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Enhanced toxicity of aerosol in fog conditions in the Po Valley, Italy

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Partitioning of PM mass and chemical components between fog droplets and interstitial aerosol

Figure S1 indicates the mass concentrations of fog water and daytime/interstitial aerosols in the Po Valley area during the study period (Nov-Dec 2015). The results pertain to concurrent aerosol and fog samples. As can be seen in the figure, daytime (i.e., out-of-fog) aerosol exhibited the highest mass concentrations (35.9±17.3 μg/m^3), whereas the average mass concentration of the interstitial aerosol was 15.7±6.3 μg/m^3. The average mass concentration of fog water (soluble and insoluble) components was also slightly higher than that of interstitial aerosols (i.e., ~17 μg/m^3). These results are in agreement with those previously observed in the area: for example, Gilardoni et al. (2014) reported an average PM_1 concentration of 32 μg/m^3 under clear conditions (i.e., during the day), while the nighttime aerosol concentrations were as low as 10 μg/m^3, indicating that the average interstitial aerosol concentration during fog episodes was 66% lower than that of daytime aerosols as a result of fog scavenging. Under the assumption that PM sources and mixing height are constant, the fog "partitioning" acts by simply transferring mass (and selectively, chemical compounds) to and from the aerosol and the fog phase, and this is supported by the results shown in Figure S1, in which the sum of mass concentrations of fog water and interstitial aerosols is almost equal to the mass concentrations of daytime aerosols.

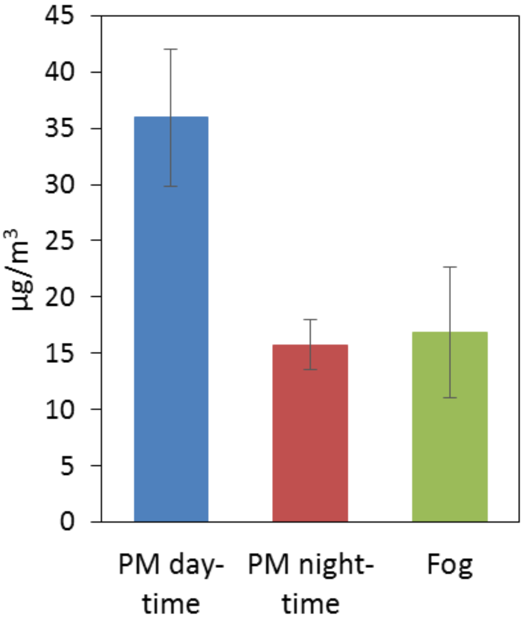

Figure S1 - Mass concentrations (μg/m^3) of aerosol (PM_1) and of fog water soluble and insoluble components in the Po Valley during the study period. Bars represent geometric means and error bars correspond to one standard error (SD).

Figure S2(a,b) illustrates the concentrations and mass fractions of WS components (inorganic and organic ionic species) in fog water and aerosol samples. As shown in the figure, the concentrations of WS components were significantly higher in daytime and fog water samples than in interstitial (or nighttime) aerosols, confirming that WS components from atmospheric aerosols partitioned to a great extent into fog water during fog episodes, reaching scavenging rates of 80% in the case of nitrate, chloride, acetate and methanesulfonate (MSA). In addition, the excess mass concentrations of certain ionic components (chloride, ammonia and especially acetate and formate) in fog samples compared to daytime PM_1 (Figure

S2 (a)) cannot be explained by a simple partitioning process, and implies the enrichment of such compounds in fog water from the gas-phase followed by aqueous-phase reactions (hydration, acid-base reactions, oxidation). Finally, as shown in the mass fraction chart (Figure S2(b)), the levels of WS components are highest in the fog water, in certain cases (e.g., acetate, formate, and ammonia) much higher than those of daytime aerosols.

