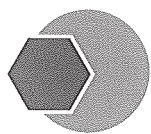Photo: Michael Bader

ICCE 2015
LEIPZIG

15th EuCheMS International Conference on Chemistry and the Environment

20 - 24 September 2015 • Leipzig, Germany

EuCheMS
European Chemical Sciences
Division of Chemistry and the Environment

Fachgruppe
**Umweltchemie &
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Tracing of aerosol sources in an urban environment using carbonaceous, major ions, Sr isotope, and mineralogical compositional data

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Understanding the chemical composition of atmospheric particulate matter (PM), particularly with a diameter less than 2.5 µm ($PM_{2.5}$), has became an emergent topic in atmospheric research due to its relation to climate change and serious health issues. In this study, a comprehensive assessment of the carbonaceous (organic carbon, water-soluble organic carbon, elemental carbon), major water-soluble inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, K^+, Na^+), $^{86}Sr/^{87}Sr$ isotope ratios, and mineralogical composition of $PM_{2.5}$ samples has been performed for a one-year period in an urban environment at the Western European Coast (Aveiro, Portugal). The concentration of each component was found to be highly dependent on the seasonal events, with the carbonaceous component being the major constituent of the $PM_{2.5}$ in almost all seasons. The concentration of SO_4^{2-} is higher in samples collected during warm seasons than in those of colder seasons, which is indicative of secondary formation (mediated by sunlight) in the atmosphere [F. Zhang et al., 2014]. On the other hand, the concentration of the more volatile NO^{3-} ion is highest for samples collected in colder seasons, which can be explained by the combined effects of lower air temperature and an increase of biomass burning and vehicles emissions during these seasons [F. Zhang et al., 2014]. The equivalent molar ratio of cations to anions was also computed, indicating that the $PM_{2.5}$ is more acidic during high air temperature periods probably due to the highest accumulation of acidic components (e.g., SO_4^{2-}) during this period [J. Zhang et al., 2014].

For the $^{86}Sr/^{87}Sr$ isotope ratios, it was possible to distinguish the labile (acid-leached) from the natural (remaining residue) Sr components (Fig.1). The highest $^{86}Sr/^{87}Sr$ ratios were observed for the residues embedded in the collection medium, being this indicative of a natural crustal dust source. The $^{86}Sr/^{87}Sr$ isotope ratios verified for the leachates are of the same order of magnitude of the reference value for seawater, thus suggesting that the urban $PM_{2.5}$ samples have also a predominant marine influence. These findings are also in agreement with the mineralogical composition data, which shows the presence of gypsum with a clear marine origin on almost all samples, besides feldspar with an anthropogenic origin, and aluminosilicates from soil dust.
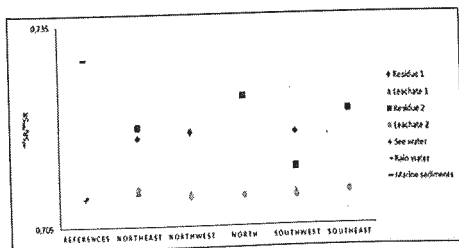

Fig. 1: $^{87}Sr/^{86}Sr$ isotope ratios in residues and leachates of $PM_{2.5}$ samples collected in the city of Aveiro (Portugal) during one-year period and under different air mass trajectories.

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Zhang, F., Cheng, H., Wang, Z., Lv, X., Zhu, Z., Zhang, G., Wang, X. *Atmos. Environ.*. **2014**, 86, 193-202

Zhang, J., Cheng, J., Yang, L., Sui, X., Lan, Y., Zheng, L., Wen, L., Xu, C., Wang, W. *Atmos. Envirot.* **2014**, 99, 641-649.

Long-term size-segregated particle (PM10, PM2.5, PM1) characterization study in the rural background of Germany – influence of air mass inflow and season

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Long-term studies allow quantifying the influence of decreasing emissions to the concentrations. The particle mass concentration is also influenced by particle formation from precursors and long-range transport. The rural-background site Melpitz (12°56' E, 51°32' N, 86 m asl.) is located in Germany in the Saxon lowlands near Torgau in the glacial valley of the river Elbe (Spindler et al. 2013). The Melpitz station is integrated in ACTRIS and EMEP and representative for a large area in central Europe.

