



Short Communication

Ozone from fireworks: Chemical processes or measurement interference?



Zheng Xu ^{a,b}, Wei Nie ^{a,b,*}, Xuguang Chi ^{a,b}, Xin Huang ^{a,b}, Longfei Zheng ^{a,b}, Zhengning Xu ^{a,b}, Jiaping Wang ^a, Yuning Xie ^a, Ximeng Qi ^a, Xinfeng Wang ^c, Likun Xue ^c, Aijun Ding ^{a,b}

^a Joint International Research Laboratory of Atmospheric and Earth System Sciences, School of Atmospheric Sciences, Nanjing University, Nanjing, Jiangsu Province, China

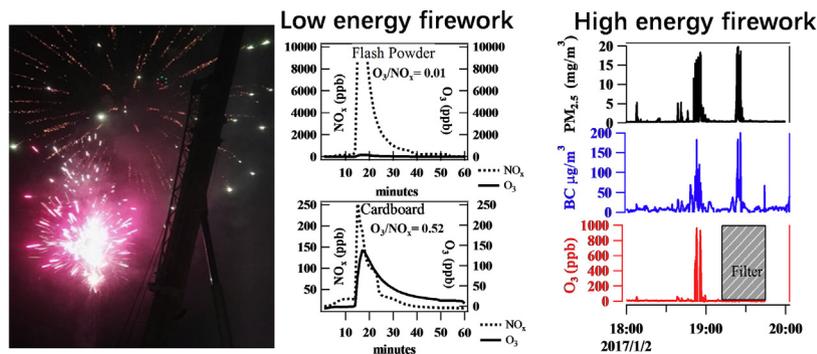
^b Collaborative Innovation Center of Climate Change, Jiangsu Province, China

^c Environment Research Institute, Shandong University, Ji'nan, Shandong Province, China

HIGHLIGHTS

- Strong ozone signal was detected in firework plumes using a UV-based analyzer.
- Photochemical processes were excluded to explain the observed ozone.
- VOCs interference was attributed to the observed ozone signal.
- Cardboard was more efficient source than flash powder to emit VOCs interferences.
- A signal of 3–8 ppbv O₃ could be detected in megacities during Chinese New Year.

GRAPHICAL ABSTRACT



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ABSTRACT

Fireworks have been identified as one ozone source by photolyzing NO₂ or O₂ and are believed to potentially be important for the nighttime ozone during firework events. In this study, we conducted both lab and field experiments to test two types of fireworks with low and high energy with the goal to distinguish whether the visible ozone signal during firework displays is real. The results suggest that previous understanding of the ozone formation mechanism during fireworks is misunderstood. Ultraviolet ray (UV)-based ozone monitors are interfered by aerosols and some specific VOCs. High-energy fireworks emit high concentrations of particular matters and low VOCs that the artificial ozone can be easily removed by an aerosol filter. Low-energy fireworks emit large amounts of VOCs mostly from the combustion of the cardboard from fireworks that largely interferes with the ozone monitor. Benzene and phenol might be major contributors to the artificial ozone signal. We further checked the nighttime ozone concentration in Jinan and Beijing, China, during Chinese New Year, a period with intense fireworks. A signal of 3–8 ppbv ozone was detected and positively correlated to NO and SO₂, suggesting a considerable influence of these chemicals in interfering with ambient ozone monitoring.

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1. Introduction

Ozone, as a strong oxidant, is harmful to human health and vegetation and plays a central role in atmospheric chemistry. Troposphere ozone is mainly produced via complex chemical reactions between

* Corresponding author at: Joint International Research Laboratory of Atmospheric and Earth System Sciences, School of Atmospheric Sciences, Nanjing University, Nanjing, Jiangsu Province, China.

