



On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation



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ABSTRACT

Peroxy acetyl nitrate (PAN) is a key component of photochemical smog and plays an important role in atmospheric chemistry. Though it has been known that PAN is produced via reactions of nitrogen oxides (NO_x) with some volatile organic compounds (VOCs), it is difficult to quantify the contributions of individual precursor species. Here we use an explicit photochemical model – Master Chemical Mechanism (MCM) model – to dissect PAN formation and identify principal precursors, by analyzing measurements made in Beijing in summer 2008. PAN production was sensitive to both NO_x and VOCs. Isoprene was the predominant VOC precursor at suburb with biogenic impact, whilst anthropogenic hydrocarbons dominated at downtown. PAN production was attributable to a relatively small class of compounds including NO_x, xylenes, trimethylbenzenes, trans/cis-2-butenes, toluene, and propene. MCM can advance understanding of PAN photochemistry to a species level, and provide more relevant recommendations for mitigating photochemical pollution in large cities.

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1. Introduction

Peroxy acetyl nitrate (PAN, CH₃C(O)O₂NO₂) is a key pollutant in photochemical smog. It is a cause of eye irritation and negatively affects vegetation, and is a potential mutagen for skin cancer (Stephens, 1969). Besides, it is an important player in atmospheric chemistry by acting as a reservoir of nitrogen oxides (NO_x). It is primarily formed in the industrialized/urbanized regions with abundant NO_x, and can be transported over long distances at low temperatures to remote regions and liberate NO_x (Singh et al., 1986). This process facilitates re-distribution of NO_x on regional (and even global) scales and controls ozone (O₃) production in both the source and downwind regions (LaFranchi et al., 2009). Consequently, investigating formation of PAN is an important part of understanding the formation of photochemical smog and assessing its impacts on human health and atmospheric chemistry.

In the troposphere, PAN is produced exclusively through photochemical reactions of volatile organic compounds (VOCs) in the presence of NO_x. Unlike O₃, precursors of PAN are only a relatively small set of VOCs that can generate peroxy acetyl radical (CH₃C(O)O₂, referred to from now on as PA, PA then combines with NO₂ to reversibly form PAN). PA comes directly from photolysis and OH/NO₃/O₃ oxidation of a small number of oxygenated VOCs (OVOCs) such as acetaldehyde, acetone, methacrolein (MACR), methyl vinyl ketone (MVK), methyl ethyl ketone (MEK) and methylglyoxal (MGLY). Besides some contribution from primary emissions (especially for acetaldehyde), most of these compounds are oxidation products (here referred to as second-generation precursors) of a certain class of hydrocarbons, e.g., ethane, propene, isoprene, and some aromatics (hereafter referred to as first-generation precursors). The relative importance of individual precursors varies from place to place depending on the VOC composition (Liu et al., 2010; and references therein). Identification of the dominant precursors is key to effective control of PAN pollution.

Numerical models built on chemical mechanisms of different complexities are widely utilized to track out the PAN precursors.

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Roberts et al. (2001) developed a sequential reaction model that considers reactions of PANs and related aldehydes, and applied it to observations made in Nashville and Houston. LaFranchi et al. (2009) employed a steady state model containing chemistry of PANs, PA and related OVOCs to understand PAN formation in the Sacramento urban plumes. These models are capable of identifying the key 2nd-generation precursors (OVOCs), but cannot 'directly' link to the 1st-generation ones (hydrocarbons). Some studies adopted more comprehensive chemistry to explore the roles of 1st-generation PAN precursors (Grosjean et al., 2002; Liu et al., 2010), but the mechanisms they used were mostly compiled with a lumped approach (e.g., the Statewide Air Pollution Research Center mechanism; usually abbreviated as SAPRC), from which the derived precursors were usually a class of hydrocarbons with similar structures/reactivities including non-PAN precursors. To our knowledge, there is lack of modeling studies that can determine the specific compounds of both generations of PAN precursors. Such information is critical for the PAN pollution control by identifying the responsible species and hence emission sources.

Here we demonstrate the application of the Master Chemical Mechanism (MCM) to better understand PAN photochemistry. MCM describes explicitly chemical degradations of individual hydrocarbon and OVOC species (Jenkin et al., 2003; Saunders et al., 2003), and hence facilitates a comprehensive evaluation of contributions from both generations of PAN precursors at a species level. In the present study, the MCM models are applied to intensive observations made both in downtown and at a downwind suburban site, to unravel formation of PAN and identify the major precursors in the atmosphere of Beijing.

2. Methodology

2.1. Field observations

Measurements were conducted in the Chinese Research Academy of Environmental Sciences (CRAES; 40°2' N, 116°25' E), a suburban site approximately 15 km north (normally downwind in summer) of city center (see Fig. 1). The site was located on the rooftop of a three-story building (~15 m above ground level). Surrounding our site there grows abundant fruit trees and landscape trees in the yard of CRAES. PAN, O₃, CO, NO, NO₂, NO_y, CH₄, non-methane hydrocarbons (NMHCs), carbonyls, aerosol size distribution and meteorological parameters were measured concurrently during 11 July–26 August 2008. In addition to the comprehensive observations at CRAES, whole air samples were taken along the 2nd and 3rd ring

roads and in urban center (see also Fig. 1) for detection of hydrocarbons at downtown Beijing.

PAN was measured in real-time by a commercial analyzer (*Meteorologie Consult GmbH*), which detects PAN based on gas chromatographic (GC) separation followed by electron capture detection. This analyzer has a time resolution of 10 min, with a detection limit of 50 pptv, 2 σ precision of 6% and uncertainty of 15%. During the campaign, the instrument baseline and sensitivity were calibrated weekly with a built-in calibration unit. Detailed information of this instrument and operation has been provided by J.M. Zhang et al. (2009) and Xue et al. (2011b).

