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PiraeusAQ

Chemical composition and source apportionment of fine aerosol in the port city of Piraeus, Greece

G. Grivas, E. Liakakou, I. Stavroulas, P. Kalkavouras, M. Lianou, M. Tsagkaraki, K. Papoutsidaki, P. Zarmpas, A. Bougiatioti, N. Mihalopoulos and E. Gerasopoulos

Dr. Georgios Grivas

Research Scientist

Institute for Environmental Research and Sustainable Development

National Observatory of Athens

APCG
NATIONAL OBSERVATORY OF ATHENS
ATMOSPHERIC PHYSICS AND CHEMISTRY GROUP

Piraeus: An Aerosol Pollution Hotspot

Local Emissions: Triple Threat

Shipping Emissions
Busiest European passenger port: >15 mil. yr^{-1}
2nd Mediterranean container port: >5 mil. TEU yr^{-1}

Traffic Emissions
Passenger, HDDV (Greek HDDV fleet: most aged in the EU)

Residential Emissions
2nd most densely populated Greek regional unit (0.5mil.), RWB

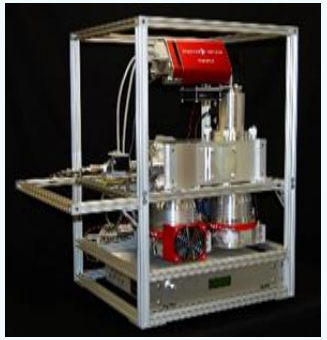
Additional Factors

Marine Aerosols

Urban and Port Development
> 3 bil. € in planned infrastructure projects

Study area and Methods

- Year-long $PM_{2.5}$ sampling campaign (12/2018-12/2019)
- Sampling site (P1) in central Piraeus, near the passenger port
- 24-h $PM_{2.5}$ quartz-fiber filter samples with LVS
- Laboratory chemical analysis in ≈300 filters for:
  - EC, OC (Sunset)
  - Major ions (IC)
  - Major and trace elements (ICP-MS)
- Q-ACSM and AE33 Aethalometer seasonal campaigns (Dec-Jan, Jun-Jul)
- Ancillary data from regulatory monitoring (CO, NO_x etc.)



Source apportionment

Annual Filter-Based $PM_{2.5}$ SA

- PMF SA (ME-2, EPA PMF5), *n* x *m* = 270 x 21
- 8-factor optimal solution (*physical, residuals, fit, Q/Qexp, IM, IS*)
- Validation (*in-profile diagnostic ratios, r vs external tracers, temporal variation, wind plots, trajectories-PSCF_90º*)
- Clears DISP, BS, BS-DISP EE methods

- 2 vehicular sources (exhaust, non-exhaust)
- Oil combustion related to shipping
- Biomass Burning
- Regionally processed aerosol
- 2 dust factors (mineral and locally resuspended dust)
- Sea Salt

Seasonal Organic Aerosol SA

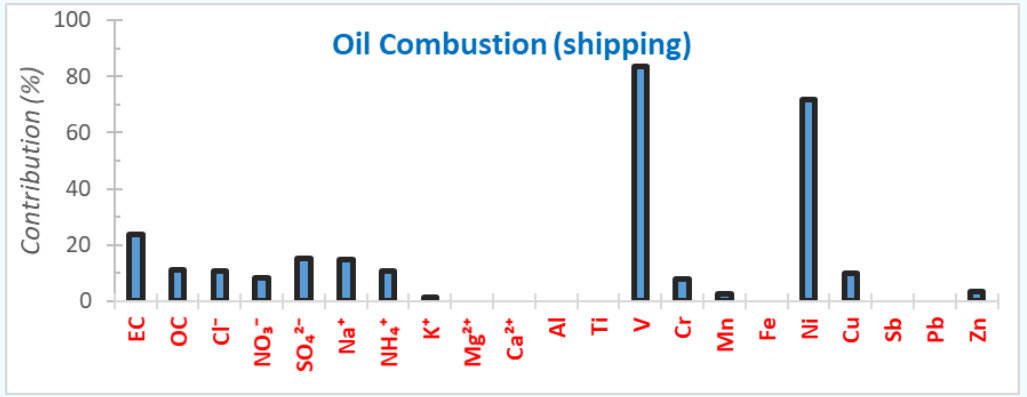
- PMF SA (ME-2, SoFi 6.1), *m/z:* 12-125, separate runs winter/summer
- Selection strategy (*physical, constrains, residual variance*)
- Validation (*temporal variation, r vs ref. FP, r vs external tracers, wind plots, PSCF plots)*

