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Mineral dust and NOx promote the conversion of SO_2 to sulfate in heavy pollution days

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Haze in China has been increasing in frequency of occurrence as well as the area of the affected region. Here, we report on a new mechanism of haze formation, in which coexistence with NOx can reduce the environmental capacity for SO_2, leading to rapid conversion of SO_2 to sulfate because NO_2 and SO_2 have a synergistic effect when they react on the surface of mineral dust. Monitoring data from five severe haze episodes in January of 2013 in the Beijing-Tianjin-Hebei regions agreed very well with the laboratory simulation. The combined air pollution of motor vehicle exhaust and coal-fired flue gases greatly reduced the atmospheric environmental capacity for SO_2, and the formation of sulfate was found to be a main reason for the growth of fine particles, which led to the occurrence of haze. These results indicate that the impact of motor vehicle exhaust on the atmospheric environment might be underestimated.

C hina's air pollution has been a global concern for decades. Reviewing the history, the "Photochemical Smog Event in Los Angeles", which took place in the 1940s–1950s, was mainly caused by photochemical reaction of NOx (= NO + NO_2) and volatile organic compounds (VOCs) from motor vehicle exhaust. The "Great Smog of 1952 in London" was mainly caused by SO_2 emitted from coal burning. The primary pollutants in these events were clearly revealed in these incidents. In contrast, up to now, the main cause of heavy haze in China has been widely studied but not yet fully elucidated. The key factors that affect the formation and evolution of haze include emission of primary pollutants, secondary aerosol formation from homogeneous and heterogeneous reactions, and hygroscopic growth of aerosols[1–3]. However, the intrinsic cause for haze formation is still not clear. The Chinese economy is undergoing high-speed development that is heavily dependent on coal consumption as its main energy source. Coal burning, motor vehicles, and industrial emission pollution, which have been seen in developed countries at different times, all contribute to a high burden and heavy composite atmospheric pollution in China nowadays. This has led to complex air pollution and is a new situation that developed countries have not experienced ever before.

Haze is a phenomenon caused by fine particles (PM_1 or $PM_{2.5}$), resulting in the decline of atmospheric visibility. In recent years, haze in China's eastern region has increased in frequency of occurrence as well as the area of the affected region. According to the statistical data from monitoring by the Chinese Academy of Sciences (CAS), the Beijing-Tianjin-Hebei regions experienced five severe haze episodes (peak concentrations of $PM_{2.5}$ over 300 μg/m³) in January 2013 alone. Therein, downtown Beijing's $PM_{2.5}$ level exceeded the Second Grade National Standard of China (75 μg/m³, the Ambient Air Quality Standard planned to be implemented in 2016) for 22 days and exceeded the First Grade National Standard (35 μg/m³) for 27 days. According to the safety standard of the World Health Organization (WHO) (10 μg/m³), downtown Beijing air conditions exceeded the standard for nearly the whole month. The haze-affected area reached 1,300,000 km² in January 2013[4].

