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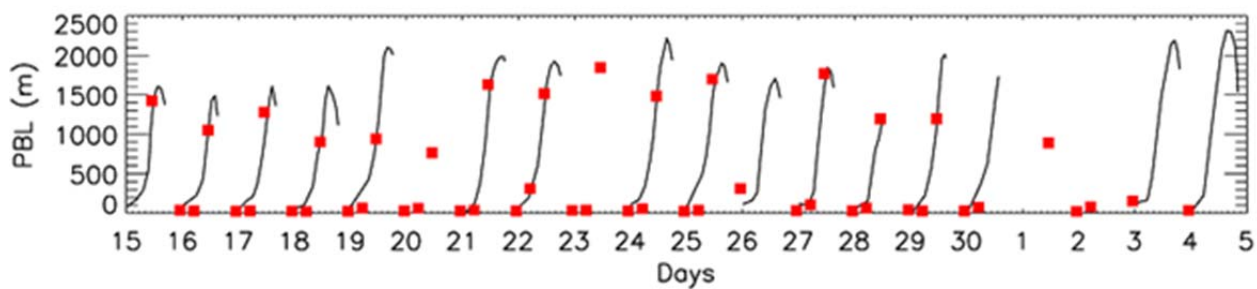
*Supplement of*

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

**Silvia Sandrini et al.**

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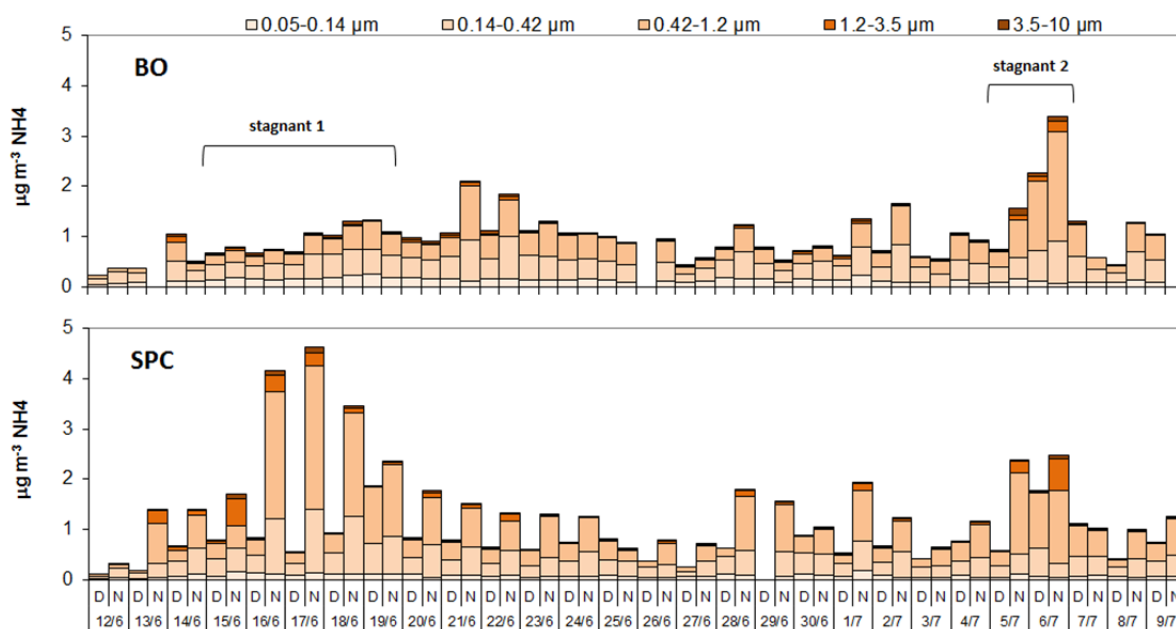


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2 **Figure S1 – PBL height from Lidar measurements (black) and from radiosoundings (red) in SPC from**  
 3 **the 15<sup>th</sup> of June to the 5<sup>th</sup> of July 2012.**

