



Evidence for NO_x Control over Nighttime SOA Formation

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Science **337**, 1210 (2012);

DOI: 10.1126/science.1221520

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Acknowledgments: The project was supported in part by the Helmholtz-Institut Mainz, the GSI Helmholtzzentrum für Schwerionenforschung GmbH, the German Federal Ministry of Education and Research (BMBF), the Max-Planck Society, the Russian Minobrnauki, and the ExtreMe Matter Institute (EMMI). Y.N.N. acknowledges support by EMMI.

4 June 2012; accepted 10 July 2012
Published online 9 August 2012;
10.1126/science.1225636

Evidence for NO_x Control over Nighttime SOA Formation

A. W. Rollins,^{1*} E. C. Browne,¹ K.-E. Min,² S. E. Pusede,¹ P. J. Wooldridge,¹ D. R. Gentner,³ A. H. Goldstein,^{3,4} S. Liu,⁵ D. A. Day,^{5†} L. M. Russell,⁵ R. C. Cohen^{1,‡}

Laboratory studies have established a number of chemical pathways by which nitrogen oxides (NO_x) affect atmospheric organic aerosol (OA) production. However, these effects have not been directly observed in ambient OA. We report measurements of particulate organic nitrates in Bakersfield, California, the nighttime formation of which increases with NO_x and is suppressed by high concentrations of organic molecules that rapidly react with nitrate radical (NO₃)—evidence that multigenerational chemistry is responsible for organic nitrate aerosol production. This class of molecules represents about a third of the nighttime increase in OA, suggesting that most nighttime secondary OA is due to the NO₃ product of anthropogenic NO_x emissions. Consequently, reductions in NO_x emissions should reduce the concentration of organic aerosol in Bakersfield and the surrounding region.

Organic aerosol (OA) constitutes about half of the total submicrometer particulate mass in the troposphere (1–3). OA is emitted to the atmosphere both directly as particles (primary OA, POA) and produced in the atmosphere through oxidation of volatile molecules (secondary OA, SOA), although evidence suggests that SOA is dominant (4). Owing to the complexity of SOA chemistry, major gaps exist in our ability to predict the time evolution of the chemical, physical, and optical properties of aerosols. A key example is our inability to predict the response of SOA to changes in emissions of nitrogen oxides (NO_x). Although laboratory evi-

dence shows that NO_x should substantially affect atmospheric SOA formation, a coherent understanding of the nonlinear SOA/NO_x relationship has not emerged (5). This issue is important because NO_x has decreased by 30% or more in the United States and United Kingdom in the last decade, while comparable increases have occurred in China (6–9). Direct evidence that these changes in NO_x affect aerosol would greatly aid in the understanding of SOA.

SOA is formed through the gas-phase oxidation of volatile organic compounds (VOCs) by reactions with the hydroxyl radical (OH), ozone (O₃), and the nitrate radical (NO₃), producing condensable material (10). Most laboratory (10, 11) and field [e.g., (2, 12)] SOA studies have focused on the role of oxidation via O₃ and OH as SOA sources. Reactions of organic compounds with NO₃ are also important for oxidizing unsaturated atmospheric compounds (13), and NO₃ is unique in that it is almost exclusively a by-product of anthropogenic NO_x emissions (reaction 1).



Due to its photolabile nature and rapid reaction with nitric oxide (NO), NO₃ is present primarily in the nighttime atmosphere. Oxidation products of nitrate radical chemistry have a unique chemical signature due to the high yields, to form

organic nitrates (RONO₂). Organic nitrates are also formed during the day by OH-initiated chemistry in the presence of NO, but with much lower yields. Laboratory studies of SOA from NO₃ have revealed both large aerosol yields, and the importance of multigenerational chemistry on compounds with multiple C-C double bonds. For example, Ng *et al.* (14) and Rollins *et al.* (15) studied the aerosol formed during NO₃ oxidation of isoprene. Both studies found large SOA yields (4 to 24%) and showed that the condensable compounds were formed not from the products of the initial NO₃ + isoprene reaction, but mostly from further oxidation of the first-generation products. Similar results were found for NO₃ + limonene (16).

