Dottorato Nazionale in Polar Sciences, Università Ca' Foscari di Venezia -

Ciclo XXXIX

Chemical characterization of atmospheric aerosols in Antarctica

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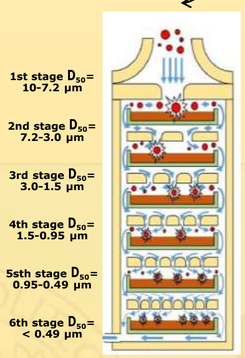
Introduction

Chemical characterization of atmospheric aerosols is crucial for understanding the sources of contaminants and the environmental status of Polar regions. These regions, often considered as traps for particulate matter (PM) transported from other locations through long-range atmospheric transport[1], offer unique insights into global pollutant dynamics. Due to its significant distance from continental sources of pollution, Antarctica serves as an ideal site for studying background aerosol concentrations and natural atmospheric processes. The isolation allows to better understand the impact of anthropogenic sources on the atmosphere and gain a clearer understanding of both local and global aerosol interactions. Understanding PM10 sources, characteristics, and behavior in the atmosphere is essential for developing effective control strategies and regulatory policies to mitigate its adverse effects.

High Volume multi-stage Cascade Impactor

Field Sampling

- M. Zucchelli Station (Terra Nova Bay, Ross Sea); the site is located at 57 m above sea level and 250 m from sea
- Antarctic sampling campaign from Nov 12, 2019 to Jan 20, 2020
- PM10 high-volume sampler with a 6-stage high-volume cascade impactor
- Flow rate at 1.13 m^3 min^{-1}
- 10-days sampling strategy using PTFE fiber filters (total samples collected: 7)
- Three field blank samples were collected



Study Area

Methodology

All analytical steps were performed in an ISO 5 clean room laboratory

For DMA-1 analysis, an aliquot (1/64) of each original PTFE fiber filters, no sampling preparation was required

For ICP-OES and GF-AAS analysis, an aliquot (1/8) of each original PTFE fiber filters were subjected to microwave acid digestion (5 mL HNO_3 / 1 mL HF/ 1 mL H_2O_2)

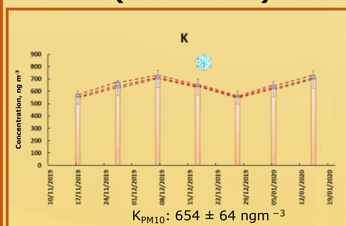
Cd, V, Cr, As, Pb, Ni and Cu were determined using the Graphite Furnace Atomic Absorption Spectrometry (GF-AAS)

Al, Ca, Fe, Mn, K, Na and Mg were determined using the Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

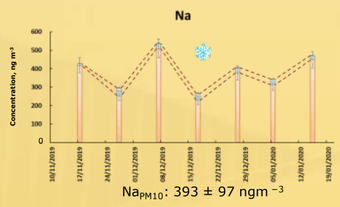
Particulate Hg from each filter of PM10 was determined by the Direct Mercury Analyzer (DMA-1, Milestone, Italy)

Results and Discussion

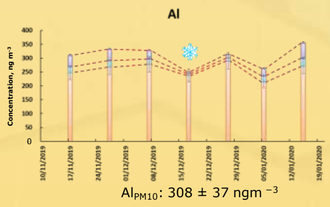
Metals (Metalloids) - Decreasing order : K > Na ≃ Al > Ca > Mg ≃ Fe > Mn >Cr > Ni > As > Cu > Pb ≃ V > Cd > Hg