The external cause for the large scope and long duration of haze which frequently appeared in China in January 2013 was the stable synoptic conditions; however, the internal cause was related to the $PM_{2.5}$ or PM_1 and their precursor pollutants, such as SO_2, NO_2, NH_3, and VOCs etc., which heavily exceeded the environmental capacity determined by conditions such as local weather and terrain. Once calm weather persists, pollutants do not disperse easily, and secondary particles produced by homogeneous and heterogeneous atmospheric chemical processes of pollutants readily accumulate, resulting in the formation of haze. Field observations of heavy haze in
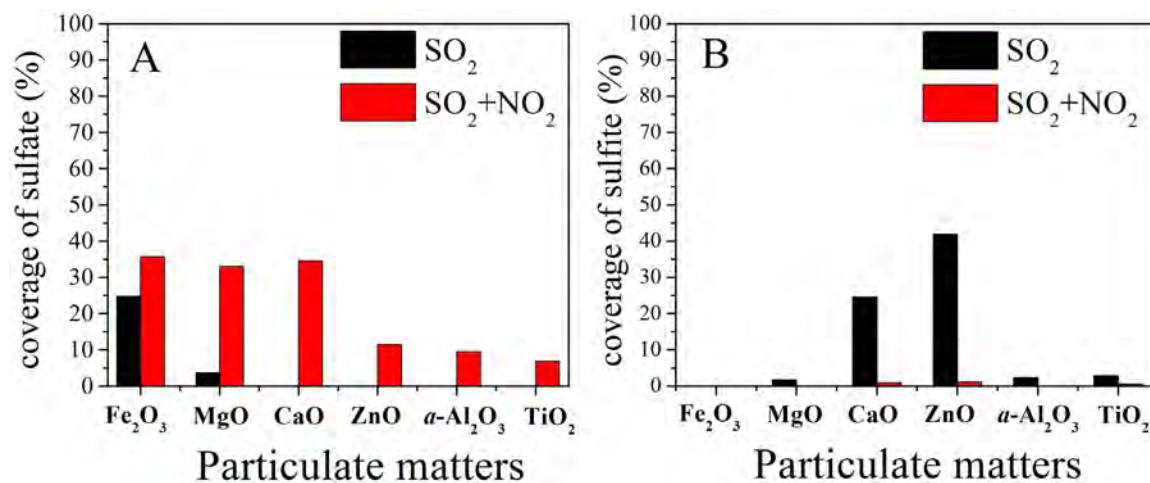
Figure 1 | Surface coverage of (A) sulfate and (B) sulfite species on mineral oxides after heterogeneous reaction of SO_2 or SO_2+NO_2 for 2 h. Reaction conditions: carrier gases: $N_2(80\%) + O_2(20\%)$ with total flow of 100 mL/min; concentrations of SO_2 and NO_2: both 200 ppm; T = 303 K. A synergistic effect between SO_2 and NO_2 was also observed when reactant concentrations were at ppb level with long reaction time (see Supplementary Information).

January 2013 also found the occurrence of a dust storm from January 10 to 15 in the Beijing-Tianjin-Hebei regions.

Here, we report on a new mechanism of haze formation, in which the coexistence of NOx can reduce the environmental capacity for SO_2, leading to a gas-particle conversion process and fine particle growth.

Results

As one of the most important components of fine particles in the atmosphere, sulfate has been the focus of research studying its formation mechanism. Atmospheric sulfate originates from a variety of sources, including volcanic ash, sea spray, and the oxidation of sulfur dioxide (SO_2) and other sulfur-containing species[5–8]. A number of models have been applied to predict the formation of sulfate aerosols on a global scale. It has been found that atmospheric SO_2 concentrations are typically overestimated while sulfate tends to be underestimated[9–11]. Sulfur dioxide can be oxidized in the troposphere to form sulfate, which may occur in the gas-phase (principally via reaction with OH to yield H_2SO_4), in cloud or fog droplets, or on aerosol particles[12–15]. The oxidation of SO_2 by a stabilized Criegee intermediate (a carbonyl oxide with two free radical sites) or its derivative was recently reported[13,16]. Furthermore, ternary nucleation (H_2SO_4-NH_3-H_2O) has been shown to be ubiquitous in the troposphere and a major source of ammonium sulfate in the atmosphere[17,18]. In recent years, field observations and modeling simulation have found large amounts of sulfate in mineral dust aerosol[19–21], though the formation mechanism remains unclear. Laboratory simulation studies have found that it is difficult for SO_2 to convert to sulfate on the surface of mineral dust other than Fe_2O_3 and MgO, but the coexistence of O_3 can convert SO_2 to sulfate[22]. As a kind of secondary pollutant, the atmospheric concentration of O_3 is closely related to illumination intensity. Under weak or no UV-light, the concentration of O_3 is low. In addition, both NOx and SO_2 are primary pollutants and are emitted from the burning processes of fossil fuels. Our previous research has demonstrated that NO_2 and SO_2 have synergistic effects when they react on the surface of mineral dust, such as Al_2O_3, CaO, ZnO, TiO_2, MgO, and α-Fe_2O_3, and thus the formation of sulfate from SO_2 is promoted by the coexistence of NO_x[23,24]. Figure 1 shows the surface coverage of sulfate and sulfite species when NO_2 and SO_2 react on the surface of a mineral oxide. Sulfate cannot be formed on the surface of CaO, Al_2O, ZnO, and TiO_2 without an oxidant under synthetic air conditions (Fig. 1A). On the surface of Fe_2O_3 and MgO, although SO_2 alone can produce

