# The Lancaster Environment Centre

**Annual Report for 2008 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network**

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# Executive Summary.

This report contains the 2008 ambient air concentration data for polychlorinated biphenyls (PCBs), polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) from the Toxic Organic Micro-pollutants Monitoring Network  (TOMPs) which is funded by the Department for Environment, Food and Rural Affairs (Defra). In 2008, 37 PCBs congeners, 4 co-planar PCB congeners, 10 furans congeners and 7 dioxin congeners were measured in each sample. The TOMPs network includes sites in London, Stoke Ferry (Norfolk), Manchester, Hazelrigg (Lancashire), High Muffles (North Yorkshire) and Middlesbrough. In July 2007 the Middlesbrough site was closed, which was followed in October 2008 by the Stoke Ferry site. These sites were replaced with two new sites located at Auchencorth Moss (Midlothian) and Weybourne (Norfolk). The aim of the TOMPs network, which has operated since 1991, is to provide information on the ambient levels of organic pollutants in the UK through monitoring of air concentrations at six sites. The results and other related scientific work are used to inform policy development on exposure to persistent organic pollutants (POPs).

The TOMPs network provides data to inform the public of air quality, and information to support the development of policy to protect the environment. The specific aims of the TOMPs programme are:

- To identify sources of a range of POPs in the UKs atmosphere.
- To quantify sources that are regarded as potentially significant.
- To measure concentrations of TOMPs in ambient air in UK cities, in order to assess both human exposure and the relationship between source emissions and levels in the ambient atmosphere.

There are a number of international instruments aimed at reducing releases into the environment, such as the 1998 UN/ECE Protocol on Persistent Organic Pollutants made under the Convention on Long-Range Transboundary Air Pollution, and the Stockholm Convention (SC) on POPs. The TOMPs network provides valuable evidence for effectiveness of such agreements on the concentrations of a range of POPs in UK urban and rural ambient air.

# Health Based standards

In order to reduce human exposure and environmental impact of POPs there are commitments from the Governments of many countries (including the UK), together with other agreed international measures, to achieve reductions of sources of these contaminants to the environment. For example, in October 2001, the European Commission published a Community Strategy for Dioxins, Furans and PCBs that set out a series of short, medium and long-term actions to address these substances in the environment, food and animal feed. The main objectives of the strategy are to:

- assess the current state of the environment and ecosystems;
- reduce human exposure to dioxins and PCBs in the short-term and to maintain human exposure at safe levels in the medium to long term;
- reduce environmental effects from dioxins and PCBs; and
- reduce human intake levels below 14 pg WHO-TEQ per kg bodyweight per week.

There are a number of international instruments aimed at reducing releases into the environment, such as the 1998 UN/ECE Protocol on Persistent Organic Pollutants, made under the Convention on Long-Range Transboundary Air Pollution, and the Stockholm Convention (SC) on POPs. The UK also has commitments under the North Sea Conference and the Oslo and Paris Commissions (OSPARCOM) to assess inputs of hazardous air pollutants to the North Sea. For many substances, atmospheric inputs provide an important contribution to the environmental burden. The UK also provides measurement data to EMEP (the co-operative programme on monitoring and evaluation of Long-Range Air Pollution in Europe) on these compounds. The UK data from the TOMPs network has been very valuable for modelling efforts conducted under EMEP at MSC-East, and under a separate Defra contract to Lancaster University on the national, regional and global scale modelling of POPs.

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## 1. Introduction

Lancaster University (LU) has been involved in the TOMPs programme since its inception in 1990. LU currently manages the programme on behalf of Defra which operates six sites, three urban, two rural and one semi-rural. Atmospheric sampling is carried out at each site, collecting a biweekly sample which are bulked to provide quarterly data. These data are reported to Defra and published on the air quality data website www.airquality.co.uk. The other sites are maintained via sub-contracts; London AEA Energy and Environment, Auchencorth Centre for Ecology and Hydrology (CEH) and Weybourne University of East Anglia. The analytes currently quantified at Lancaster University are PCDD/Fs ('dioxins') and PCBs. PAHs are quantified and reported separately under another monitoring programme currently run by AEA Energy and Environment.

This annual report for polychlorinated biphenyls (PCBs) polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) includes:

- Information on PCBs, PCDDs and PCDFs
- A summary of network operations including details of monitoring sites, equipment employed, details of site installations/removals, site calibration visits and equipment servicing and breakdowns
- A summary of the analytical procedure used to detect PCBs, PCDDs and PCDFs.
- Trends in estimated sources of PCBs, PCDDs and PCDFs in the UK
- Review of annual mean and quarterly concentration.