4

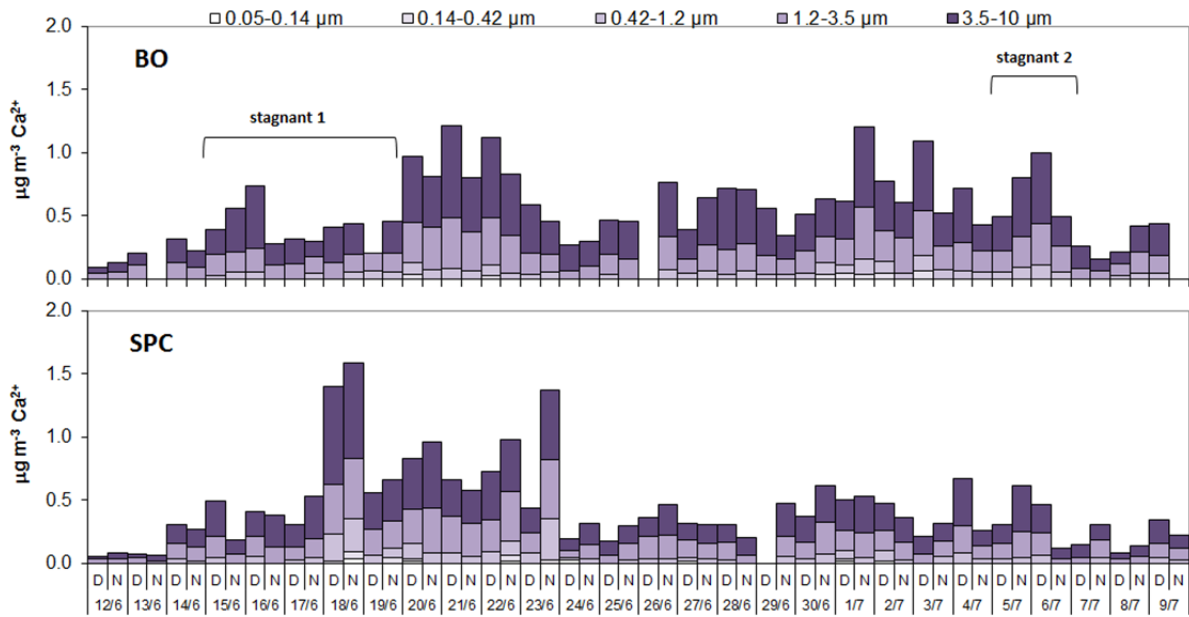
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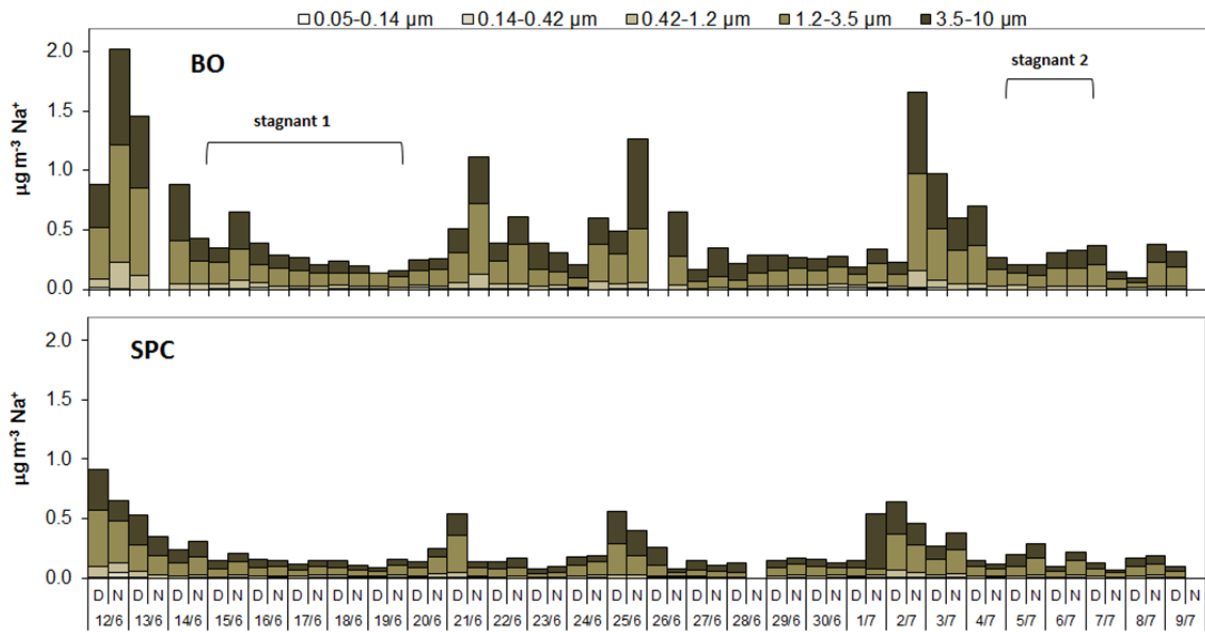
7 **Figure S2 – Size segregated time series of ammonium ( $\text{NH}_4^+$ ) in BO and SPC.**