sulfate, the coexistence of NO_2 further increased the amount of sulfate. Surface sulfite species were formed on the surface of mineral oxides other than Fe_2O_3 exposed to SO_2 alone (Fig. 1B). When NO_2 and SO_2 coexisted, the content of sulfite on the surface of all oxides was reduced significantly, or disappeared entirely. This shows that the coexistence of NO_2 significantly promotes the oxidation of surface sulfite to sulfate. Further analysis indicates that, in the process of NO_2 promoting SO_2 oxidation to sulfate, O_2 plays a critical function in the reaction atmosphere. As shown in Fig. 2, sulfate can be formed on the CaO surface only in the presence of O_2. Similar phenomena were also found on Al_2O_3, ZnO, and TiO_2 surfaces (see Supplementary Information). Therefore, O_2 was the key oxidant in the process of SO_2 oxidation, while NOx and mineral oxides acted as catalysts to promote the conversion of SO_2 to sulfate on the surface of mineral oxides. The catalytic oxidation mechanism of SO_2 on the surface of mineral oxides by NOx is proposed as shown below:
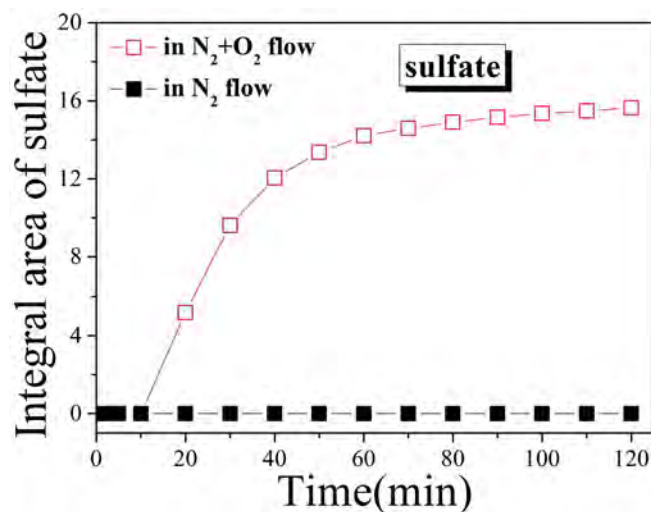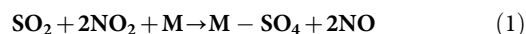
$$SO_2 + 2NO_2 + M \rightarrow M - SO_4 + 2NO \qquad (1)$$

Figure 2 | Comparison of integral infrared peak area of sulfate when NO_2+SO_2 was exposed to the surface of CaO with pure N_2 (black solid squares) and synthetic air ($80\%N_2+20\%O_2$) (red hollow squares) as carrier gas. Reaction conditions: total flow = 100 mL/min; concentrations of SO_2 and NO_2 both 200 ppm; T = 303 K.
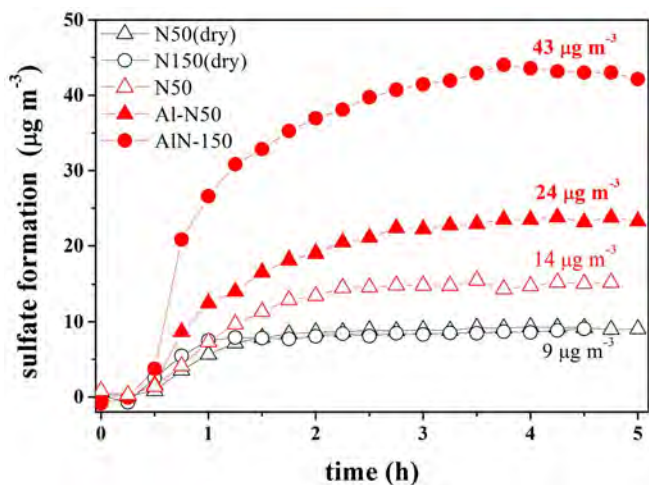
Figure 3 | Sulfate formation in heterogeneous reactions of NO_x and SO_2 in the smog chamber. N50(dry) and N150(dry) represent NO_2 concentrations of 50 and 150 ppb in the absence of Al_2O_3 with a RH of 12%, respectively; N50 represents an NO_2 concentration of 50 ppb in the absence of Al_2O_3 at 50% RH while Al-N50 and Al-N150 represent NO_2 concentration of 50 and 150 ppb in the presence of Al_2O_3 at 50% RH, respectively.

$$2NO + O_2 + M \rightarrow 2NO_2 \qquad (2)$$
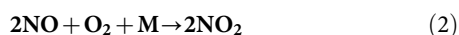
where M represents the surface of mineral oxides. This process is analogous to the lead chamber process for manufacturing sulfuric acid, in which nitrogen oxides serve as a catalyst for conversion of SO_2 to H_2SO_4[25].

