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Releases of chlorobenzenes, chlorophenols and dioxins during fireworks

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HIGHLIGHTS

- Hexachlorobenzene has been found as an additive in fireworks.
- Air concentrations of hexachlorobenzene were measured during the National Day with fireworks in the city of Zurich.
- During fireworks, concentrations of hexachlorobenzene increased by a factor of 10.
- Multimedia mass balance modeling was used to interpret the field measurements.
- Hexachlorobenzene from fireworks contributes up to 10% to the total emissions in Switzerland.

GRAPHICAL ABSTRACT

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ABSTRACT

In fireworks, organic additives with high chlorine content such as hexachlorobenzene (HCB) are used for the improvement of illumination effects. In the course of a monitoring campaign for the detection of HCB in fireworks, atmospheric concentrations of chlorobenzenes (CBs), chlorophenols (CPs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), were measured during the Swiss National holiday August 1, 2011 which is celebrated with fireworks nationwide. Samples were collected in the city of Zurich using high-volume air samplers equipped with quartz fiber filters and poly-urethane foam plugs. With one sampling period of 3 h, a peak HCB concentration of 297 pg m^{-3} was detected. Maximum total concentrations of pentachlorophenol and PCDD/Fs were 218 pg m^{-3} and 61 fg I-TEQ m^{-3}, respectively. These levels are in the order of ten times above background concentrations measured one week before and two weeks after the event. Atmospheric emissions of HCB and CPs were quantified using a multimedia mass balance model to interpret the field measurements resulting in total emissions of HCB and CPs during the event of 23 g and 25 g, respectively. Based on *per capita* amounts this corresponds to total annual emissions from fireworks of 1.5 kg for each of the two pollutants in Switzerland. Starting from an estimation of the total worldwide emissions of HCB, in Switzerland emissions from fireworks may represent about 2–14% of total HCB releases.

1. 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

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combustion products of gun powder, metals used for colorization and many other additives. For example, earlier studies have shown significant formation and emission of particulate matter, metals, and also organic micropollutants, such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from fireworks (Dyke et al., 1997; Fleischer et al., 1999; Lee et al., 1999; Croteau et al., 2010). 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 (Shimizu, 1981). However, certain of these organochlorine compounds, in particular the above mentioned PCDD/Fs, are of concern because of their hazardous properties, predominantly their environmental persistence (i.e. low degradability), their faculty to bioaccumulate, and their long-term toxic effects. They were therefore banned by the international Stockholm Convention on Persistent Organic Pollutants (POPs) that was enforced in 2004 (UNEP, 2004). Investigations of additives in consumer fireworks by the Chemical Legislation European Enforcement Network (CLEEN) (CLEEN Chemical Legislation European Enforcement Network, 2012) in Denmark (2008–2010) and Austria (2009–2010) have revealed concentrations up to 4.4 wt% of hexachlorobenzene (HCB), which was added to the Annex A (elimination) of the Stockholm Convention in 2004. 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 (Umweltinstitut Vorarlberg, 2009). 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 (CLEEN Chemical Legislation European Enforcement Network, 2012). Within the scope of the project, a total of 409 samples were analyzed in eleven countries, of which 41 samples contained HCB above the limit value of 50 mg kg^{-1} within the EuroPOP project.

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, Switzerland, around the Swiss National Day on August 1, 2011, which was celebrated by setting off of fireworks after nightfall. Samples were taken by high-volume air sampling using quartz fiber filters and polyurethane foam plugs. As firework activities in the evening of August 1 consist of many small-scale consumer fireworks let off nationwide, an urban environment was considered as a suitable and representative sampling location. For comparison, air samples were taken one week before and two weeks after the event. Furthermore, 24-h filter samples from the same site were analyzed for metals.

2. Material and methods

2.1. Air sampling

Sampling was performed in 2011 in the period around August 1, the Swiss National Day. Nationwide in Switzerland including Zurich, this day is celebrated with numerous small-scale private fireworks let off organized by inhabitants of the city (not large-scale public fireworks displays organized by the municipalities). The time resolution of the sampling was conceived to optimally cover the dynamics of the aerial emissions (see Table 1). Aerosols were collected on quartz microfiber filters (QFF; diameter 15 cm, type QMA, Whatman) backed out at 500 °C and downstream polyurethane foam plugs (PUF; diameter 10 cm, length 14 cm) pre-extracted with toluene in a Soxhlet extractor. Two high-volume air samplers (Digitel DA-80, Hegnau, Switzerland) were used.

The initial volumetric flow rate was 30 $m^3 h^{-1}$; due to overload caused by high ambient temperatures of the drawing pump it was reduced to 21 $m^3 h^{-1}$ from sample 6 onwards. For comparison, samples were collected on weekends one week before and two weeks after the event, *i.e.* on days with traffic density in the city comparable to the August 1 holiday, but no firework activities. In order to test the comparability of the two samplers, samples 1A and 1B were simultaneously collected. After collection, QFF and PUF samples were wrapped in aluminum foil, shrink-wrapped in polyethylene bags and stored at −20 °C until analysis. The samplers were deployed in the city center of Zurich (Kasernenhof, E 8°31′49″, N 47°22′39″, 409 m above sea level). This sampling station is located in a large courtyard (approx. 9000 m^2) and belongs to the Swiss National Air Pollution Monitoring Network (NABEL). Combustion-related air pollutants (particulate matter with an aerodynamic diameter lower than 10 μm (PM10), carbon monoxide (CO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2)), which are continuously monitored at this station are of additional interest for this study.

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 (Table 1).

Table 1
Sampling schedule (samples with suspected incomplete collection volume are marked with an asterisk) and meteorological conditions prevailing during the sampling campaign.

Sample	Start	Sampling duration (h)	Sampling rate ($m^3 h^{-1}$)	Sampling volume (m^3)	Average (min-max) air temperature (°C)	Average (min-max) wind speed (km h^{-1})
1A	07–24 00:00	24	30	720	13.5 (11.0–16.6)	8.5 (4.4–15.6)
1B	07–24 00:00	24	30	720	13.5 (11.0–16.6)	8.5 (4.4–15.6)
2	08–01 00:00	9	30	270	14.5 (13.0–16.9)	7.6 (4.8–10.)
3	08–01 09:00	9	30*	270	19.3 (14.7–23.6)	7.8 (5.0–10.3)
4	08–01 18:00	3	30*	90	22.8 (22.0–23.5)	6.6 (5.4–7.7)
5	08–01 21:00	3	30*	90	20.3 (19.4–21.1)	2.8 (2.4–3.1)
6	08–02 00:00	3	21	63	17.8 (16.9–18.6)	3.5 (2.6–5.1)
7	08–02 03:00	3	21	45	15.9 (15.4–16.4)	7.1 (5.5–8.8)
8	08–02 06:00	9	21	189	21.0 (15.2–27.8)	5.0 (3.1–7.8)
9	08–02 15:00	9	21	135	26.7 (22.1–29.0)	5.2 (1.6–8.2)
10	08–13 23:00	24	21	504	21.2 (17.3–25.5)	5.3 (2.8–10.2)
11	08–14 23:00	24	21	504	22.0 (17.6–27.9)	9.9 (1.5–22.1)