High-Volume (HV) quartz filter samples for particles < 10 μm aerodynamic-diameter (PM_{10}) were collected daily (since November 1992). Particles $PM_{2.5}$ and PM_1 were collected daily respective every six days (since January 2003). The determination of the particle mass was done gravimetrically. Main water-soluble ions (NO_3^-, SO_4^{2-}, Cl^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were analyzed by ion chromatography. The determination of OC and EC (available since 2003) performed by a two-step thermographic method (according to VDI 2465 part 2). PAH and n-alkanes were determined by CPP-GC-MS (Curie point 510°C) for PM_{10} samples in 2012.

Daily samples were evaluated at first as yearly means and quarterly means (per year), at second for spatial and seasonal discrimination days were sorted for air mass transport from a western sector (W, 210-320°, mostly maritime influenced) and a broad eastern sector (E, 35-140°, continentally influenced) using backward trajectories (96 h) Days with a strong change in transport direction (often more local influenced by inversion) were excluded here. A seasonal discrimination was done for winter (Wi, November-April) and for summer (Su, May-October). The result are the four categories WiW, WiE, SuW and SuE in which 68% of the whole time (November 1992 until December 2014) can be sorted (53.3% for W, 15.1% for E).

15 EuCheMS International Conference on Chemistry and the Environment

Tracing of aerosol sources in an urban environment using carbonaceous, major ions, Sr isotope, and mineralogical compositional data

Andreia Paula[1], Sónia Lopes[1], Sara Ribeiro[2], José Francisco Santos[2], Carla Patinha[2], Eduardo Anselmo[2], Rosário Teixeira[3], Regina Duarte[1,3] Armando Duarte[1]

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Introduction

Understanding the chemical composition of atmospheric particulate matter (PM), particularly with a diameter less than 2.5 μm ($PM_{2.5}$), has became an mergent topic in atmospheric research due to its relation to climate change and serious health issues.
This study aims at performing a comprehensive assessment of:

➢ carbonaceous species (organic carbon, water-soluble organic carbon, elemental carbon) and major water-soluble inorganic ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, K^+, Na^+) in $PM_{2.5}$ samples collected over 1-year period in an urban environment at the Western European Coast (Aveiro, Portugal);

➢ $^{87}Sr/^{86}Sr$ isotope ratios and mineralogical composition of the urban $PM_{2.5}$ samples.

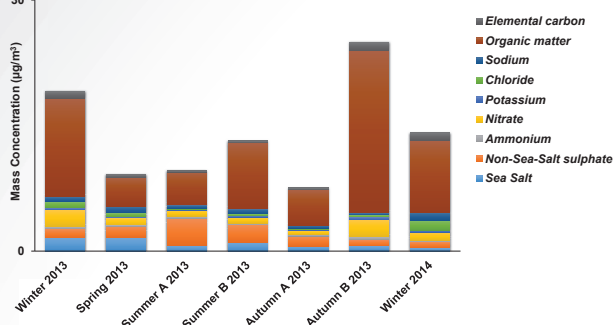## Chemical Composition of $PM_{2.5}$

Fig. 1 - Chemical mass closure for urban $PM_{2.5}$ samples.

• During the course of the measuring period, seasonal $PM_{2.5}$ mass concentrations were extremely variable.
• The carbonaceous component is the major constituent of the $PM_{2.5}$ samples.
• The average ambient concentrations of SO_4^{2-} and NO_3^- follow an opposite trend between warm and cold seasons, the reason for which is depicted in **Fig. 2**.
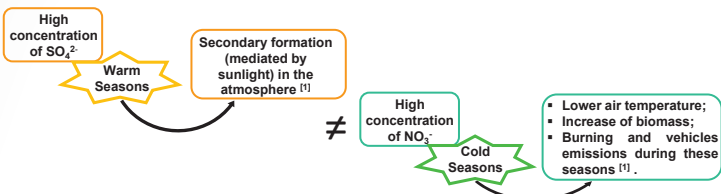

Fig. 2 - Justification for the different SO_4^{2-} and NO_3^- concentrations in warm and cold seasons.

