


Application of PMF analysis for assessing the intra and inter-city variability of emission source chemical profiles



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Background

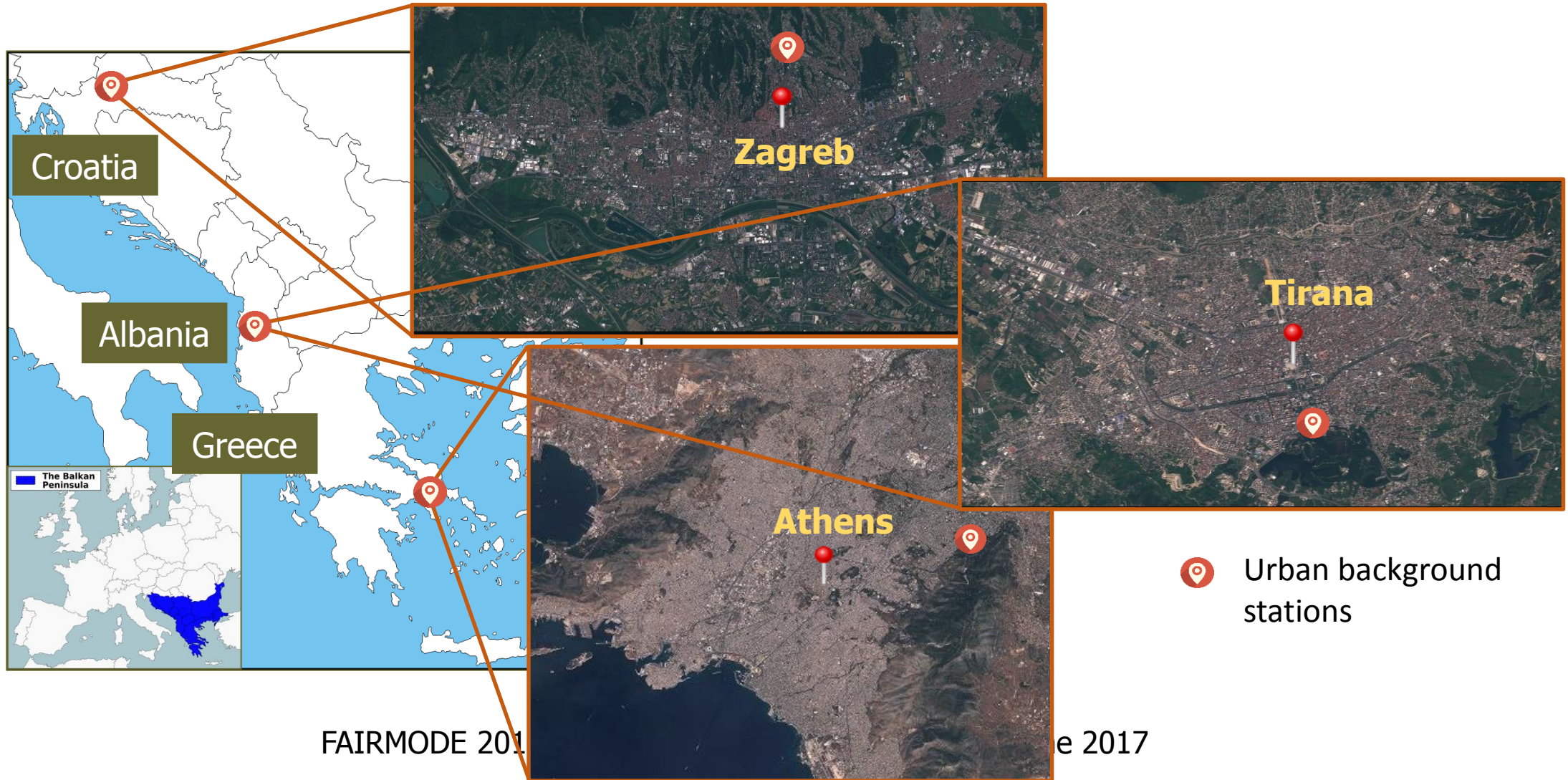
- ✔ Unregulated anthropogenic activities, both local and regional
- ✔ Hot and dry climate
- ✔ Significant impact from natural sources



+ lack of quantitative knowledge on source contributions to PM levels

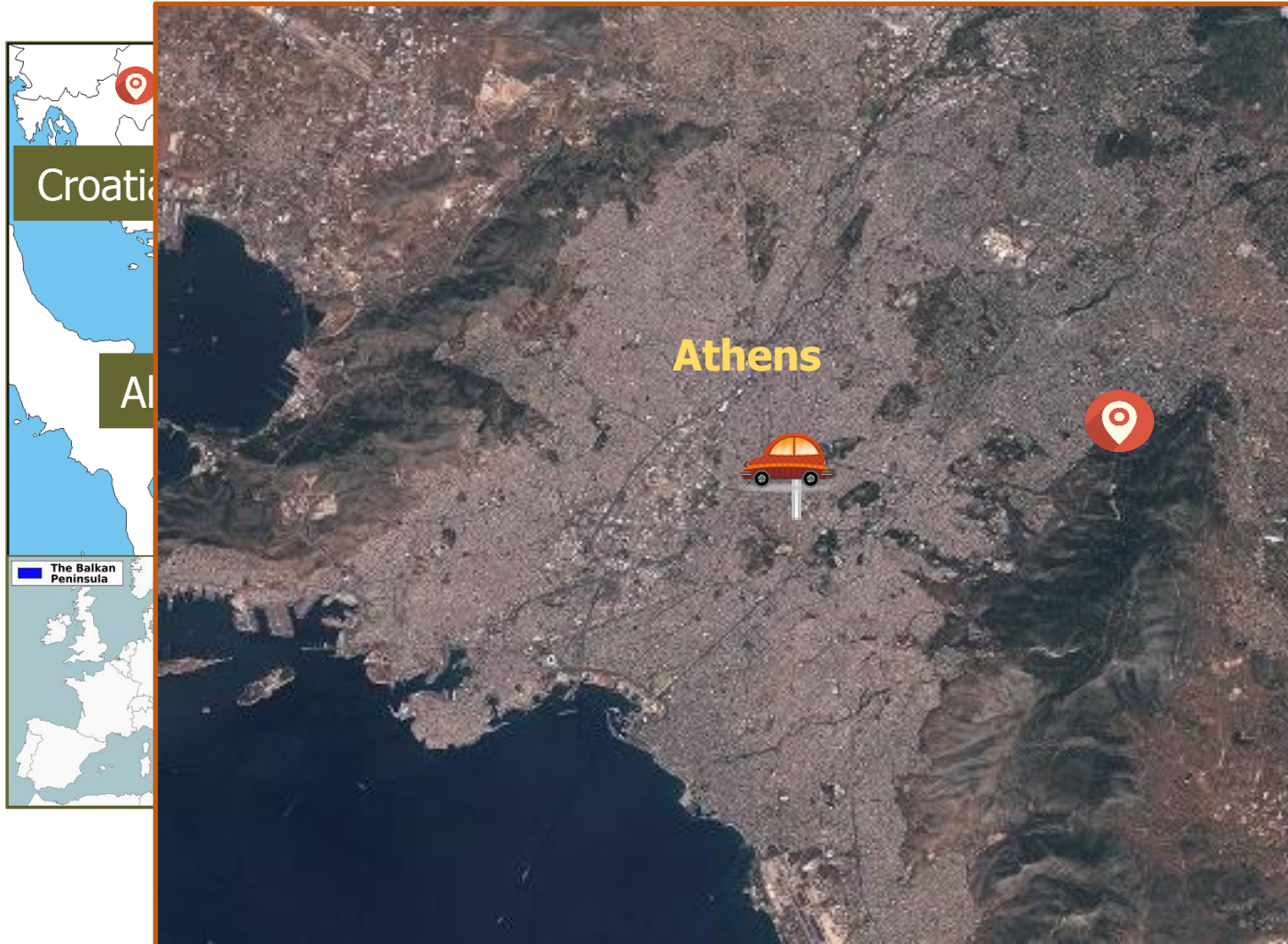
Motivation

- Assess the variability in source contributions and **chemical profiles** in urban background sites of big urban centres in the Balkan region



Motivation

- Assess the variability in source contributions and **chemical profiles** in sites with different characteristics in the city of Athens



Urban traffic station



Urban background stations

Methods – Intra-city variability (Athens, Greece)

- 24 h measurements of $PM_{2.5}$ and PM_{10} at
 - an urban background during 02/2013-02/2014 and
 - An urban traffic site during 07-08/2013 & 01-02/2014
- Chemical speciation by:
 - Ion chromatography for major ionic species
 - Thermal-optical analysis for EC, OC
 - PIXE and ICP-MS analysis for major and trace elements