On the other hand, the formed surface nitrate species can promote the hygroscopicity of mineral oxides and content of surface water[26]. This allows the oxidation process of SO_2 to occur in the liquid phase and improves the efficiency of SO_2 conversion to sulfate[27]. Under haze weather conditions, the concentration of O_3 is low while NO_2 is high, and mineral dust constitutes a high proportion (about 10%) of $PM_{2.5}$ in Beijing (see Table S2 in supplementary information). Therefore, the synergistic effect between SO_2 and NO_2 on the surface of mineral dust is an important potential source of sulfate aerosol in China. Even in an atmosphere in which the O_3 concentration is low, the primary pollutant NO_x can also promote the oxidation of SO_2 to sulfate. In addition, SO_2 oxidized by NO_3 radicals may also occur under haze conditions[16].

A 2-m^3 smog chamber, equipped with an aerosol composition speciation monitor (ACSM), was used to investigate sulfate generation in heterogeneous reactions of NO_x and SO_2 on mineral oxides. Detailed conditions of the smog chamber experiments are shown in Table S3 in Supplementary Information. Figure 3 shows the sulfate yields in the smog chamber under different conditions. Without Al_2O_3 seed (black empty triangles), the sulfate yields were low (~ 9 μg m^{-3}) and the increase in NO_2 concentration exhibited no promotion effect on the formation of sulfate (black solid circles). When RH was increased to 50% in the reactor without seed, the formation of sulfate was enhanced slightly (~ 14 μg m^{-3}, red empty triangles). In contrast, if Al_2O_3 seed aerosols were introduced at 50% RH, sulfate formation increased significantly to ~ 24 μg m^{-3} (red solid triangles). It is interesting to note that the sulfate yield was further increased (~ 43 μg m^{-3}) by increasing NO_2 concentration (red solid circles). These results provide distinct evidence that Al_2O_3 seed aerosols and NO_2 greatly promote the formation of sulfate.