E-mail address: niewei@nju.edu.cn (W. Nie).

nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the presence of sunlight (Seinfeld and Pandis, 2016; Wang et al., 2017). Recently, a few studies reported that O₃ can be generated from fireworks. Attri et al. (2001) first observed up to ppm ozone level near areas of firework displays and attributed this to the “stratosphere-like” mechanism of photolyzing O₂. The same mechanism was confirmed to have a significant positive correlation between ozone and UV irradiance during fireworks in the city of Alicante (Caballero et al., 2015). In addition to this “stratosphere-like” mechanism, Nishanth et al. (2012) ascribed fireworks related ozone to the photolysis of NO₂, since the light spectrum from the tested fireworks did not cover the cross section that can photolyze O₂.

O₃ is typically measured by using UV-absorption technology, which is possibly subjected to interference by water vapor, Hg and some VOCs (Kleindienst et al., 1993; Turnipseed et al., 2017; Williams et al., 2006; Wilson and Birks, 2006). Since these interferents generally have low concentrations in the atmosphere and are less sensitive to O₃ cross-section, their influence on O₃ measurement should be negligible in most cases. However, fireworks are intensive sources of plenty of air pollutants, such as sulfur dioxide, carbon dioxide, carbon monoxide, suspended particles and VOCs (Li et al., 2013; Lin, 2016; Nishanth et al., 2012). These intensive emissions have the potential to interfere with ozone measurements. In a recent study by Fiedrich et al. (2017), O₃ formation was not detected using a selective O₃-Long Path Absorption Photometer (O₃-LOPAP) during firework displays in the laboratory. They attributed the observed ozone during ambient fireworks to the co-emitted VOCs. This is, to our best knowledge, the only work that notes that the O₃ signal from fireworks is artificial. However, there are still several open questions left. First, is the entire observed ozone from fireworks artificial? Is it possible that some high-energy fireworks (e.g., display shell) can form ozone with stronger light and higher temperature released? Second, which specific species of VOCs interfere with these measurements? Third, what is the influence of these interferences on the ambient O₃ monitoring at a city level?

China is the world's largest producer, consumer and exporter of fireworks (<http://english.cntv.cn/program/newshour/20140118/102468.shtml>). Large mount fireworks are intensively displayed during national festivals, especially Chinese New Year, which can induce serious air pollutions (Huang et al., 2012; Shi et al., 2011; Wang et al., 2007). If ozone is really formed from fireworks, they will produce considerable additional oxidants during the nighttime to exacerbate air pollution. In this study, we conducted both lab and field experiments to investigate whether the observed O₃ signal is real or artificial. Two types of fireworks with different energy levels were tested. The source profiles of VOCs emitted from fireworks were measured to identify the speciation of potential interferents. The influence of fireworks on ambient O₃ monitoring during Chinese New Year was finally evaluated in several megacities in China.

2. Experiments

2.1. Laboratory experiment

Pyrotechnical material was burnt inside a cylindrical acrylic glass flow reactor with an inner diameter of 10 cm and a length of 80 cm. The burning time was manually controlled to 5 s to avoid too high of concentrations of emissions. The smoke from fireworks was carried by 500 cm³ clean air through the flow tube and diluted 20 times before being detected with an ozone analyzer and a NO_x analyzer. In the experiment, gas bags were used to collect the sample gases to be detected using a Proton-transfer-reaction mass spectrometry (PTR-MS) after further dilution. The setup was shown in Fig. 1.

2.2. Field experiment

Display shell samples were selected as a form of high-energy fireworks, which cannot be tested in the flow reactor. A field study was

thus conducted to measure the possible ozone signals inside the firework plumes. The display shell was launched to the height of 70 m before exploding. The emitted smoke plume from the display shell was measured by using a rotor-unmanned helicopter loading the portable analyzer on the downwind of ~20 m. Two-group 10-minute display shells were tested.