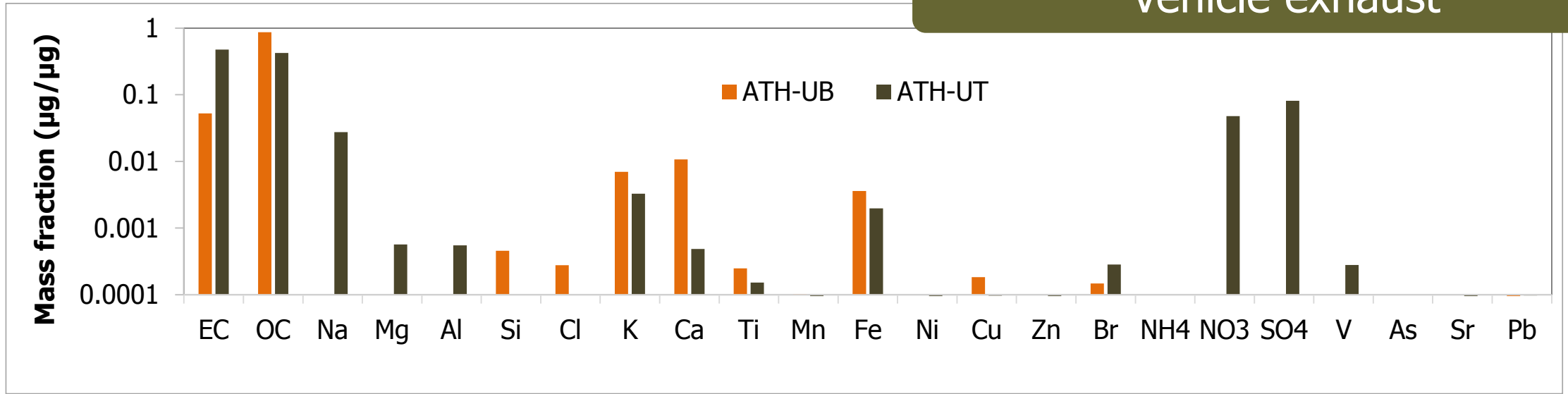
EPA PMF 5.0

Methods – Intra-city variability (Athens, Greece)

| | Urban background | Urban traffic |
|-----------------------------|---|--|
| Number of samples | 256 (PM ₁₀ +PM _{2.5}) | 140 (PM ₁₀ +PM _{2.5}) |
| Strong species | EC, OC, Na, Mg, Al, Si, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, V, As, Pb, NH ₄ ⁺ , NO ₃ ⁻ , SO ₄ ²⁻ | EC, OC, Mg, Al, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Na ⁺ , NH ₄ ⁺ , K ⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ |
| Weak species | Sr, Cd, Sb | V, As, Br, Sr, Ba, Pb |
| Extra modelling uncertainty | 5% | 10% |
| Constraints (dQ≤0.5%) | PM _{2.5} < PM ₁₀ OC pulled up in Heavy oil combustion and set to initial value in Biomass burning | - |

Results – Intra-city variability (Athens, Greece)

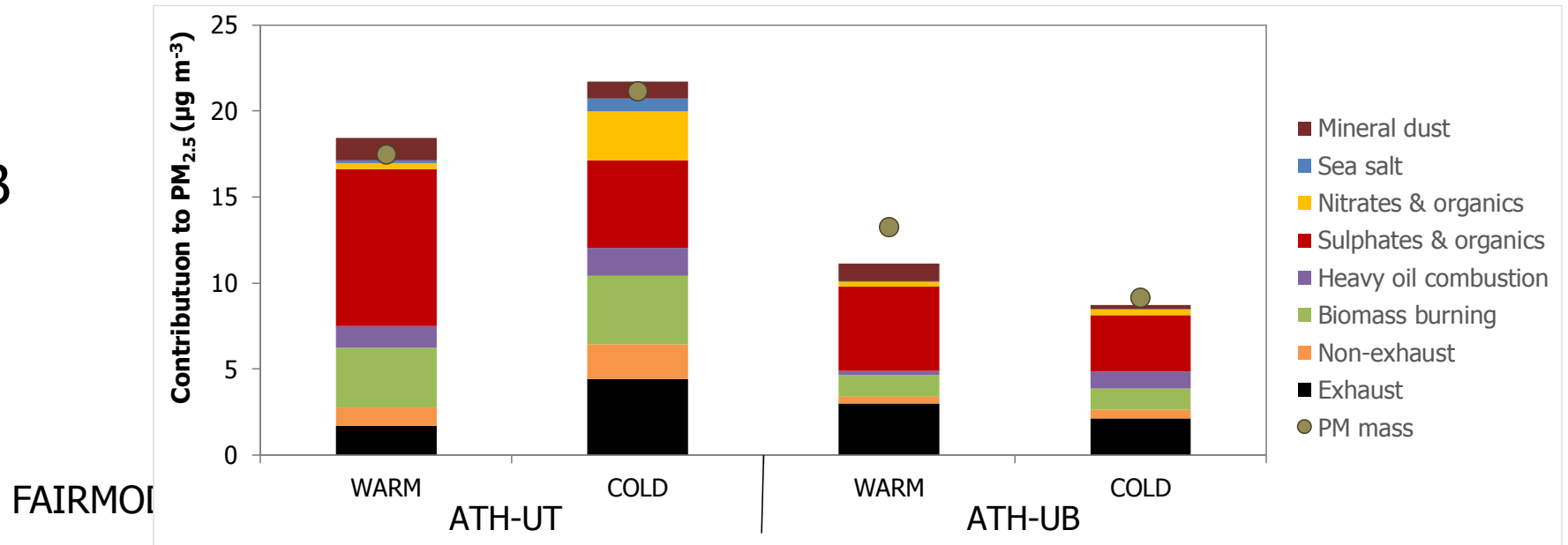
Vehicle exhaust



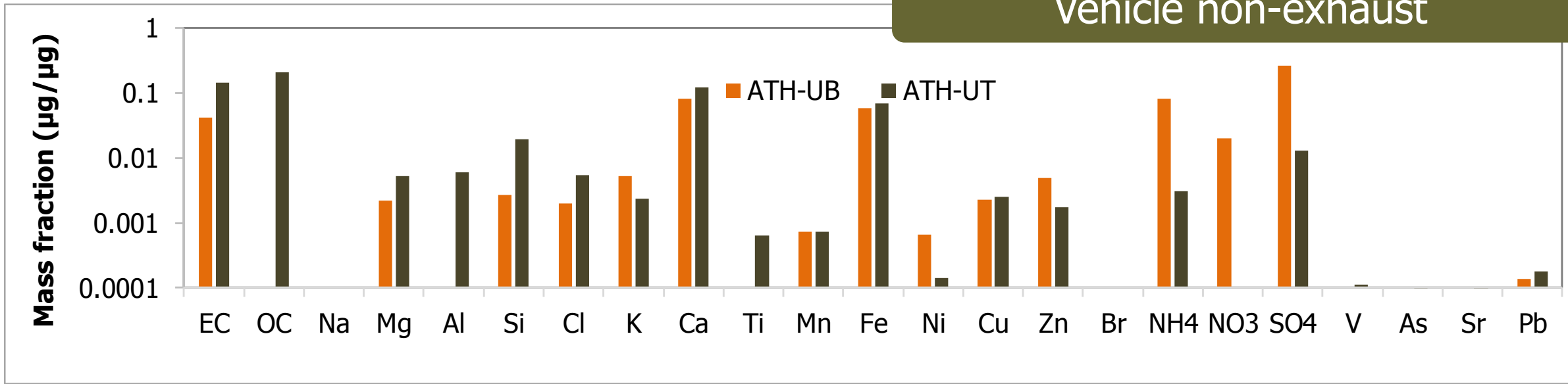
OC/EC:

- <1 at ATH-UT
- 16.4 at ATH-UB

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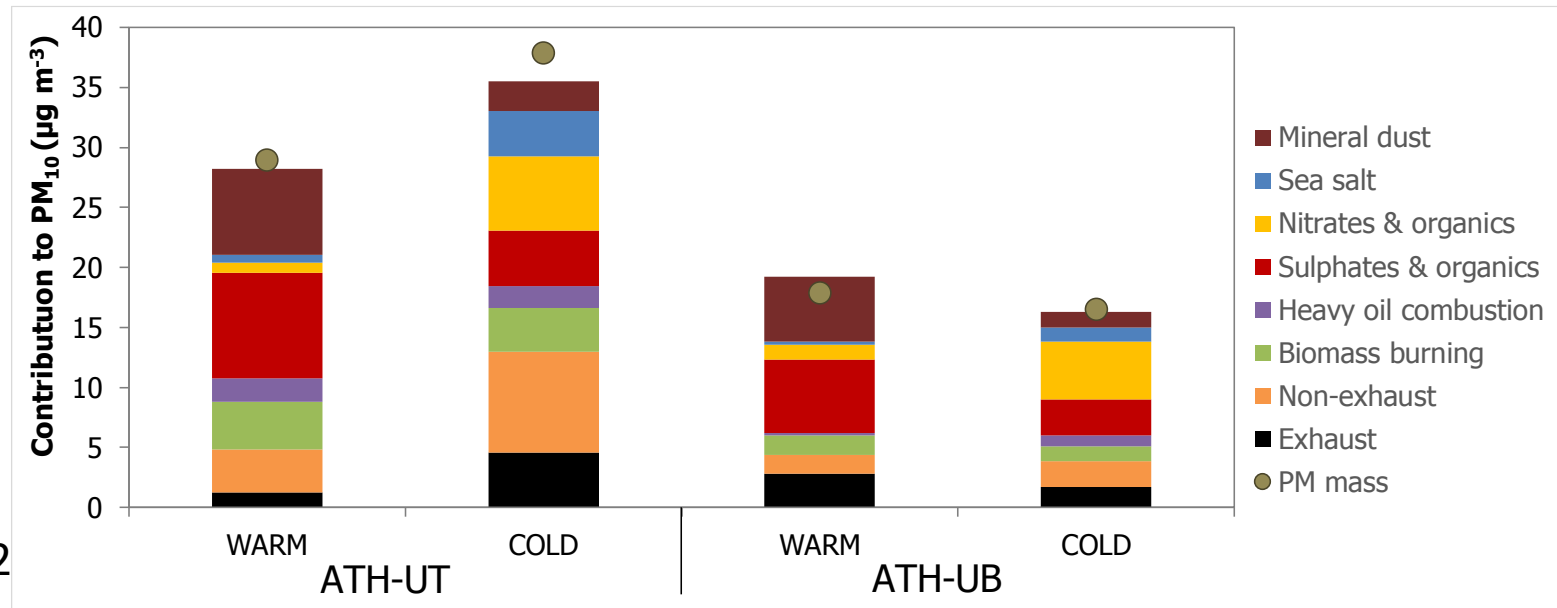
Results – Intra-city variability (Athens, Greece)



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- Fe, Ca and EC at both sites
- OC in ATH-UT
- SIA mainly in ATH-UB