Field observations of heavy haze in January 2013 confirmed the above mechanism. Figure 4 shows the variation trend in the
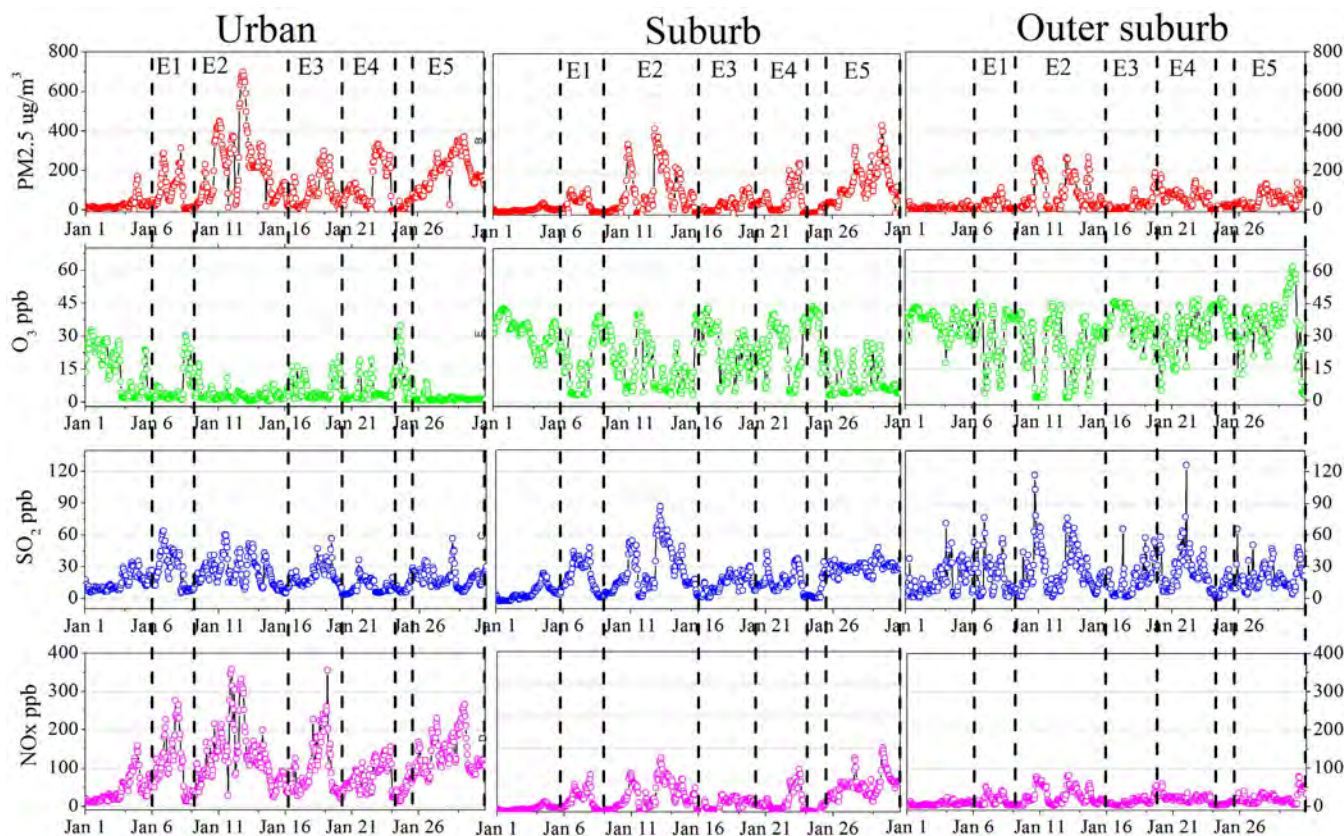

Figure 4 | Variation trend of $PM_{2.5}$, O_3, SO_2, and NOx concentrations in Beijing (urban site), Mangshan (suburb site) and Xinglong (outer suburb) stations in January 2013.
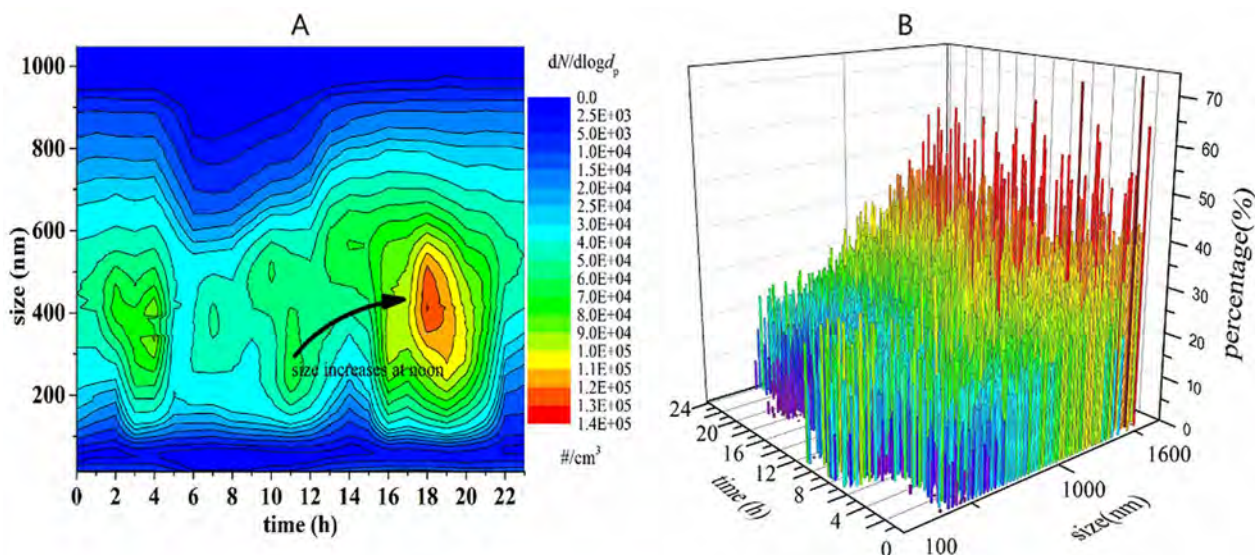
Figure 5 | Time variations of grain size distribution (A) and size-dependent sulfate mass percentage (B) of fine particles in Beijing station on January 12, 2013. Particle size was measured with a scan mobility particle sizer (SMPS) in the range of 14–1048 nm and sulfate mass fraction was calculated according to the mass concentrations measured by an aerosol mass spectrometer (AMS) with a size range of 90–1758 nm.