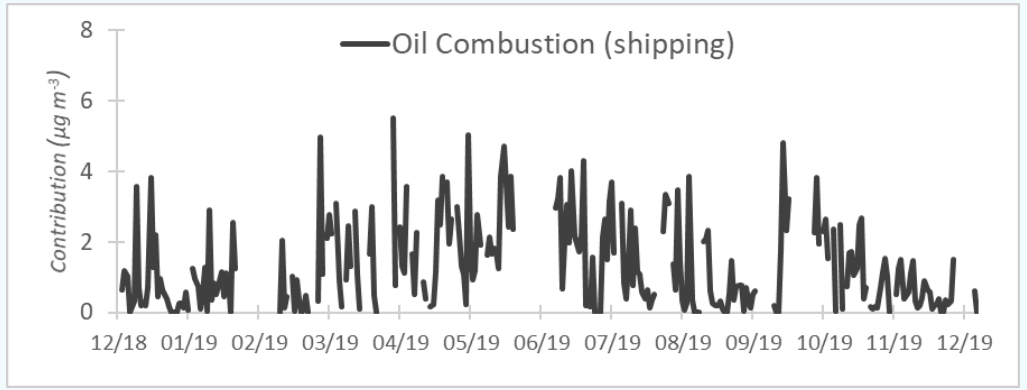
- Constrained HOA-1 factor in both seasons, linked to local traffic
- HOA-2 factor in both seasons, linked to port emissions
- Constrained BBOA factor only in winter
- Unconstrained LO-OOA, MO-OOA in both seasons
- Winter LO-OOA clearly associated with BBOA oxidation

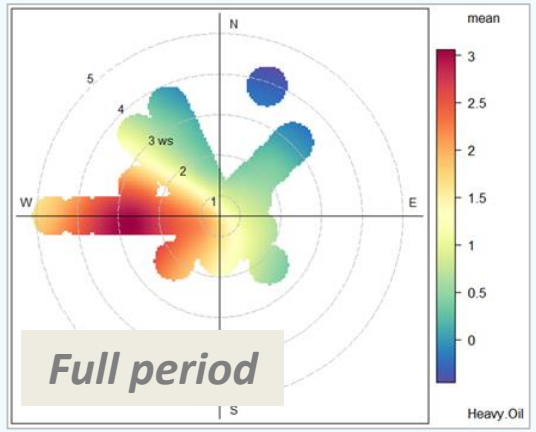
Stavroulas et al., 2021
https://doi.org/10.3390/atmos12121686

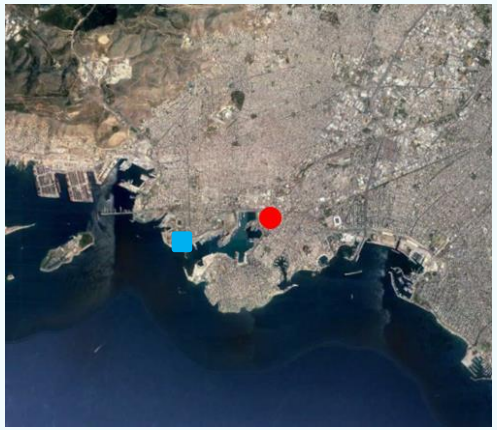
Oil combustion (shipping)

- Source profile: V, Ni, EC, OC
- V/Ni = 1.8
- Warm-period enhancement (+68%)
- High contributions in summer, in spite of increased dilution (increased BLH)
- Linked to westerlies year-round (port sector)
- Correlates with SO_2 (r = 0.58) measured to the W
- Correlates with BC_{ff} (r = 0.55)