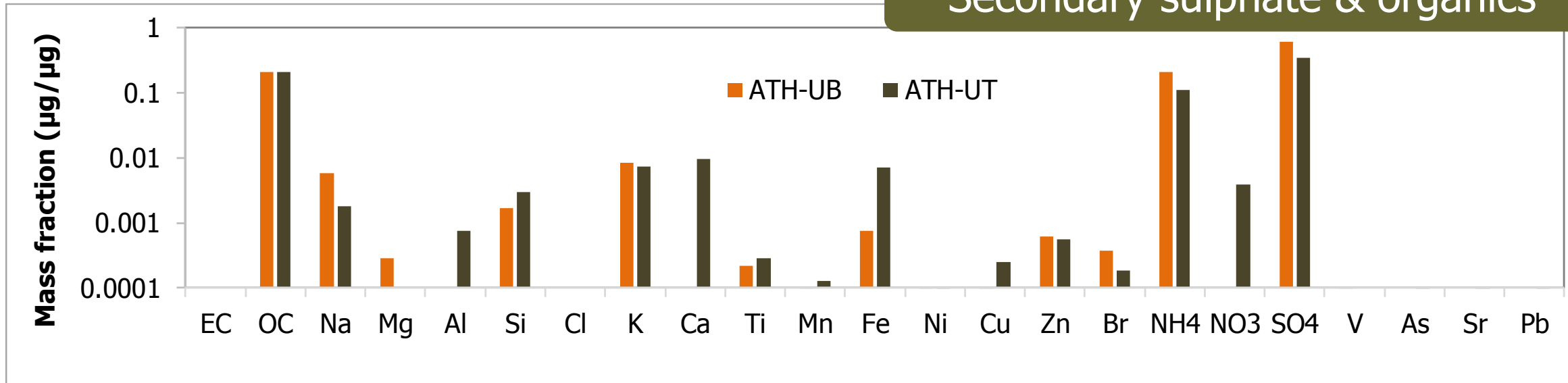
FAIRMODE 2



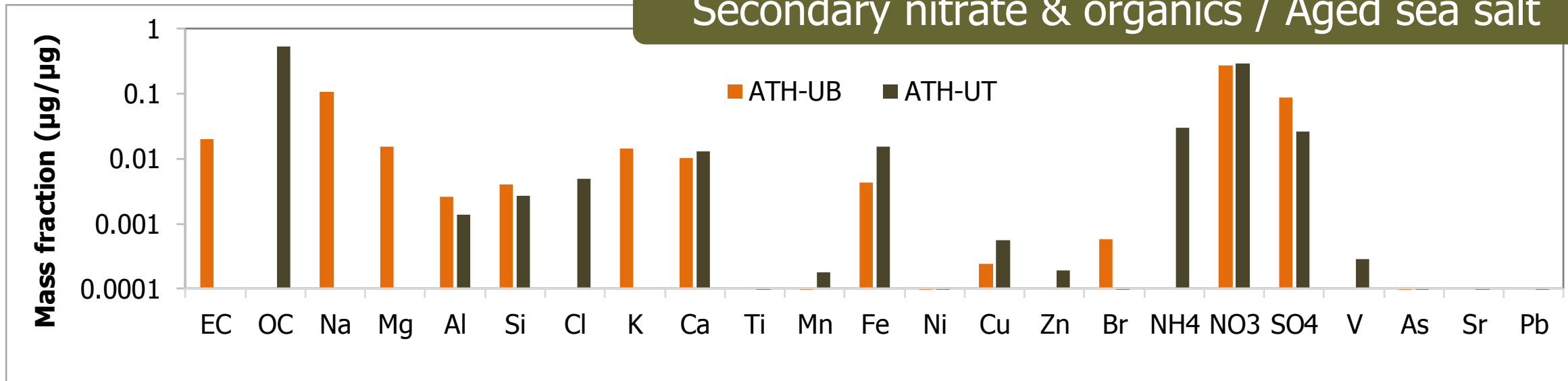
Results – Intra-city variability (Athens, Greece)



Secondary sulphate & organics

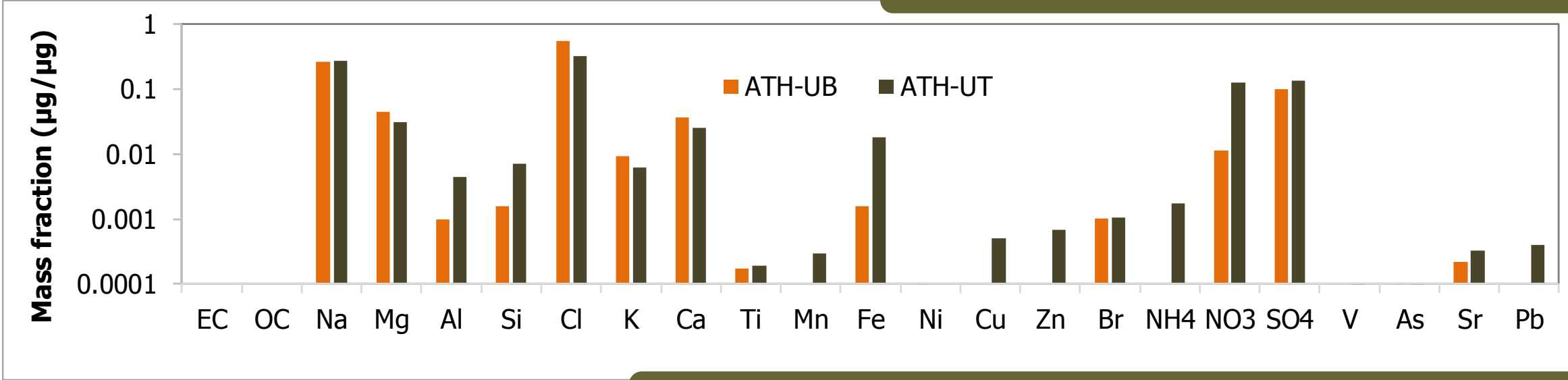


Secondary nitrate & organics / Aged sea salt

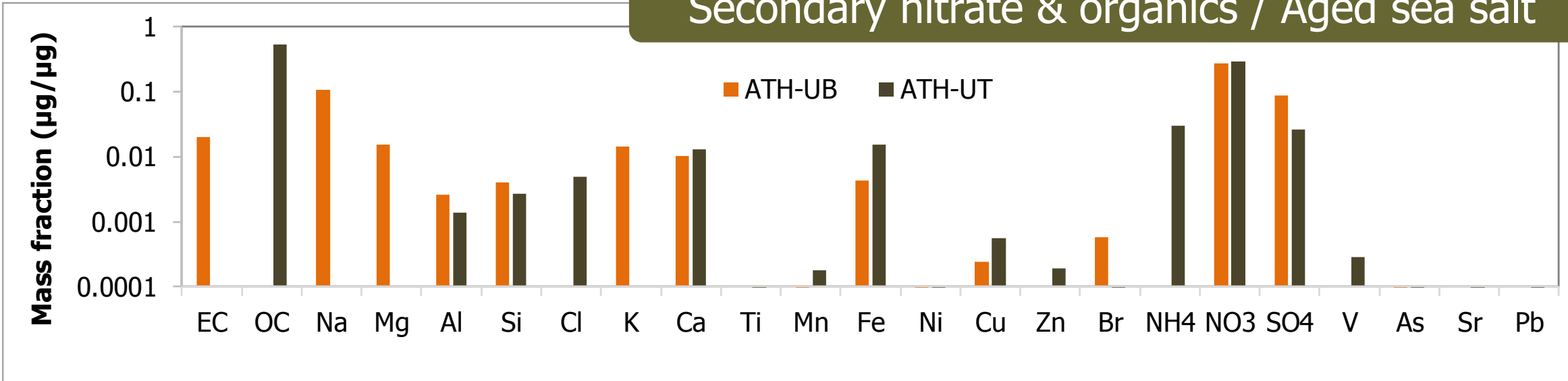


Results – Intra-city variability (Athens, Greece)