## 2. Background to PCBs, PCDDs and PCDFs.

PCBs were first synthesized in 1881 by Schmidt and Schulz but their commercial production only began in 1929 in USA (*Danse et al.,* 1997). They were marked as mixed products under various trade names depending on the country where they were produced such as Aroclor (Monosanto, USA), Phenochlor and Clophen (Bayer, EU). Because of high chemical and thermal stability, electrical resistance, low or no flammability, PCBs had extensive applications. They have been used as dielectric fluids in capacitors and transformers, in plasticizers, adhesives, inks,

sealants and surface coatings (*Eduljee*, 1988; *de Voogt and Brinkman*, 1989; *Herrad et al.,* 1994). Their basic structure is a biphenyl backbone with one to ten chlorine substituents and a general structure of $C_{12}H_{10-n}Cl_n$ (n=1-10) (Figure 2).

$$Cl_n \qquad Cl_m$$
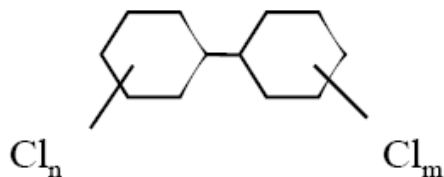
There are 209 different congeners with one to ten chlorines atoms attached. The International Council for the Exploration of the Seas (ICES) 7 PCB congeners generally reported in environmental samples are PCB 28 (2,4,4'-triPCB), PCB 52 (2,2',5,5'-tetraCB), PCB 101 (2,2',4,5,5'-pentaCB), PCB 118 (2,3',4,4',5-heptaCB), PCB 138 (2,2',3,4,4',5-heptaCB), PCB 153 (2,2',4,4',5,5'-heptaCB), PCB 180 (2,2',3,4,4',5,5'-heptaCB), although several dozen different congeners can be found in the environment.

Production of PCBs peaked in the 1960s in Europe and USA and terminated in the mid 1970s, when they where ultimately banned in the late 1970s/early 1980s (*de Voogt and Brinkman*, 1989). The most recent inventory of PCB production estimates the cumulative global production of PCBs at 1.3 million tonnes (*Breivik et al*., 2002). Approximately 97% of this has been used in the Northern Hemisphere, mostly between 30 °N and 60 °N (*Breivik et al.,* 2002). Before the ban, PCBs had entered the environment through point and diffusive sources such as landfill sites, accidental releases/spillages via leaking during commercial use of electrical equipment and transformer and capacitor fires, incineration of PCB waste etc. (*de Voogt and Brinkman*, 1989; *Danse et al.,* 1997). Current atmospheric levels of PCBs in the environment are due to on-going primary anthropogenic emissions (e.g. accidental release of products or materials containing PCBs), volatilization from environmental reservoirs which have previously received PCBs (e.g. sea and soil) or incidental formation of some congeners during combustion processes (*Breivik et al*., 2002).

The term Dioxin is commonly used to refer to a family of toxic chemicals that all share a similar chemical structure and a common mechanism of toxic action. This family includes seven of the polychlorinated dibenzo dioxins (PCDDs), ten of the polychlorinated dibenzo furans (PCDFs) and twelve of the polychlorinated biphenyls (PCBs). PCDDs and PCDFs are not commercial chemical products but are trace level unintentional byproducts of most forms of combustion and several industrial chemical processes. PCBs were produced commercially in large quantities until production was stopped in 1977. Dioxin levels in the environment have been declining since the early seventies and have been the subject of a number of federal and state regulations and clean-up actions; however, current exposures levels still remain a concern.
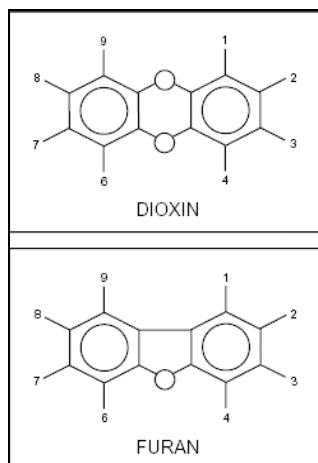