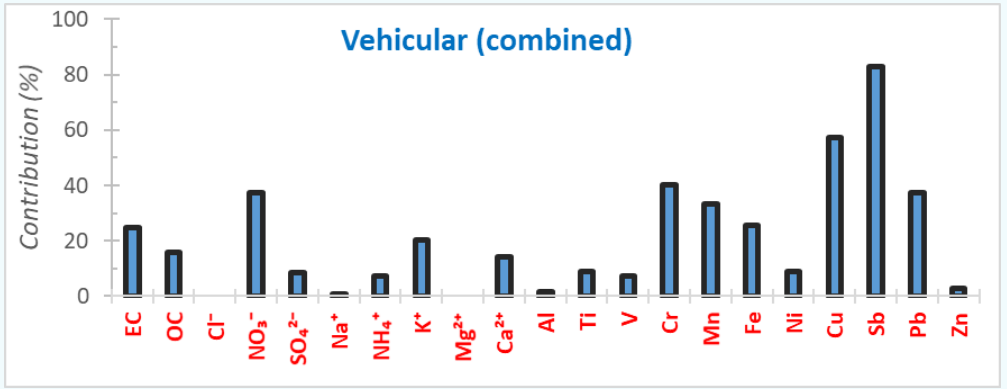
Vehicular Sources

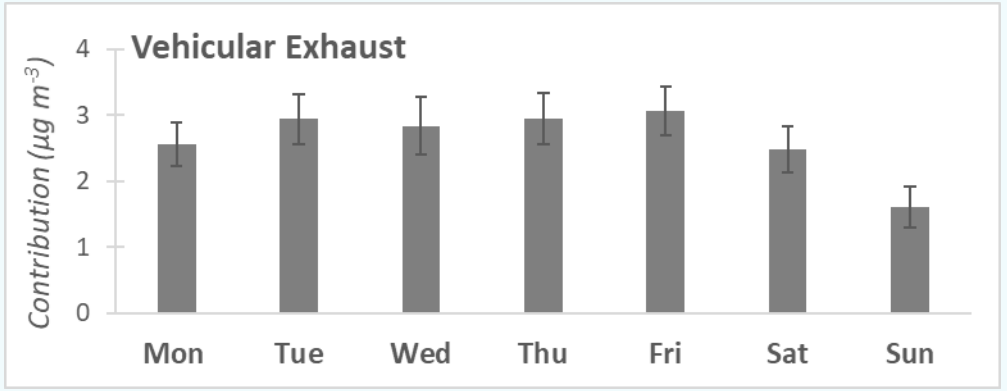
Vehicular Exhaust

- Source profile: OC, EC, nitrate
- OC/EC: 1.8
- Weekday enhancement (+48%)
- Correlates with CO (r = 0.92), NO_x (r = 0.66), BC_{ff} (r = 0.45)
- Correlates with HOA-1 (r = 0.69)

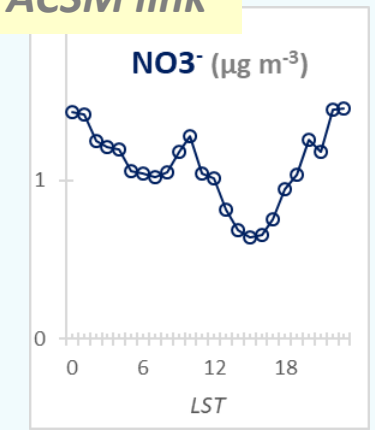
Vehicular Non-Exhaust

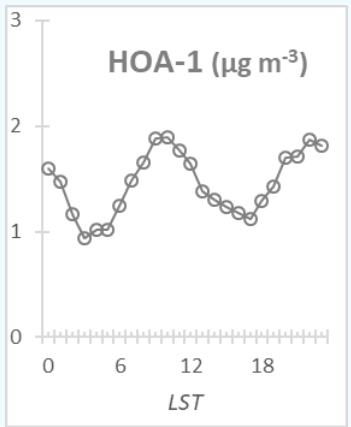
- Source profile: Cu, Sb, Fe
- Weekday enhancement (+19%)