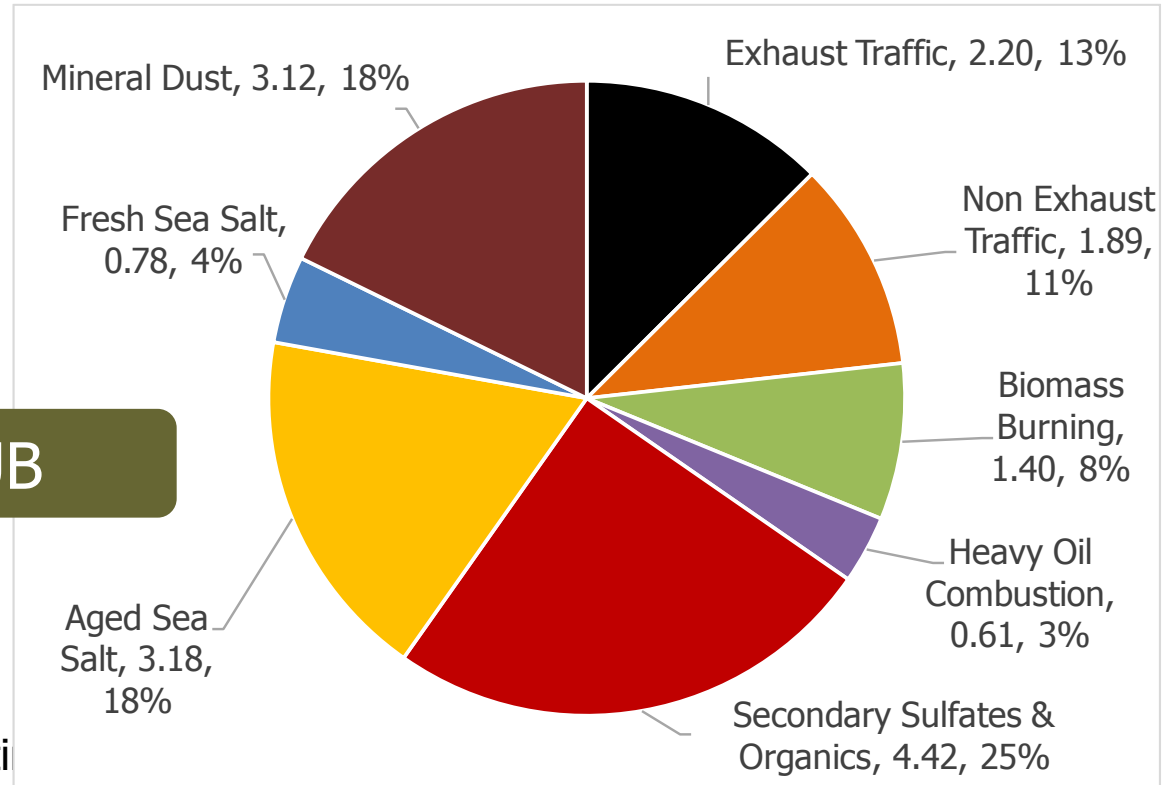
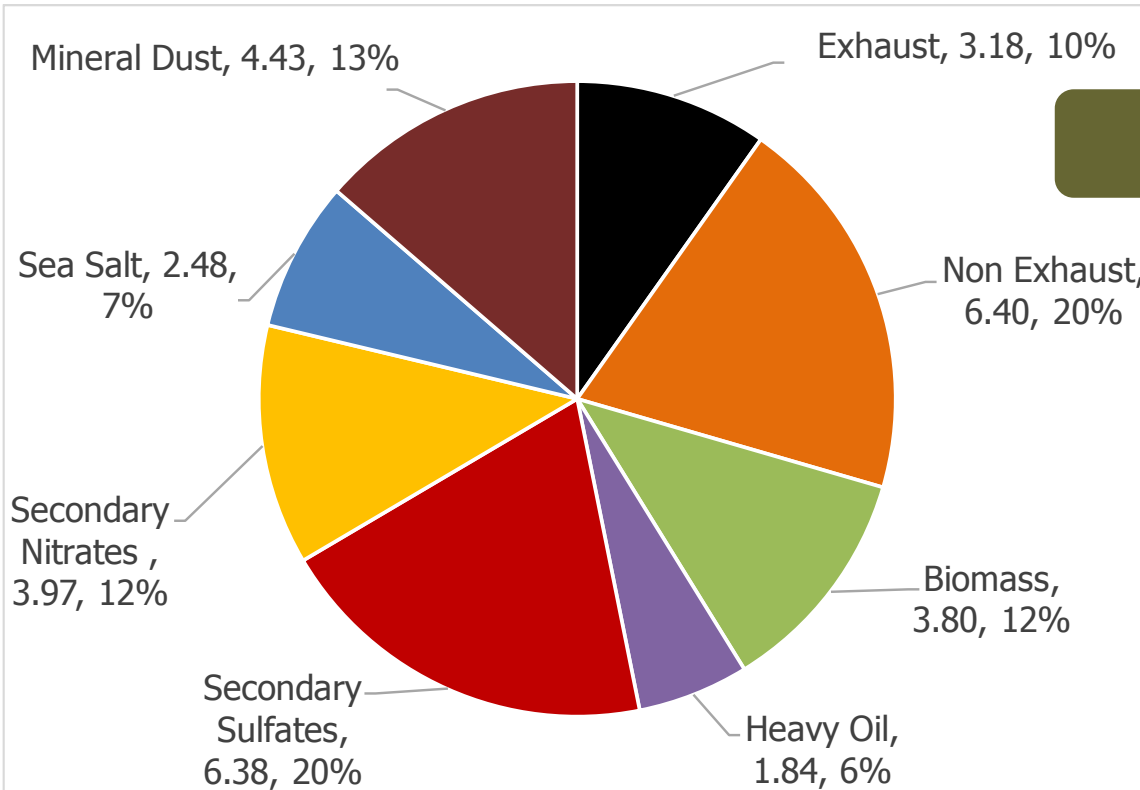
Fresh sea salt



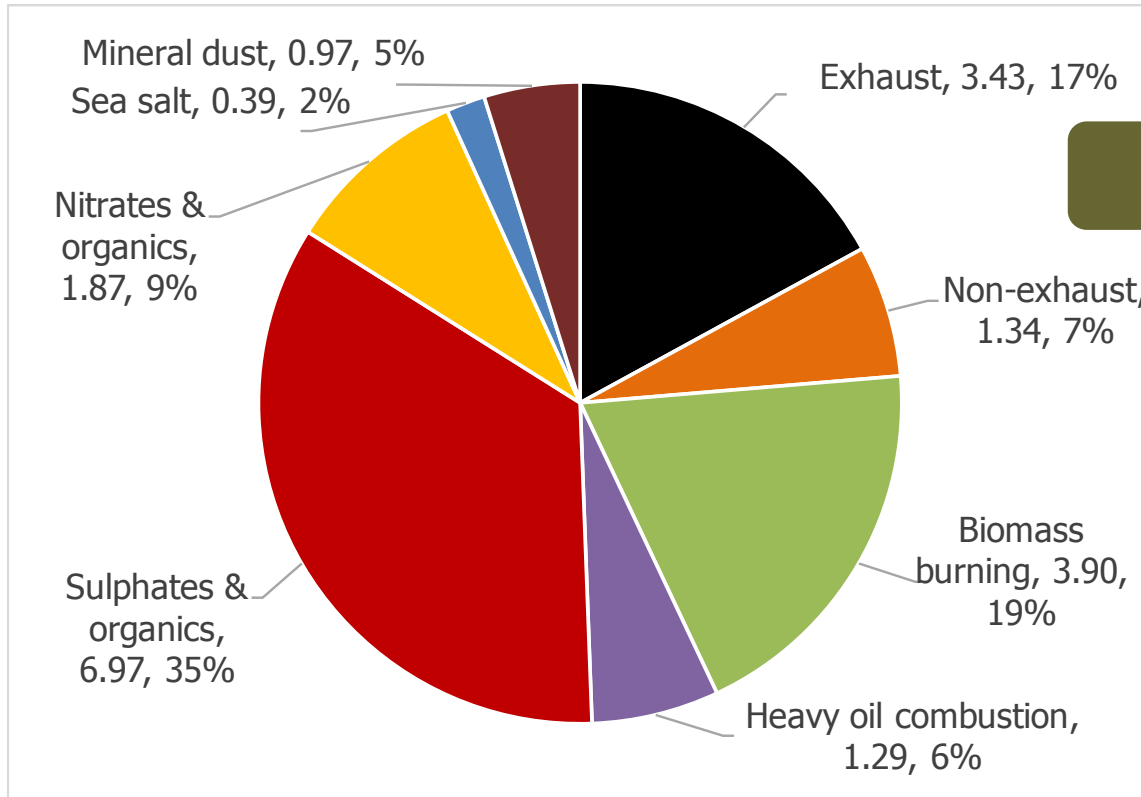
Secondary nitrate & organics / Aged sea salt



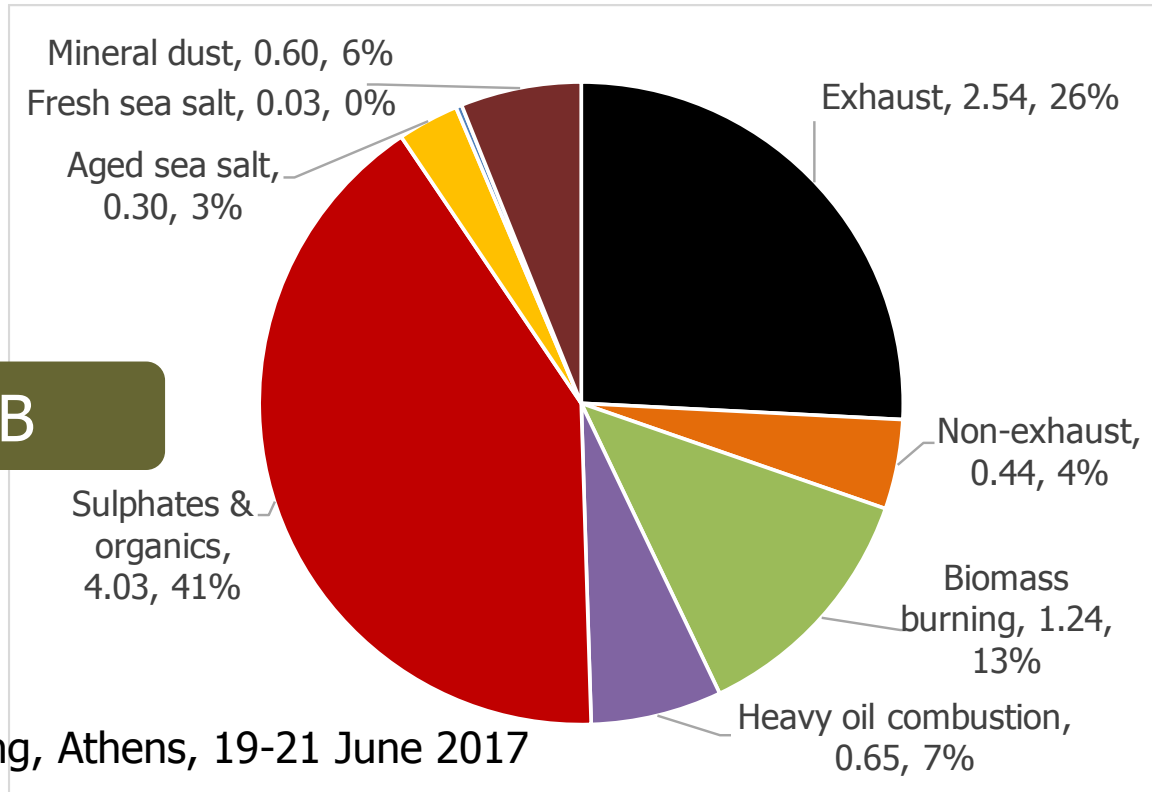
Results – Intra-city variability (Athens, Greece)