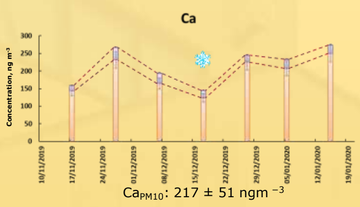
K_{PM10}: 654 ± 64 ngm $^{-3}$



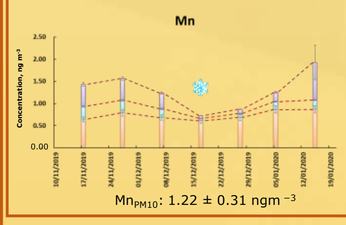
Na_{PM10}: 393 ± 97 ngm $^{-3}$



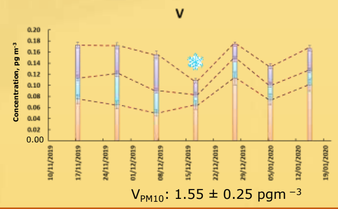
Al_{PM10}: 308 ± 37 ngm $^{-3}$



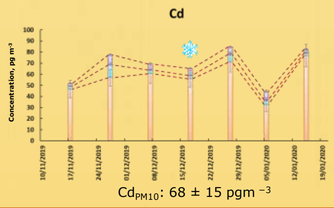
Ca_{PM10}: 217 ± 51 ngm $^{-3}$



Mn_{PM10}: 1.22 ± 0.31 ngm $^{-3}$

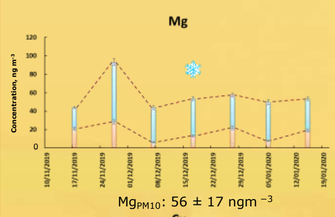


V_{PM10}: 1.55 ± 0.25 pgm $^{-3}$

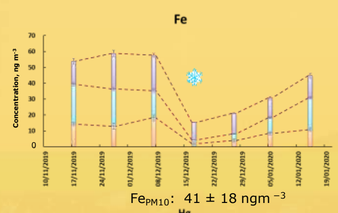


Cd_{PM10}: 68 ± 15 pgm $^{-3}$

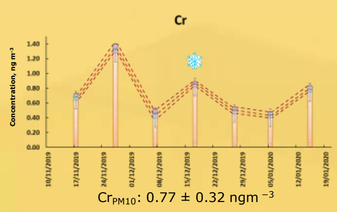
I - Constant trend - Elemental concentrations in total Antarctic PM10 follow a constant trend over the sampling period.



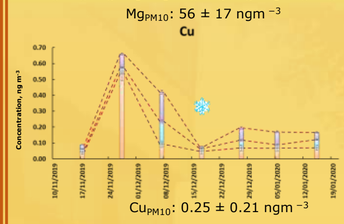
Mg_{PM10}: 56 ± 17 ngm $^{-3}$



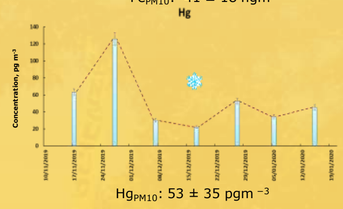
Fe_{PM10}: 41 ± 18 ngm $^{-3}$



Cr_{PM10}: 0.77 ± 0.32 ngm $^{-3}$



Cu_{PM10}: 0.25 ± 0.21 ngm $^{-3}$



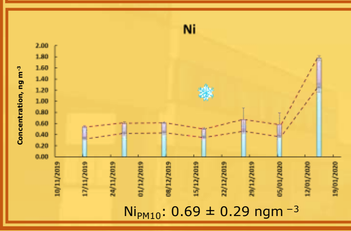
Hg_{PM10}: 53 ± 35 pgm $^{-3}$

II - Decreasing trend - as a result of ice melting and the sea spray emission, elements peak at the end of November/mid-December and then show lower values in the end of the campaign. Episodes of snowfall were observed in the inner of the campaign.

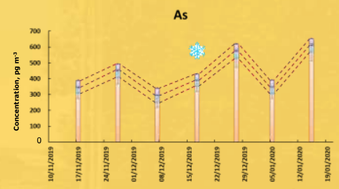
Snowfall characterized the study area from the 12 of December to the 22 of December

Source Meteo-Climatological Observatory

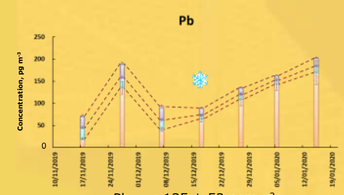
Legend
- CM2
- CM1
- ACM



Ni_{PM10}: 0.69 ± 0.29 ngm $^{-3}$



As_{PM10}: 474 ± 121 pgm^{-3}



Pb_{PM10}: 135 ± 52 pgm $^{-3}$

III - Increasing trend - The elements exhibit an increasing trend, with elevated concentrations observed toward the end of the campaign. After the halfway point of the campaign, a progressive rise is detected, in contrast to the previous trends exhibited by the other elements