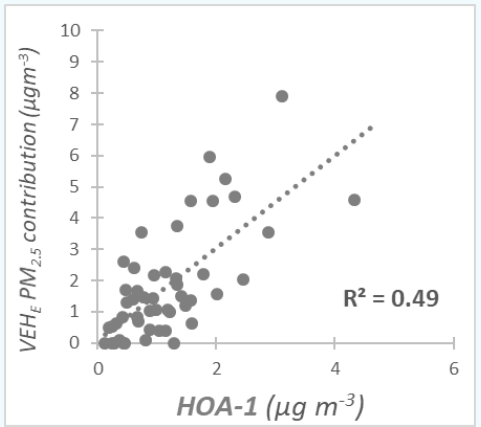


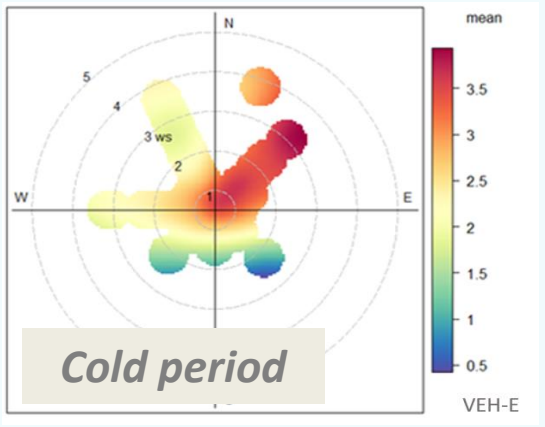


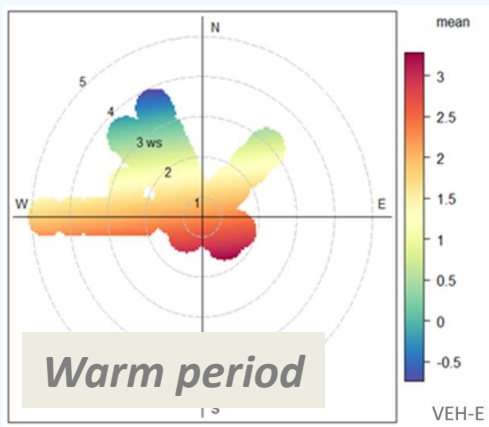
ACSM link









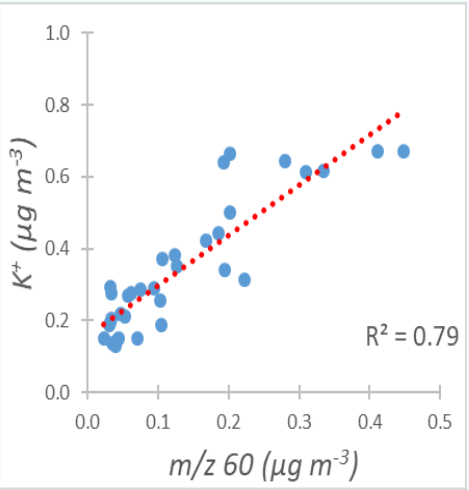


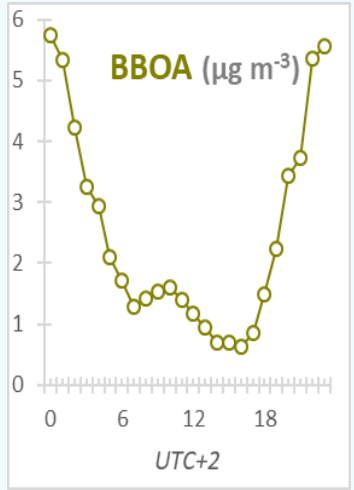
Biomass Burning

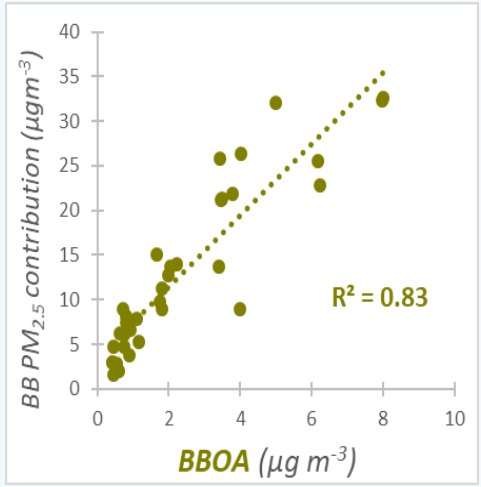
- Source profile: OC, EC, water-soluble K, nitrate
- Impact of local RWB emissions – winter heating
- Cold-period enhancement (*4.4, 7.0 vs 1.3 μg m^{-3})
- Correlates with BC_{bb} (r = 0.96)
- Correlates with BBOA in winter (r = 0.91)

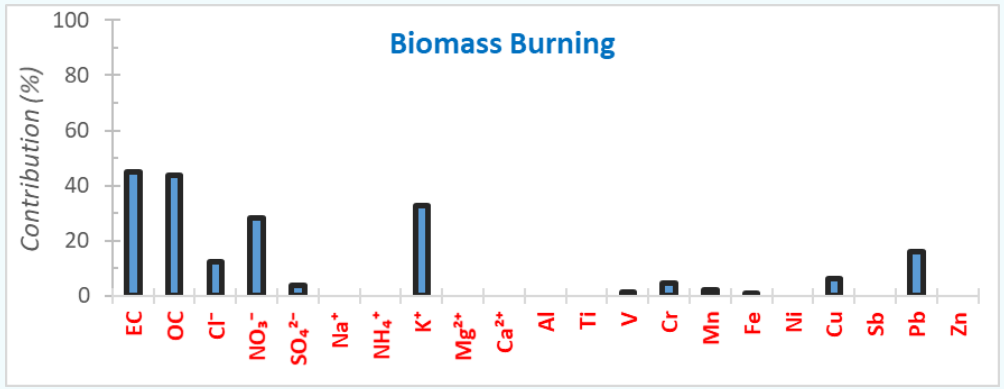
ACSM link

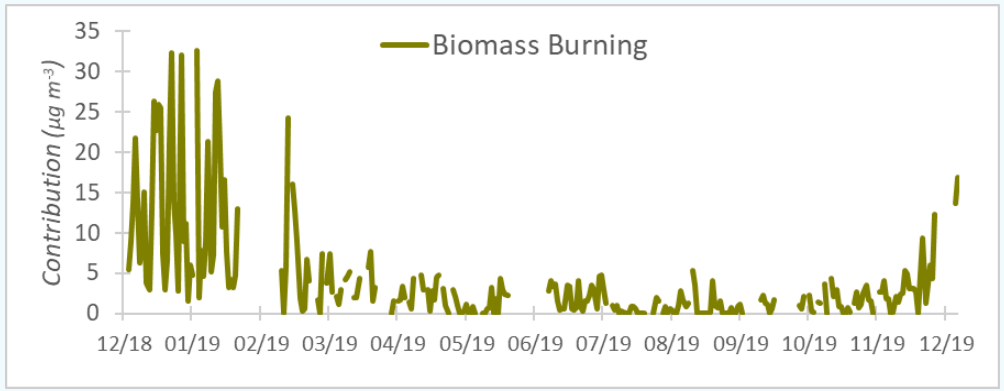
- Night-time enhancement of winter BBOA (*3.2)