### 3. TOMPs sites operating in 2008

In 2008 the TOMPs programme operated 6 sites:

| London | urban site established in 1991 |
|---|---|
| Manchester | urban site established in 1991 |
| Middlesbrough | urban site established in 1991, closed summer 2008 |
| Hazelrigg | semi-rural site established in 1992 |
| High Muffles (North Yorkshire) | rural site established in 1999 |
| Auchencorth Moss | rural site established in 2008 |
| Weybourne | Rural site established at the end of 2008 |

The sites consist of three urban locations in London (LON), Manchester (MAN), and Middlesbrough (MB), two rural sites at High Muffles (HM, North Yorkshire) and Auchencorth Moss (Mid Lothian), and one semirural site at Hazelrigg (HR, Lancashire). At the rural and semirural sites, samplers are located away from major roads, whereas at the urban sites samplers are located in the city centre on the roof of a building. The locations of the current samplers in the network are shown in Figure 1.
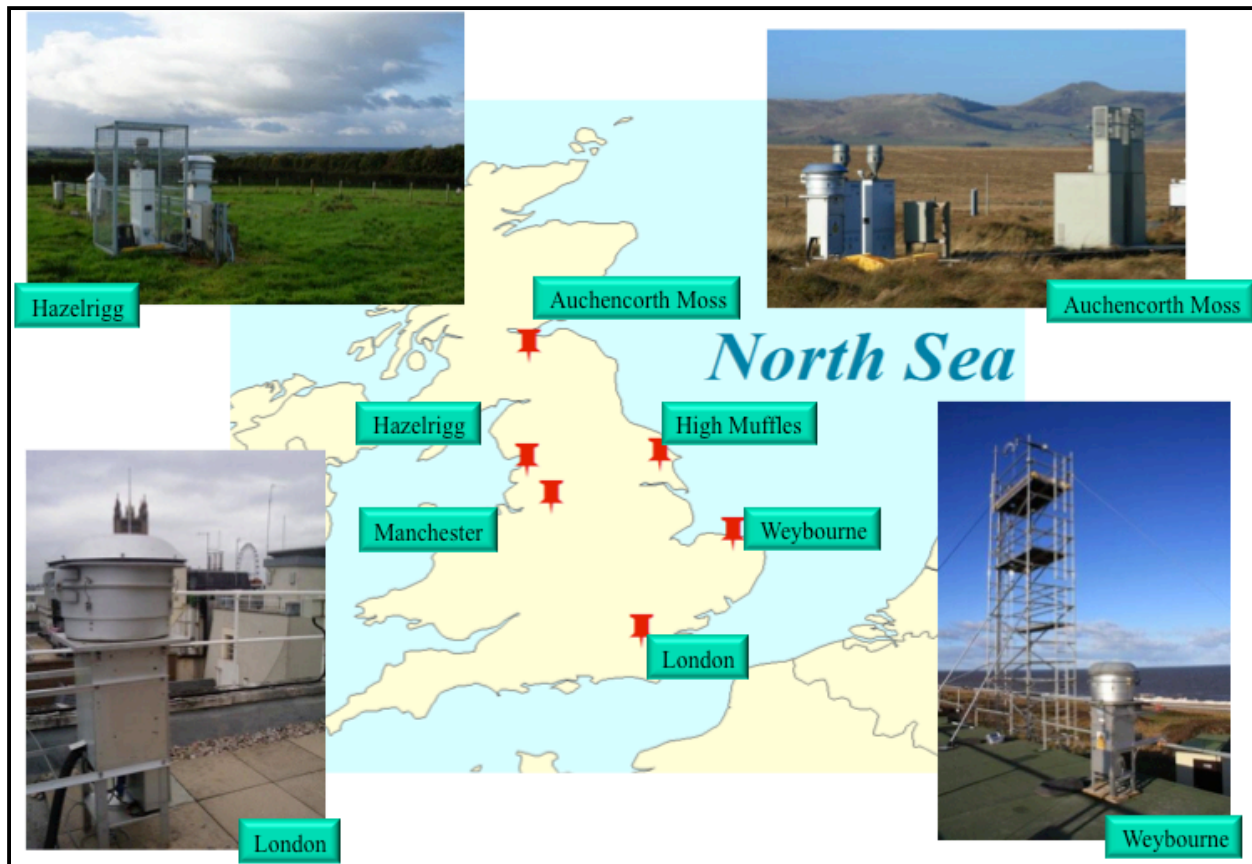


Figure 1. Location map of the current TOMPs sites.

