

Metallic Trace Elements Shipping Profile by PM1 Source Apportionment in a Mediterranean Port City

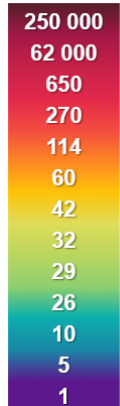
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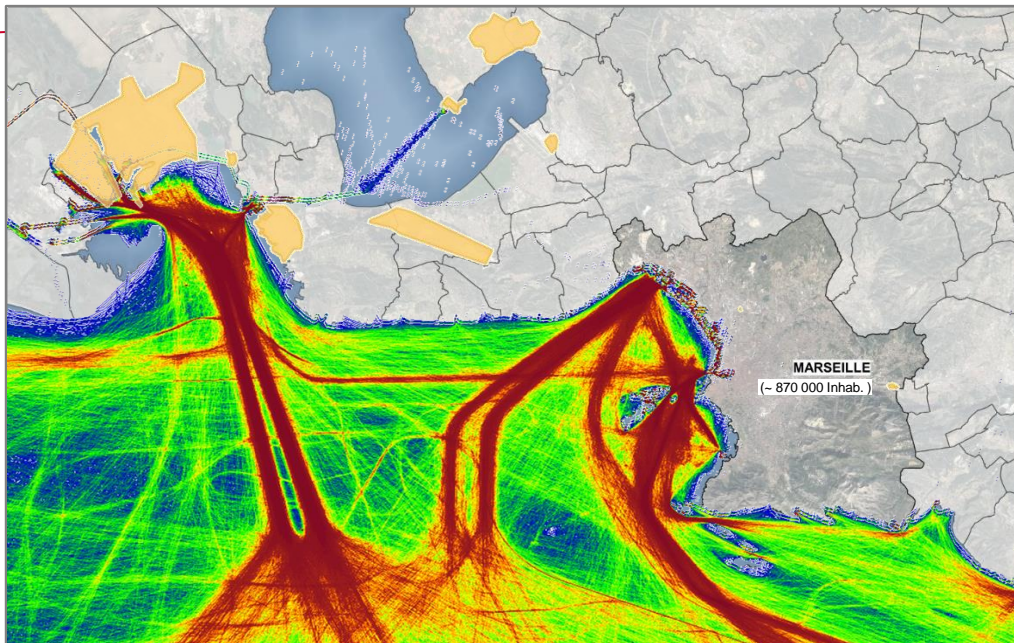
AAAR 40TH annual conference – October 4, 2022



Marseille



Nb of ship
/ km² / year



Marine traffic Density Maps 2021

Multiple sources



Conventional sources



Industrial area



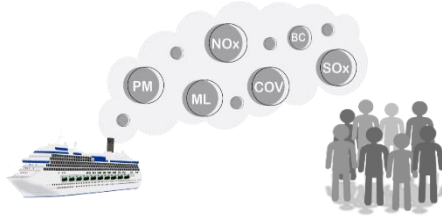
Shipping

⇒ In top 5
Mediterranean port

A real **hotspot** in France, where the population is clearly exposed to a complex mixture of pollutants

Shipping emissions

- Impacts on air quality and population health



~250,000 premature
deaths per year worldwide
attributable to shipping
(Sofiev et al, 2018)

Previous study on Organic Aerosol in Marseille

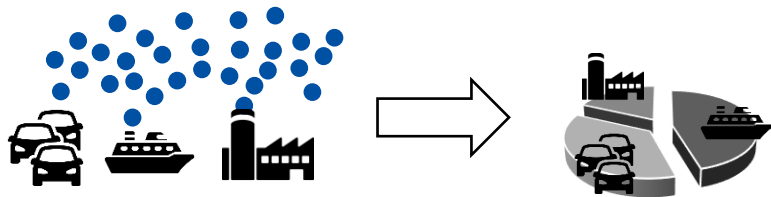
(Chazeau et al, 2022)

