

Size-resolved aerosol composition at an urban and a rural site in the Po Valley in summertime: implications for secondary aerosol formation

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14 Figure S1 – Size segregated time series of ammonium (NH₄⁺) in BO and SPC.





2 Figure S2 – Size segregated time series of calcium (Ca²⁺) in BO and SPC.



5 Figure S3 – Size segregated time series of sodium (Na⁺) in BO and SPC.









5 Figure S5 – Size segregated time series of oxalate in BO and SPC.



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2 Figure S6 – Size segregated time series of methansulfonate (MSA) in BO and SPC.

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5 SI-1. Comparison of Berner impactor concentrations with co-located measurements

A problem which can arise when using low-pressure impactors for the collection of aerosols is represented
by sampling artifacts which can affect aerosol collection (e.g., evaporative losses of semivolatile
compounds) and result in a systematic error in the reported mass-diameter distribution (Markowski, 1984) as
well as in an underestimation of the total mass concentration.

10 In order to evaluate the presence of negative artifacts in the Berner impactor sampling, the size-integrated 11 ($PM_{1.2}$, sum of the first three stages) impactor concentrations for sulfate, nitrate and ammonium were 12 compared with those obtained by another off-line system, a High Volume Digitel PM_1 sampler, and by 13 integrated HR-ToF-AMS (PM<1) measurements. Figures S7 and S8 reports the results for the site of SPC, 14 for which both High Volume and AMS datasets were available. In general there was a reasonable good 15 agreement between the impactor measurements and the co-located observations, with the exception of sulfate 16 which was slightly lower for the impactors in correspondence with the diurnal samples.





Fig. S7 - Comparison between PM₁ high volume sampling filters and Berner Impactor concentrations

3 integrated over the first three stages $(PM_{1,2})$, for sulfate, nitrate and ammonium during the whole 4 observation period.



Fig. S8 - Comparison between Berner Impactor concentrations integrated over the first three stages (PM_{1.2}) and AMS (PM1) concentrations averaged over the impactor sampling times, for sulfate, nitrate

- 3 and ammonium during the whole observation period.
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5 The evaluation of possible negative artifacts affecting the Berner Impactor concentrations was carried out also in respect to size distributions of the main inorganic chemical components by comparing the size-6 7 segregated concentrations of the Berner Impactor with the AMS PToF data. To the aim of comparison with 8 impactor size-distributions, the dry diameters measured by AMS were converted into ambient (humid) 9 particle diameters based on published hygroscopicity parameter κ for ammonium nitrate, ammonium sulfate 10 and organic matter (OM) (Petters and Kreidenweis, 2007, and references therein) and assuming an internal mixing. For this purpose AMS PToF data were first averaged over 3 hours in order to have time intervals 11 characterized by less variable RH values than over 12 hours. Once transformed the original diameters into 12 wet diameters according to the average RH, discrete distributions obtained by HR-PToF-AMS were fitted by 13 14 a lognormal curve to obtain a continuous size distribution, which finally allowed to average again 15 dM/dlogD_{pw} data (where D_{pw} stands for the wet diameter of particles) over the 12 hours of Berner Impactor 16 sampling.

17 The resulting size distributions for two samples – one day-time and one night-time (16/6 day and night) – 18 selected during the late June stagnation period, are reported (Fig. S9). The results indicate only a very 19 moderate loss of ammonium nitrate in the very fine stages of the impactor ($PM_{0.4}$), while for particles in the 20 range $0.4 - 1.2 \mu m$, the AMS concentrations are smaller than those determined by the impactor, but this can 21 be put in relation to the loss of collection efficiency in the AMS for particle diameters larger than 0.7 μm , 22 hence to an upper size cutting effect. In conclusion, there is no strong evidence of ammonium nitrate 23 evaporation in the small impactor stages.



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Fig. S9 – Comparison between Berner Impactor (black line histogram) and PToF-AMS size distribution. AMS size distributions have been fitted by a lognormal curve both on the original data (red dotted line) and after correction of dry particle diameters into humid diameters (blue dotted line). D_{pw} stands for humid diameter (diameter of wet particles). The blue dashed histogram represents $dNO_3^{-}/dlogD_{pw}$ data averaged over the first three size bins of the Berner Impactor (0.05 – 0.14 µm; 0.14 – 0.42 µm; 0.42 – 1.2 µm).

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2 References

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