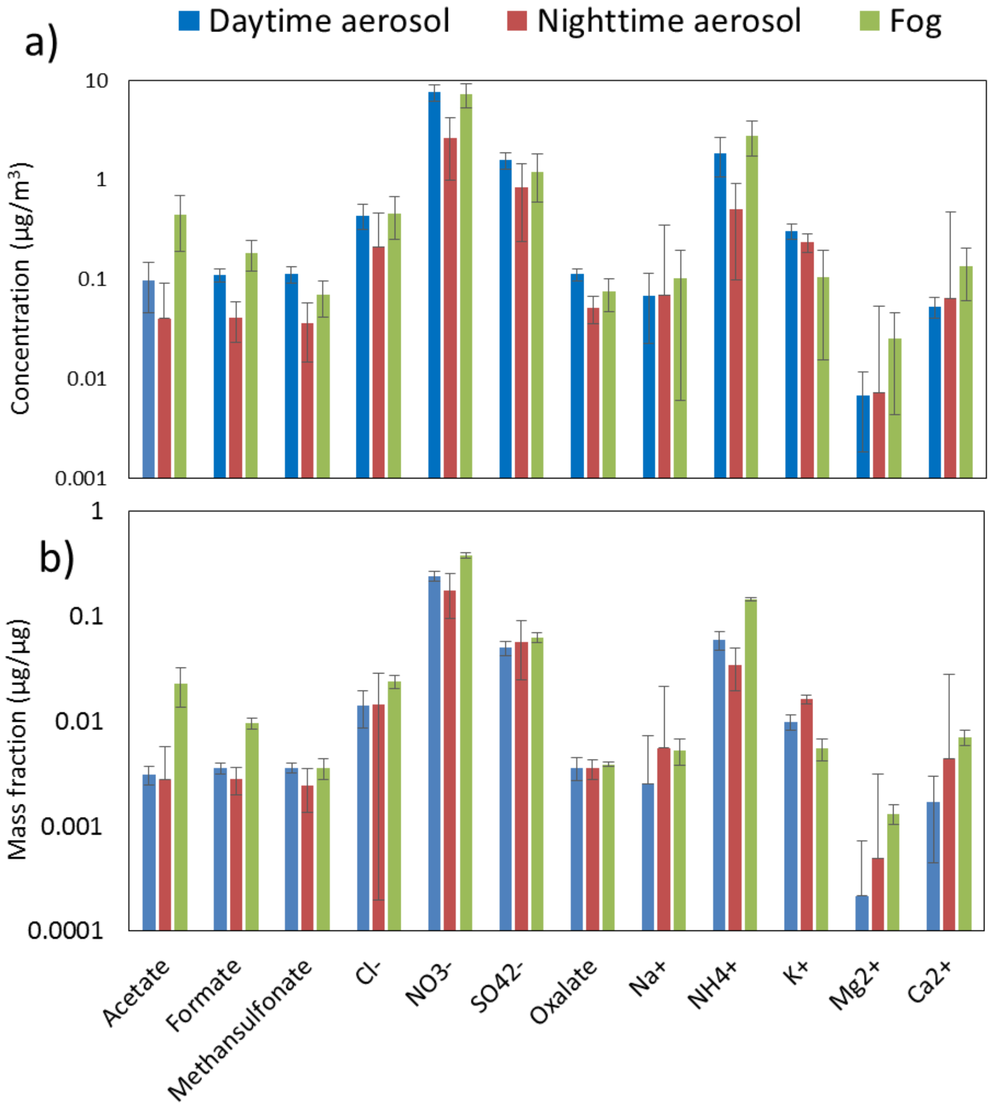

Figure S2 - Concentrations (a), and mass fractions (b), of the water-soluble components in the fog water and aerosols. Bars represent geometric means and error bars correspond to one standard error (SE).

Figure S3(a, b) illustrate the airborne concentrations (ng/m^3) and mass fractions (ng/µg) of the metals/elements in fog water and aerosol samples. The results pertain to parallel aerosol and fog samples. Our results are comparable with those of previous studies in the Po Valley area in terms of the concentrations of metals/elements in the aerosol samples (Mancinelli et al., 2005; Canepari et al., 2014; Perrino et al., 2014). For species with usually high WS fractions (including Ca and Mg), mass fractions were higher in fog water than within interstitial aerosol. However, mass fractions of combustion-related species (including V, Mn, Fe, Cu, and Pb) were greater in the interstitial aerosol with respect to fog water. Their scavenging rates (daytime minus nighttime concentrations) are lower than 60% and much smaller than those of WS ionic compounds (Figure S2). Therefore, combustion-related metals are enriched in aerosol particles that are poor condensation nuclei and, therefore, remain in the particle phase during fog episodes, while the particles carrying the WS components are efficiently scavenged into fog water (Gilardoni et al., 2014).