- Difficulty to separate « industrial » and « shipping » sources by Positive Matrix Factorization (PMF) model

⇒ Objectives :

- To isolate « shipping » and « industrial » sources
- To evaluate the contribution of « shipping » source to the air quality degradation of Marseille

Source apportionment analysis



Focus on metallic trace elements in PM₁

- Ship emissions are associated with ultrafine particles (Merico et al., 2020)
- Metals recognized as tracers to separate « shipping » and « industrial » sources (Chang et al., 2018; Chu Van et al., 2020)

Using Positive Matrix Factorisation (PMF)

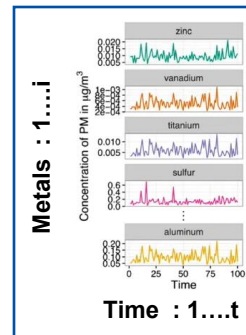
- SoFi Pro toolkit (Canonaco et al., 2013)

- Minimization of $Q = \sum_i \sum_j \left(\frac{e_{i,t}}{\sigma_{i,t}} \right)^2$
- Rotation ambiguity (a-values)

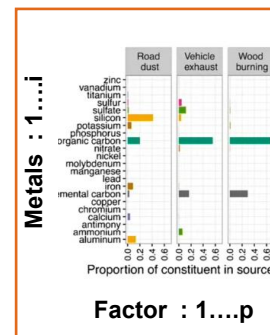
$$X_{i,t} = \sum_{p=1}^p (F_{i,p} \times G_{p,t} + E_{i,t})$$

Residual matrix

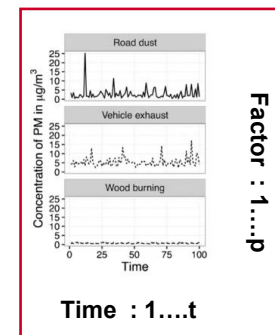
Metal measured matrix



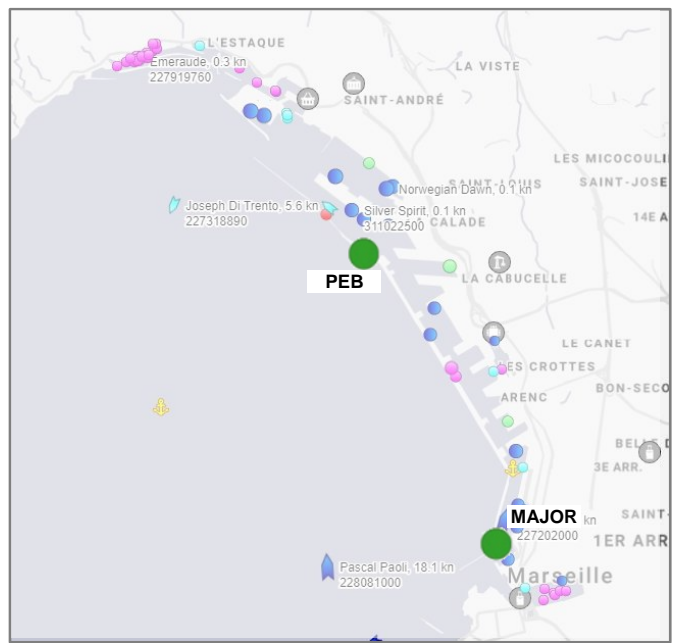
Factor profiles (chemical composition)



