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Level of uncertainty on $PM_{2.5}$ mass concentrations introduced by inorganic sampling artifacts

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Inorganic aerosol compounds such as reactive acidic (SO_2, HNO_2 and HNO_3) and basic gases (NH_3) contribute to positive and negative artefacts significantly affecting $PM_{2.5}$ mass concentrations. The evaporative loss of the semi-volatile ammonium nitrate from the aerosol phase (negative artefact) or adsorption of nitric acid and sulphur dioxide gases (positive artefact) can occur during or after sampling. This work presents results obtained during a campaign for the assessment of sampling artefacts on the gravimetrically determined $PM_{2.5}$ mass concentration during winter.

The field campaign was carried out at the "Demokritos" urban background site in the periphery of the Athens Metropolitan area, Greece. An annular denuder system (ADS) and a filter pack (FP) were deployed in parallel for the evaluation of mass concentrations. A cyclone inlet preceded the annular denuder/filter pack system in order to remove coarse particles, while gases and fine particles are quantitatively transferred into the annular denuder and filter pack components. SO_2, HNO_2 and HNO_3 vapours are trapped by a Na_2CO_3 – coated annular denuder. A second Na_2CO_3 – coated annular denuder is used to retain excess nitrate and nitrite. The third denuder was coated with citric acid for trapping NH_3. The filter pack after the denuders contained a Teflon filter where the particulate matter was collected, a KOH coated cellulose filter where the gases evaporating due to the disequilibrium between gas and particulate phase were collected and a citric acid coated cellulose filter where the evaporating NH_3 was collected. The annular denuders and the triple filter pack together comprised the annular denuder sampling system (ADS). An identical triple filter pack equipped with a cyclone inlet was also sampling in parallel. Samples were collected at 24h intervals, where the sampling flow rate was set at 10 lt/min and values of ambient temperature, R.H. and pressure were monitored. After sampling, the aerosol mass concentration was determined gravimetrically on the Teflon filters from the ADS and FP systems. Filters were conditioned in a 20 0C and 50 % R.H. weighing room for 24h before and after sampling. Weighing was performed on a 10^{-5} gr resolution Sartorius Balance.

A control experiment was performed comparing the mass concentrations on Teflon filters obtained by an un-denuded ADS system and the filter pack, when sampling in parallel. Mass concentrations displayed an excellent correlation (R^2 =0.99) and a ratio of 0.8 for the FP concentration over the ADS concentration. Results of the equivalent mass concentrations measured by the ADS and FP during the winter period (February – March – April) are shown in Fig 1.

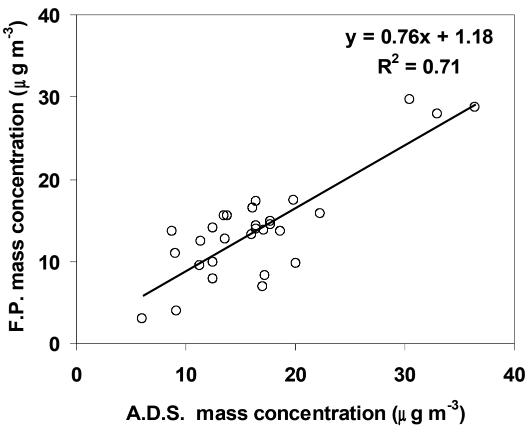

Figure 1. Relationship between denuder and filter pack system concentration in PM2.5 samples

Preliminary conclusions from the current results indicate that increased scatter in the data is apparent when the ADS and FP ratios are compared to the control experiment data. This is due to the variability in positive/negative artifact due to the disequilibrium between gas/particle phases at variable conditions. Below the effect of increasing RH is demonstrated to lead to FP/ADS ratio closer to unity as the particulate phase is favoured.

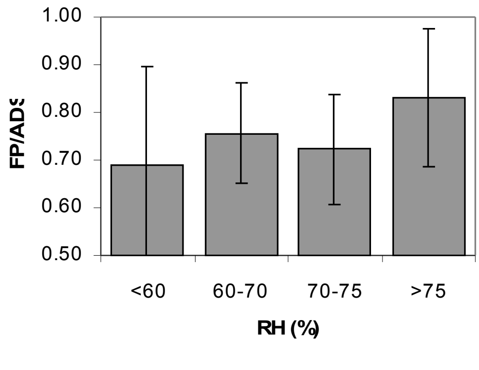

Figure 2.FP/ADS ratios with respect to ambient RH