2.3. Instrumentation

In the flow tube laboratory experiment, NO and NO₂ were measured using a chemiluminescence analyzer with a molybdenum converter (Teledyne API, T200, with a molybdenum converter). The time resolution was 1 min, and the detection limits (3 s) were 2 ppb for NO and 3 ppb for NO₂. Ozone (O₃) was measured using a commercial O₃ monitor (Teledyne API, T300), which is based on UV absorption at λ = ~254 nm. The time resolution and detection limit (3 s) were 1 min and 5 ppbv, respectively. The VOCs were measured using the PTR-TOF-MS (IONICON, PTR-TOF 1000), with the sensitivity of >40 cps/ppbv (Benzene) and the resolution of >1500.

In the field experiment, ozone was measured using a portable analyzer based on UV absorption at λ = 254 nm (2B Technologies, POM). The PM_{2.5} and BC were also measured using the portable analyzers (TSI Sidepak AM510 and Magee Scientific AE51, respectively). The eight-rotor unmanned helicopter (DJI, SPREADING WINGS S1000+) was used to load the portable analyzers.

3. Results and discussion

3.1. Ozone-like substances from fireworks

A flow reactor study was conducted with a pencil sparkler to investigate the influence of firework emissions on ozone measurement. The results are shown in Fig. 2(a). Compared to a previous study by Attri et al. (2001), in which the concentrations of NO and NO₂ remained constant during the O₃ burst, the increased ozone observed in this experiment strongly correlated to NO, with the ratio of O₃/NO_x being approximately 0.12. During the well-known reaction between O₃ and NO, the lifetime of O₃ under these conditions (NO ~ 1000 ppbv, O₃ ~ 180 ppbv) was approximately 5 s, which is much lower than the resistance time (2 min) of the flow tube. These results suggest that the observed O₃-like substance here was likely caused by measurement interference. The light spectrum was measured to investigate if some ozone, beside the interferent, can be formed by the photolysis of O₂ or NO₂. As shown in Fig. S1, the light released from the fireworks was concentrated in the visible region of 500–550 nm, which is hard to photolyze oxygen (<240 nm) and NO₂ (350–450 nm), further confirming that interference, but not real ozone, was formed from the fireworks.

To investigate the source of these O₃-like substances, the pencil sparker was separated into its flash powder and cardboard components in the following experiments. Since NO_x is a well-known chemical emitted from fireworks, we used the O₃/NO_x ratio to evaluate the relative O₃ signal. As shown in Fig. 2b–c, burning of flash powder, which should release stronger light and more heat, revealed much lower O₃ signals (O₃/NO_x ~ 0.01) than from burning cardboard (O₃/NO_x ~ 0.52). One possible explanation for this is that the material of cardboard is similar to biomass, which can emit large amounts of VOCs (Yuan et al., 2010) to

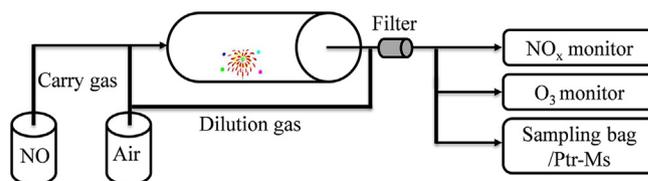


Fig. 1. Laboratory experimental setup for the measurements of emission of firework.

interfere with O₃ measurements. We double-checked this phenomenon with another type of biomass, tobacco, which showed an even higher O₃ to NO_x ratio (~0.58). These results suggest that the detected ozone using a UV-based instrument during fireworks was more likely due to measurement interferences induced by VOCs, emitted mostly from the packaging papers.