concentrations of PM$_{2.5}$ and gaseous pollutants such as O$_3$, SO$_2$, and NO$_2$ in Beijing (urban), Mangshan (suburban) and Xinglong (outer suburban) monitoring stations in January 2013. Detailed information on the stations is shown in the Supplementary Information. Five episodes of heavy haze (Episode 1-Episode 5) occurred in January 2013 (Fig. 4). In Beijing station, the 1-hour maximum value of PM$_{2.5}$ reached 700 µg/m³. In Mangshan station, it was 440 µg/m³, while Xinglong station had only 268 µg/m³. However, the concentration of O$_3$ in Beijing station was lower than the other two stations, especially on the heavy haze days. This illustrates that the photochemical reaction was negligible and O$_3$ is not the key oxidant causing heavy haze. The concentrations of SO$_2$ in Beijing, Mangshan, and Xinglong stations were relatively close (monthly mean values were 19 ppb, 20 ppb, and 21 ppb, respectively). But the monthly mean concentrations of NOx were 100 ppb (Beijing station) > 42 ppb (Mangshan station) >18 ppb (Xinglong station). These data strongly corroborate the results of the laboratory simulation study. That is, NOx reduced the environmental capacity for SO$_2$, so that the oxidation of SO$_2$ to sulfate was promoted in the presence of high concentrations of NOx. Clearly, the high concentration of NOx in Beijing station was mainly due to the contribution of vehicle emissions. As seen in Fig. 5A, the fine particle concentration increased rapidly and particle size was enlarged over several hours around noon. Along with the growth in particle size, the relative amount of sulfate increased notably (Fig. 5B). Therefore, the formation of sulfate was a main reason for the growth in size of fine particles (also seen Fig. S4 in SI[28]). Dupart et al.[29] reported that metal oxides present in mineral dust can act as atmospheric photocatalysts promoting the formation of fine H$_2$SO$_4$ and sulfate particles, which strongly supports the experimental and observation results from the present study. Moreover, the mass fraction of different components in PM$_{2.5}$ in Beijing during non-haze and haze episodes also indicated that the formation of sulfate was closely related to mineral content during haze episodes. As seen in Fig. 6, the increase of sulfate fraction on haze days accompanied the increase of mineral fraction, indicating mineral dust may have a promoting effect on the formation of sulfate during haze episodes.

Discussion

The London smog of 1952 was mainly caused by SO$_2$ emitted from coal burning. On clear days, the concentration of SO$_2$ was in the

range of 140–470 ppb while during smog days it reached levels as high as 1.34 ppm[30]. By contrast, cities in northern China had heavy haze pollution even when the concentration of SO$_2$ was only 60–120 ppb. This indicates that the environmental capacity for air pollutants has declined due to the complex air pollution of coal burning, motor vehicles, and industrial emissions. Therefore haze incidents occur frequently. China's population reached 1.4 billion in 2010, with over half living in cities. Considering its unique megacity scale and high population density, and the fact that the environmental capacity for single pollutants has declined under complex air pollution conditions, eastern China requires a stricter air pollution emission standard than developed countries. In fact, China has implemented an emission standard for coal-fired flue gas emissions that is the most restrictive in the world; however, it is still necessary to strengthen law enforcement. Considering the environmental sensitivity toward NOx leading to haze, and the increasing trend of total NOx emissions, China should prioritize the reduction of NOx emissions. Emission control of vehicles is critical in megacities. Vehicle exhaust emission standards in China should catch up with the current
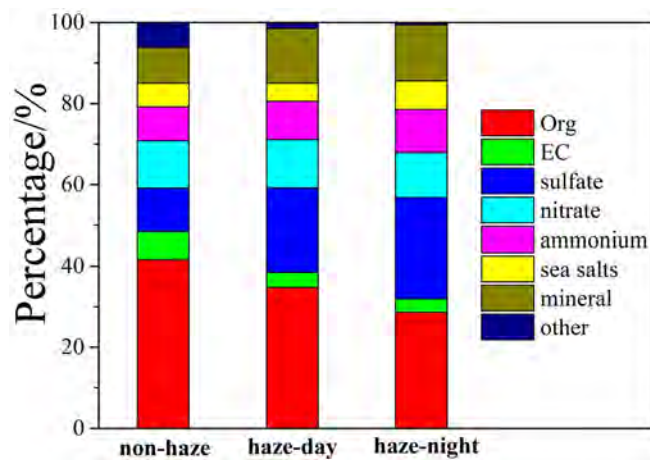