8



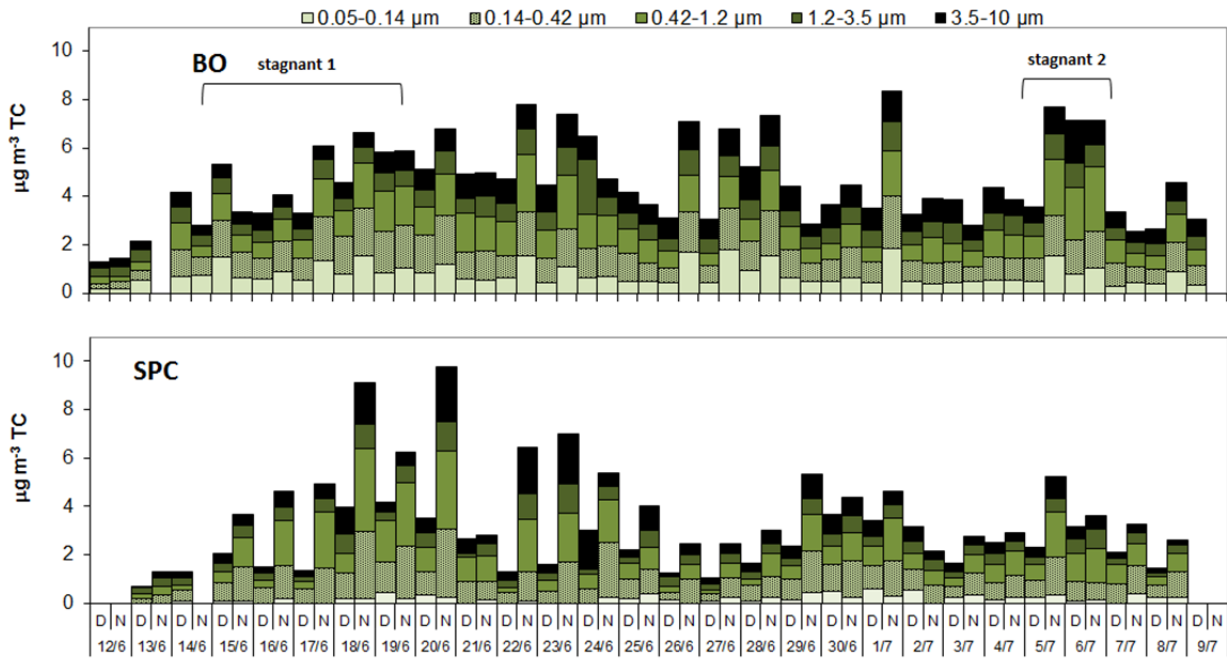
1  
 2 **Figure S3 – Size segregated time series of calcium ( $\text{Ca}^{2+}$ ) in BO and SPC.**