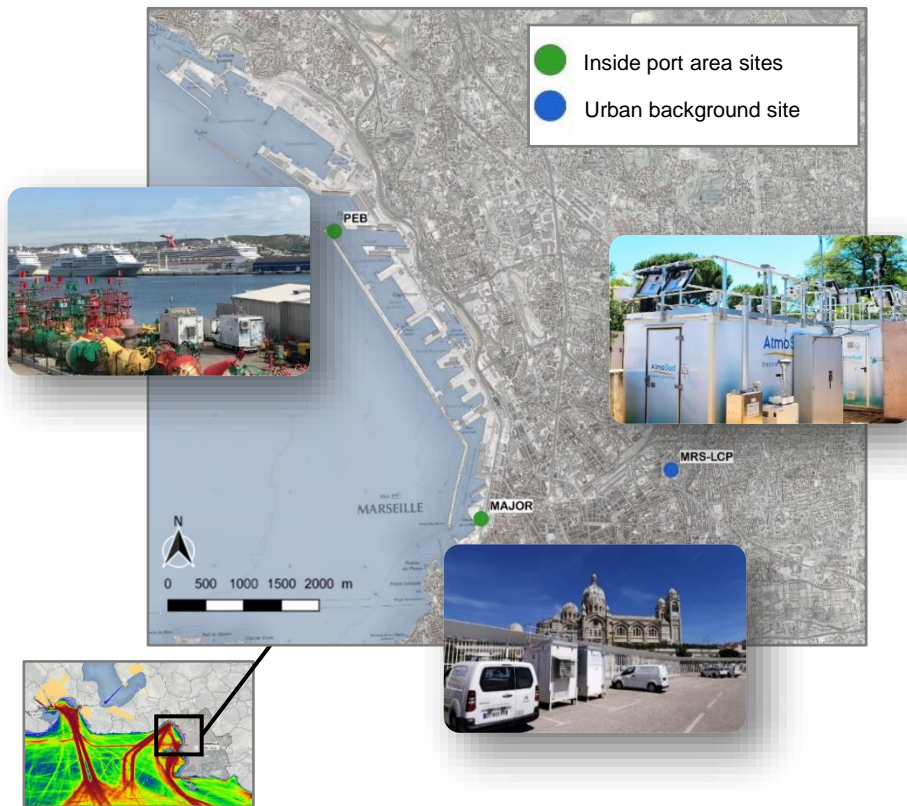
Factor contribution (time series)



Measurement sites



Measurement sites



Substances monitored

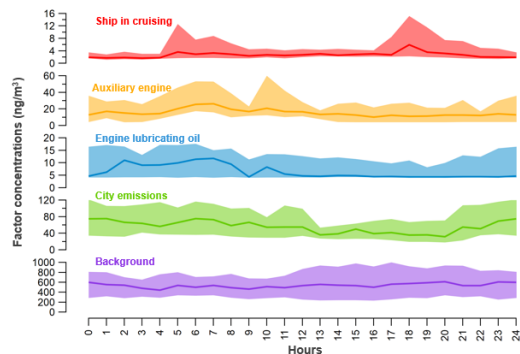
- **More 30 trace metals in PM₁**
 - Online metal analyser Xact 625i
 - High time resolution
- In addition
 - PM₁ chemical composition : BC, sulfate, OA...
 - Ultrafine particle number and size distribution
 - Gaseous compounds : SO₂, NO_x, VOC, ...



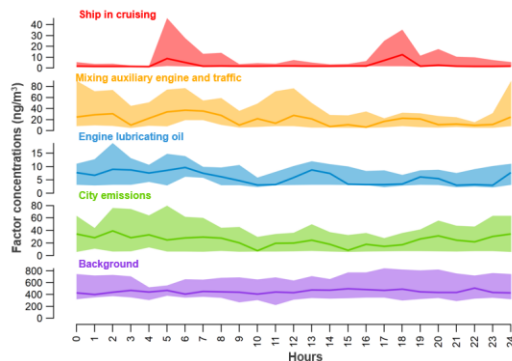
⇒ **Original metals database with high time resolution**