References

[1] Zhang, F., Cheng, H., Wang, Z., Lv, X., Zhu, Z., Zhang, G., Wang, X. Atmos. Environ.. 2014, 86, 193-202

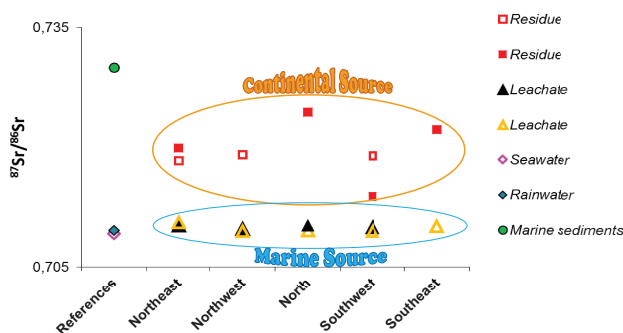## $^{87}Sr/^{86}Sr$ isotopic signature of $PM_{2.5}$

Fig. 3 - $^{87}Sr/^{86}Sr$ isotope ratios in reference matrices (rainwater, seawater, and marine sediments), and in residues and leachates fractions of urban $PM_{2.5}$ samples collected under different air mass trajectories.

The highest $^{87}Sr/^{86}Sr$ ratios were found in the $PM_{2.5}$ residues, being this indicative of a natural crustal dust source. The $^{87}Sr/^{86}Sr$ ratios of the $PM_{2.5}$ leachates are of the same order of magnitude of the reference value for seawater, thus suggesting that the urban $PM_{2.5}$ samples have also a predominant marine influence.

Mineralogical composition of $PM_{2.5}$

Mineral	Compound name	Chemical Formula	Potential source
Illite	Potassium Calcium Magnesium Aluminum Iron Aluminum Silicate Hydroxide	$(K_{0.74}Ca_{0.03})(Al_{1.92}Mg_{0.09}Fe_{0.01})((Si_{3.22}Al_{0.78})O_{10}(OH)_2)$	Continental crust
	Calcium Sodium Aluminum Silicate Hydroxide Hydrate	$(Ca,Na)_{0.3}Al_2(Si,Al)_4 O_{10}(OH)_2 \cdot xH_2O$	
	Potassium Aluminum Silicate Hydroxide Hydrate	$(K,H_3O)Al_2(Si_3Al)O_{10}(OH)_2 \cdot xH_2O$	
Muscovite	Potassium Aluminum Silicate Hydroxide	$KAl_2Si_3AlO_{10}(OH)_2$	
Kaolinite	Aluminum Silicate Hydroxide	$Al_2Si_2O_5(OH)_4$	
Hydrotalcite	Magnesium Aluminum Carbonate Hydroxide Hydrate	$Mg_{0.67}Al_{0.33}(CO_3)_{0.165}(OH)_2(H_2O)_{0.48}$	
Chlorite	Magnesium Aluminum Silicon Oxide Hydroxide	$Mg_{2.45}Al_{1.1}Si_{1.45}O_5(OH)_4$	
Gypsum	Calcium Sulfate Hydrate	$Ca(SO_4)(H_2O)_2$	Marine derived
Halite	Sodium Chloride	$NaCl$	
	Sodium Nitrate	$NaNO_3$	Anthropogenic

Table 1 - Mineralogical composition obtained by X-ray diffraction analysis of urban $PM_{2.5}$ samples.

A similar profile of mineral phases was observed for all $PM_{2.5}$ samples: 1) aluminosilicates are likely related to the resuspension of soil dust, 2) gypsum is typical of marine aerosols, and 3) feldspar has an anthropogenic origin.

Conclusions

• The major constituent of urban $PM_{2.5}$ is organic matter, followed by SO_4^{2-} (secondary origin) and NO_3^- (anthropogenic origin) ions.
• The difference in the $^{87}Sr/^{86}Sr$ isotopic composition of the leachates (i.e. labile, soluble marine Sr fraction) and residues (i.e. natural crustal Sr fraction) suggests that urban $PM_{2.5}$ has both marine and crustal dust influence. These findings are in agreement with the mineralogical composition data..