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QUANTIFICATION OF A MAJOR ANTHROPOGENIC COMBUSTION EMISSION PULSE OF POPS TO THE UK ATMOSPHERE

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Introduction. In the early hours of November the 5th, 1605, Guy Fawkes was discovered under the Houses of Parliament with the intention of killing King James I. After his capture, many Londoners celebrated by lighting fires in a thanksgiving for the saving of their King. Later, fireworks were introduced into the celebration and effigies of Guy Fawkes were burned. 'Guy Fawkes Night' or 'Bonfire Night' as it is more commonly known, manifests itself in the United Kingdom by the burning of bonfires accompanied by firework displays.

To lessen the impact on air quality, the Environment Agency advises people to attend public displays, as the cumulative effect of many small fires at individual homes is thought to have a greater adverse effect on air quality. Large scale public celebrations are usually more controlled, with measures being taken to ensure that materials placed on the fire are non-toxic, i.e. not from industrial sources. Conversely, it is very difficult to monitor small domestic fires and even industrial fires which are lit illegally, many of which are carried out on private property.

By the nature of their construction, mainly wood, and the potential temperature gradients found within a single bonfire, the release of PAHs as a consequence of incomplete combustion is possible. Previous work by Lee (1999)[1] has shown evidence of dioxin production under similar conditions. As domestic fires may include other man-made materials (i.e refuse), PAHs may not be the only SVOC found to increase during this period.

This study was designed to quantify the episodic release of persistent organic pollutants during the Bonfire celebrations of November 2000. Although previous work has been carried out to assess dioxin release during this event (Lee 1999)[1], this study focussed upon PAHs, PCBs and PBDEs. Such data are important, as national emission estimates may not include realistic data for this unique event. Back trajectory analysis (using the HYSPLIT model) will hopefully allow the origin of air masses throughout the sampling campaign to be determined.

Method. In order to assess the magnitude of any potential increase in POPs during the Bonfire event, it was important to measure air concentrations before, during and after the 5th of November. This was carried out by using Graseby-Anderson high volume air samplers, beginning on the 01/05/2000 and finishing on 13/05/2000. Samples were taken every day during the campaign, with greater temporal resolution from the 4th to the 7th of November. Each sampling point during these days was carried out in triplicate, to assess variation between samples and to allow bulked samples to be prepared if certain compounds were found to be below instrument detection limits. All samples were taken at a semi-urban location in Lancaster, North –West England.

A standard PS-1 module was used to house the sampling train, in this case being a combination of 2 pre-extracted (Soxhlet for 18 hours using DCM) polyurethane foam (PUF) plugs and 1 glass fibre filter (GFF) which had been baked out for 18 hours at 450°C in a muffle furnace. Following aspiration with ambient air, PUF plugs were stored in solvent rinsed jars (3x acetone, 3x hexane, 3x DCM) and GFFs were placed in solvent rinsed (same solvents used previously) foil packets. Both were subsequently placed in storage at -10°C.

Extraction and clean-up. Vapour phase (PUF) and particulate bound (GFF) samples were extracted separately in a soxhlet system.

A novel clean-up was developed and validated which utilised a combination of silica and neutral alumina (acting as a crude clean up column) and gel permeation chromatography (GPC). A chromatography column of 8mm internal diameter was constructed by slurry packing 1 g of activated alumina (baked out at 450°C), on top of which a slurry of 2g silica (baked out at 450°C) was added. A 1:1 mixture of hexane/DCM was used to create the slurry and introduce the sorbent to the column. The column was protected by finally introducing 0.5g of sodium sulphate (baked out at 450°C). Following sample introduction, 25ml of 1:1 hexane/DCM mixture was used to elute all the compounds of interest. The eluent was then reduced under a gentle flow of nitrogen to approximately 500µl.

A 12g GPC column, pre-washed with 30ml of 1:1 hexane/DCM, was used as the final method of clean-up. The reduced sample was introduced to the column and eluted with a total of 48ml of 1:1 mixture. The first 16ml of solution was found to contain unwanted co-extractives and was discarded. The remaining 32 ml of solvent was collected and reduced under nitrogen to 500µl.

Analysis. The reduced eluent was transferred, with three washes, to an injection vial. Deuterated PAH internal standards were added and the final injection solution was blown down to 500µl. The 1µl injection was equivalent to a volume loss of 0.2 % and was thought to be insignificant. After the addition of dodecane, which contained internal standards for PCB and PBDE analysis (^{13}C labelled), samples were further concentrated to 25µl. All analysis was carried out using GC-MS.

Results and discussion. *PAHs.* As expected, levels of PAH increased significantly over the sample period, with ∑PAH increasing from 43 ng/m^3 on 01/11/2000 to 200 ng/m^3 on 05/11/2000. Although the concentration of each compound increased during this period, the increase was not uniform. Naphthalene contributed most, accounting for 16 % of the observed total, with phenanthrene making up a further 14 %. However, phenanthrene had a higher background concentration, meaning the overall increase was approximately 7.5x, whereas naphthalene increased by ~ 17x.

PCBs. ∑PCB also increased, again with a maximum atmospheric concentration of 370 pg/m^3 found on the 05/05/2000, compared to background concentrations of ~ 150 pg/m^3. It is interesting to consider what the source of PCBs would have been. Usually, the bulk of the bonfires consist of wood / leaves, but some individuals undoubtedly use the bonfire as an opportunity to burn refuse.