The site at **Middlesbrough** was closed to coincide with the redevelopment of the site, which occurred during 2007. This site was not relocated, freeing resources for elsewhere in the network. A new TOMPs site was established **Auchencorth Moss**, an upland remote peat site close to Edinburgh. This site, operated by CEH Edinburgh, is part of the heavy metal network and is one of the EMEP network of superstations. These high quality EMEP stations have extended measurement programmes, detailed documentation and trained technical staff. This site is an ideal TOMPs site as it represents a rural/remote location and is likely to be removed from

the influence of local sources. As a result, it will provide an important quantification of temporal trends of atmospheric POP concentrations with a regional background influence. Auchencorth Moss started operating in October 2008. In order to replace the Stoke Ferry sampler, a new site was established at the University of East Anglia's **Weybourne** field station, a rural coastal site. Sampling at this site started in December 2008.

### 4. Network sampling operations

The sampling modules for the Andersen GPS-1 sampler are prepared just prior to deployment which involves disassembling, inspecting and cleaning the modules. Modules are stored frozen in sealed bags prior to deployment. All parts of the modules that come into contact with the glass fibre filter (GF/A Whatman ) and polyurethane plugs (PUFs, Klaus Ziemer GmbH Langerwehe, Germany) are routinely solvent cleaned between each sample. In addition, the modules are fully disassembled and all parts thoroughly cleaned in solvent. The GF/As are pre-cleaned by baking out in a muffle furnace at 450 ºC for 24 hours. They are then transferred to aluminium foil packages (the aluminium foil has also been baked out) and stored sealed until they are used. PUFs and GF/As filters are regularly sent to AEAT, who manage the London site, to CEH in Edinburgh who manage the Auchencorth Moss site and University of East Anglia who manage the Weybourne site.  The PUFs are prepared for all the sites from the same batches, by a rigorous pre-extraction procedure. This involved a soxhlet extraction in dichloromethane (DCM), with subsequent DCM removal in a solvent cleaned desiccator, maintained under vacuum. PUFs are also prepared to serve as field and laboratory blanks. The GF/As and PUFs are placed in the sampling modules using solvent cleaned stainless steel tongs and are exposed to the laboratory environment for the minimum amount of time possible.

The modules are changed every 14 days at all sites. In addition, sample information and temperature data are recorded, airflows adjusted, data loggers exchanged and preventative maintenance carried out when necessary. The time during which the sampler operates is recorded with a timer, and the flow rate determined using the flow venturi and MagnaHelic gauge. Each sampler is also fitted with a pressure transducer and a data logger that records the pressure drop during the sampling period, so that the sampling rate can be accurately determined. Log books are used to record sampling data at each site, but sampling data are also available electronically.

The following are recorded routinely for each sample at each of the sites: start time, date, counter reading, MagnaHelic reading; stop time, date, counter reading, MagnaHelic reading; maximum, minimum and actual temperature (ºC). Cross-checks are possible between the manually calculated air volume and the electronically calculated air volume. During each visit, the sampler, sampler platform and auxiliary pieces of equipment are checked for corrosion or breakages. A number of spare parts are routinely taken to each site and preventative or remedial maintenance carried out when necessary. Long life brushless motors are used to minimise samples lost through motor failures.

## 5. Extraction and clean-up procedures

Preparation of the samples takes place in a laboratory with restricted access. All glassware is thoroughly solvent cleaned prior to use and where necessary baked out at 450 ºC overnight following established procedures. Each sample (gas + particle) was spiked with a recovery standard of $^{13}C_{12}$-labeled PCB congeners ($^{13}C_{12}$ PCB 28, 52, 101, 138, 153, 180, 209) and an isotope dilution/recovery standard containing $^{13}C_{12}$-labelled PCDD/Fs. Samples are individually extracted in a Buchi extraction unit for 18 hours with hexane and 4 hours with toluene. PAHs, PCBs and tri, tetra and penta PCDD/Fs are extracted in the hexane fraction. The remaining PCDD/Fs are extracted in the toluene fraction. The extracts are concentrated using rota-evaporation and nitrogen-evaporation. The hexane and toluene fraction are combined for each sample and extracts pooled before purification to obtain quarterly data (Jan-March (Q1), April-June (Q2), July-Sept (Q3), and Oct-Dec (Q4)). The 6 hexane fractions of each quarter are then bulked together. The samples are transferred into a 250ml round bottom flask using hexane. If necessary this can then be rotary evaporated to 2ml for splitting. The toluene fractions are then bulked in the same way using hexane. Each quarter will consist of 6-7 two week samples, representing approximately 4500 $m^3$ of air. The hexane fraction (50 ml) is then split: 10% (5mL) is used for the PAHs analysis, 40% (20 mL) for the analysis and 50% (25 mL) is archived. The toluene fraction (50 mL) is also split: 10% (5mL) is discarded, 40% (20 mL) is analyzed and 50% (25 mL)is archived. The toluene and hexane fractions for archive are combined in the same vials. The same is done for the fractions (40%) that will be analyzed. The extracts are then eluted through a multilayer 20 mm id acid silica column containing a small layer of sodium sulphate, 1