CH₄ and C₂–C₁₀ NMHCs were measured by collecting whole air samples in evacuated 2-L stainless-steel canisters followed by laboratory analyses. At CRAES, samples were taken every day with at least one sample in the afternoon (12:00–17:00 LT) on clean days and up to seven samples throughout the daytime (07:00–19:00 LT) on episode days (Wang et al., 2010b). The sampling frequency was 2 h and sampling duration was 2 min. A total of 130 samples were collected during the measurement period. At urban center, 18 samples were taken during the morning rush hours (07:00–09:00 LT) on 14 and 23 August 2008. After the campaign, the canisters were shipped to the University of California at Irvine for analyses by using a five-column multiple GC system coupled with flame ionization detection, electron capture detection and mass spectrometer detection (Simpson et al., 2010; Xue et al., 2011a; 2013b).

C₁–C₈ carbonyls were measured by collecting air samples in sorbent cartridges coated by 2,4-dinitrophenylhydrazine (DNPH) equipped with an O₃ scrubber. The samples were taken generally every 2 h from 07:00 to 19:00 LT on selected O₃ episode days, with a sampling duration of 2 h for each sample and a flow rate of 1 L per minute. A total of 98 samples were collected at CRAES during the campaign. The collected samples were then eluted with acetonitrile and analyzed by a high-pressure liquid chromatography (*PerkinElmer, Series 2000*) in the laboratory of the Hong Kong Polytechnic University (Ho et al., 2011; Ho and Yu, 2004). Seventeen carbonyl species were detected, and only the data of acetaldehyde, acetone, MEK (mainly PAN precursors) and formaldehyde were used in the present study.

Ozone was measured by a commercial UV photometric analyzer (*TEI Model 49i*). CO was detected with a non-dispersive infrared analyzer (*API Model 300EU*). NO and NO₂ were observed with a chemiluminescence instrument (*TEI Model 42i*) equipped with a blue light converter (*Meteorologie consult GmbH*; Xu et al., 2013). NO_y was analyzed by another chemiluminescence analyzer (*TEI, Model 42cy*) with an externally placed molybdenum oxide converter. Particle number and size distributions (10 nm–10 μ m) were measured in real-time by a wide-range particle spectrometer (*MSP, WPS model 1000XP*; Gao et al., 2012). Ambient temperature, pressure, relative humidity (RH), solar radiation and winds were monitored by a weather station. All these techniques and quality assurance and control procedures have been described elsewhere (Wang et al., 2010b; Xue et al., 2011b; J.M. Zhang et al., 2009).

2.2. The Master Chemical Mechanism models

Two sets of photochemical box models were set up to evaluate formation of PAN and its sensitivity to precursors at CRAES and in urban plumes. The model frameworks were largely similar to that described in our previous studies (Xue et al., 2013a, 2013b). Briefly, they were built on the latest version of MCM (v3.2) that explicitly describes degradation of 143 primary VOCs together with the latest IUPAC

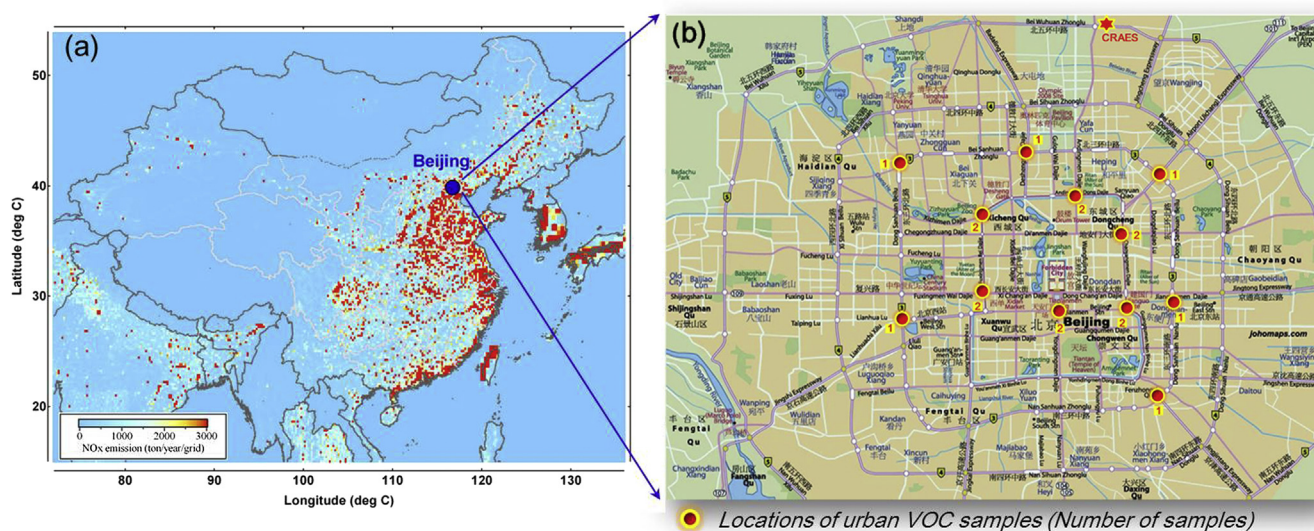


Fig. 1. (a) Map showing the study area and anthropogenic NO_x emissions (Q. Zhang et al., 2009) and (b) Locations of the CRAES site and urban VOC samples.

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