Results – Intra-city variability (Athens, Greece)

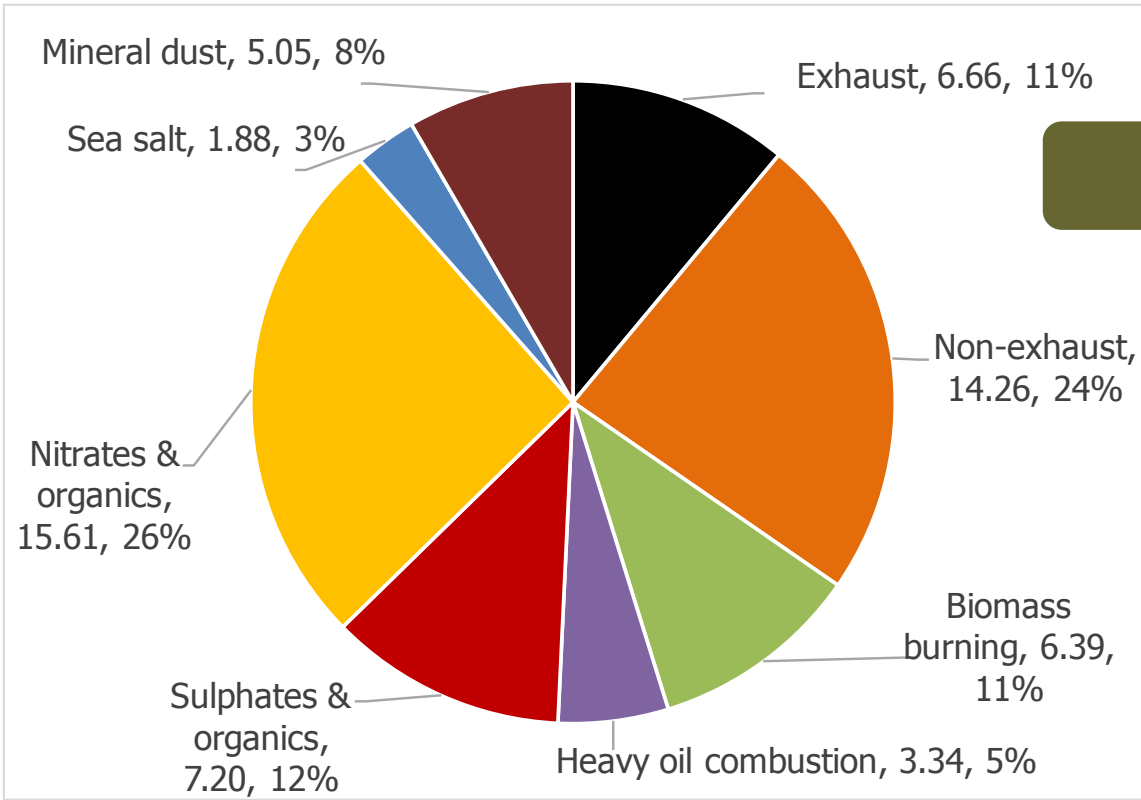


PM_{2.5} / ATH-UT

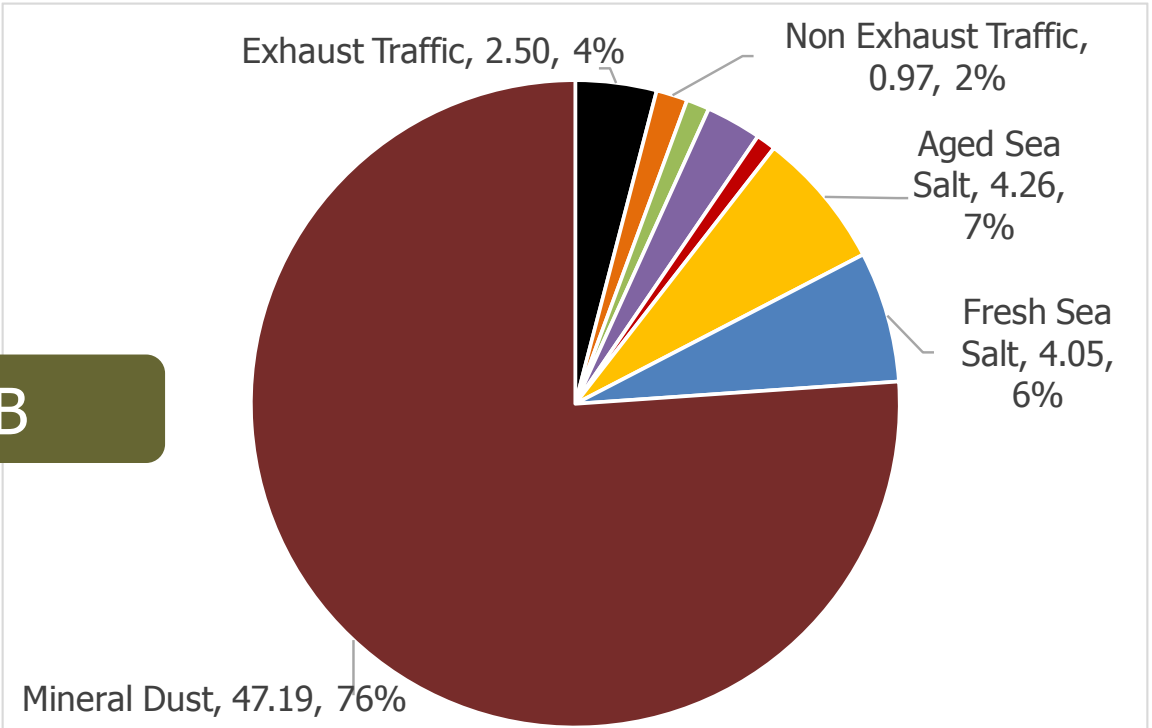


PM_{2.5} / ATH-UB

Results – Intra-city variability (Athens, Greece)