A PTR-MS was then used to detect the VOCs emitted from the above four types of materials to investigate the specific VOCs species that interfere with O₃ measurements during fireworks. The concentrations of 5 selected VOC species that have overlapped absorption cross-sections and can exist in potentially high concentrations, including xylene, phenol, o-Nitrophenol, benzene and toluene, as well as O₃ signal and NO_x, are illustrated in Table 1. In general, high concentrations of VOCs were emitted from the combustion of all these four materials. Total emitted VOCs were more than one order of magnitude higher than the detected O₃ signal. Flash powder, benzene and toluene emitted ozone intensively and were potentially the major contributors that interfered with O₃ measurements. Meanwhile, for cardboard and tobacco, phenol was the most abundant species that interfered with O₃ measurements. Noting that the burning rates of flash powder were much higher than those of biomass-like substances (e.g., cardboard and tobacco), the related emission intensity was thus significantly stronger, which resulted in a higher detected instantaneous signal of O₃. However, the effective emission of flash powder, indicated by O₃/NO_x, was much lower.

3.2. Field test for high energy display shells

In case of the numerous types of fireworks, our lab experiment using a pencil sparkler, which is low-energy firework, cannot exclude the possibility that some high-energy fireworks can produce ozone by photochemistry. We therefore tested a display shell, a typically high-energy firework, with a field experiment. Portable equipment fixed on an unmanned helicopter was used to monitor the PM_{2.5}, BC and O₃ concentrations in the smoke plume emitted from the firework display. Two rounds of experiments were conducted with the portable ozone monitor without or with an inline filter. As shown in Fig. 3, high concentrations of

Table 1

The VOCs, O₃ and NO_x concentrations detected from the burning plumes of four different materials, including a pencil sparkler, flash powder, cardboard covering of the flash powder and tobacco.

	Pencil sparkler	Flash powder	Cardboard	Tobacco
Total VOCs (ppm)	1.1	5.1	3.3	10.1
Xylene (ppb)	74.4	60.9	79.5	105
Phenol (ppb)	107.1	92.7	105.9	300
o-Nitrophenol (ppb)	7.08	6.09	6	6
Benzene (ppb)	132	840	72	375
Toluene (ppb)	57.9	122.7	64.5	222.6
O ₃ (ppb)	103	152	92	208
NO _x (ppm)	1.02	15.4	0.13	0.32
O ₃ /NO _x	0.1	0.01	0.71	0.65

PM_{2.5} (up to 20 mg/m³) and O₃ (up to 2 ppm) were detected and strongly correlated to each other in the first experiment. In the second experiment, the ozone was removed using an inline filter, suggesting that the “ozone signal” observed in the first experiment was interference induced by the aerosols emitted from the display shell. These results confirmed that fireworks cannot produce O₃ via a photochemical pathway, even with high-energy display shell. In addition, since the displaying of the display shell was mainly due to the combustion of the flash powder, these results supported that flash powder had a very low efficiency to release the gas phase ozone-like substance.

3.3. The influence of firework-induced artificial O₃ in the ambient environment

To evaluate the influence of artificial O₃ from fireworks on the ambient environment, we analyzed a field campaign dataset in Jinan during Chinese New Year of 2007 (Yang et al., 2014) and a routine air pollution monitoring dataset from 6 stations in Beijing during Chinese New Year of 2016. During the Jinan campaign, high concentrations of NO_x and SO₂ were observed in the firework plumes (See Figs. 4b, S2). Considerable O₃ concentrations were detected by the monitor, and showed a