We have developed a fast, sensitive, and precise instrument capable of measuring the particulate total alkyl and multifunctional nitrates (pΣANs) (17). Using this instrument, we made observations of pΣANs along with key precursors (NO₂, O₃, VOC) and aerosol properties in Bakersfield, California, as part of the CalNex-2010 experiment. Bakersfield is of interest due to its location in California's San Joaquin Valley, with abundant sources of biogenic VOC (BVOC) and NO_x and (for the United States) relatively severe particulate matter (PM) air pollution. We interpret the observations as evidence for a substantial nighttime chemical source of pΣAN.

Air parcels arriving at the site had traveled typically through the agricultural San Joaquin Valley, and then through the Bakersfield urban center for 1 to 2 hours before reaching the site. During the experiment, OA concentrations exceeding 10 μg/m³ were frequently observed at night. A possible contributor to these high concentrations is the reduction in the boundary layer (BL) depth before sunset in the San Joaquin Valley. At a site near Bakersfield, Bianco *et al.* (18) observed that during May and June, the BL on average would decrease from ≈1.7 km at noon to ≈300 m just before sunset. The nighttime increase in OA observed in this study, however, occurred after sunset (Fig. 1), and thus after the BL is thought to have reached its minimum depth. We do not know the extent to which the aerosol that we measured at the surface was well mixed through the nocturnal BL; however, the diurnal

¹Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, USA. ²Department of Earth and Planetary Sciences, University of California, Berkeley, Berkeley, CA 94720, USA. ³Department of Civil and Environmental Engineering, University of California, Berkeley, Berkeley, CA 94720, USA. ⁴Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley, CA 94720, USA. ⁵Scripps Institution of Oceanography, University of California, San Diego, San Diego, CA 92093, USA.

*Present address: NOAA Earth System Research Laboratory and Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, Boulder, CO 80309, USA. †Present address: Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, Boulder, CO 80309, USA.

‡To whom correspondence should be addressed. E-mail: rccohen@berkeley.edu

patterns vary little from day to day, suggesting the observations shown in Fig. 1 are characteristic of a large spatial scale and not dominated by local surface layer plumes. There was no appreciable change in the prevailing wind direction (west-northwest) from 6 p.m. to 11 p.m., and back-trajectories for air arriving at this site in this time interval follow a common path arriving from the west-northwest (fig. S1).

The average diurnal trends in pΣAN, OA, and the ratio of these two are shown in Fig. 1. Additionally, diurnal averages in NO₂, O₃, temperature, and relative humidity are shown in fig. S2. The OA and pΣAN have both a midday maximum and a nighttime/early morning maximum. The average OA maximum at night exceeds that of the midday by 24%, which is an unusual observation compared to studies in other large urban areas that have observed the daily OA maxima midday (19–21). Although aerosol mass spectrometer (AMS) data did not readily quantify POA and SOA individually at night, size distributions and tracers suggest that POA was at most 10 to 20% of OA (see materials and methods SI).

On average, the pΣAN nitrate groups increased from 2.3% of OA at sunset to 4.7% at 23:30 local time. The rapid increase in the pΣAN fraction begins immediately after sunset, when NO₃ chemistry becomes possible. Although temperature is expected to affect SOA through changes in vapor pressures, it does not appear to have

played the dominant role in the trends; temperatures peaked near 15:00 local time and decreased significantly before sunset (fig. S1). The RONO₂ contribution to OA is relatively constant in the morning hours between 6:00 and 9:30 before obvious SOA production. After 10:00, when OA concentration is increasing, the observations indicate that as photochemistry generates SOA, pΣAN becomes a smaller fraction of the total OA mass. Factor analysis of AMS measurements are consistent with this interpretation. A unique nighttime factor was identified that becomes less important as the aerosol mass increases during daylight, and daytime SOA factors did not increase until after 9:00.

