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Understanding unusually high levels of peroxyacetyl nitrate (PAN) in winter in Urban Jinan, China

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ABSTRACT

Peroxyacetyl nitrate (PAN), as a major secondary pollutant, has gained increasing worldwide attentions, but relevant studies in China are still quite limited. During winter of 2015 to summer of 2016, the ambient levels of PAN were measured continuously by an automatic gas chromatograph equipped with an electron capture detector (GC–ECD) analyzer at an urban site in Jinan (China), with related parameters including concentrations of O_3, NO, NO_2, $PM_{2.5}$, HONO, the photolysis rate constant of NO_2 and meteorological factors observed concurrently. The mean and maximum values of PAN concentration were (1.89 ± 1.42) and 9.61 ppbv respectively in winter, and (2.54 ± 1.44) and 13.47 ppbv respectively in summer. Unusually high levels of PAN were observed during severe haze episodes in winter, and the formation mechanisms of them were emphatically discussed. Study showed that high levels of PAN in winter were mainly caused by local accumulation and strong photochemical reactions during haze episodes, while mass transport played only a minor role. Accelerated photochemical reactions (compared to winter days without haze) during haze episodes were deduced by the higher concentrations but shorter lifetimes of PAN, which was further supported by the sufficient solar radiation in the photolysis band along with the high concentrations of precursors (NO_2, VOCs) and HONO during haze episodes. In addition, significant PAN accumulation during calm weather of haze episodes was verified by meteorological data.

Introduction

Peroxyacetyl nitrate (PAN), a typical secondary pollutant, is formed by photochemical reactions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) in the atmosphere (Aikin et al., 1982). PAN is often considered as a marker of photochemical pollution due to its exclusive secondary origin, and it is a harmful substance for human health and vegetation (Peak and Belser, 1969). Because of its low solubility in water and thermal instability, thermal decomposition is the main sink mechanism of PAN compared to wet deposition and photolysis (Gaffney et al., 1993). Because of its long lifetime at low temperature, PAN can be transported over long distances in the upper troposphere from polluted regions, and

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it could release NO_x in some remote areas through thermal decomposition (Beine et al., 1997; Kenley and Hendry, 1982). Thus, PAN is considered as a temporary NO_x reservoir that may affect the NO_x level and consequently O_3 production in remote areas.

PAN was first detected in the photochemical smog events of Los Angeles in the 1950s (Stephens et al., 1956) and has been extensively measured around the globe since then. Field measurements showed that the mixing ratios of atmospheric PAN range from a few pptv (in remote areas) (Bottenheim and Gallant, 1989; Moore and Remedios, 2010) to over 40 ppbv (in fragmented metropolitan regions) (Grosjean, 1983, 2003). These values are usually one order of magnitude lower than those of O_3, but the overall bio-toxic effect of PAN is always one or two orders of magnitude greater than that of O_3 (Zhang et al., 2015). In China, photochemical pollution has become a severe environmental issue in recent years due to rapid economic development. However, available data of atmospheric PAN were scarce in China, except in a few regions (Pearl River Delta, Beijing, Lanzhou) (Liu et al., 2010; Wang et al., 2010; Zhang et al., 2009), while researches on O_3 and VOCs were fairly extensive (Shao et al., 2009; Wang et al., 2003; Xu et al., 2008). In addition, previous studies of PAN had been conducted mainly during summer rather than winter, because PAN had obvious diurnal variation and high concentrations during summer. In comparison, wintertime researches were much harder because the high-occurrence of serious pollution events might entail more complex formation and sink mechanisms of gas pollutants.

In this study, the ambient concentrations of PAN were measured from November 2015 to July 2016 in Jinan, China, and this was the first measurement of PAN in the urban area of Shandong Province. We primarily analyzed the mechanism of the unusually high concentrations of PAN in winter (especially during haze episodes) combined with the concurrent data of CCl_4, O_3, NO, NO_2, $PM_{2.5}$, HONO, photolysis rate constant and local meteorological information. Additionally, backward trajectory analysis was used to determine the long-range transport of PAN. Comprehensive analysis of PAN behavior in this study helped to explain the formation and sink mechanisms of PAN, especially in winter.

