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## Chemical characterization of the inorganic fraction of aerosols and mechanisms of the neutralization of atmospheric acidity in Athens, Greece

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**Abstract.** The  $PM_{10}$  mass concentration levels and inorganic chemical composition were determined on 12-h resolution sampling during August 2003 and March 2004, in the centre of Athens, Greece. The August 2003 campaign mean  $PM_{10}$  mass concentration, obtained by Beta Attenuation at 5 m above ground in Athinas Street, was  $56 \mu\text{g m}^{-3}$  while the corresponding value for March 2004 was  $92 \mu\text{g m}^{-3}$ . In both campaigns the E.U. imposed daily limit of  $50 \mu\text{g m}^{-3}$  was exceeded on several days. During the March campaign, in Athinas Street, additionally obtained DSFU- $PM_{10}$  ( $PM_{10-2.5}+PM_{2.5}$ ) gravimetric mass concentrations (mean:  $121 \mu\text{g m}^{-3}$ ) in the "breathing zone", at 1.5 m above ground were significantly higher compared to the respective mean  $PM_{10}$  mass concentrations obtained by the same method at 25 m above ground, in a second site (AEDA; mean:  $86 \mu\text{g m}^{-3}$ ) also in the centre of the city. The above findings suggest that, for a realistic estimation of the exposure of citizens to particulate matter,  $PM_{10}$  sampling in the "breathing zone" (1.5–3 m above ground) is necessary. Such data are presented for the first time for the centre of Athens. In both campaigns, calcium was found to be the predominant component of the coarse fraction while crust-related aluminosilicates and iron were the other major components. The above elements constitute the most important components of the fine fraction, together with the predominant sulphur. All toxic metals were found in concentrations below the established air quality limits, and most of them in lower concentrations compared to older studies. Lead in particular, appeared mostly in the fine fraction and in very low concentrations compared to studies dating more than a decade back. The predominant ions of the coarse fraction have been found to be  $Ca^{2+}$ ,  $NO_3^-$ ,  $Na^+$  and  $Cl^-$ , while  $SO_4^{2-}$ ,  $Ca^{2+}$  and  $NH_4^+$  were the major ionic components of the fine fraction. In the fine particles, a low molar ratio of  $NH_4^+/SO_4^{2-}$  indicated an ammonium-poor ambient air, and together with inter-ionic correlations suggested that atmospheric ammonia is the major neutralizing agent of sulfate, while being insufficient to neutralize it to full extent. The formation of  $NH_4NO_3$  is therefore not favored and additional contribution to the neutralization of acidity has been shown to be provided by  $Ca^{2+}$  and  $Mg^{2+}$ . In the coarse particle fraction, the predominantly abundant  $Ca^{2+}$  has been found to correlate well with  $NO_3^-$  and  $SO_4^{2-}$ , indicating its role as important neutralizing agent in this particle size range. The proximity of the location under study to the sea explains the important concentrations

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of salts with marine origin like NaCl and MgCl<sub>2</sub> that were found in the coarse fraction, while chloride depletion in the gaseous phase was found to be limited to the fine particulate fraction. Total analyzed inorganic mass (elemental+ionic) was found to be ranging between approximately 25–33% of the total coarse particle mass and 35–42% of the total fine particle mass.

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