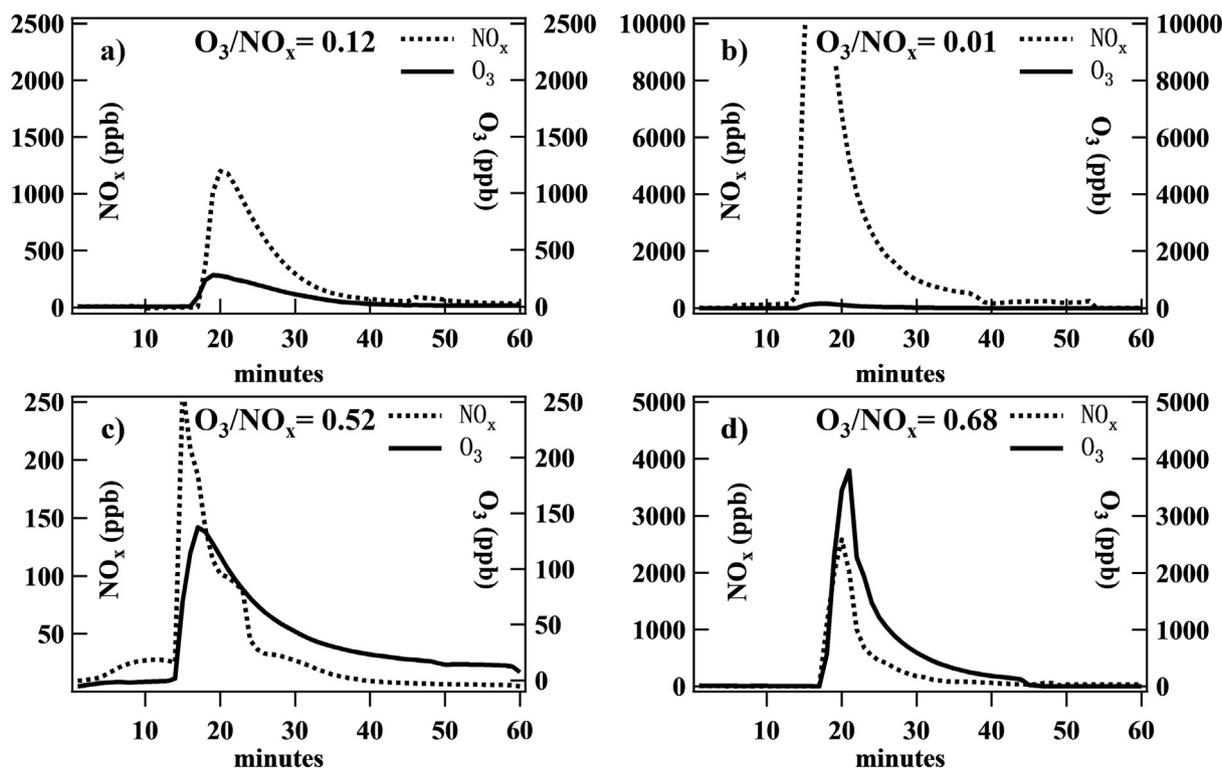


Fig. 2. The concentration of NO_x and O₃ as a function of time after lighting the pencil sparkler (a), flash powder (b), cardboard covering flash powder (c) and tobacco (d).

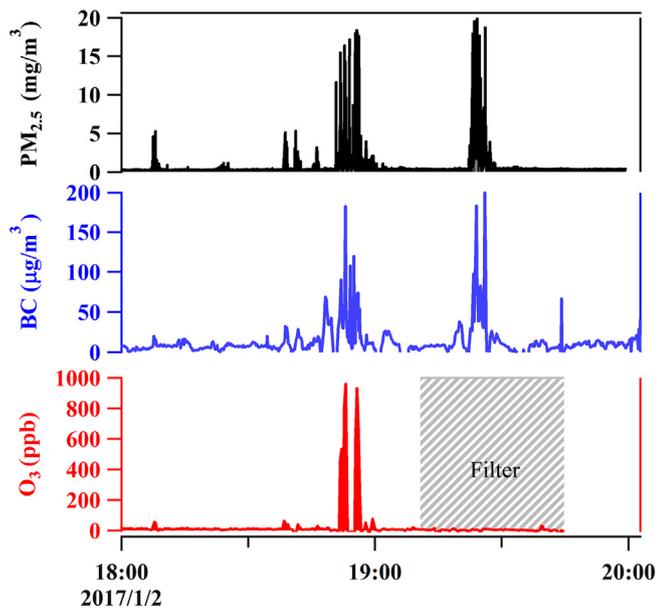


Fig. 3. Unmanned rotorcraft measurement of $PM_{2.5}$, BC and O_3 in the plumes of display shell emission.

positive correlation with NO concentrations, indicating that the observed O_3 signal was interference induced by the fireworks. The maximum ozone signal was approximately 8 ppb when the NO concentration was approximately 180 ppb and SO_2 was approximately 500 ppb.