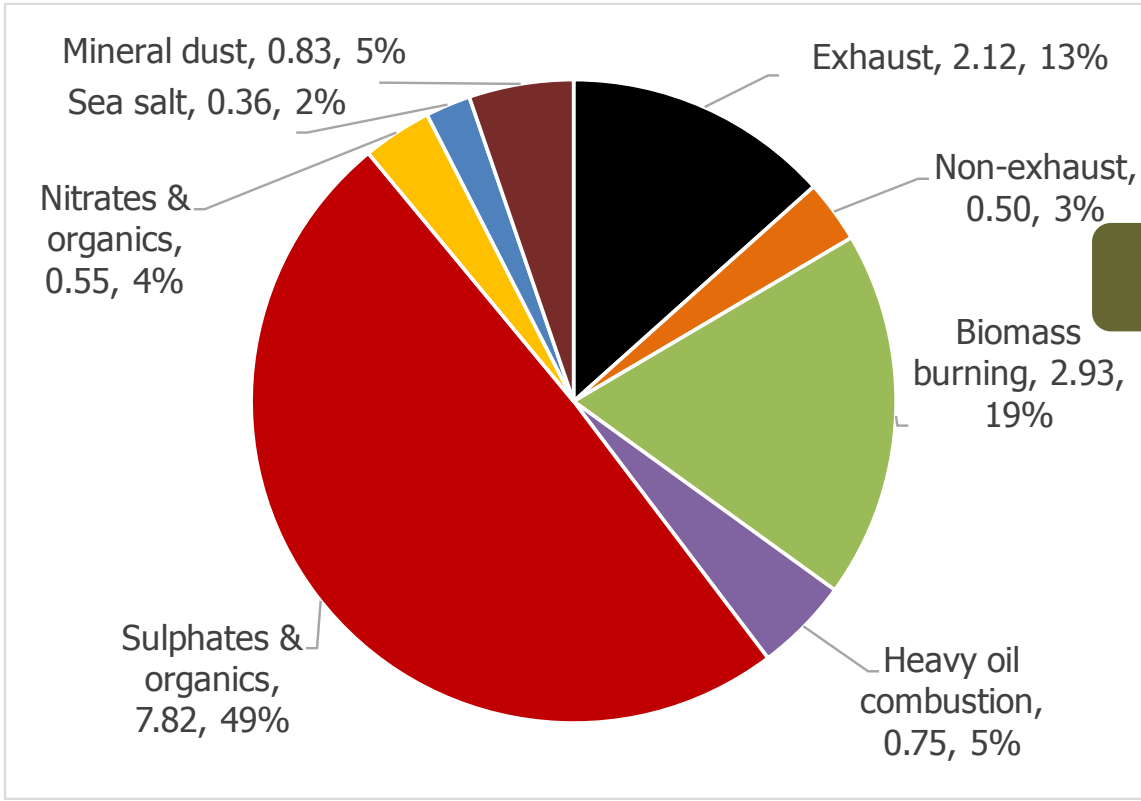
PM₁₀ / ATH-UT



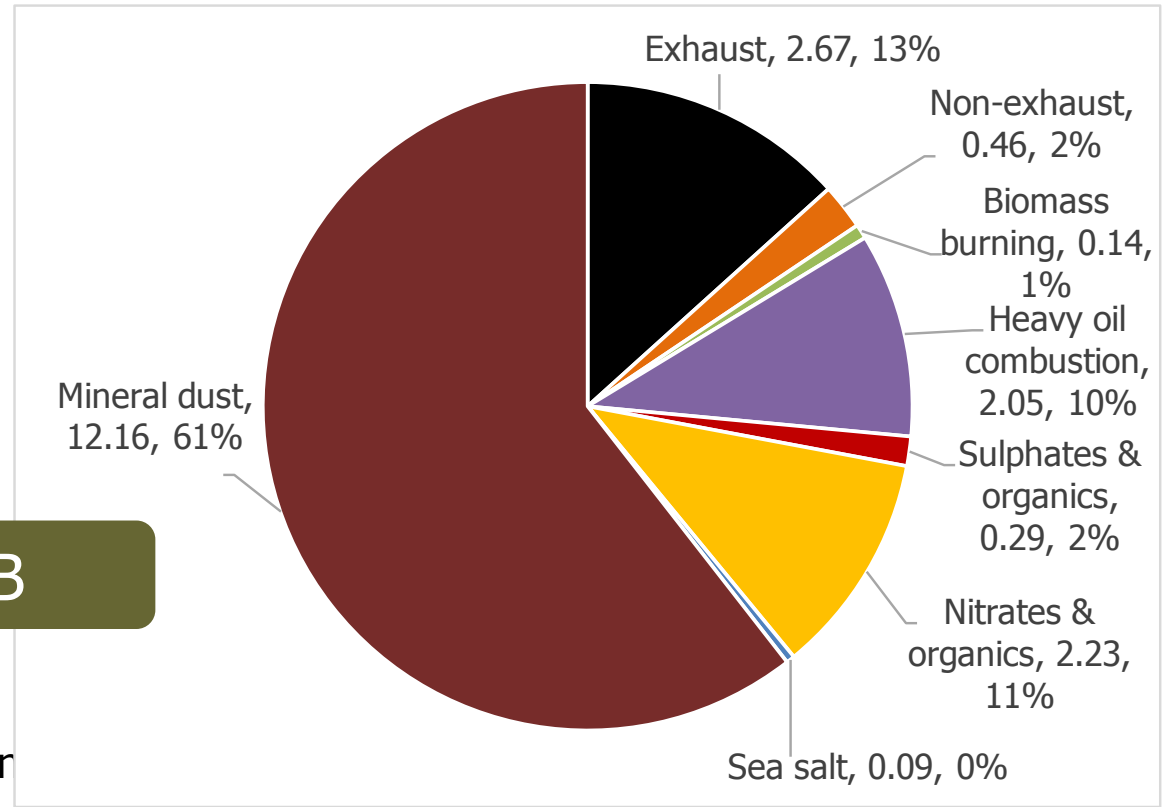
PM₁₀ / ATH-UB

Results – Intra-city variability (Athens, Greece)

PM_{2.5} / ATH-UT



PM_{2.5} / ATH-UB



Methods – Inter-city variability (Balkan region)

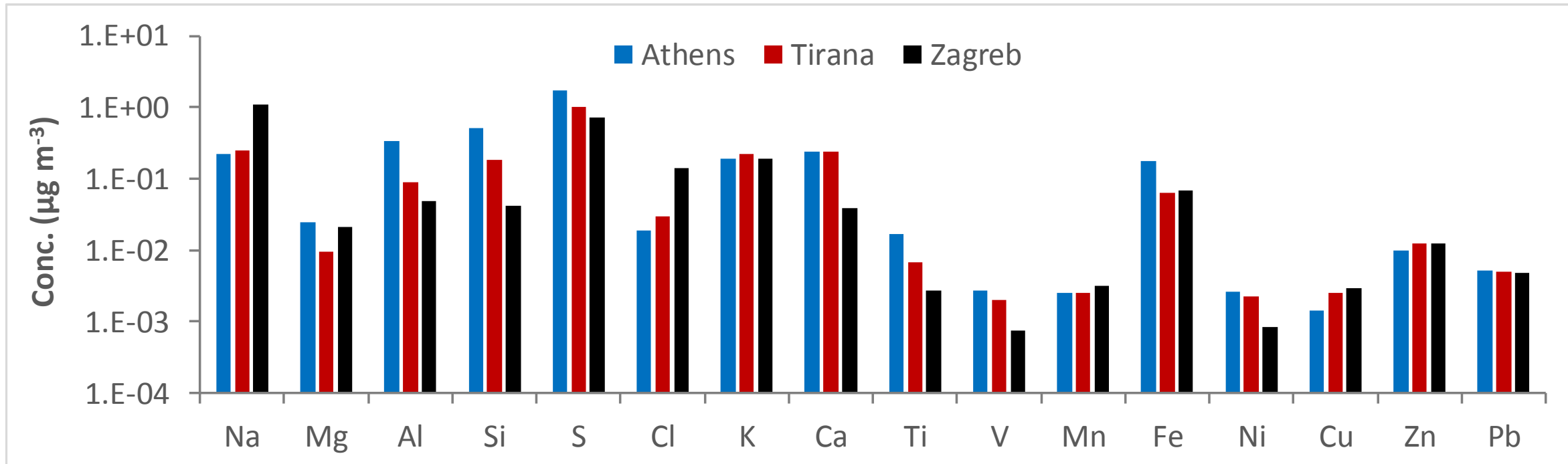
- **24-hr PM_{2.5}** samples were collected at **urban background** sites in Athens, Zagreb and Tirana, during **2014-2015**.
- **Black carbon (BC)** concentrations were calculated for Tirana and Zagreb through light attenuation coefficient measured by EEL reflectometer.
- **Elemental (EC) and organic carbon (OC)** concentrations were recorded in Athens by Semi-continuous OCEC Field Instrument (Sunset Lab., Inc.).
- XRF analysis for: **Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Pb**.



EPA PMF 5.0

Methods – Inter-city variability (Balkan region)

| $\mu\text{g m}^{-3}$ | PM _{2.5} | OC | EC / BC | S | Si | Na | K |
|----------------------|-------------------|-----------|-----------|-----------|-------------|-----------|-----------|
| Athens | 11.4 ± 6.3 | 3.4 ± 1.5 | 0.6 ± 0.2 | 1.7 ± 2.0 | 0.50 ± 1.20 | 0.2 ± 0.3 | 0.2 ± 0.2 |
| Tirana | 19.5 ± 8.7 | - | 3.4 ± 1.3 | 1.0 ± 0.6 | 0.20 ± 0.50 | 0.2 ± 0.3 | 0.2 ± 0.2 |
| Zagreb | 18.1 ± 16.2 | - | 0.9 ± 0.4 | 0.7 ± 0.6 | 0.04 ± 0.09 | 1.1 ± 0.6 | 0.2 ± 0.2 |



Methods – Inter-city variability (Balkan region)

| | Athens | Tirana | Zagreb |
|--------------------------|--|---------------------------------------|---|
| Sampling period | 01-12/2014 | 01/2014-10/2015 | 01/2014 – 09/2015 |
| Number of samples | 116 | 218 | 619 |
| Strong species | OC, EC, Al, Si, S, Cl, K, Ca, Ti, Fe, Zn | S, K, Ca, Ti, Fe, Zn | Al, Ca, Cl, Cu, Fe, K, Mg, Mn, Ni, Pb, S, Si, Ti, V, Zn, BC |
| Weak species | Na, Mg, V, Mn, Ni, Cu, Pb | BC, Na, Al, Si, Cl, V, Mn, Ni, Cu, Pb | Na |

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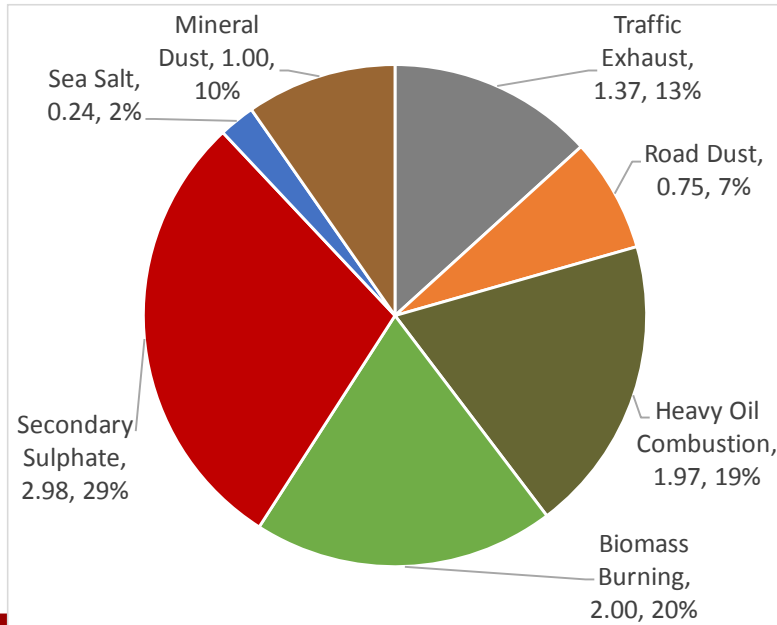
PMF analysis:

5 % extra modelling uncertainty

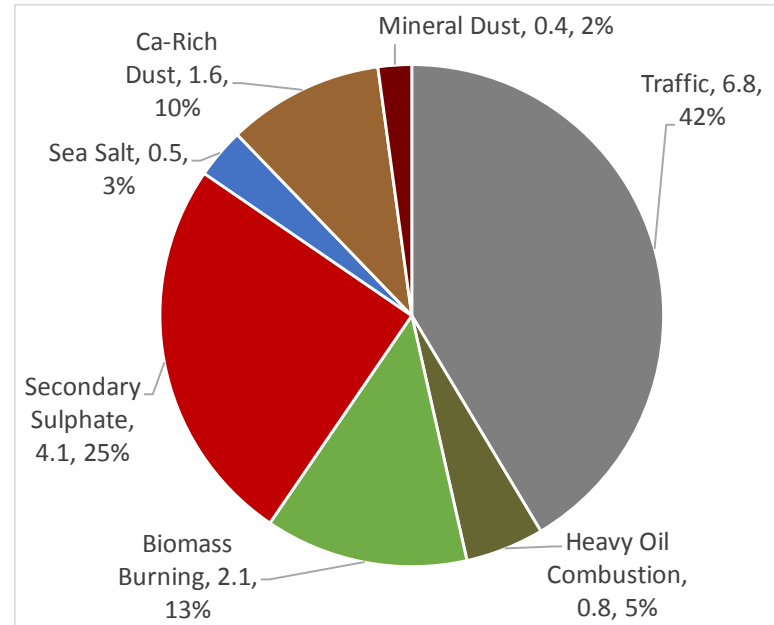
$f_{peak} = 0$ for Athens and Tirana and -1.5 for Zagreb

