

## Characteristics and formation of heavy winter haze pollution during 2014-2015 in Tianjin, China

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With the rapid increase in the amount of vehicles and energy consumption during the past two decades, China faces a serious air pollution in urban areas, which has produced negative impact on the society development and human health. Tianjin, locating on the southeast of Beijing-Tianjin-Hebei region in north China, has been one of the heavy polluted cities during 2013-2016 of which the haze occurred frequently in particular in winter while the knowledge on its sources and formation mechanism are limited. For better understanding of the characteristics and the formation mechanisms of  $PM_{2.5}$  (particulate matter with an aerodynamic diameter  $\leq 2.5 \mu m$ ), especially secondary water-soluble inorganic species in these haze events, continuous and online hourly field observations in Tianjin urban area were carried out during 2014-2015 winter, that were, hourly concentrations of  $PM_{2.5}$ , sulfate, nitrate, and ammonium (SNA) as well as the concentrations of gaseous pollutants and meteorological parameters.  $PM_{2.5}$  concentrations ranged from  $5.6 \mu g \cdot m^{-3}$  to  $495.5 \mu g \cdot m^{-3}$ , with an average of  $112.1 (\pm 96.1) \mu g \cdot m^{-3}$ . In general, SNA (sulfate, nitrate and ammonium) was the most abundant secondary water-soluble inorganic species and contributed to 35% of  $PM_{2.5}$  mass concentration. The most severe  $PM_{2.5}$  pollution was observed in January 2015 with four haze episodes observed. The chemical composition of four episodes was characterized by high level of  $SO_4^{2-}$  (22%~38%), together with high concentration of  $NO_3^-$  (22%~34%), suggesting the contribution of secondary conversion. NOR and SOR increased with elevated  $PM_{2.5}$  levels and heterogeneous processes seemed to be the most plausible explanation of this increase. Nitrogen oxidation ratio (NOR) was much higher than sulfur oxidation ratio (SOR), indicating the  $NO_2$  was easily oxidized in low temperature condition than that of  $SO_2$ . Relative humidity (RH) played a considerable role in the formation of secondary inorganic aerosols, accelerated the secondary transformation of gaseous precursors, and further aggravated haze pollution.

Key words: winter haze; secondary formation; high relative humidity; heterogeneous processes