g activated silica (Merck Silica 60), 2 g of basic silica (Merck Silica 60), 1 g of activated silica (Merck Silica 60, 4 g of acid silica (Merck Silica 60), 1 g activated silica and a small layer of sodium sulphate (all baked at 450°C overnight), followed by an acid digestion concentrated $H_2SO_4$, for 2 days and a second multicolumn. The extracts are eluted through gel permeation columns containing 6 g of Biobeads SX 3 and concentrated to 100 μL. Each sample is then fractionated with a basic alumina column to obtain three fractions. Fraction 1 contained PCBs, Fraction 2 contained co-planar PCBs and Fraction 3 contained PCDD/Fs. Fraction 1 containing PCBs is solvent exchanged to 160 μL of dodecane (for urban site) and 80 μL of dodecane (for the more remote sites) containing PCB 30 [$^{13}C_{12}$] PCB 141 and [$^{13}C_{12}$] PCB 208 as internal standards. The PCB fractions are analyzed by gas-chromatography mass spectrometry (GC-MS) with an EI+ source operating in selected ion mode (SIM). Details of the instruments, temperature programme and monitored ions are given elsewhere (*Thomas et al., 1998 and Gouin et al., 2002*). Thirty-seven PCB congeners are constantly measured in all samples, but only the following PCB congeners are reported: PCBs 28, 52, 90/101, 118, 138, 153/132 and 180. Some congeners co-elute and are hence reported as a pair, for example, 153/132. Fractions 2 and 3 are solvent exchanged to 15 μL of nonane containing an injection standard of $^{37}Cl$-labeled 2,3,7,8-TCDDwas added to both the PCDD/F. Analysis is performed on a Micromass Autospec Ultima HR-MS operated at a resolution of at least 10,000. Dioxins, furans and co-planar PCBs are generally found in mixtures containing several kinds of dioxins and dioxin-like compounds, each having its own degree of toxicity. To express the overall toxicity of such a mixture as a single number, the concept of "Toxic Equivalents" (TEQ) has been developed. The concentration of co-planar PCBs and PCDD/Fs are expressed in units of $fgTEQm^{-3}$. The concentration in $fgm^{-3}$ is multiplied by the WHO Toxic equivalency factors (TEF) to obtain the final concentration in $fgTEQm^{-3}$.

QA/QC A number of steps are taken to obtain data that would allow an assessment of the accuracy and reliability of the data. Recoveries are monitored by quantifying 7 $^{13}C_{12}$-labelled PCBs standards and they ranged between 70-110%. Recoveries are monitored by quantifying 20 $^{13}C_{12}$-labelled PCDD/F isotope dilution standards, using the injection standard as an internal standard. The average recoveries ranged between 61 and 101%. The criteria for the

quantification of analytes are a retention time found within 2s of the standard, isotope ratio found within 20% of standard and a signal to noise ratio of at least 3. Analytical blanks, consisting of solvent are included at a rate of one blank for every 12 samples. The method detection limit was calculated as 3 times the standard deviation of the concentrations found in the analytical blanks. If the concentrations in the blanks are below the instrumental detection limit, then the method detection limit is defined as equal to the instrumental detection limit. All results are blank corrected using the concentration of the field blanks. Field blanks are produced for each site and each quarter and they are used to calculate method detection limits (MDLs). When compounds are not detected in the field blanks, laboratory blanks produced for each quarter and are used to estimate MDLs.