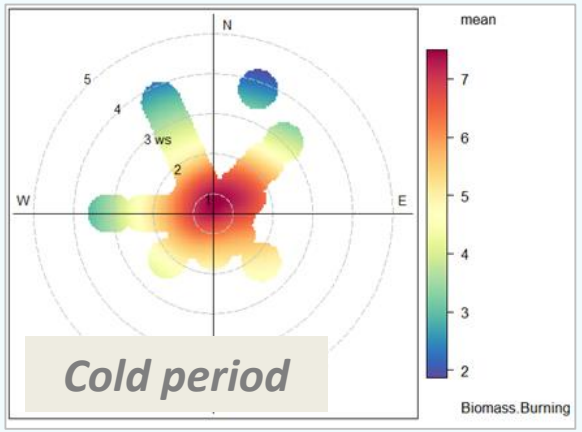


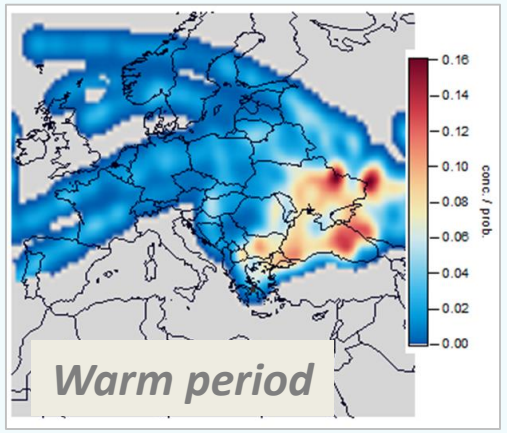






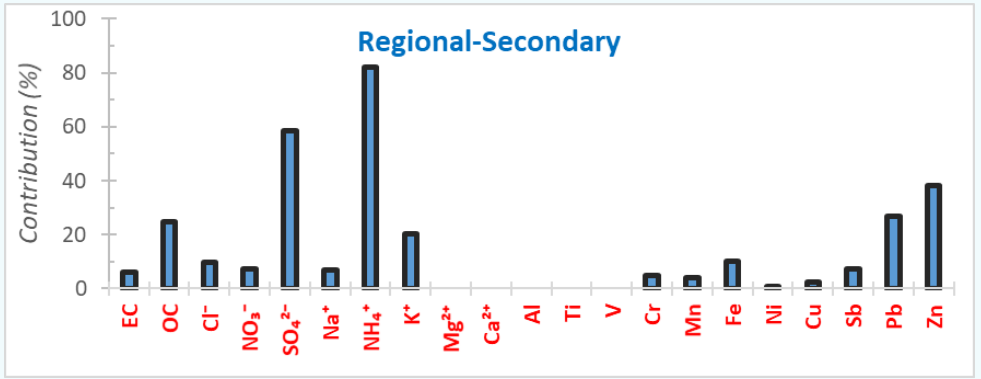


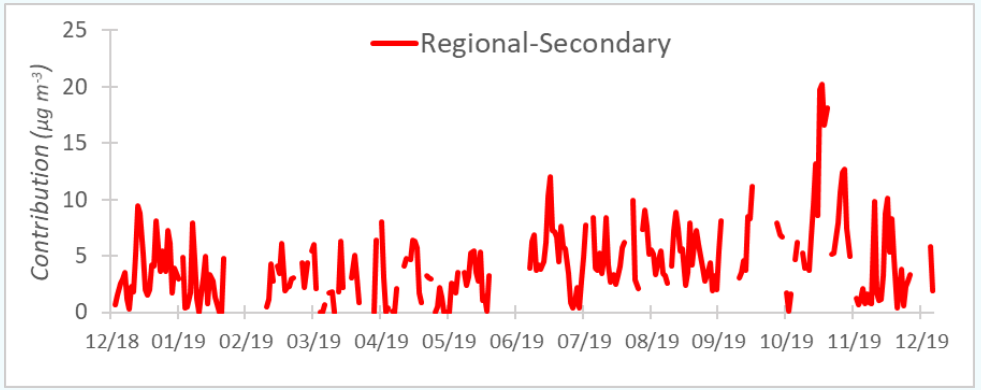




Regional-Secondary

- Source profile: SO_4^{2-}, NH_4^+, OC, EC
- OC/EC > 10
- Small warm-period increase (+4%)
- Higher levels associated with transport from the N
- Main LR source origins: Balkans, Ukraine, SW Russia





