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Short Communication

Ozone from fireworks: Chemical processes or measurement interference?

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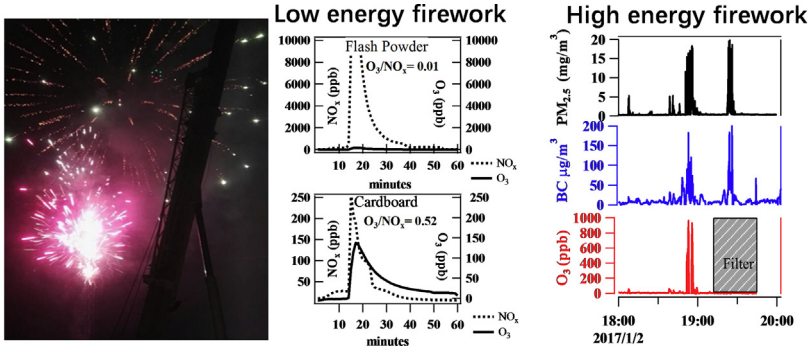
HIGHLIGHTS

- 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 O_3 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 NO_2 or O_2 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 SO_2, 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

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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 O_3 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 O_2. 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 NO_2, since the light spectrum from the tested fireworks did not cover the cross section that can photolyze O_2.

O_3 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 O_3 cross-section, their influence on O_3 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), O_3 formation was not detected using a selective O_3 -Long Path Absorption Photometer (O_3-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 O_3 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 O_3 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 O_3 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 O_3 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 cm^3 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 NO_2 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 NO_2. Ozone (O_3) was measured using a commercial O_3 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 NO_2 remained constant during the O_3 burst, the increased ozone observed in this experiment strongly correlated to NO, with the ratio of O_3/NO_x being approximately 0.12. During the well-known reaction between O_3 and NO, the lifetime of O_3 under these conditions (NO ~ 1000 ppbv, O_3 ~ 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 O_3-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 O_2 or NO_2. 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 NO_2 (350–450 nm), further confirming that interference, but not real ozone, was formed from the fireworks.

To investigate the source of these O_3-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 O_3/NO_x ratio to evaluate the relative O_3 signal. As shown in Fig. 2b–c, burning of flash powder, which should release stronger light and more heat, revealed much lower O_3 signals (O_3/NO_x ~ 0.01) than from burning cardboard (O_3/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

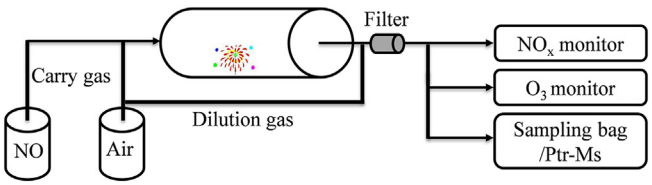

Fig. 1. Laboratory experimental setup for the measurements of emission of firework.

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