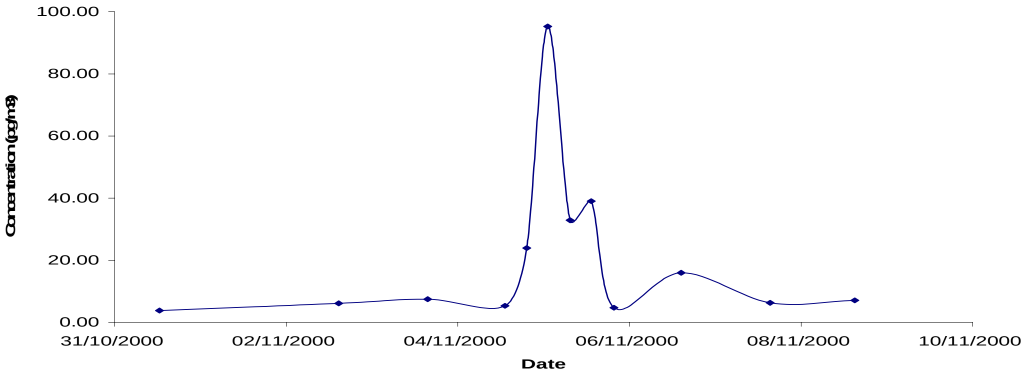

Figure 1. Total PBDE levels over the Bonfire Night period.

PBDEs. ∑PBDE concentrations over the Bonfire event are shown in figure 1. Background concentrations of ~ 4 pg/m^3 are consistent with data measured previously (Lee, 2003)[2]. However, a peak value of 95 pg/m^3 occurred on the 05/11/2000. Similar to PCB emission, the release of PBDEs from fires is thought to occur on the domestic scale where the burning of household waste is potentially more common. We hypothesise that the inclusion of soft furnishings and mattresses on smaller scale fires provide a source of PBDEs which are released during the early stages of combustion. This indicates that the temperatures within a bonfire are not sufficient enough to cause complete debromination of PBDEs.

Particulate fraction. Table 1 displays the percentage contribution made by particulate associated compounds to the observed total, clearly showing that unlike the low-molecular weight PAHs and PCBs, PBDEs are predominantly found in the particulate phase. Harrison (1999)[3] has shown an increase in PM_{10} particles as a consequence of combustion related activities over the Bonfire Night period. It is postulated that the rapid cooling of man made fibres in ambient air at 8°C, originating from soft furnishings, slows down and stops the rapid debromination that would be expected to occur at temperatures in excess of 700°C found within the fire. It is the association of PBDEs with PM_{10} that would enable their dispersion and inhalation.

Air Masses. Determination of the air mass origin is of great importance when attempting to calculate emissions estimates for such a unique event. Consequently, backwards air trajectories were calculated using the HYSPLIT model (NOAA Air Research Laboratories) for each sample. Figure 2 shows the potential origin of the air mass responsible for the concentration pulse seen on 05/05/2000, a time point in which increases in all compounds were observed. This would indicate that the measured air concentrations were the result of local emissions within the Lancaster region.

Table 1. The % contribution made by the particulate fraction to the observed total (A) and the total contribution of that compound to the overall total (B) on 05/05/2000.

Compound	A	B
PBDE 47	100	7.7
PBDE 99	100	15.1
Naphthalene	1	16.7
Phenanthrene	1.7	14.7
PCB 22	1.5	14.2
PCB28	2.2	15.2

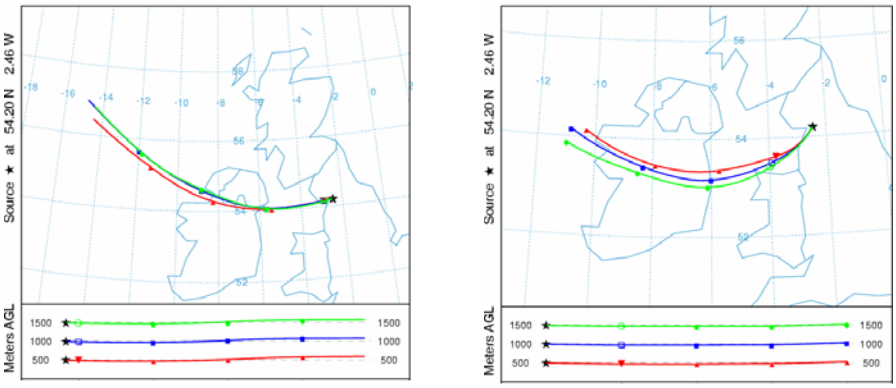

Figure 2. Back trajectories for 05/05/2000 (using HYSPLIT isobaric model) showing the origin of air masses at two time points and at three altitudes above ground level (AGL).

Conclusions. The episodic release of pollutants by a large scale anthropogenic event, such as Bonfire Night, has been shown to release a wide range of persistent organic pollutants. The observed increase has been assigned to the burning of a wide range of materials. Wood used to fuel the fires is potentially responsible for the increases in PAH, with higher levels of PCBs and PBDEs thought to be the result of smaller, domestic fires with a more heterogeneous fuel content. High levels recorded during this campaign were assigned to local emissions along the West coast, indicating that concentrations found on the East coast are potentially even higher.

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References:

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