The observation that pΣAN and pΣAN/OA increase at night suggests not only that NO₃ chemistry is important for SOA production at night, but also that the organic nitrate tracers of this chemistry contribute appreciably to the total OA. Over the 5-hour time period after sunset (18:30 to 23:30), the average total OA increase was 1.54 μg/m³. The added mass of -ONO₂ functional groups alone accounted for 0.129 μg/m³ (8.4%) of this total mass. That this ratio increased continuously for 5 hours after sunset while Bakersfield is only 1 to 2 hours upwind suggests that the effect is somewhat regional. Assuming that the organic molecules with nitrate functional groups have an average molecular weight of 200 to 300 g/mol (22), we calculate that 27 to

40% of the OA growth was due to molecules with nitrate functionalities. This fraction of OA molecules that are nitrates is similar to the nitrate yields from a number of NO₃ + BVOC reactions (23). Thus, these numbers do not preclude all of the SOA production, including non-nitrates, being a result of NO₃ chemistry. The other potential source of nighttime SOA, O₃ + alkenes, is unlikely to be nearly as important because the rates of these reactions are typically at most one-tenth of the NO₃ rates (materials and methods S1.3).

To examine the role of NO_x emissions for SOA formation, we used observations of [NO₂] and [O₃] to calculate the nitrate radical production rates ($PNO_3 = k_1[NO_2][O_3]$) and compared these to the rate of net increase in pΣAN at night, defined as the difference ($\Delta p\Sigma AN = ([p\Sigma AN]_{23:30} - [p\Sigma AN]_{18:30})/5$ hours) on each night. Figure 2 compares $\Delta p\Sigma AN$ to the average PNO₃. The correlations with PNO₃ are modest ($r = 0.44$). However, if we exclude those nights when the NO₃ lifetime to gas-phase reactions was short ($\tau < 65$ s), a much stronger correlation between the PNO₃ and $\Delta p\Sigma AN$ ($r = 0.73$) is inferred. A linear fit to this data ($\Delta p\Sigma AN/PNO_3 = 0.015$) suggests that ~1.5% of NO₃ reacts to form particle-bound nitrates, a number that is somewhat lower than expected from chamber studies and could be used to estimate the efficacy of NO_x emission reductions for reducing fine PM at this location.

Generally, NO₃ reactivity at the site is dominated by BVOC from the valley and surrounding mountains (fig. S3). When the NO₃ lifetime is short, we find that a larger fraction of the reactivity is due to primary biogenic VOC than on other nights, suggesting that BVOC can suppress aerosol formation. Previous in situ observations have shown that biogenics react rapidly with NO₃, reducing the NO₃ concentration (24). We believe this is the likely mechanism for aerosol suppression. The removal of NO₃ by primary VOC results in production of first-generation gas-phase nitrates with vapor pressures that are too high ($C^* \approx 10^3$ to 10^6 μg/m³) for the molecules to be incorporated into aerosol to an