1. Experiment and methodologies

1.1. Site description

Field measurements were carried out continuously in Jinan (N36°40′, E117°03′), 400 km south of Beijing, from Nov. 2015 to Jul. 2016 (except for a data-deficient gap from Feb. to Mar. in 2016). The population of Jinan is seven million with an urban population of nearly five million. In general, Jinan has a plain topography, but the elevation is higher on the south side than on the north side, and there are small hills on the east and west sides. Thus, the entire area forms a half basin. Due to rapid urbanization, Jinan has faced many air quality problems recently, especially haze and smog (Cui et al., 2016; Gao et al., 2011; Yang et al., 2007). In this study, the monitoring site was located at the Atmospheric Environment Observation Station of Shandong University, on the rooftop of a seven-story building (at a height of approximately 25 m above ground level), and all the gas data (such as NO_x, O_3) were measured at the same location. The monitoring site was surrounded by several residential areas, commercial strips and schools, without large-scale industrial sites or construction projects.

1.2. Measurement techniques

The technique used a gas chromatograph equipped with an electron capture detector (GC–ECD) to simultaneously measure ambient concentrations of PAN, peroxypropionyl nitrate (PPN), and carbon tetrachloride (CCl_4). The detailed introduction of this instrument had been given in many published papers (Zhang et al., 2012, 2015), thus we only briefly mentioned the basic principles of PAN measurement and calibration in this paper. Ambient air was sampled through a Teflon tube (3 mm OD, 6 m length) at a flow rate of 1.5 L/min by a built-in pump (NMP830KNDC, KNF Inc.). Each sampling lasted for 20 sec, and the air sample was temporarily stored in a 0.5-mL GC loop. Then, the pump was switched off for 5 sec to allow the pressure to equilibrate. After that, ten-port switched to make carrier gas (Helium) push the gas sample into the GC–ECD, a well-studied instrument with high sensitivity and selectivity of PAN quantification. In addition, PPN and CCl_4 were measured by the ECD detector at the same time. Because the signals of PPN were always below the detection limits, the PPN data were not included in this study. The minimal variation in CCl_4 concentration could reflect the precision of the instrument due to the constant level of CCl_4 in the ambient air. Analysis of each gas sample took 10 min to complete, and 144 sets of data were obtained every day when the instrument worked continuously. To calibrate the instrument, PAN was generated by irradiation (254 nm) of a gaseous mixture of acetone and NO, and the concentration of PAN was deduced by the flow of the standard NO gas due to the excess acetone. The calibration repeated twice per month and the results showed only small variations (approximately 15%) (Zhang et al., 2012). The detection limits of the GC–ECD (estimated as three times the signal to noise ratio) for PAN, PPN and CCl_4 were 22, 36 and 5 pptv, respectively; the overall uncertainties in the GC–ECD were estimated to be ±13% (IC calibration) and ±15% (NO_x analyzer calibration) (Zhang et al., 2012). There were some modifications from conditions of the previous studies (Zhang and Mu, 2014; Zhang et al., 2014): we changed the carrier gas from nitrogen to high purity helium to ensure the stability of the instrument, and we used acetone solution instead of acetone gas to ensure an excess of acetone.

During the measurement period, a set of supporting parameters including O_3, NO, NO_2, $PM_{2.5}$, HONO, photolysis rate constant and meteorological data, were collected to explain the variations in the concentrations of PAN. O_3 was measured continuously using the ultraviolet absorption technique (Model 49C, USA) (Wang et al., 2012). NO and NO_2 were detected by the chemiluminescence technique (NO, NO_2, NO_x Analyzer, Thermo Environmental Model 42C, USA), and the NO_2 concentration was corrected by subtraction concurrent PAN concentration to reduce the interference of oxidation of nitrogen oxides (NO_2). The mass concentration of $PM_{2.5}$ was obtained by using a Synchronized Hybrid Ambient Real-Time Particulate Monitor (SHARP Monitor Model 5030, Thermo Fisher Scientific, USA) (Wen et al., 2015). The concentration of HONO was measured by a commercial long path

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