RELEASES OF HEXACHLOROBENZENE AND OTHER POPS FROM FIREWORKS

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Introduction

Combustion is a major source of airborne pollutants. Among many combustion processes, setting off of fireworks stands out due to its emissions of a large variety of air pollutants including combustion products of gun powder, metals used for colorization and many other additives. Earlier studies have shown significant formation and emission of organic micropollutants, such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from fireworks[1]. In contrast to other combustion processes, air pollutants from deflagration of fireworks are released without the possibilities of restraining techniques such as filtration. Thus, any additives, which may lead to discharge of hazardous air pollutants, have to be well considered.

Additives acting as chlorine donors are used for flame coloring in fireworks, e.g. blue color of copper is intensified with organic chemicals with high chlorine content. For this purpose, organochlorine compounds such as chlorobutyl rubber, hexachloroethane, polyvinyl chloride and hexachlorocyclohexanes (HCH) were suggested in a standard reference on fireworks[2]. Investigations of additives in consumer fireworks by the Chemical Legislation European Enforcement Network (CLEEN)[3] in Denmark (2008-2010) and Austria (2009-2010) have revealed concentrations up to 4.4 wt% of hexachlorobenzene (HCB) that is also banned by the Stockholm Convention on persistent organic pollutants (POPs)[4]. Release of HCB into the air was documented by increased atmospheric concentrations of HCB observed in Dornbirn (Austria) during the traditional fireworks in celebration of the New Year[5]. As a consequence, in 2010 the project EuroPOP was set up by CLEEN aimed at a survey of the content of HCB in consumer fireworks used in European countries. Within the scope of the project a total of 409 samples have been analyzed in 11 countries and revealed 41 samples that contained HCB above the EuroPOP limit value of 50 mg/kg.

The present work is intended as a complementary field study on the trend of the atmospheric concentrations of chlorobenzenes (CBs, including HCB), chlorophenols (CPs, including pentachlorophenol (PCP)), and PCDD/Fs during firework events. Atmospheric concentrations of these air pollutants were determined in the city of Zurich around the Swiss National Day on August 1, 2011, which was celebrated by setting off of fireworks after nightfall. Results and multimedia mass balance modeling of total emissions and *per capita* amounts are comprehensively presented in Schmid at al.[6].

Materials and methods

Aerosols were collected at flow rates of 20 - 30 m^3/h on quartz microfiber filters (QFF) and downstream polyurethane foam filters (PUF) using high volume air samplers deployed in the city center of Zurich, Switzerland, (Kasernenhof, E 8°31'49'', N 47°22'39''). Sampling intervals were between 3 h during the firework event and 24 h for reference samples taken before and after the event. Meteorological conditions around August 1, 2011, were favorable for the study with a stable high pressure system remaining during the whole sampling period. Also one week before and two weeks after the holiday of August 1 when samples were taken for comparison, meteorological conditions were comparable to the holiday.

PUF and QFF were extracted separately with toluene followed by group separation of CBs, CPs, and PCDD/Fs. Phenols were converted to the corresponding anisoles with diazomethane. Quantitative determination of the analytes was achieved using gas chromatography/electron ionization high resolution mass spectrometry and selected ion monitoring (SIM). Quantification was based on signal areas of the SIM mass chromatograms. The target analytes included: hexachlorobenzene (HCB), pentachlorobenzene (PeCB), 1234-/1235-/1245-/tetrachlorobenzene (sum of tetrachlorobenzenes denoted Σ TeCB), pentachlorophenol (PCP), 2345-/2346-tetrachlorophenol (sum of tetrachlorophenols denoted Σ TeCP), and the 17 2,3,7,8-chlorosubstituted PCDD/Fs (Σ PCDD/Fs).

Extraction recoveries of QFF and PUF were between 33% and 90%. Limits of detection (LOD) based on a signal-to-noise ratio >3 were <30 fg/m^3, <200 fg/m^3 and 1-10 fg/m^3 for single CBs, CPs and PCDD/Fs, respectively.