The dataset of air pollution monitoring in Beijing was further analyzed during Chinese New Year of 2016 to evaluate the potential influence of O_3 interference at a city level (Fig. S3). Since firework displays were not homogeneously distributed, ambient O_3 around the stations far from the firework source regions cannot be fully titrated by the emitted NO and make the VOC-induced interference hard to be evaluated. Therefore, we selected 6 stations that experienced obvious emission plumes from the total 12 air quality stations. Noting that NO

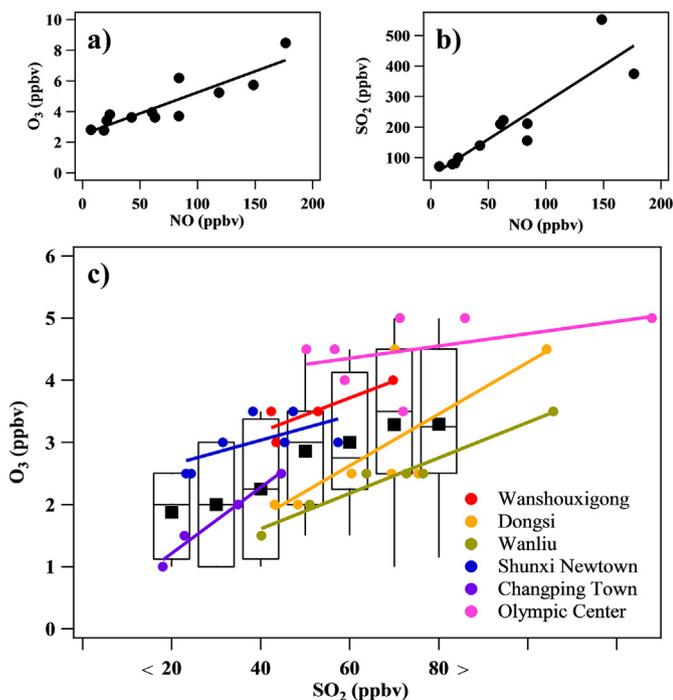


Fig. 4. Scatter plot of (a) O_3 and NO, (b) SO_2 and NO during the Chinese New Year 2007 in Jinan, and (c) O_3 and SO_2 during the Chinese New Year 2016 in Beijing.

concentrations were unavailable from this database, SO_2 concentration was used as a trace of firework plume (Fig. S4). As shown in Fig. 4(C), a positive correlation between O_3 and SO_2 was commonly observed in these six stations with stronger firework plumes. On average, the artificial O_3 can reach approximately 5 ppb in the firework plumes in Beijing. This artificial O_3 may mislead our understanding of nighttime chemistry.

4. Summary

In this study, we demonstrated that the previously reported ozone formation from fireworks is actually interference induced by UV-absorbed VOCs. Both low- and high-energy fireworks cannot photolyze NO_2 or O_2 to produce O_3 via photochemical pathways. Compared to the flash powder, the combustion of cardboard is a more efficient source to release VOCs that interfere with UV-based O_3 monitor. Benzene and phenol are recognized as the major contributors to the artificial ozone signal. This artificial ozone could contribute a ppb-level ozone signal (with an observed maximum of 8 ppb) during nights of intensive fireworks, and may mislead our understanding on the nighttime chemistry. For the further implication, the UV-based method with the conventional O_3 scrubber (MnO_2) should be carefully used for measurement of O_3 in the environment with strong VOCs emission, such as vehicle or biomass burning. In these areas, more selective method, such as the UV absorbance with the O_3 scrubber based on the titration of NO to O_3 or O_3 -LOPAP, are recommended.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.03.203>.

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