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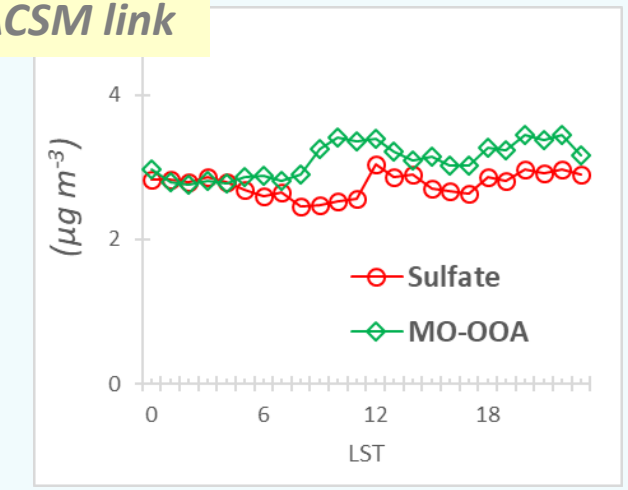
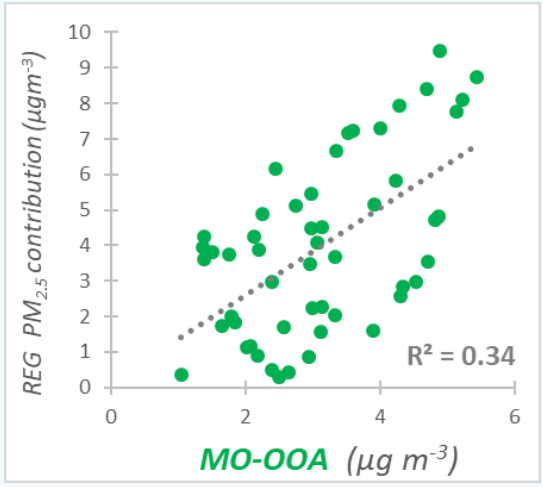
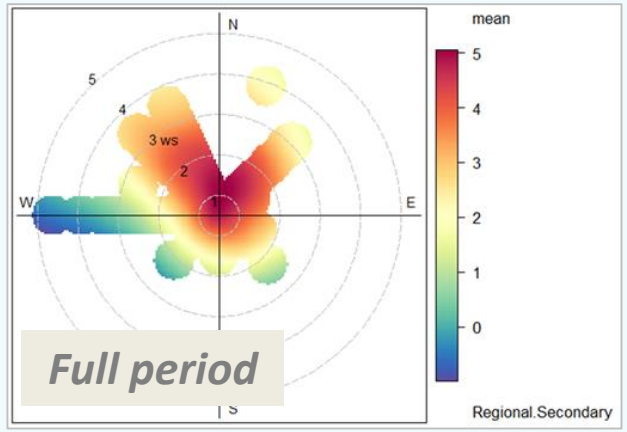
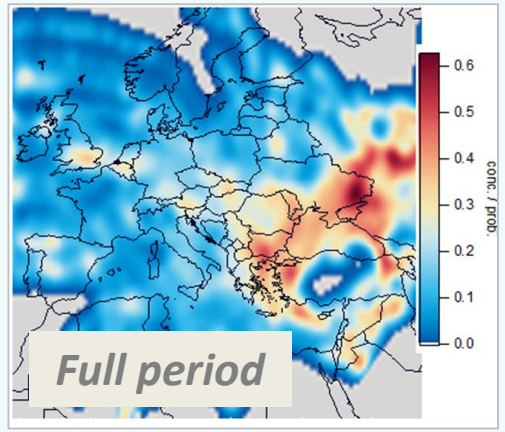






Full period



Full period

"Natural" Sources

Local dust resuspension

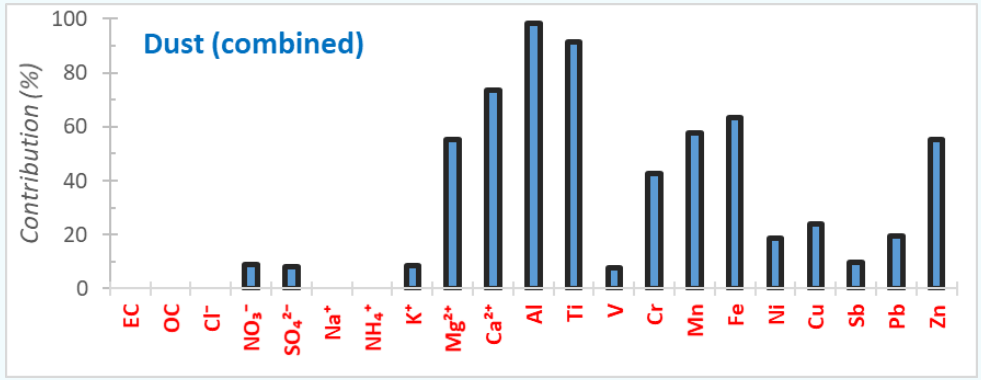
- Source profile: Mg^{2+}, Ca^{2+}, Al, Fe, Cu, Pb, Zn
- High in-profile EFs of Zn, Cu, Cr, Pb > 50
- Local resuspension
- Soil enriched by decades of anthropogenic activity in Piraeus