Results and discussion

Air concentrations of CBs, CPs and PCDD/Fs are shown in Figure 1. The temporal trends of the air pollutants during the firework event exhibit culmination in the sampling intervals during and after the main firework activities. Detailed inspection reveals that the HCB air concentration peaks before the lower chlorinated CB homologues, the CPs and the PCDD/Fs that culminate in the subsequent interval. This finding insinuates different formation processes of these substances, e.g. formation of the retarded lower chlorinated CB homologues, the CPs and PCDD/Fs through transformation of HCB as a precursor. However, there is no dominating species. Hence, it is not clear which of these chemicals were already present in fireworks and released in the deflagration or which were the transformation products.

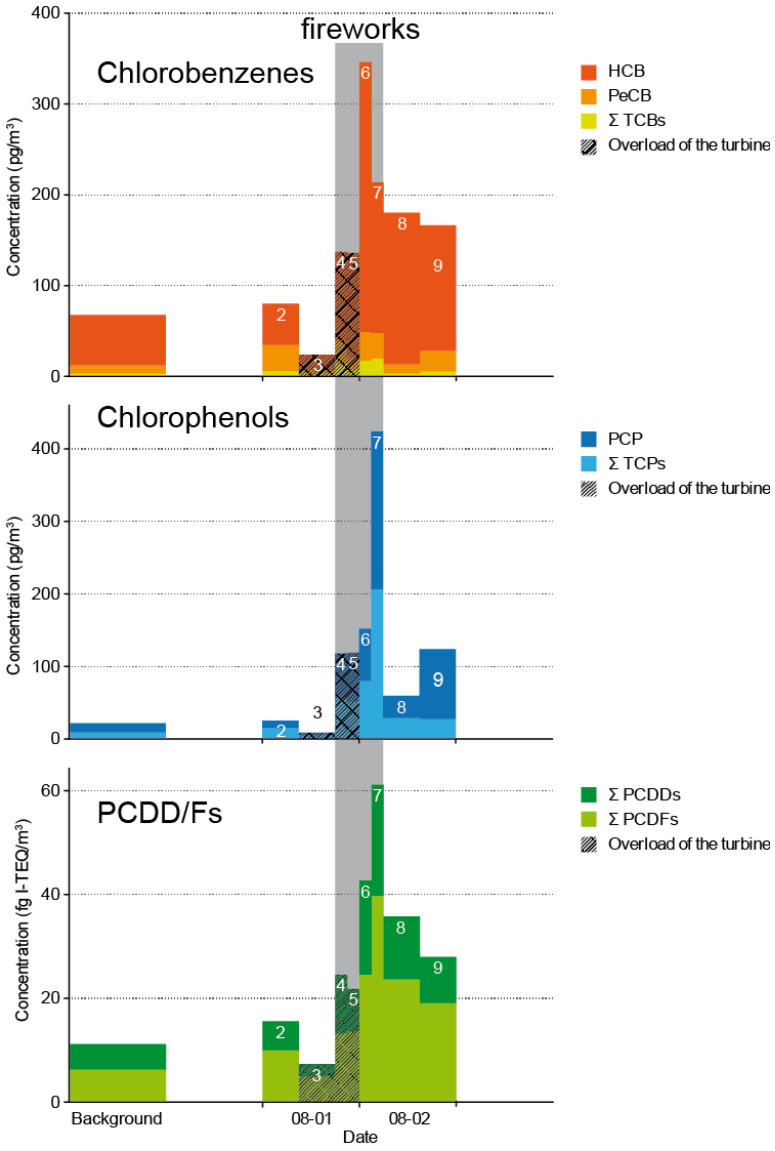

Figure 1: Atmospheric concentrations of CBs, CPs, and PCDD/Fs with phase of firework activities highlighted with grey bar. Background denotes average 24-h concentrations 1 week before and 2 weeks after August, 1.

The formation of air pollutants during the firework event is also documented by the observed sharp peaks of PM10, SO_2, CO and NMVOC (non-methane volatile organic compounds), which peaked simultaneously to HCB at around midnight, apart from SO_2 that peaked somewhat earlier (around 22:00, see Figure 2).

