend to think of P as being derived from mineral dust. However, contribution of mineral dust to aerosol P was low. P could be a special case in this region due to the presence of open cast P mines (Morocco is second largest exporter of P in the world)



(3) Relationship between dust events & elemental ratios

- Al is a proxy for mineral dust
- Dust events (peaks in Al concentration) have little effect on the mass ratio of lithogenic elements to Al (e.g. Ti/Al), suggesting mineral dust is main source of these elements
- Dust events reduce the ratio of anthropogenic elements to Al (e.g. Cd), suggesting these elements have lower relative abundances in mineral dust than industrial emissions
- On low dust days (low Al) there were peaks in ratio of anthropogenic elements to Al

### (4) Enrichment Factors

- Normalised to Al
- Only enrichment > 10 considered significant (marked by horizontal line)
- Lithogenic elements not significantly enriched (top row)
- Generally highest enrichment in Agadir samples
- P most enriched in Laayoune samples
- Cd enriched at all locations but...
- Cd/Al (mass/mass) at all stations (Agadir = 2.1x10<sup>-5</sup> - 2.7x10<sup>-4</sup>; Laayoune = 8.4x10<sup>-6</sup> - 2.9x10<sup>-4</sup>; Dakhla = 3.0x10<sup>-6</sup> - 2.0x10<sup>-4</sup>) fall close to the range observed at nearby locations (e.g., Cap Spartel = 4.6x10<sup>-5</sup> - 2.3x10<sup>-4</sup> [8] & Gran Canaria = 4.6x10<sup>-5</sup> - 1.84x10<sup>-4</sup> [5])
- Same trend seen for other anthropogenic TEs, e.g. Pb/Al

## Conclusions

- No strong seasonal pattern in aerosol Al concentration/dust deposition, but tendency towards higher frequency of dust events in winter
- Mineral dust proportionately contributes least to the bulk aerosol in Agadir, most in Dakhla
- Dust events are characterised by aerosols that originate from sources in Sahara/Sahel
- In terms of elemental ratios, Cd/Al looks like other locations in the region, but it was significantly enriched in samples from all locations & had little to no mineral dust source during this study
- Mineral dust dilutes anthropogenic TE aerosols during dust events

## Acknowledgements

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## References

- [1] Prospero et al., 1996; [2] Kaufman et al., 2005; [3] Carr et al., 2003; [4] Rudnick and Gao, 2003; [5] Gelado-Cabellero et al., 2012; [6] Fomba et al., 2013; [7] Torres-Padron et al., 2002; [8] Gieue et al., 2010