

# Ionic composition of PM<sub>10</sub> and PM<sub>2.5</sub> in the area of Thessaloniki, Northern Greece - Estimation of secondary inorganic aerosols and sea spray contribution

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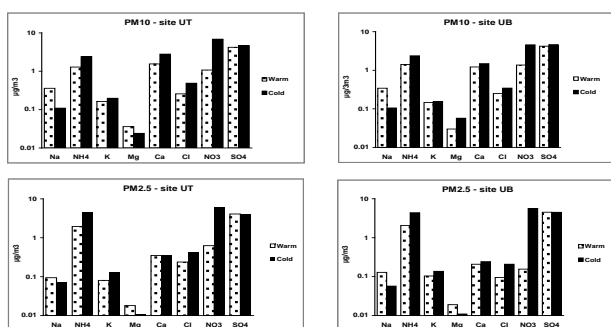
Keywords: ionic constituents; PM10/PM2.5; secondary ionic aerosol; sea spray

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Ionic constituents represent a significant component of atmospheric particles (Putaud et al., 2010). Thessaloniki, Greece (40°62'E, 22°95'N) is a densely populated city suffering from high concentrations of airborne particulate matter. Previous studies at urban sites of the city indicated that ionic species were major components of PM<sub>10</sub> (Voutsas et al., 2002; Terzi et al., 2010). However, there, there are no data available for PM<sub>2.5</sub> fraction.

The aim of the present study was to investigate the ionic composition of both PM<sub>10</sub> and PM<sub>2.5</sub> in the Major Area of Thessaloniki, Northern Greece. For this purpose, PM<sub>10</sub> and PM<sub>2.5</sub> fractions were collected from an urban-traffic (UT) and an urban-background (UB) site. At both sites, PM<sub>10</sub> and PM<sub>2.5</sub> samples were concurrently collected during the warm and the cold months of the year (July-Sept 2011 and Febr-April 2012). Sampling was carried out according to EN12341 and EN14907 using Low Volume Samplers operating at constant flow rate 2.3 m<sup>3</sup>/h. PM<sub>10</sub> and PM<sub>2.5</sub> fractions were collected on  $\Phi$  47 mm Teflon filters (Zefluor<sup>TM</sup> membranes, Pall 2 $\mu$ m). Each sampling had a 24-h duration starting at 00:00. Ionic chromatography has been employed for the determination of water soluble ions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>).

The average concentrations of ions associated with PM<sub>10</sub> and PM<sub>2.5</sub> are shown in Fig. 1.



**Figure 1.** Average concentrations of ions associated with PM10 and PM2.5 at two sampling sites

The PM<sub>10</sub> fractions of ions were almost similar at the two sampling sites. The PM<sub>2.5</sub> fractions of Ca<sup>2+</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> (in summer) were higher at the UT site. Mg<sup>2+</sup> and Ca<sup>2+</sup> were mainly associated with the coarse fraction whereas NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> with the fine fraction. Higher concentrations of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> were observed during winter. This trend is probably due to higher NO<sub>x</sub> emissions during winter as well as to loss of nitrate or chloride ammonium during summertime. Moreover, K<sup>+</sup>

exhibited higher concentrations during winter probably due to emissions from the increasing residential wood burning in the area.

Average contributions of ionic species to total PM<sub>10</sub> mass were 25% at UT and 32% at UB. The corresponding contributions to total PM<sub>2.5</sub> mass were 30% and 43% at UT and UB, respectively. Sulfate was the predominant PM<sub>10</sub> ionic constituent, followed by NO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>. The main ion in PM<sub>2.5</sub> was also SO<sub>4</sub><sup>2-</sup>, followed by NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup>.

Secondary inorganic aerosol (SIA) calculated as the sum of non-sea salt of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> exhibited similar concentrations (~10%  $\mu$ g/m<sup>3</sup>) at both sites. This may indicate common origin and removal processes, suggesting that SIA dynamics are more linked to regional processes than to local sources. The average contributions of SIA to PM<sub>2.5</sub> mass were 35% at UT vs. 45 % at UB. The corresponding contribution to PM10 mass was 20% at UT vs. 29% at UB. At both sites the concentration of SIA was almost two folds higher in winter. Similar SIA concentrations and temporal variation was also reported by other investigators (EEA, 2012; Squizzato et al., 2012). The sulfur oxidation ratio (SOR) showed that sulfate is photochemically oxidized in the atmosphere from its precursor SO<sub>2</sub>. The nitrogen oxidation ratio exhibited higher values at the UB in cold period suggesting favorable conditions for gas conversion processes.

The marine contribution was calculated as the sum of Na<sup>+</sup> concentration and sea salt fractions of Cl<sup>-</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and SO<sub>4</sub><sup>2-</sup>. The sea spray contribution to particulate matter on a mass basis was low (<2%) similar to the reported values from other Mediterranean coastal areas (Querol et al., 2008; Terzi et al., 2010; Eleftheriadis et al., 2011). The low PM<sub>2.5</sub>/PM<sub>10</sub> ratio of sea spray showed the predominant coarse grain size of marine constituents.

## References

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## Acknowledgements

This work was supported by the European Community (LIFE + Environment Policy and Governance).