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4  
 5 **Figure S4 – Size segregated time series of sodium ( $\text{Na}^+$ ) in BO and SPC.**

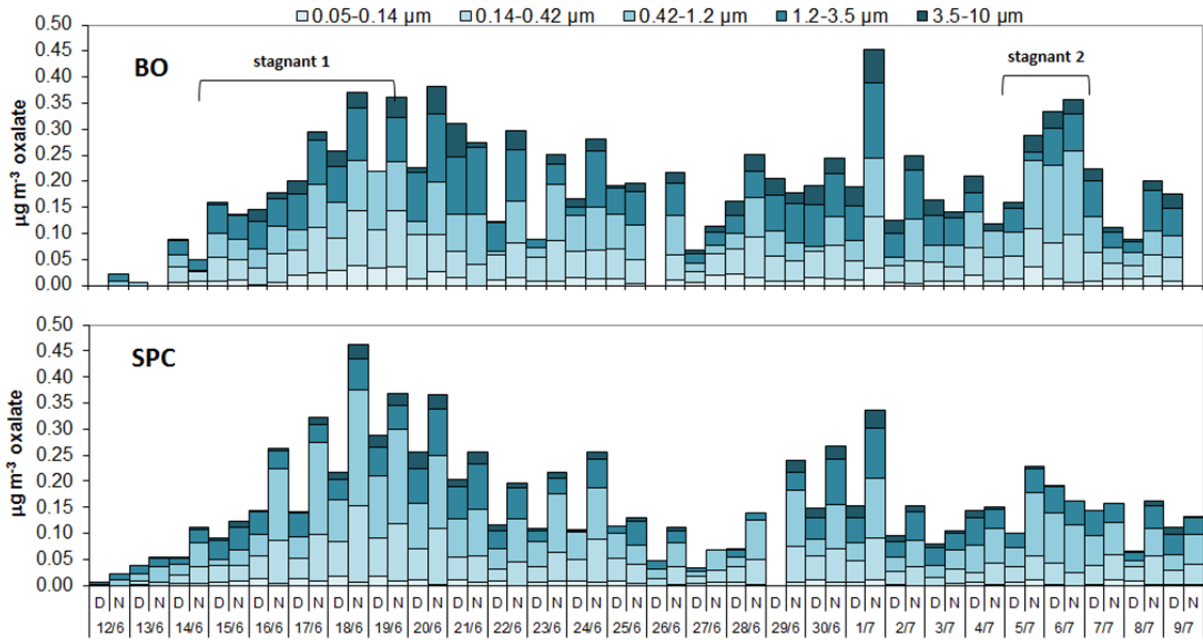
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2 **Figure S5 – Size segregated time series of Total Carbon (TC) in BO and SPC.**