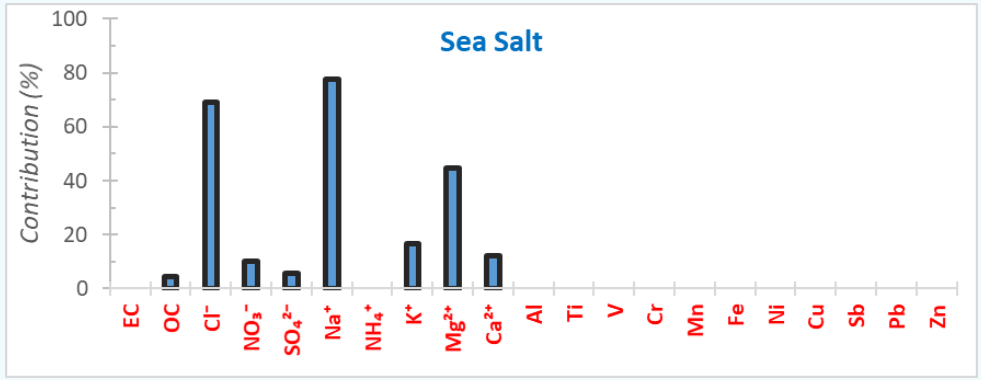
Mineral dust

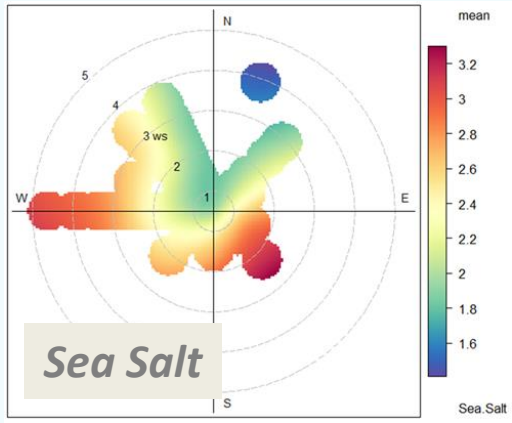
- Source profile: Al, Ti, Ca^{2+}, Mg^{2+}, K^{+}, Fe
- Low in-profile EFs (<10) for Cu, Cr, Mn, Ti, V
- Linked to episodic dust intrusions (LRT), mostly in spring

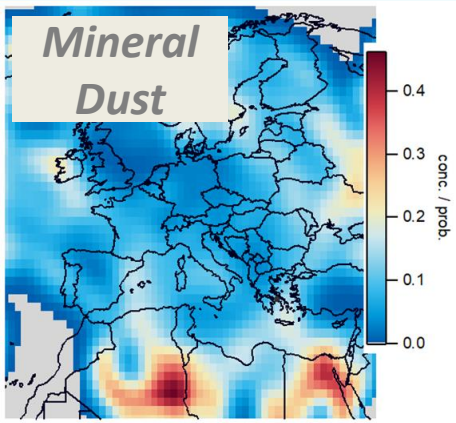
Sea Salt

- Source profile: Na^{+}, Cl^{-}, Mg^{2+}
- Warm-period enhancement (+45%, 2.6 vs 1.8 μg m^{-3})
- Sea-breeze effect (correlates with Temp.: r = 0.4)
- Associated with winds of the marine sector (S-W)