### 6. Data storage.

The data are reported to DEFRA and published on the UK air quality website (www.airquality.co.uk). Archived samples for each year (50% of the samples) are stored in the freezer in the laboratory at Lancaster University. More information can be found at:

http://www.lec.lancs.ac.uk/research/chemicals_management/tomps.php

## 7. Results.

PCDD/Fs. PCDD/Fs enter the environment from various combustion processes and as impurities from the manufacture and use of various chlorinated compounds. Considerable effort has been expended in the UK and elsewhere to try and quantify and rank these sources and their emissions into the environment, principally the atmosphere, so that cost-effective source reduction measures can be taken. The concentration data for 2008 are contained in Appendix 1.

Statistical analysis of the time trends for the sum of PCDD/Fs was carried out to investigate the statistical significance of the decreasing trends and to calculate apparent half-lives. Assuming first-order kinetics, the concentration of the chemical in air is given as

$$C = C_0 e^{-kt} \qquad \text{or}$$

$$\ln C = \ln C_0 - kt$$

where $C$ is the concentration of the compound in air (ng m$^{-3}$), $k$ is the rate constant, and $t$ is time (years). Therefore, regressing the natural logarithm of the concentration against time should yield a straight line with intercept $\ln C_0$ and slope $-k$. Half-lives can then be calculated as $t_{1/2} = \ln 2/k$.

The first-order decay curves are shown in Figures 2a to e. Out of the 5 regressions, 3 were statistically significant at Middlesbrough, Manchester and London, where PCDD/Fs continue to decline in the atmosphere. Regressions at High Muffles and Hazelrigg are not statistical significant. This indicates that at more remote sites far from sources, the dioxins/furans signal is more weathered and influenced by meteorology and less dependent on source patterns. The time series for Stoke Ferry and High Muffles is shorter, and therefore the likelihood of detecting significant trends is decreased given the variability in the data. Half-lives range from 3.8 years at London to 5.3 years at Middleborough, with an average half-life of 6.3 years for the sum of PCDD/Fs at all sites.
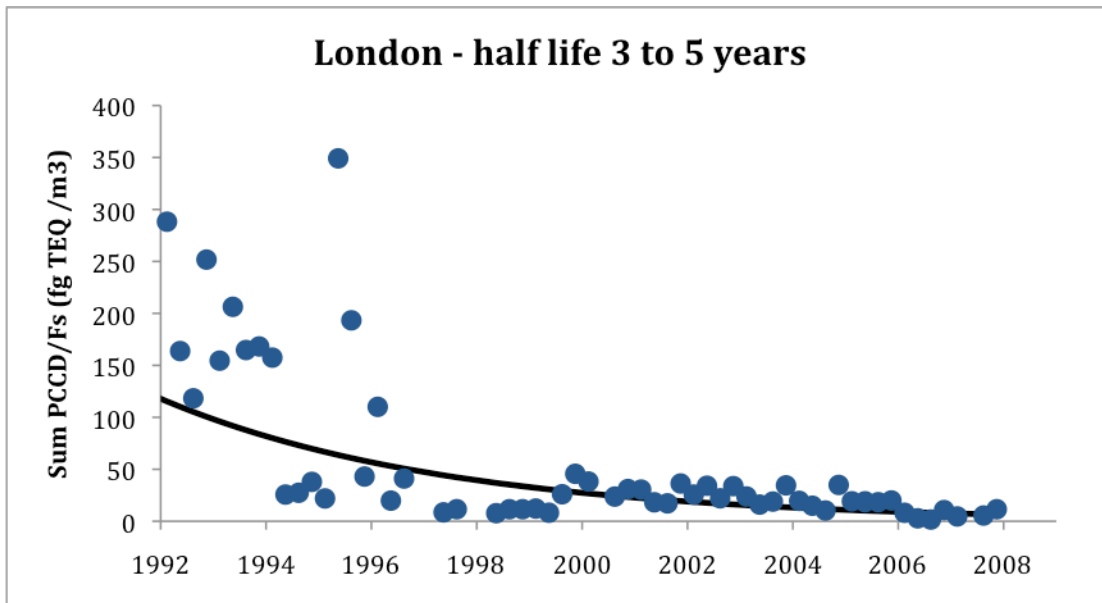
Figure 2a. PCDD/F data for the London TOMPs site
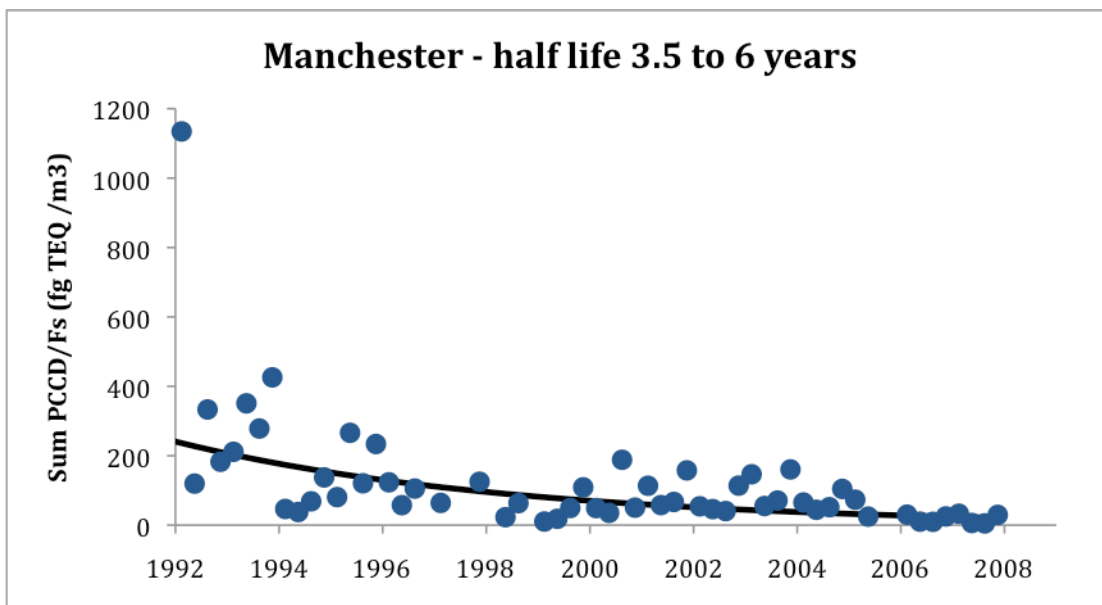