Methods – Inter-city variability (Balkan region)

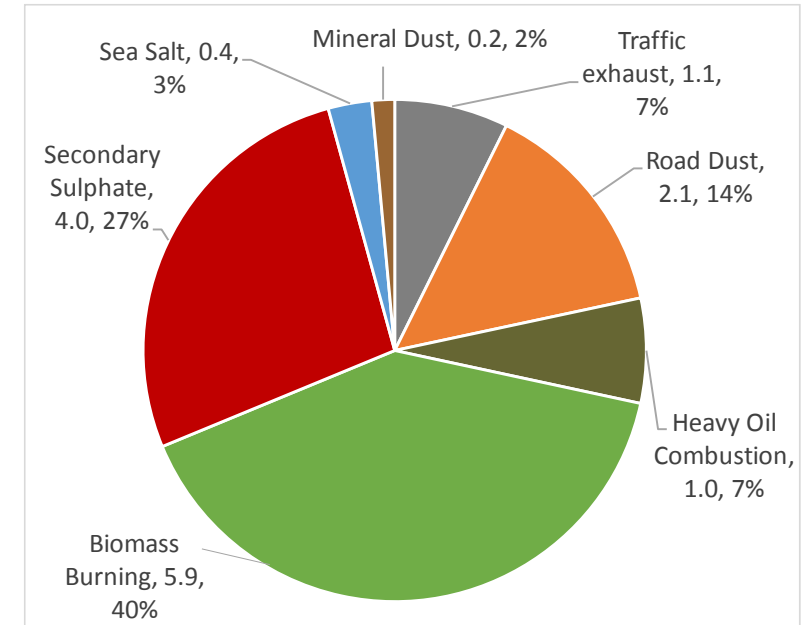
Athens



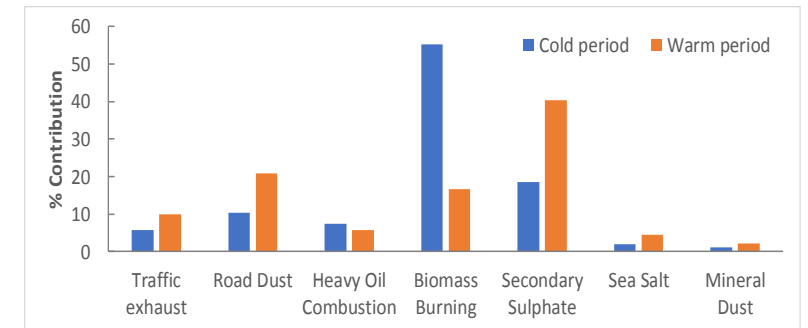
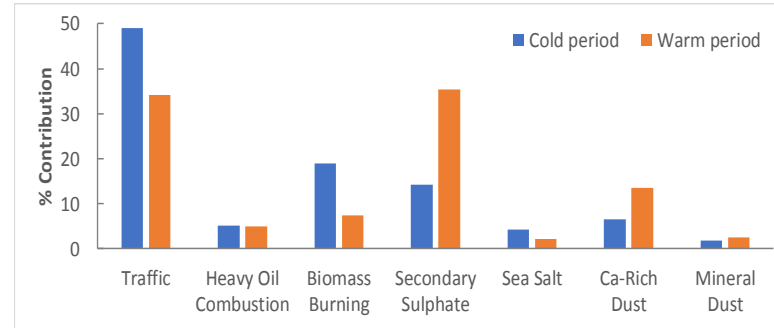
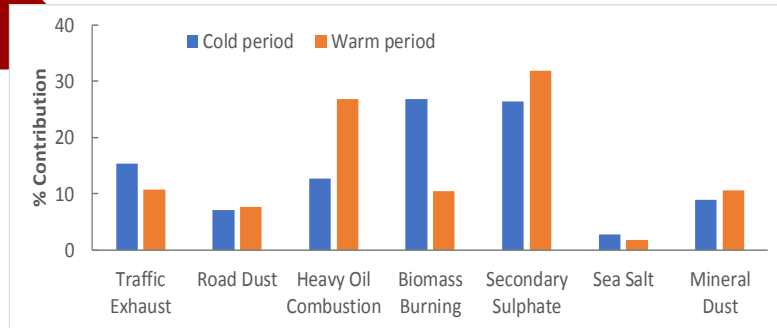
Tirana



Zagreb

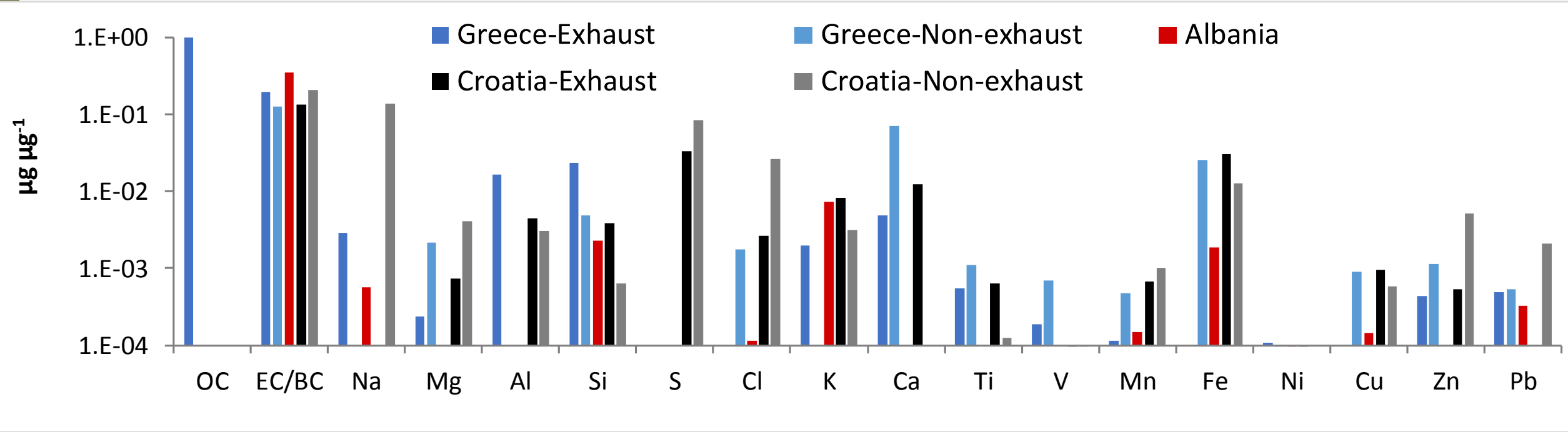


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Methods – Inter-city variability (Balkan region)

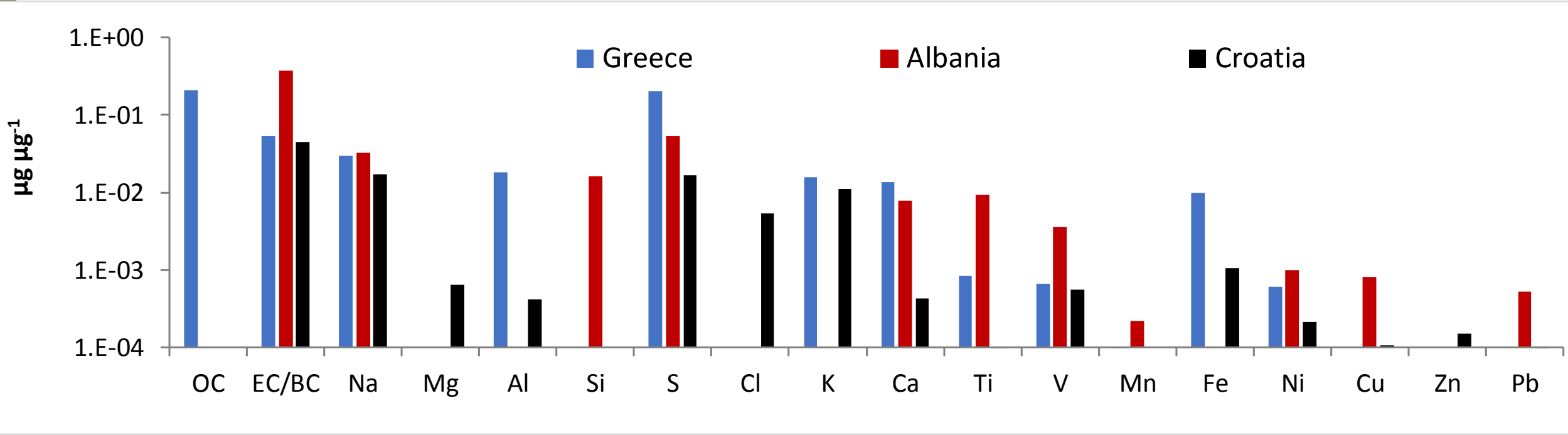
Traffic



- Mainly EC/BC and OC
- Sulphur only in Croatia
- Ca from the combustion of lubricating oil and soil (in road dust)
- NaCl in Zagreb due to salting of the streets during winter-time

Methods – Inter-city variability (Balkan region)