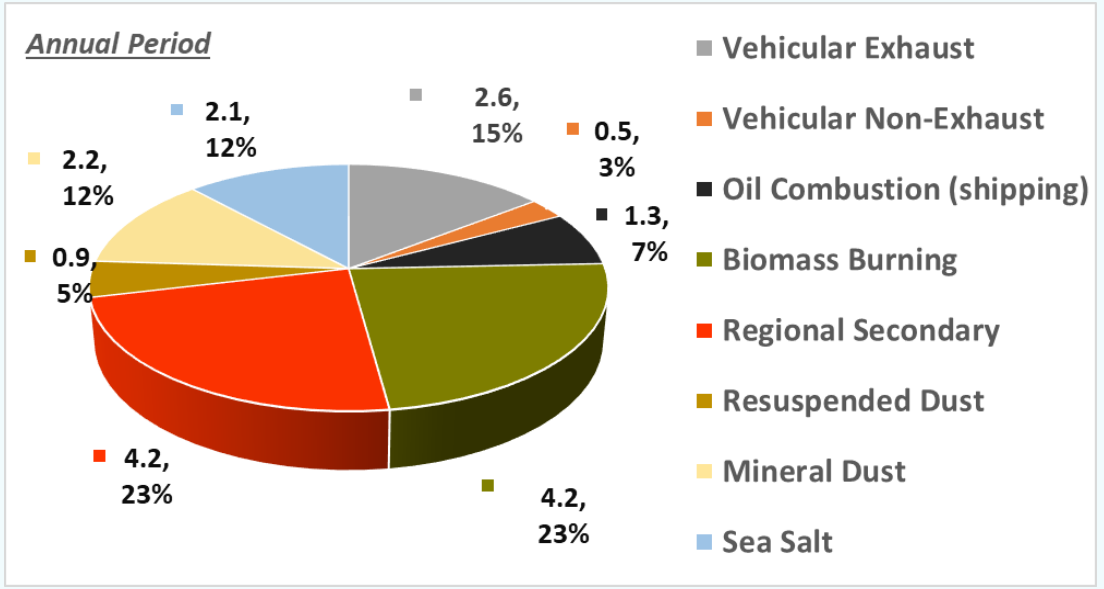


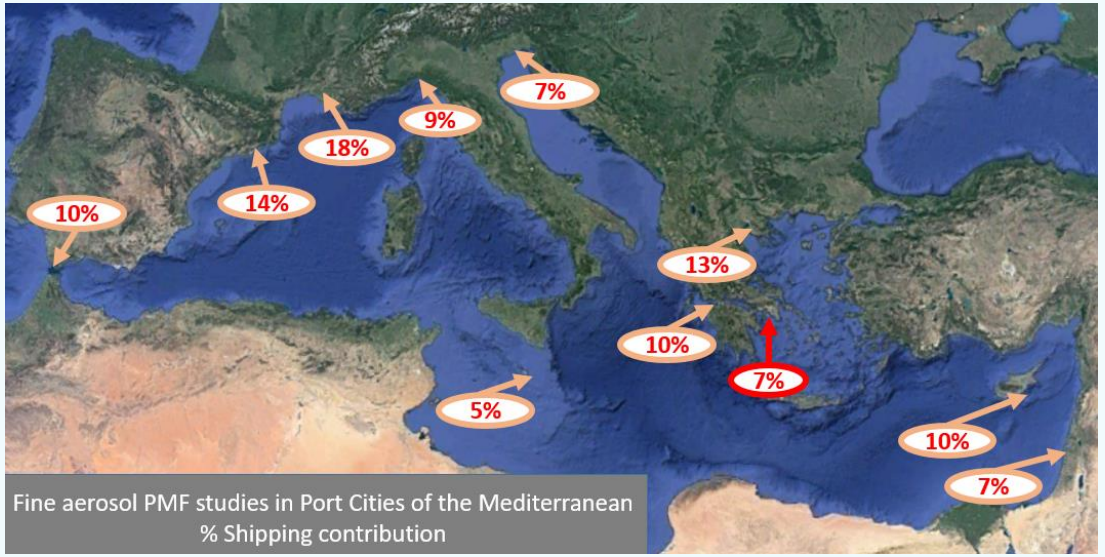




$PM_{2.5}$ Source Contributions

- Mean annual $PM_{2.5}$ (18 μg m^{-3}) at a 15-year low
- Moderate annual contribution of oil combustion (7%, 1.3 μg m^{-3}). Summer enhancement related to the passenger port
- Combined traffic sources account for 17% annually, lower compared to Greek urban sites in the past
- Residential wood burning (54% in winter) is a major contributor leading to wintertime "smog" events
- Regional-Secondary inputs form a background of 4 μg m^{-3}, indicating a declining trend in Southern Greece
- Frequent LRT dust events in 2019 led to an increased contribution
- Sea Salt contribution at the coastal site higher than typically observed at inland GAA sites





…some conclusions…

- *Anthropogenic local sources contributed almost ½ of $PM_{2.5}$ suggesting the potential of control measures to further reduce the mean annual concentration, in case of a revised EU standard*
- *The annual contribution of shipping didn't exceed 10%, even close to a major port like Piraeus. However, more research is needed to identify its effects on a sub-daily basis and at a spatial level*
- *Residential wood burning is a major $PM_{2.5}$ source, especially in winter, leading to episodic events. It has emerged as a result of the last decade's recession in Greece and persists during the current global energy crisis. Mitigation actions should be coordinated at the EU level*
- *The regional secondary contribution was about 25%, originating mostly from countries to the Northeast, not bound by EU legislation. Combined with the natural inputs, it forms a considerable $PM_{2.5}$ background for SE European cities, that will be difficult to mitigate*

Thank you!

ggrivas@noa.gr

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