Similar PMF results on both sites

• Northern pass site



• Southern pass site



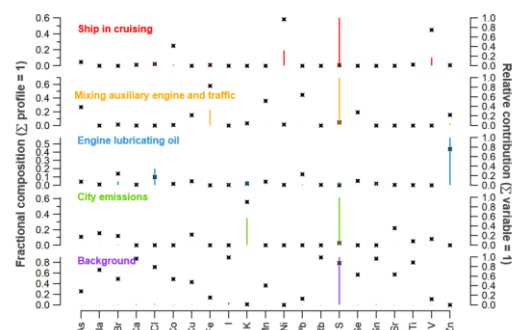
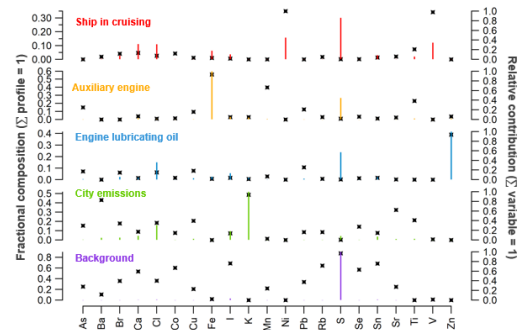
⇒ 3 shipping factors identified

Reminder of PMF strategy

- Input data :
 - Metals in PM₁ with Xact
 - Time resolution : 30 min
 - Periods :
 - June on North site
 - July on South site
- 21 elements used
As, Ba, Br, Ca, Cl, Co, Cu, Fe, I, K, Mn, Ni, Pb, Rb, S, Se, Sn, Sr, Ti, V, Zn
- No constrained PMF
- 5 factors selected

Diurnal factor profiles

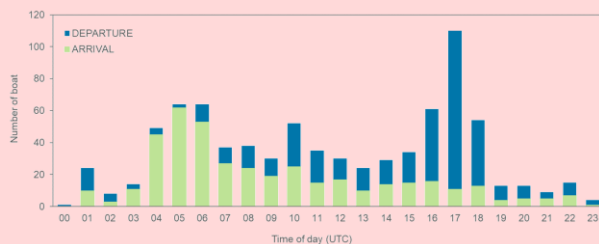
Chemical factor profiles



Ship in cruising phase factor

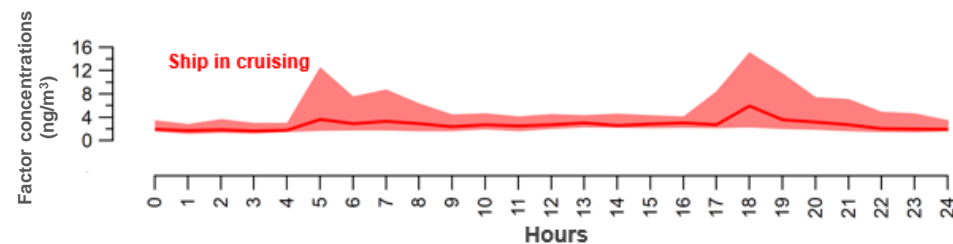
(FSC < 0.5 %)

- Daily profile correlated with ship arrivals/departures

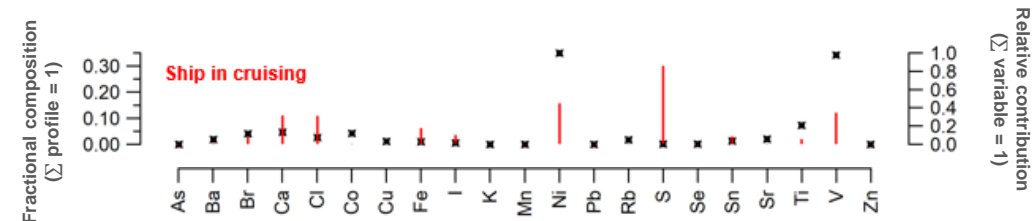


- Factor contributes > 90% of V and Ni while the mass is dominated by S (30-50%).
- V/Ni mass ratio between 0.5 - 0.8 as found in recent studies (Yu et al., 2021)