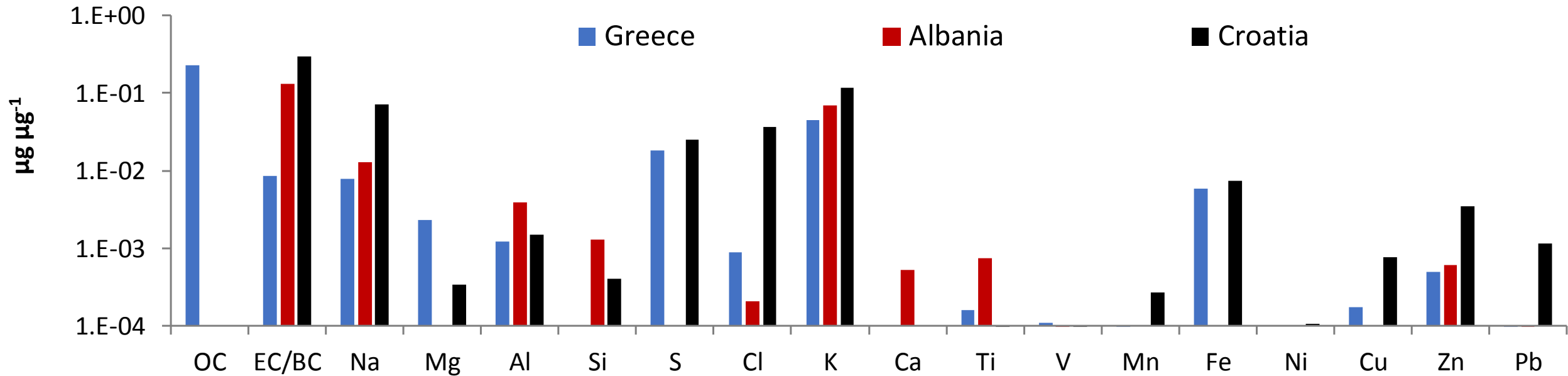
Heavy oil combustion



- Mainly EC/BC and OC + Sulphur
- Na in all cities
- V/Ni ratio varies (~ 1 in Athens, 3.6 in Tirana and 2.7 in Zagreb)

Methods – Inter-city variability (Balkan region)

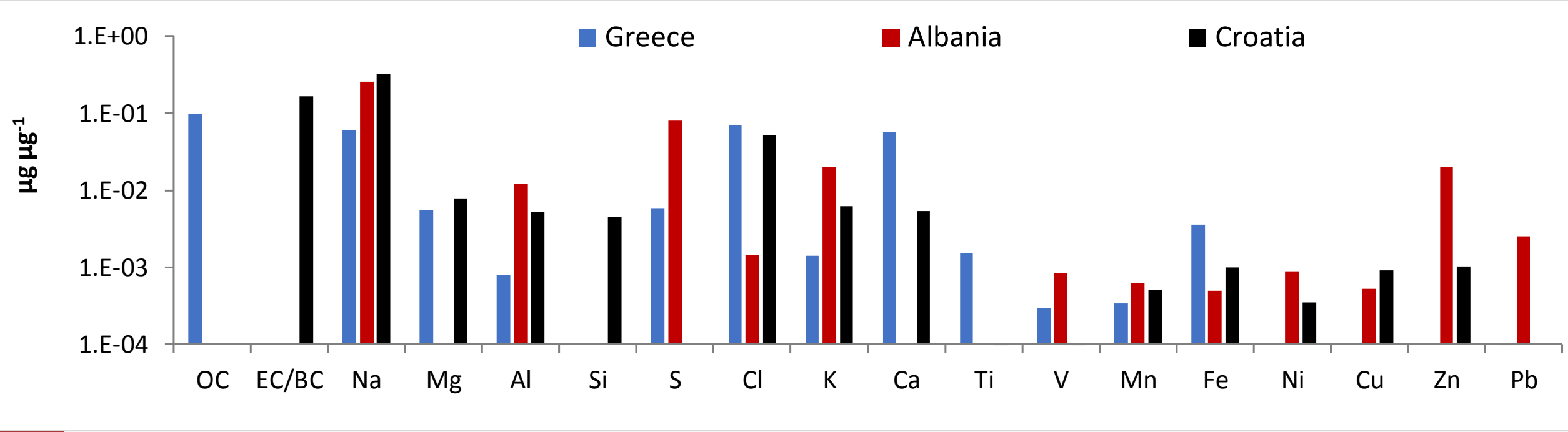
Biomass burning



- EC/BC and OC and K
- OC >> EC
- Na and Cl also present in much lower concentrations
- Zn and Pb indicate the burning of waste and/or treated wood

Methods – Inter-city variability (Balkan region)

Sea salt



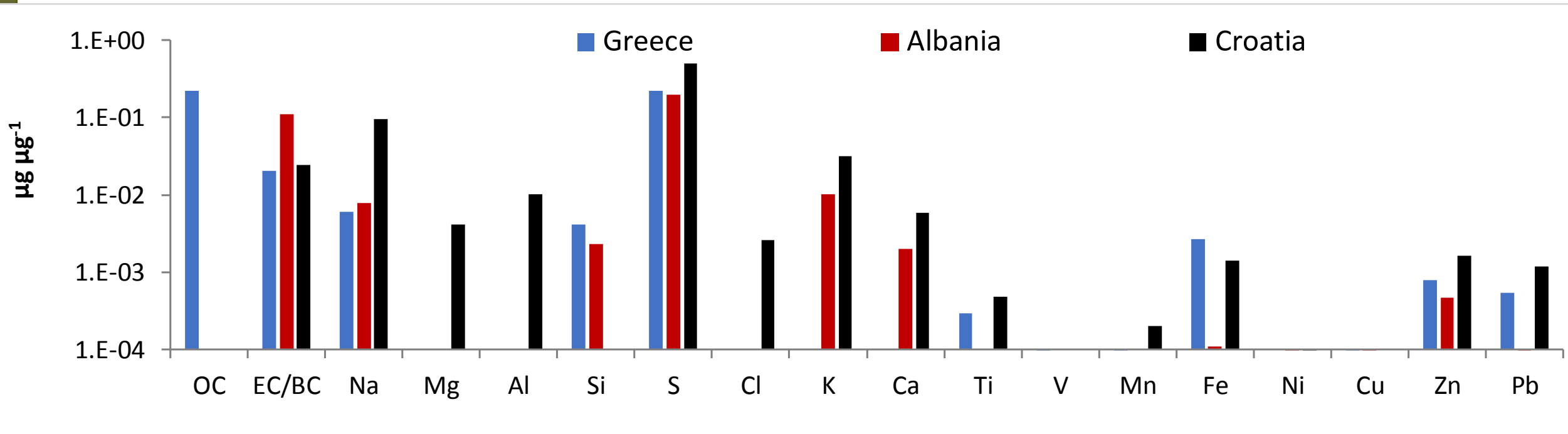
Cl/Na ratio:

- 1.16 in Athens
- 0.16 in Zagreb and 0.01 in Tirana (aged sea salt)

Methods – Inter-city variability (Balkan region)



Secondary aerosol

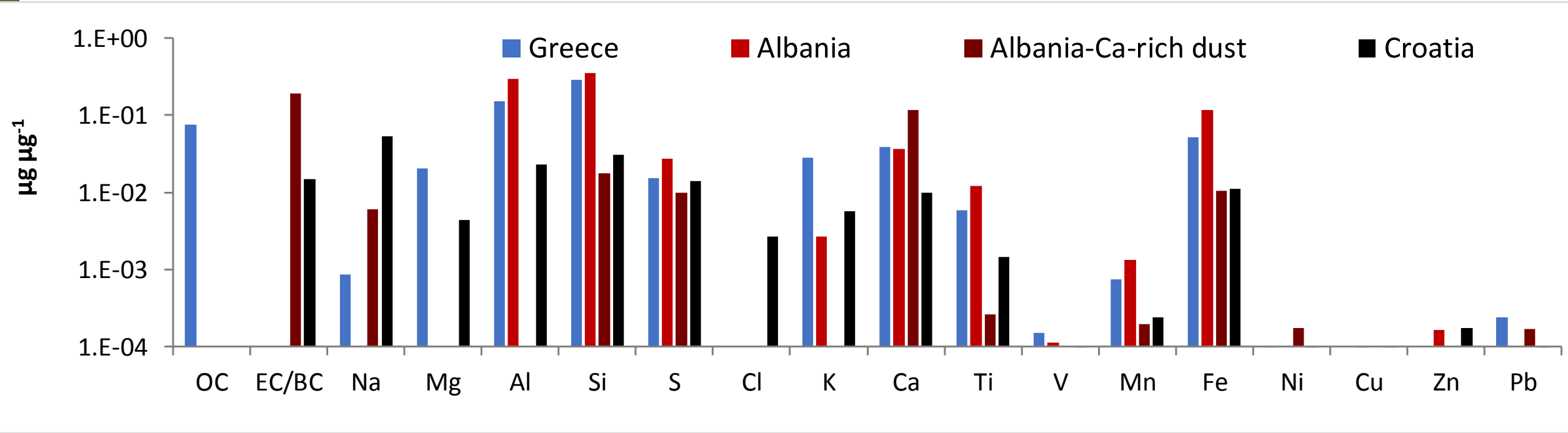


- Not so clear due to the absence of ion data
- With secondary organics in Athens



Methods – Inter-city variability (Balkan region)

Mineral dust



➤ Ca-rich dust source may be connected to construction activities and/or a cement industry located at a distance of around 15 km

Summary remarks

- ✔ While the profiles for the urban traffic and urban background sites in Athens were in general similar, site-specific PMF analysis may provide insight into the emission sources and transport / secondary formation mechanisms affecting PM levels at each site.
- ✔ On average, the relative contribution of the different sources was comparable at the two Athens sites, even though the absolute contributions were much higher at the ATH-TR site.
- ✔ During exceedance days, source contributions were very different between sites.

Summary remarks

- ✔ Sulphate accounted for a large fraction of $PM_{2.5}$, with very similar mass and relative contributions at all urban background sites ($3 - 4 \mu\text{g m}^{-3}$), pointing towards a regional source of secondary aerosol affecting the Balkan region.
- ✔ High contributions from biomass burning during the cold period, reflecting the impact wood burning for residential heating.
- ✔ Heavy oil combustion was related to shipping emissions at all sites.