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Influence of relative humidity on aerosol composition: Impacts on light extinction and visibility impairment at two sites in coastal area of China

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ABSTRACT

Investigation on the aerosol characteristics, surface visibility (Vis) and meteorology at BGS (Baguanshan, Qingdao) and LNA (Lin'an, Zhejiang) shows that the ambient aerosol chemical composition and light extinction are relative humidity (RH) dependent. At higher RH, both the strengthened hygroscopic growth and the more efficient oxidization (of the precursor gases and formation of the secondary sulfate and nitrate) contribute to the increase of the mass fraction of the hygroscopic species, which consequently results in the increase of the aerosol mass extinction efficiency (MEE) and Vis reduction at the two Chinese coastal sites. MEE and chemical composition of the aerosol vary significantly under different regional transport ways; the airmasses from the ocean directions are associated with higher RH, higher sulfate mass fraction and greater MEE at BGS, while MEEs are smaller and associated with lower RH and lower sulfate fraction for the airmasses from the continent directions. Vis shows better correlation with $PM_{2.5}$ and PM_{10} mass concentrations when RH effect on aerosol hygroscopic growth is considered. At BGS, the sulfate mass fraction in $PM_{2.5}$ and PM_{10} (in average 32.4% and 27.4%) can explain about 60.7% and 74.3% of the variance of the aerosol MEE, respectively; sulfate and nitrate contribute to about 61% of the light extinction. RH plays a key role in aerosol extinction and visibility variation over this coastal area of China. Formation of the secondary aerosol (especially sulfate and nitrate) as well as hygroscopic growth under favorable (more stable and humid) meteorological conditions should be paid adequate attention in regulation of air quality and Vis improvement over eastern China in addition to the routine emission control measurements.

1. Introduction

Increase in energy consumption along with urbanization and industrialization has led to more frequent air pollution episodes (Chan and Yao, 2008) and low visibility (Vis) events in China (Qiu and Yang, 2000; Fan et al., 2005; Che et al., 2007; Deng et al., 2008; Chang et al., 2009), which have raised worldwide concern (Tao et al., 2012; Zhao et al., 2013). Although a lot of efforts have been implemented to improve air quality as well as to control the occurrence of fog and haze events in China, the effects of these measurements (without full understanding and consideration of the weather and climate background of the recently accelerated intensification of these severe haze and fog events) are mostly limited. A key challenge that still remains is to find and pay *adequate* attention

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to the major contributors to the aerosol extinction and Vis impairment during these typical air pollution episodes over the region.

It is well known that the hygroscopic growth of the aerosol affects its optical characteristic (such as the single-scattering albedo and the refractive index; Zieger et al., 2013) and size distribution, which have important implications to the radiative forcing (Chýlek et al., 1995; Kotchenruther et al., 1999; Wang et al., 2008; Rastak et al., 2014) and the variation of Vis (Noll et al., 1968; Charlson, 1969). Aerosol hygroscopicity is also important for accurate satellite retrieval (Wang and Martin, 2007). A recent study over eastern China (ECN) found that in addition to emission, the relative humidity (RH) is an important meteorological factor (except for the wind speed and regional transport of the pollutants) contributing to the variation of Vis (Qu et al., 2014), and regional statistics for the 136 stations show that RH is strongly correlated with the detrended Vis (calculated through subtracting the linear trend from the original time series of Vis) in winter over ECN from 1973 to 2012 ($R = -0.81$, $P < 0.0001$, $n = 40$); higher RH and more humid environment are found to be more favorable for the hygroscopic growth of the particles and subsequently Vis decline.

Along the same line, increase of the aerosol optical depth (AOD) is found to be associated with increase of the total column water vapor content (CWV, Smirnov et al., 2002; Eck et al., 2008). Bi et. al (2014) found a strong positive correlation between AOD and CWV at Beijing during the severe haze episodes in January 2013, and they attributed the large accumulation mode particles then to the coagulation through both condensation and gas-to-particle conversion processes. Through comparison of the dry and ambient aerosol light extinction coefficient (B_{ext}), Jung et al. (2009a) estimated the contribution of the aerosol water content to light extinction. The aerosol water content was found to contribute significantly to the light extinction (about 51.4% and 68.4% during the biomass burning and the long-range transport periods) under Asian continental outflow (Jung and Kim, 2011). Jung et al. (2009a) further found that the effect of aerosol water content on Vis impairment and light extinction is mainly due to increases of the $(NH_4)_2SO_4$ and NH_4NO_3 concentrations in the Pearl River Delta region.