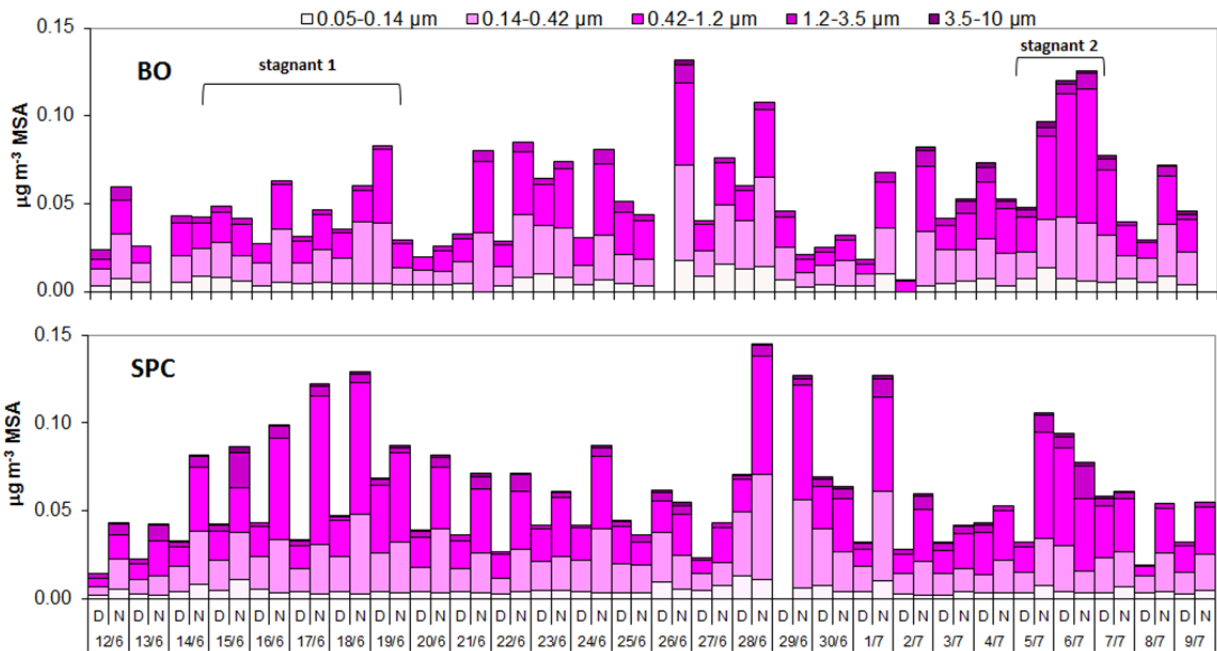
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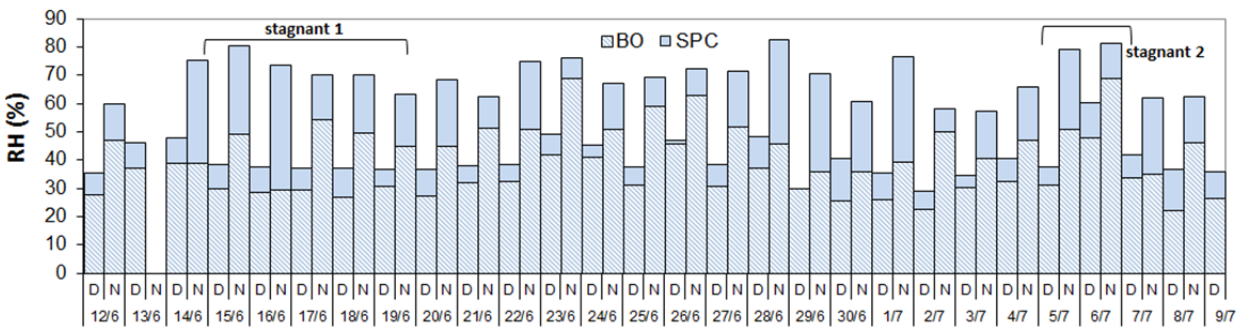
5 **Figure S6 – Size segregated time series of oxalate in BO and SPC.**

6



1

2 **Figure S7 – Size segregated time series of methansulfonate (MSA) in BO and SPC.**



3

4 **Figure S8 – Size segregated time series of Relative Humidity (RH) in BO and SPC, averaged over the**  
 5 **sampling periods of the Berner Impactor.**