Figure 2b. PCDD/F data for the Manchester TOMPs site
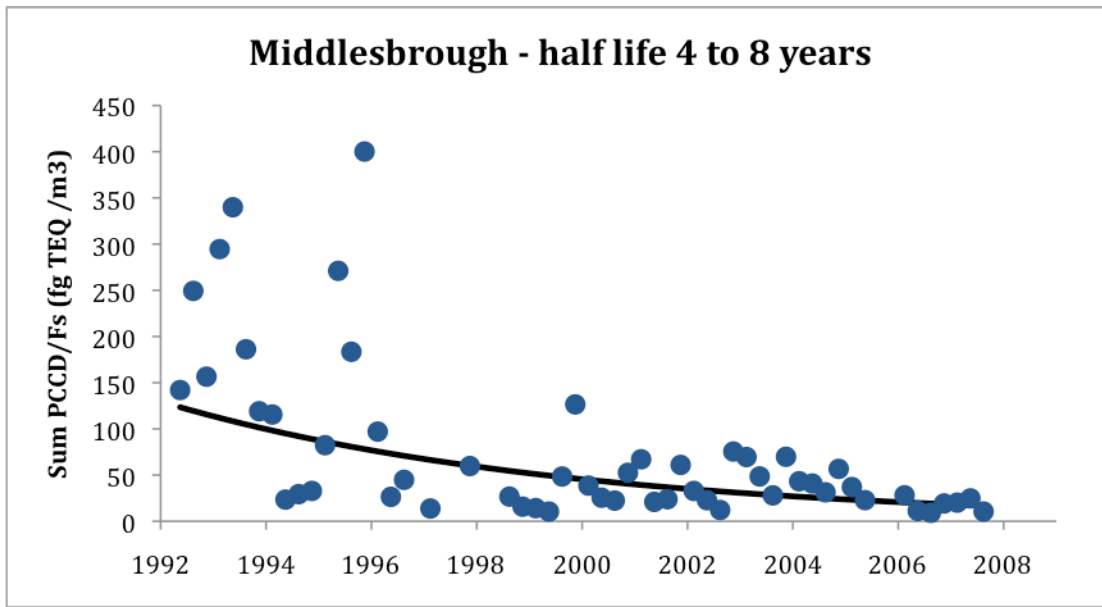
Figure 2c. PCDD/F data for the Middlesbrough TOMPs site
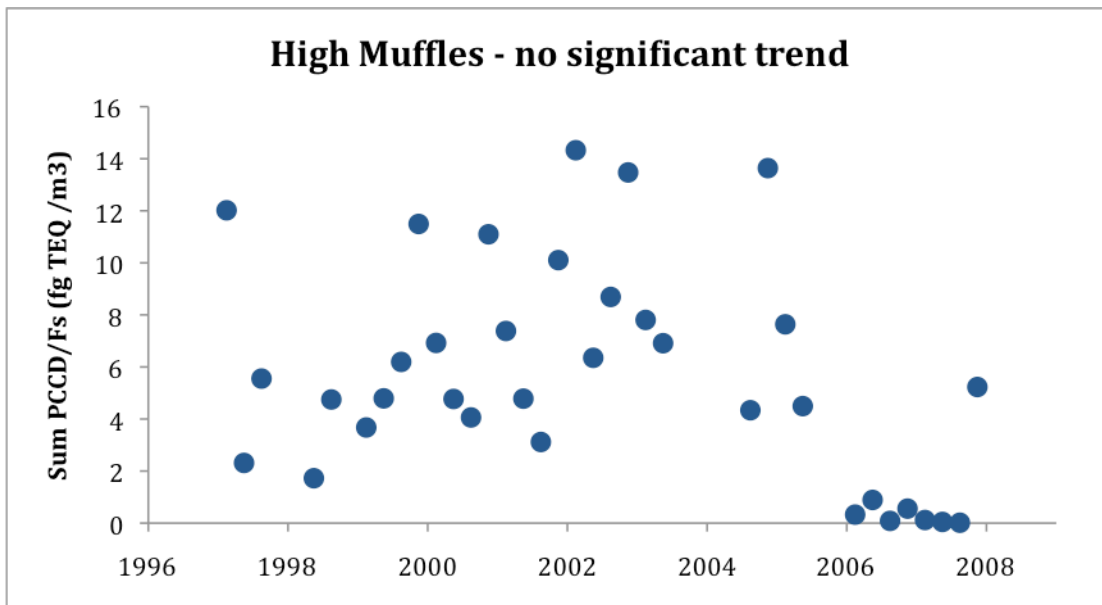