Diurnal factor profiles



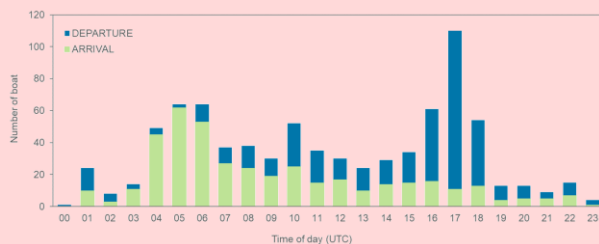
Chemical factor profiles



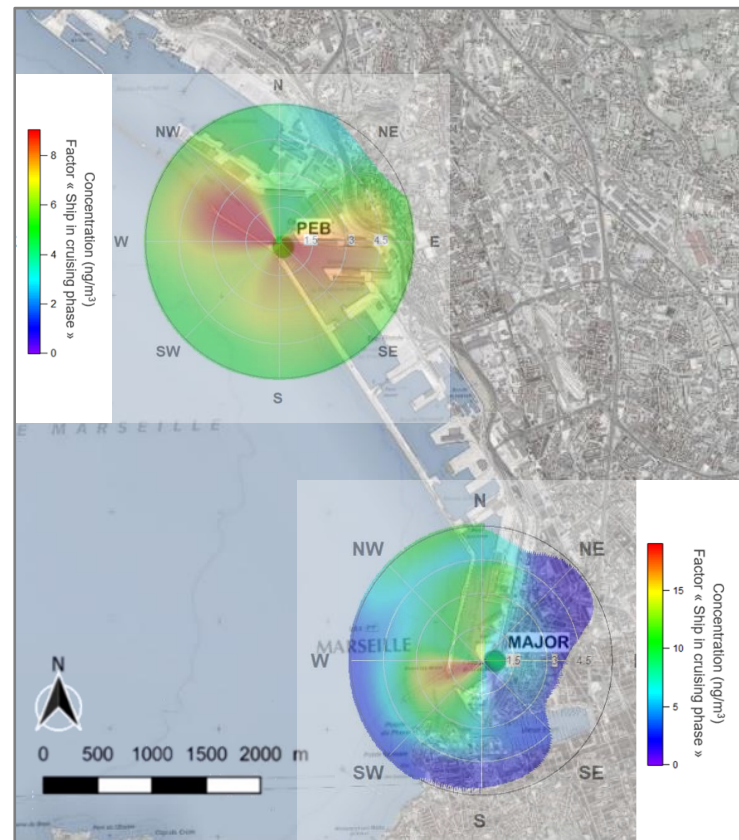
Ship in cruising phase factor

(FSC < 0.5 %)

- Daily profile correlated with ship arrivals/departures



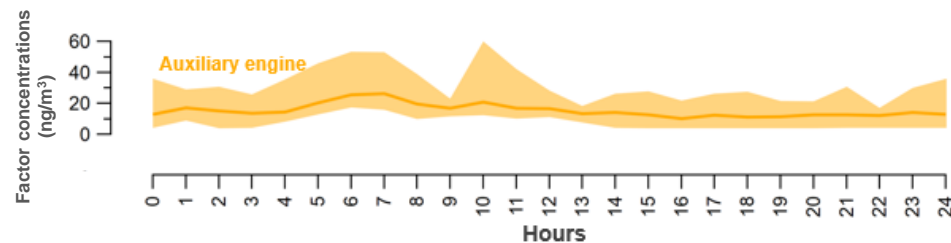
- Factor contributes > 90% of V and Ni while the mass is dominated by S (30-50%).
- V/Ni mass ratio between 0.5 - 0.8 as found in recent studies (Yu et al., 2021)
- Maximum concentrations are observed along ship access routes to the port