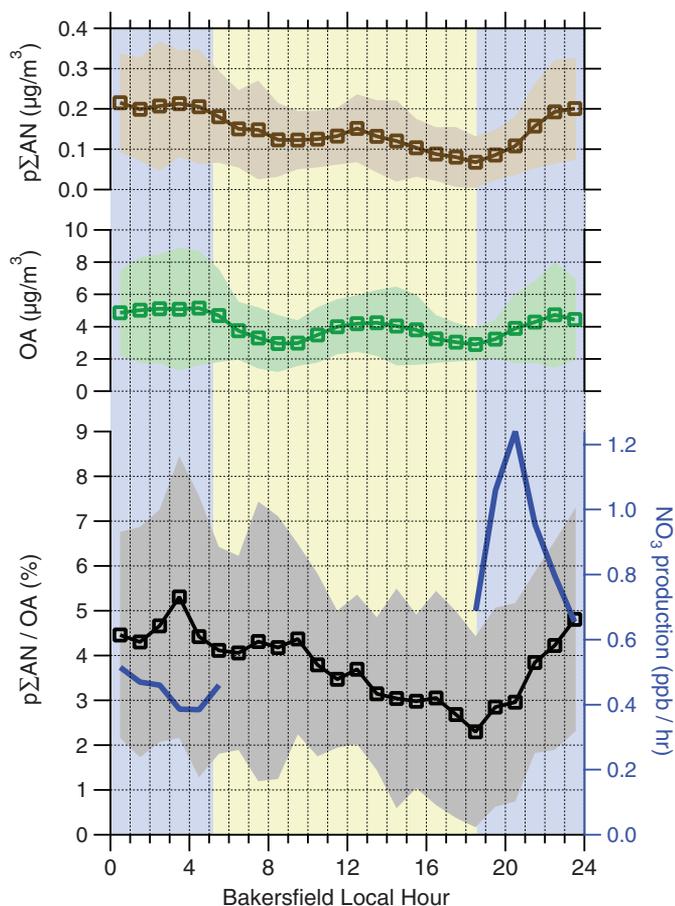


Fig. 1. Diurnal trends (means shown with $\pm 1\sigma$ ranges in shading) in pΣAN (brown), OA (green), pΣAN/OA (black), and NO₃ production rate (blue). Blue shading indicates nighttime (solar zenith angle > 85°), and yellow indicates daytime.

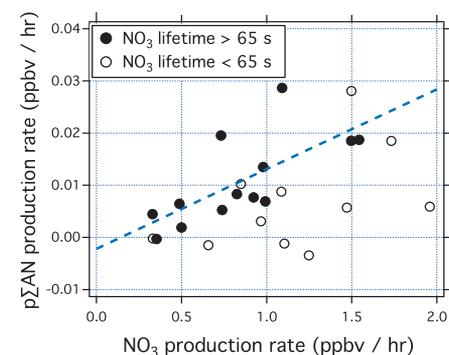
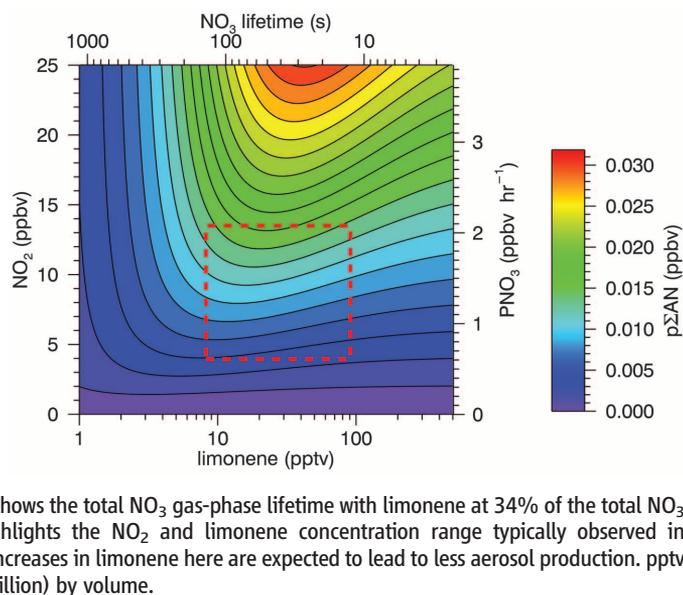


Fig. 2. Observations of trends in nighttime production rate of pΣAN with NO₃ production rate. Data are high NO₃ reactivity (open circles) and lower NO₃ reactivity (solid circles). Dashed blue line is a linear fit to low-reactivity data with a slope of 0.015 and $r = 0.73$.

Fig. 3. Simulation of multigenerational SOA formation from the reaction of NO_3 with limonene as a function of NO_2 and limonene at 50 ppb O_3 . We assume that Bakersfield (1 to 2 hours upwind) is the major NO_x source and therefore show contours that are ppb of $\text{p}\Sigma\text{AN}$ after 2-hour model runs. For longer runs (up to 5 hours), the $\text{p}\Sigma\text{AN}$ scaled approximately linearly with time. The production rates of NO_3 corresponding to the NO_2 concentration are shown



on the right axis. Top axis shows the total NO_3 gas-phase lifetime with limonene at 34% of the total NO_3 loss. Red dashed box highlights the NO_2 and limonene concentration range typically observed in Bakersfield, showing that increases in limonene here are expected to lead to less aerosol production. pptv (ppbv), parts per trillion (billion) by volume.