Figure 6 | Mass fraction of different chemical compositions in PM$_{2.5}$ in Beijing station. Non-haze, haze-day, and haze-night represent the sampling times of 12:00 on Jan. 9th, 12:00 on Jan. 12th, and 00:00 on Jan. 13th, 2013, respectively.

standard of the EU, and China must progress to a stricter standard suitable for its severe and complex air pollution.

Solving China's haze pollution problems requires judicious energy structure planning, a reduction in coal and oil usage as well as other traditional energy sources, an increase in the proportion of clean energy, rational industrial distribution planning, the elimination of productive force lags, an upgrade of industries, and the development of environmental protection. With such measures, China will mitigate complex air pollution and achieve sustainable development.

Methods

Heterogeneous reactions of NOx and SO$_2$ on mineral oxides were investigated by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The experimental methods and integral IR peak area of surface species can be referenced to a previous study[24].

The smog chamber is a 2-m^3 cuboid reactor, constructed with 50 μm-thick FEP-Teflon film (Toray Industries, Inc.). The reactor was irradiated by 40 black lights (GE F40T12/BLB, peak intensity at 365 nm) and located in a temperature-controlled room (Escpec SEWT-Z-120) at a constant temperature. To generate Al$_2$O$_3$ seed aerosols, liquid alumisol (AlOOH, Kawaken Fine Chemicals Co., Ltd.) was sprayed into droplets by an atomizer and dried by a diffusion dryer. The generated particles were then carried into a corundum tube embedded in a tubular furnace with the temperature maintained at 1373 K. Details on the chamber and experimental methods can be found in previous studies[31,32]. An aerosol composition speciation monitor (ACSM) was used to measure the chemical species in the aerosol phase. The principle and structure of ACSM are similar to aerosol mass spectrometry (AMS). Ng et al.[33] presented a detailed introduction to this instrument and found that measurement results agreed well with AMS.

The urban station is located in downtown Beijing (116°22′21″E, 39°58′28″N), the suburban station is located in Mangshan (116°16′10″E, 40°16′3″N), and the outer suburb station is located in Xinglong (117°34′34″E, 40°23′40″N). All air quality monitoring stations were selected and set up according to US EPA method designations (US EPA, 2007). Concentrations of NOx, SO$_2$, O$_3$ and PM$_{2.5}$ were measured using a NO-NO$_2$-NOx chemiluminescence analyzer (Model 42i, Thermo-Fisher Scientific (TE)), a pulsed fluorescence SO$_2$ analyzer (Model 43i, TE), an ozone analyzer (Model 49 I, TE) and a Tapered Element Oscillating Microbalance (Model 1400A, R&P), respectively. The instruments were operated and maintained properly to ensure data integrity. Scheduled quality control procedures included daily zero and span checks, biweekly precision checks, quarterly multiple-point calibrations, and data validations.

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Acknowledgments

Author contributions

H.H. initiated the project and designed the experiments, Q.M. and J.M. performed the laboratory experiments, B.C. and C.L. performed the smog chamber experiments, Y.W., D.J., G.T. and H.Z. conducted the field measurements. H.H., Y.W., Q.M., J.M. and B.C. analyzed the data and contributed to the interpretation and to manuscript preparation. J.H. contributed to new tools. Correspondence and requests for materials should be addressed to H. He (honghe@rcees.ac.cn) and Y. Wang (wys@mail.iap.ac.cn).

Additional information