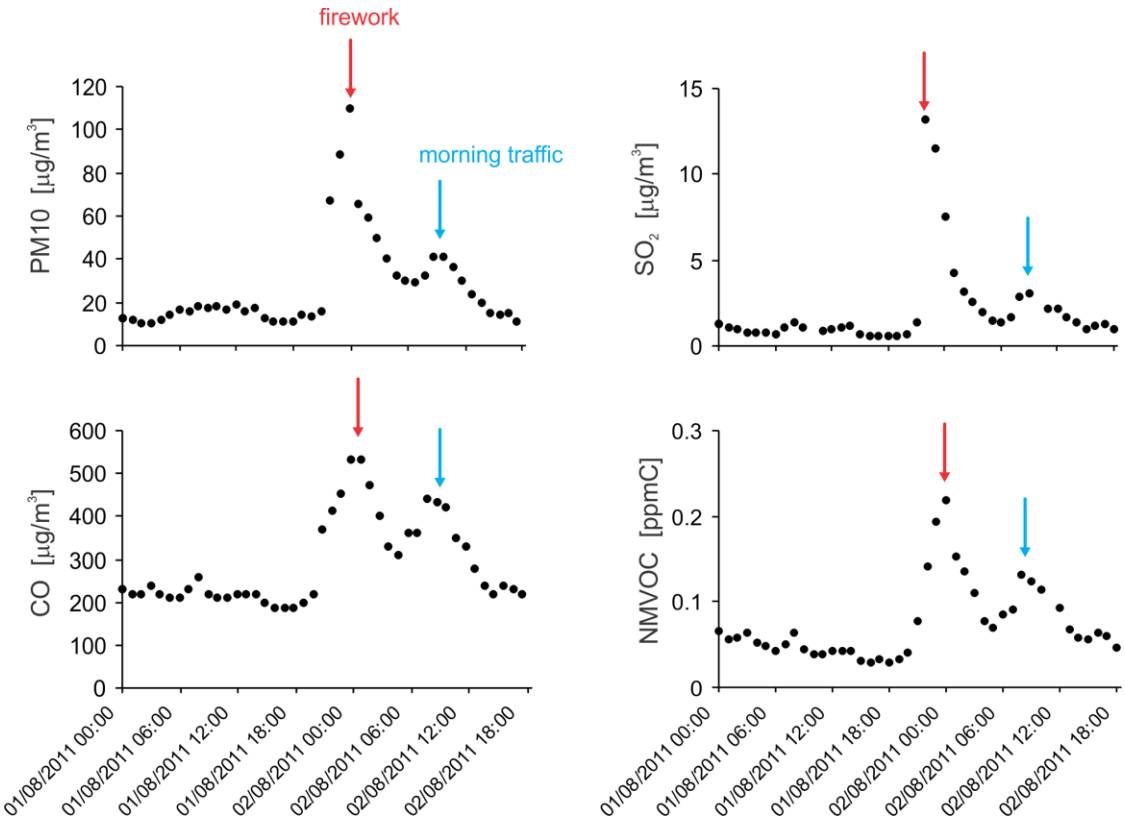

Figure 2: Concentrations of particulate matter with an aerodynamic diameter smaller than 10 µm (PM10), sulfur dioxide (SO_2), carbon monoxide (CO), and non methane volatile organic compounds (NMVOC) measured at the sampling site Zurich Kasernenhof around the Swiss National Day of August 1, 2011[7].

The study demonstrates substantial increases of atmospheric concentrations of CBs, CPs, and PCDD/Fs during widespread setting off of fireworks in celebration of holidays such as the National Day on August 1 in Switzerland in an urban environment. Maximum atmospheric concentrations are in the order of 10 times above background concentrations measured one week before and two weeks after the event, as well as above literature data surveyed in urban environments. Concentration increase affects all chlorination levels of the three compound classes to a similar degree. Thus, no distinct main component can be identified. It is, therefore, unclear which of the detected chemicals are already present in fireworks and which are formed during the deflagration of fireworks. Thus, the observed increase of air concentrations of CBs, CPs, and PCDD/Fs may be as well due to non-specific formation in the deflagration process similar to other processes such as waste incineration.

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