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8

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

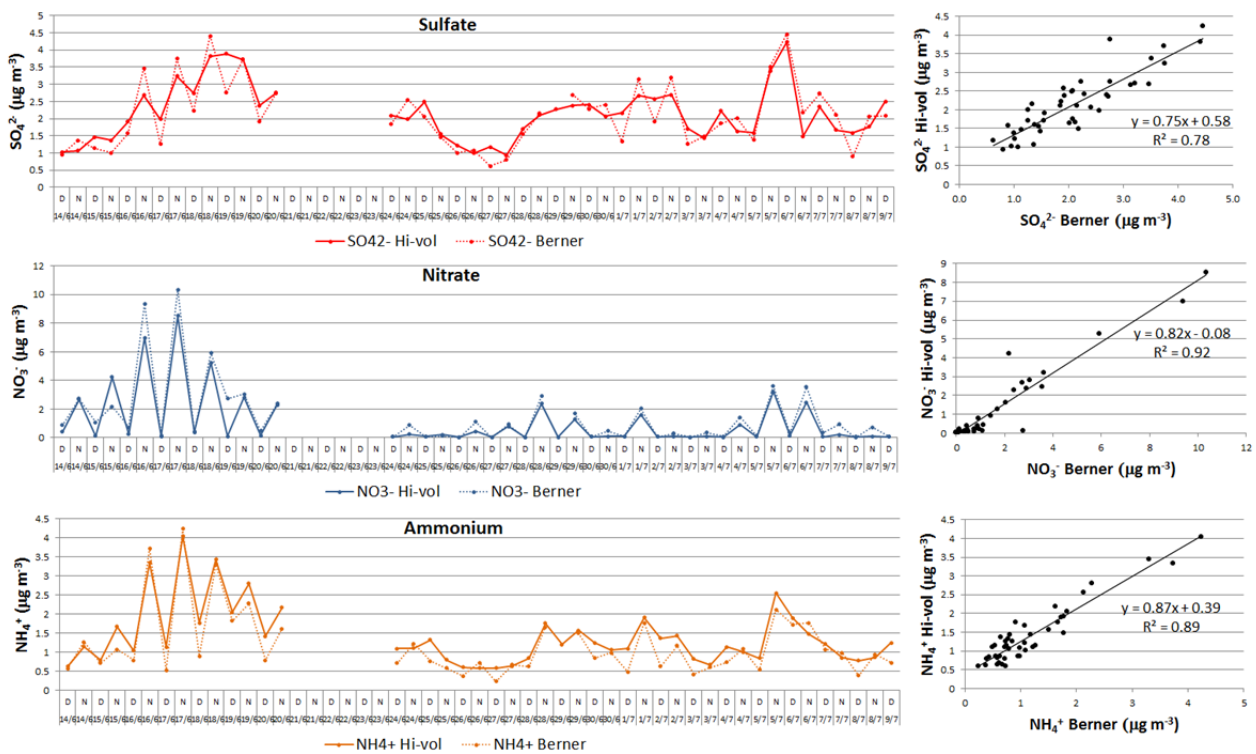
10 A problem which can arise when using low-pressure impactors for the collection of aerosols is represented  
 11 by sampling artifacts which can affect aerosol collection (e.g., evaporative losses of semivolatile  
 12 compounds) and result in a systematic error in the reported mass-diameter distribution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

14 In order to evaluate the presence of negative artifacts in the Berner impactor sampling, the size-integrated  
 15 (PM<sub>1.2</sub>, sum of the first three stages) impactor concentrations for sulfate, nitrate and ammonium were  
 16 compared with those obtained by another off-line system, a High Volume Digital PM<sub>1</sub> sampler, and by  
 17 integrated HR-ToF-AMS (PM<1) measurements. Figures S9 and S10 report the results for the site of SPC,

1 for which both High Volume and AMS datasets were available. In general there was a reasonable good  
 2 agreement between the impactor measurements and the co-located observations, with the exception of  
 3 sulfate which was slightly lower for the impactors in correspondence with the diurnal samples.