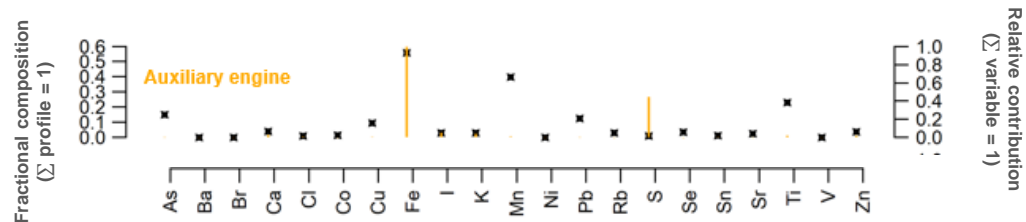
Auxiliary engine factor
(FSC < 0.1 %)

- Mass factor dominated by Fe and S

Diurnal factor profiles



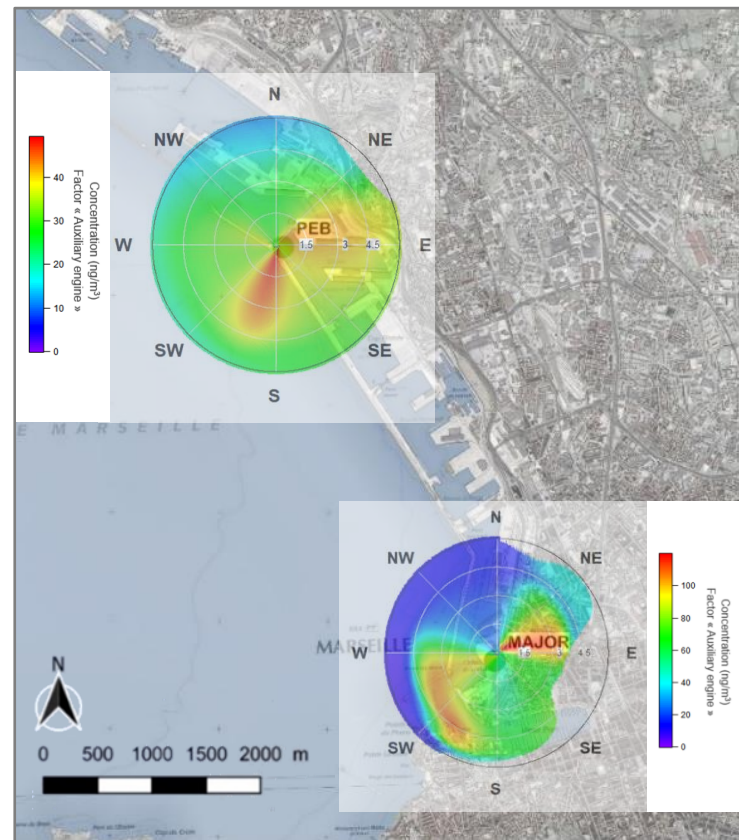
Chemical factor profiles



Auxiliary engine factor

(FSC < 0.1 %)

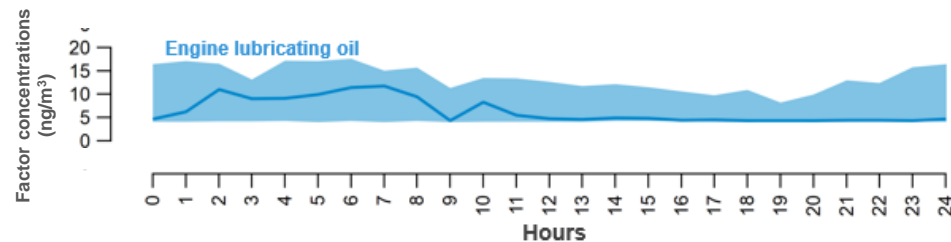
- Mass factor dominated by Fe and S
- Maximum concentrations are observed along the berths or along ship access routes to the port
- On south site, could be mixed with traffic



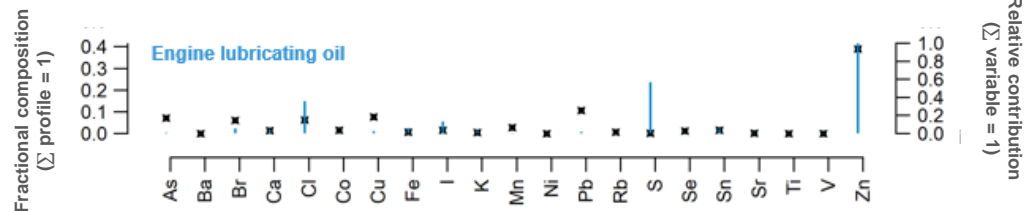
Engine lubricating oil

- Mass factor dominated by Zn and S
- Maximum concentrations are observed when sites are downwind of several categories of ships.