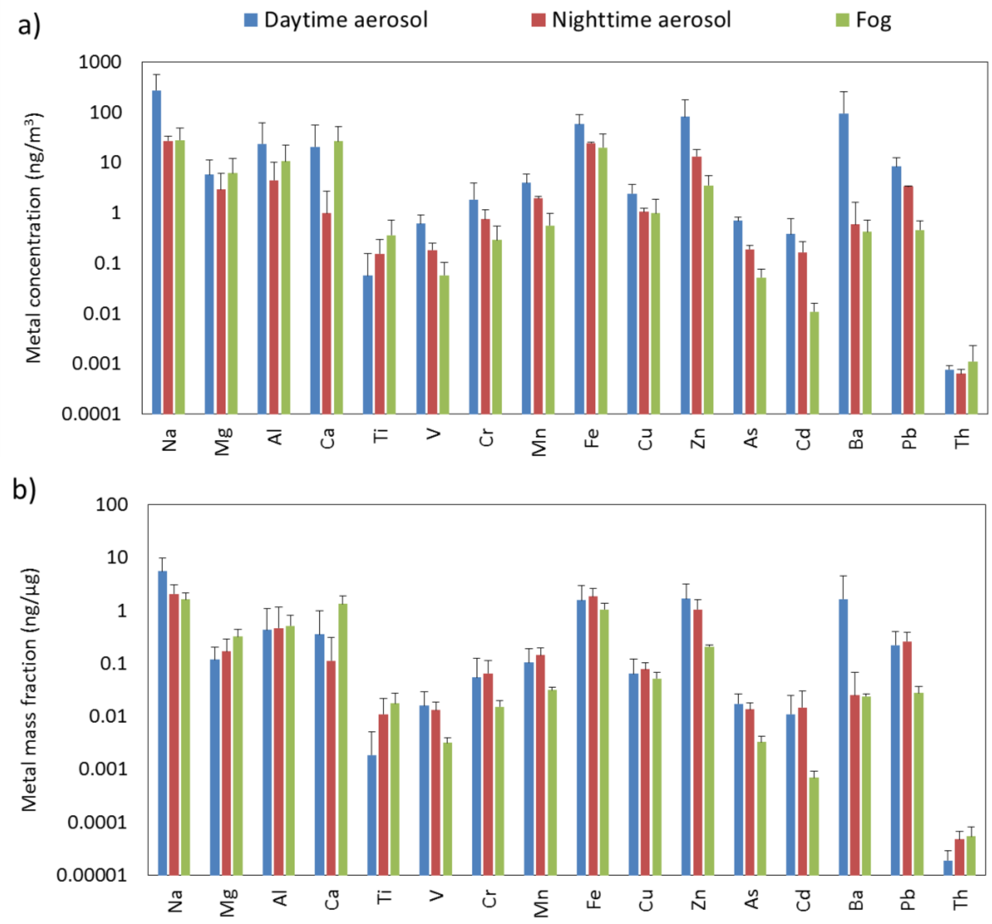

Figure S3 - Mass fractions (ng/m^3) (a) and airborne concentrations (ng/µg) (b) of metals/elements in fog water and aerosol samples collected in the Po Valley area in Fall 2015. Bars represent geometric means and error bars correspond to one standard error (SD).

Table S1 - Spearman rank correlation coefficients between WSOC and inorganic species in the fog water samples. Correlation coefficients which were statistically significant (at P<0.05) are highlighted in bold.

Species	Correlation Coefficient	Species	Correlation
	Water-soluble components		
Acetate	**0.86**	**Cl$^-$**	**0.78**
Dimethylamine	**0.81**	**K$^+$**	**0.99**
Ethylamine	**0.81**	**Mg^{2+}**	**0.89**
Formate	**0.89**	Na$^+$	0.75*
Methansulfonate	**0.96**	**NH$_4^+$**	**0.96**
Methylamine	**0.88**	NO$_2^-$	-0.53
Oxalate	0.68*	**NO$_3^{2-}$**	**0.96**
Trimethylamine	**0.96**	**SO$_4^{2-}$**	**0.79**
Ca^{2+}	**0.96**		

*Denotes statistical significance at P<0.1.

Table S2 - Results of the Principal Component Analysis (PCA) performed on the aerosol samples (N=6).

Species	Source factors	
	Transition metals (tracers of combustion-related sources)	Water-soluble components (tracers of secondary aerosol)
Fe	**0.98**	0.19
Mn	**0.96**	0.24
V	**0.93**	0.35
Ni	**0.94**	-0.08
Cu	**0.96**	0.23
WSOC	0.03	**0.98**
MSA	0.49	**0.85**
Oxalate	0.46	**0.79**
NO$_3^-$	-0.17	**0.99**
SO$_4^{2-}$	0.22	**0.96**

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