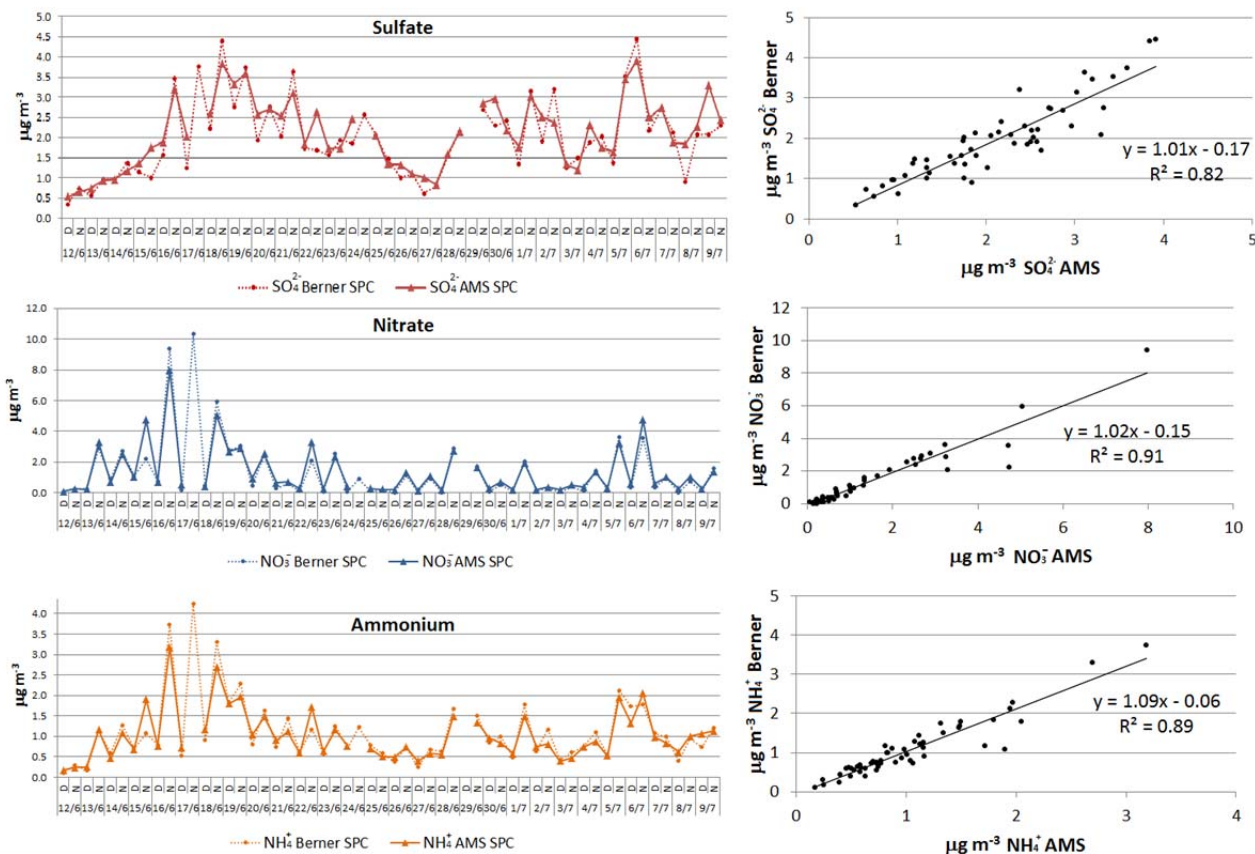
4 To quantify the particle losses due to bouncing we compared sulfate concentrations, which is not volatile,  
 5 for diurnal samples. Bouncing, in fact, is more effective at low relative humidity. The simple linear  
 6 regression of Berner Impactor concentrations versus the two co-located instruments, when forced to the  
 7 origin, highlights a 15% loss with respect to both High Volume ( $R^2 = 0.73$ ) and AMS ( $R^2 = 0.75$ ), which could  
 8 be attributed to bouncing. More precisely, since High Volume quartz fibre filters can also absorb  $SO_2$ , this  
 9 15% would represent the extent of negative artifacts on impactors due to bouncing, assuming that no  
 10 positive artifacts from  $SO_2$  absorption occurred on the HiVol.