Indeed, Li et al. (2013) reported that the chemical composition of the aerosol has an influence on its optical properties (especially the single scattering albedo) in urban Shanghai. Sulfate is found to be a major aerosol species contributing to Vis reduction in USA (Malm et al., 1994). A study in Beijing found that sulfate, nitrate and organic carbon mass contributed to about 42.2%, 24.9% and 15.7%, respectively, of light extinction in summer 2006 (Jung et al., 2009b). On the other hand, the formation of secondary hygroscopic aerosol (such as SO_4^{2-}, NO_3^-, and NH_4^+) is found to be an important mechanism of haze over Beijing (Zhao et al., 2013). Secondary pollutants including the hygroscopic species were the major chemical components during haze days in Guangzhou (Tan et al., 2009). Sun et al. (2014) also reported that the secondary inorganic species play enhanced roles in the haze formation and their contributions elevated during haze episodes in Beijing in January 2013. Furthermore, RH is found to have important impacts on aerosol composition (especially sulfate and coal combustion organic aerosol) during winter in Beijing (Sun et al., 2013).

How does RH influence the chemical composition and optical properties of the aerosol (and consequently contribute to Vis degradation)? As RH and water vapor are important to light extinction and AOD, what is the impact of the variation in water vapor supply and RH under different regional atmospheric transport ways to aerosol extinction and Vis impairment? Further clarifying these questions in coastal area of China is important to air quality regulation and Vis improvement measurements over the region.

Here we use observations of surface Vis and meteorology as well as measurements of aerosol mass concentration and chemical composition at two sites over coastal China to investigate the RH influences on aerosol composition, extinction and Vis variation. The enhanced aerosol extinction is linked with the increase of the mass fraction of sulfate and nitrate at elevated RH. Both the RH effects on formation of the secondary species and on hygroscopic growth are considered. The results of this study will be helpful to better understand the effect of meteorology (in this case RH variation) on the light extinction of aerosol and Vis decline over the coastal area of China.

2. Data and method

2.1. Sampling and chemical analysis of PM

Measurements of aerosol mass concentration and chemical composition were conducted during a year-round campaign at two sites: (1) Baguanshan (BGS, 36° 04′ N, 120° 20′ E, 76 m above sea level) in a residence district of Qingdao, a coastal city; (2) Lin'an (LNA, 30° 17′ N, 119° 44′ E, 138 m asl), a rural site in the east of the Plain of Yangtze River Middle and Lower Reaches. The two sites are located in ECN (with the Yellow Sea or the East China Sea to the east and mainland China to the west), a region with dense population, upgrowth industry, and significant anthropogenic emissions. In summer, East Asian summer monsoon is the major synoptic system with humid climate; in spring there is input of Asian dust to the region.

Bulk 24-h (from 9:00 AM to 9:00 AM the next day) $PM_{2.5}$ and PM_{10} (particulate matter with diameter less than 2.5 μm and 10 μm) samples were collected every other day from May 2007 to June 2008 at BGS with a MiniVol™ air sampler (Airmetrics, Oregon USA) operating at a flow of 5 l min^{-1}. At LNA, bulk 24-h (9:10 AM to 9:10 AM the next day) $PM_{2.5}$ samples were collected from March 2004 to June 2005 with an R&P 2025 sampler (Rupprecht & Patashnick, USA) at a flow rate of 16.7 l min^{-1}; except for sampler maintenance, from March 3, 2004 to January 11, 2005 one sample was collected every other day, while from January 12 to June 8, 2005 one sample was collected every day.

Aerosol particles were collected on 47 mm diameter Whatman quartz microfibre filters (QM/A, Whatman Ltd, Maidstone, UK) (preheated at 800 °C for 4 h to remove contaminants). The filter samples were equilibrated for at least 24 h under a constant RH between 30% and 40%, then aerosol mass was determined gravimetrically using an electronic microbalance with 1 μg sensitivity (ME 5-F, Sartorius AG, Goettingen Germany), which is referred to as dry mass in this study. Samples were stored in a refrigerator at 4 °C before chemical analysis.

The analytical techniques used have been described previously (Qu et al., 2008). Chemical analyses of the water-soluble ions, including SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, NO_2^-, Cl^- and F^-, were conducted using a Dionex® 600 ion