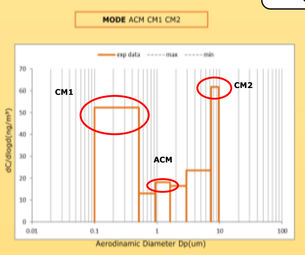
Size Distribution

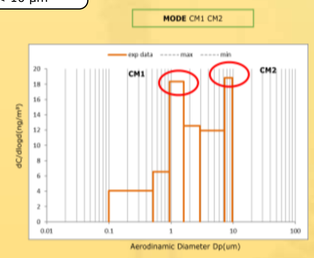
Al, Fe, K, Mn, As, Cu, Cd, Cr, Pb and V have a Trimodal distribution

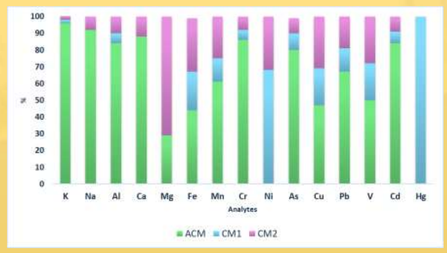
Ca, Mg, Na, and Ni have a bimodal distribution

Hg has a unimodal distribution

ACM → 0.1 < Dp < 1.0 µm
CM1 → 1.0 < Dp < 3.0 µm
CM2 → 3.0 < Dp < 10 µm







K, Na, Ca, Cr, Cd, Al, Pb , Mn and As : mainly present in the accumulation mode (ACM > 60%)

Hg, Ni and Mg mainly present in coarse modes (at least 71%)

Cu, Fe and V : equally distributed between Fine (ACM ~ 48%) and coarse modes (CM1 ~22% and CM2 ~30%)

Conclusions

- The seasonal evolution of size-segregated PM10 was element-specific and strongly affected by the catabatic wind events and pack-ice melting. Three different trend are recorded :a Constant trend (K, Na, Al, Ca, Mn, V and Cd); Decreasing trend (Mg, Fe, Cr, Cu and Hg); and an increasing trend (Ni, As and Pb)
- A trimodal distribution for Al, Fe, K, Mn, As, Cu, Cd, Cr, Pb and V, unimodal for Hg and a bimodal distribution for Ca, Mg, Na, and Ni are recognized
- Enrichment factor's results, suggesting an anthropogenic contribution to be further investigated for Hg and Cd while a moderately enrichment for As and Cr.
- These preliminary results highlighted the importance of monitoring aerosols in Antarctic to better understand their contribution and impact on polar ecosystems.

Future Perspectives

- To Conclude this approach for Mario Zucchelli's Campaigns 2017-2018 and 2018-2019
- Assess the potential sources (natural and/or human-related sources of Me.
- Application of statistical analysis (PMF) and air mass back-trajectories model (HYSPLIT model) during the host period at ARPAM
- Measurements of Rare Earth Elements during the host period at Norwegian University of Science and Technology

Source Evaluation: Enrichment Factors

$$EF_m = \frac{\left(C_m / C_{Al}\right)_{PM}}{\left(C_m / C_{Al}\right)_{UCC}}$$

Aluminium as reference element (Wedepohl, 1995)

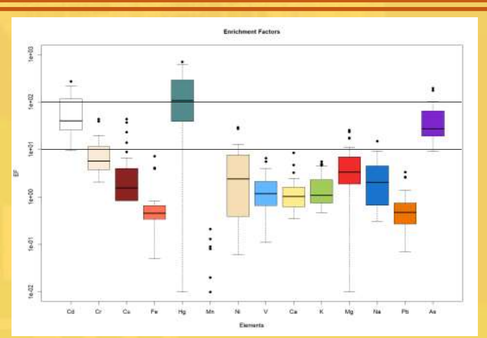
EF<10 No Enrichment
10<EF<100 Moderate Enrichment
EF>100 Severe Enrichment

Hg Cd → Severe Enrichment

As Cr → Moderately Enrichment

POTENTIAL ANTHROPOGENIC ORIGIN

Fe Mn Ca K Cu Mg V Na Pb Ni → No Enrichment



References

[1] Bargagli, R., 2016. Chemosphere 163, 202–208. [2] Vagnoni, Flavio, et al. Atmosphere 12.8 (2021): 1030. [3] Grotti, Marco, et al. Antarctic Science 17.2 (2005): 289-300.