11



12

13 **Fig. S9 - Comparison between  $PM_1$  high volume sampling filters and Berner Impactor concentrations**  
 14 **integrated over the first three stages ( $PM_{1.2}$ ), for sulfate, nitrate and ammonium during the whole**  
 15 **observation period.**



1

2 **Fig. S10 - Comparison between Berner Impactor concentrations integrated over the first three stages**  
 3 **(PM<sub>1.2</sub>) and AMS (PM<sub>1</sub>) concentrations averaged over the impactor sampling times, for sulfate, nitrate**  
 4 **and ammonium during the whole observation period.**

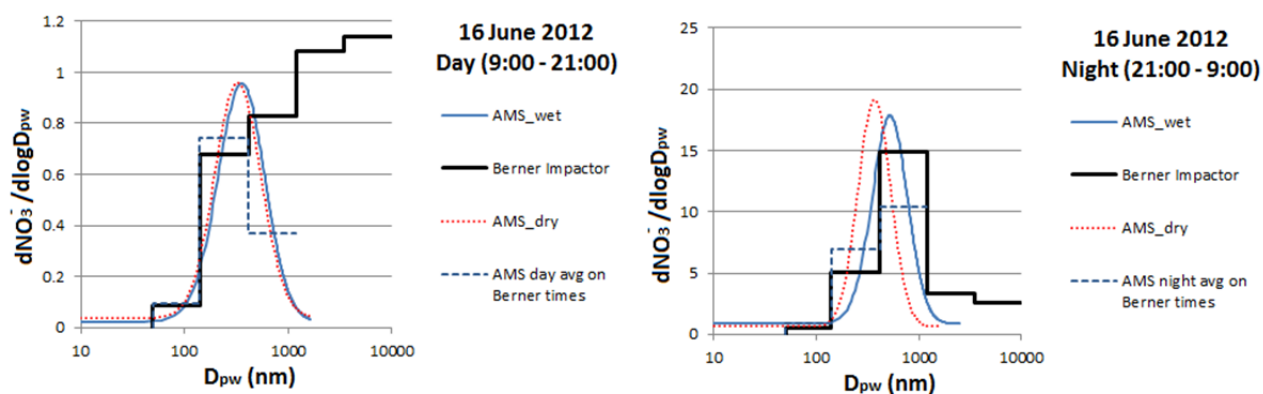
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6 The evaluation of possible negative artifacts affecting the Berner Impactor concentrations was carried out  
 7 also in respect to size distributions of the main inorganic chemical components by comparing the size-  
 8 segregated concentrations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

18 The resulting size distributions for two samples – one day-time and one night-time (16/6 day and night) –  
 19 selected during the late June stagnation period, are reported (Fig. S11). The results indicate only a very  
 20 moderate loss of ammonium nitrate in the very fine stages of the impactor (PM<sub>0.4</sub>), while for particles in the  
 21 range 0.4 – 1.2  $\mu\text{m}$ , the AMS concentrations are smaller than those determined by the impactor, but this can  
 22 be put in relation to the loss of collection efficiency in the AMS for particle diameters larger than 0.7  $\mu\text{m}$ ,  
 23 hence to an upper size cutting effect. In conclusion, there is no strong evidence of ammonium nitrate  
 24 evaporation in the small impactor stages.



1



2

3 **Fig. S11 – Comparison between Berner Impactor (black line histogram) and PToF-AMS size**  
4 **distribution. AMS size distributions have been fitted by a lognormal curve both on the original data**  
5 **(red dotted line) and after correction of dry particle diameters into humid diameters (blue dotted line).**  
6  **$D_{pw}$  stands for humid diameter (diameter of wet particles). The blue dashed histogram represents**  
7  **$dNO_3^- / d\log D_{pw}$  data averaged over the first three size bins of the Berner Impactor (0.05 – 0.14  $\mu m$ ; 0.14**  
8 **– 0.42  $\mu m$ ; 0.42 – 1.2  $\mu m$ ).**

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10

11

## 12 **References**

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15 Petters, M. D., and S. M. Kreidenweis, 2007, A single parameter representation of hygroscopic growth and  
16 cloud condensation nucleus activity: Atmospheric Chemistry and Physics, v. 7, p. 1961-1971.

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