appreciable extent. The condensable nitrates that we observe in the particle phase are likely second- or higher-generation oxidation products, produced by the slower oxidation of the first-generation products (15, 16). Based on the measurements of RH, and aerosol surface area and composition, we estimate that N_2O_5 heterogeneous loss has a small impact on NO_3 concentration (<10%), and thus NO_3 variability is dominated by its source term (reaction 1) and gas-phase reactivity. Figure 2 also shows that the kinetics of aerosol RONO_2 formation are approximately linear with PNO_3 , indicating that aerosol precursors are abundant and that NO_3 production is rate limiting. Because this SOA is produced by reactions of NO_3 , it can be considered anthropogenic. Although the carbon may be of biogenic origin, without high NO_x emissions it would not be produced.

The observation that VOC with high SOA yields may suppress SOA formation is surprising. To demonstrate that this is kinetically possible in the NO_x/VOC regime observed in Bakersfield, we modeled SOA formation from NO_3 oxidation of limonene (Fig. 3). We use limonene as an example VOC because of its relatively high concentrations in Bakersfield and its high SOA yield, and because we have some knowledge of the kinetics of its oxidation products (16). Details of the box model used are included in the materials and methods SI. We find that because the second-generation products have SOA yields ~2.5 times as large as those of the first-generation products and that high concentrations of limonene inhibit the formation of these less-volatile products, SOA production slows in the high-limonene regime. At the same time, given sufficient O_3 , increases in NO_2 always lead to more SOA owing to the higher NO_3 production rate.

Our findings suggest that SOA formation via nighttime nitrate radical chemistry in Bakersfield is a large PM source, which frequently results in the daily maximum OA concentration during the sum-

mer. The high concentrations of NO_2 and O_3 at night resulted in very high NO_3 production rates [frequently greater than 1 part per billion (ppb) hour^{-1}]. Nevertheless, concentrations of reactive BVOCs were frequently high enough that $\text{p}\Sigma\text{AN}$ formation was inhibited, suggesting that the $\text{p}\Sigma\text{AN}$ precursors are less reactive than the primary VOCs and have a somewhat reduced volatility. A good correlation between production rates of NO_3 and $\text{p}\Sigma\text{AN}$ was observed, suggesting that the targeted reductions in NO_x at this location should reduce OA mass. Although attributing sources of daytime SOA as biogenic or anthropogenic remains challenging, our results show that $\text{p}\Sigma\text{AN}$ s are a large fraction of nighttime growth and likely a result of NO_3 chemistry. That this SOA would not be produced in the absence of NO_x makes nighttime $\text{p}\Sigma\text{AN}$ s a clear tracer for anthropogenically controlled SOA, regardless of the carbon source.

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Acknowledgments: This work is supported by the California Air Resources Board under grants CARB 08-316 and 09-328. E.C.B. was supported by NASA ESSF fellowship.

Supplementary Materials

www.sciencemag.org/cgi/content/full/337/6099/1210/DC1
Materials and Methods

Figs. S1 to S4

Table S1

References

6 March 2012; accepted 24 July 2012

10.1126/science.1221520

Predatory Fish Select for Coordinated Collective Motion in Virtual Prey

C. C. Ioannou,^{1,2*} V. Guttal,^{1,3} I. D. Couzin^{1*}

Movement in animal groups is highly varied and ranges from seemingly disordered motion in swarms to coordinated aligned motion in flocks and schools. These social interactions are often thought to reduce risk from predators, despite a lack of direct evidence. We investigated risk-related selection for collective motion by allowing real predators (bluegill sunfish) to hunt mobile virtual prey. By fusing simulated and real animal behavior, we isolated predator effects while controlling for confounding factors. Prey with a tendency to be attracted toward, and to align direction of travel with, near neighbors tended to form mobile coordinated groups and were rarely attacked. These results demonstrate that collective motion could evolve as a response to predation, without prey being able to detect and respond to predators.

From herding ungulates to shoaling fish, nesting birds, and swarming crickets, animals living in groups are generally less at risk from predators (1). Mechanisms include the

ability of groups to detect predators sooner and from a greater distance (the "many eyes" effect) and cognitive confusion of the predator, caused by having to choose among many possible targets