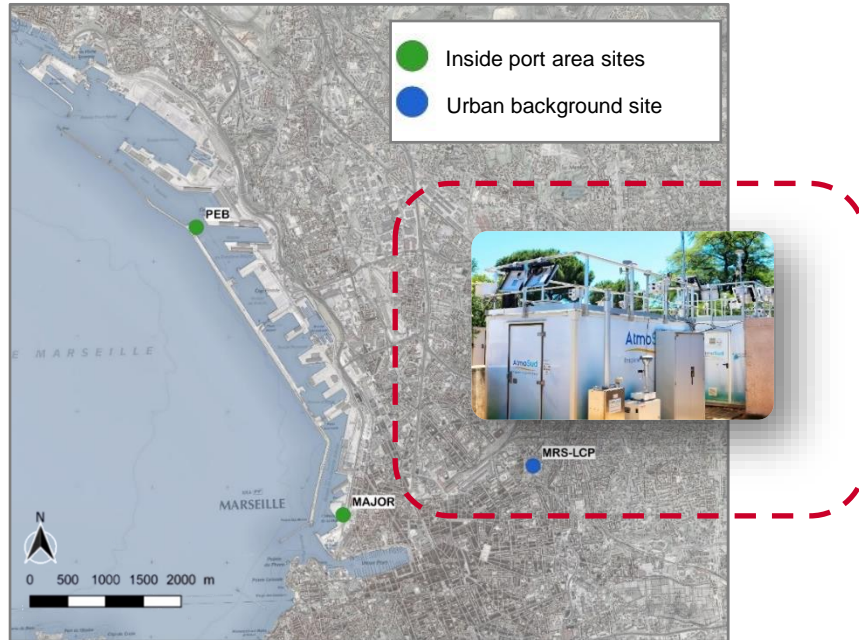
Diurnal factor profiles



Chemical factor profiles

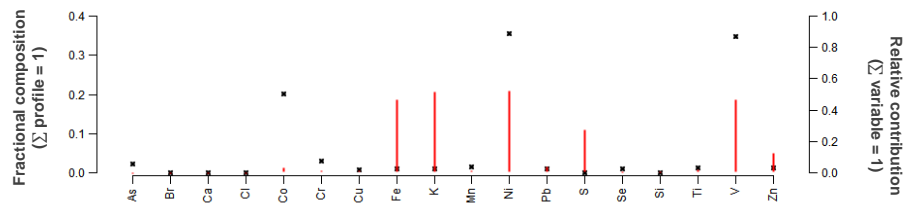
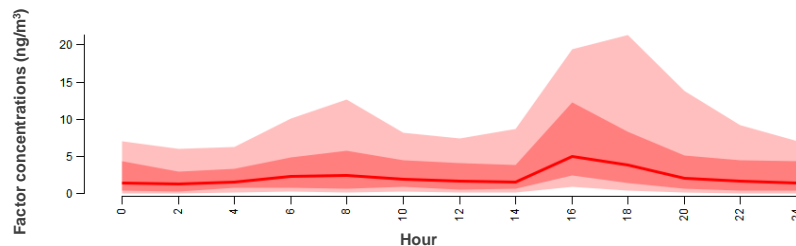


Measurement sites



Focus on shipping factors

- Urban background site : Marseille-Longchamp 2021
 - Only one factor could be retrieved



⇒ V/Ni mass ratio = 0.9

Reminder : V/Ni mass ratio inside port area = 0.5-0.8

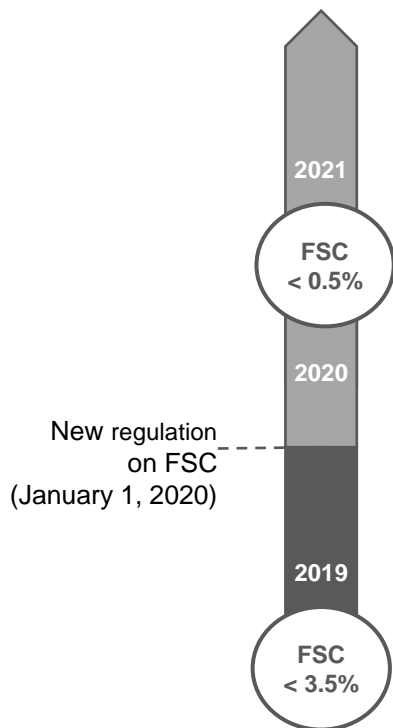


Reminder of PMF strategy

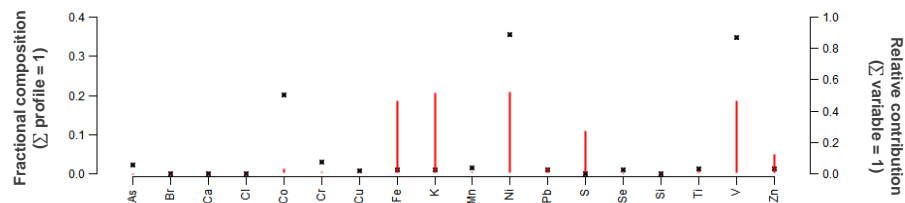
- Input data :
 - Metals in PM₁ with Xact
 - Time resolution : 2 hours
 - Periods: June-September 2021
 - Fireworks periods excluded (July 14, 2021)
- 18 elements used
As, Br, Ca, Cl, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Se, Si, Ti, V, Zn
- No constrained PMF
- **6 factors selected**

Focus on shipping factors

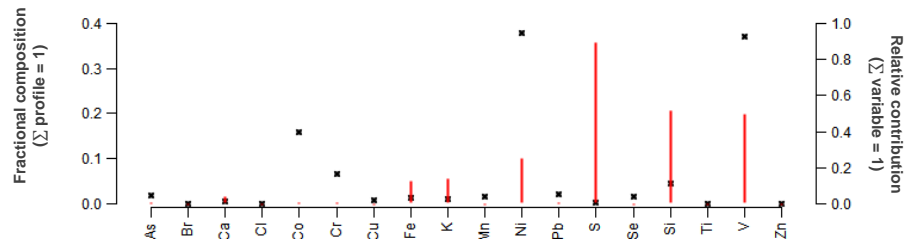
- Urban background site : Marseille-Longchamp



Summer 2021



Summer 2019



⇒ Decrease in the quantity of sulfur

⇒ Change in V/Ni mass ratio from 2 to 0.9

Conclusions

- Shipping factors identified
 - 3 profiles on sites inside the port area
 - Only 1 retrieve on urban background site
- New regulation in Mediterranean sea change shipping chemical profile
- Contribution of shipping activity
 - Low (< 10%) for total mass of metals
 - High (> 90%) for mass of specific toxic metal such as V and Ni

Outlooks

- For the PMFs on sites inside port area :
Need to constrain specific profiles to stabilize the runs
- For the PMFs on the urban background site :
Some factors of the PMF solutions need to be refined
- Next step : achieve a complete PM₁ source apportionment with OA, BC and metals



THANK YOU FOR YOUR ATTENTION

Acknowledgements



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PAREA project « Fine particles in fields close to maritime traffic in Marseille » which has received funding from the French Agency for ecological transition (ADEME) as part of CORTEA research program 2019 (June campaign)



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