Figure 2d. PCDD/F data for the High Muffles TOMPs site
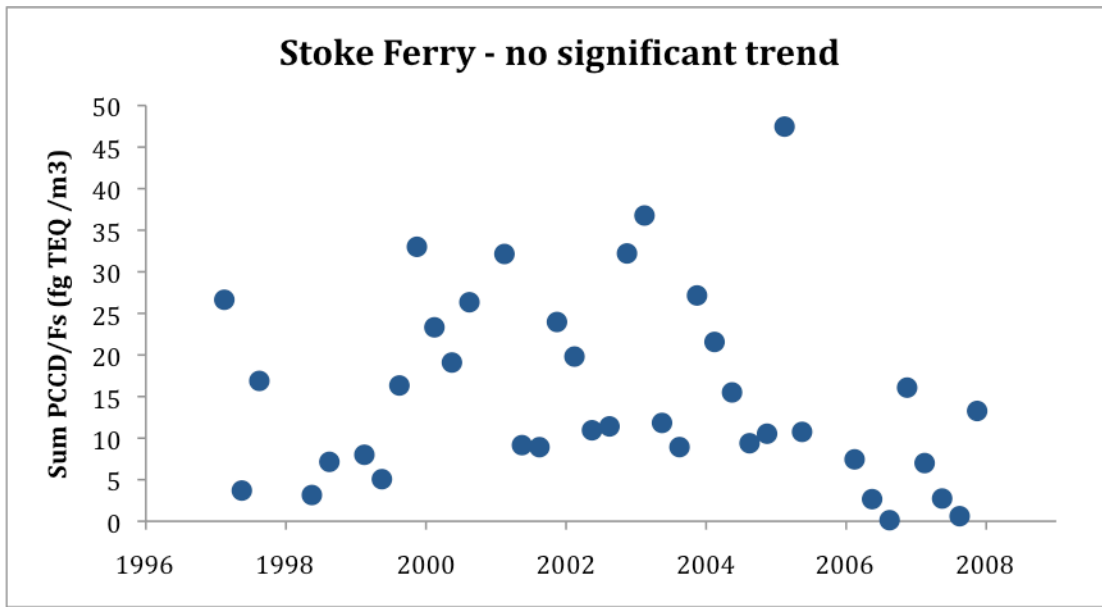
Figure 2e. PCDD/F data for the Stoke Ferry TOMPs site
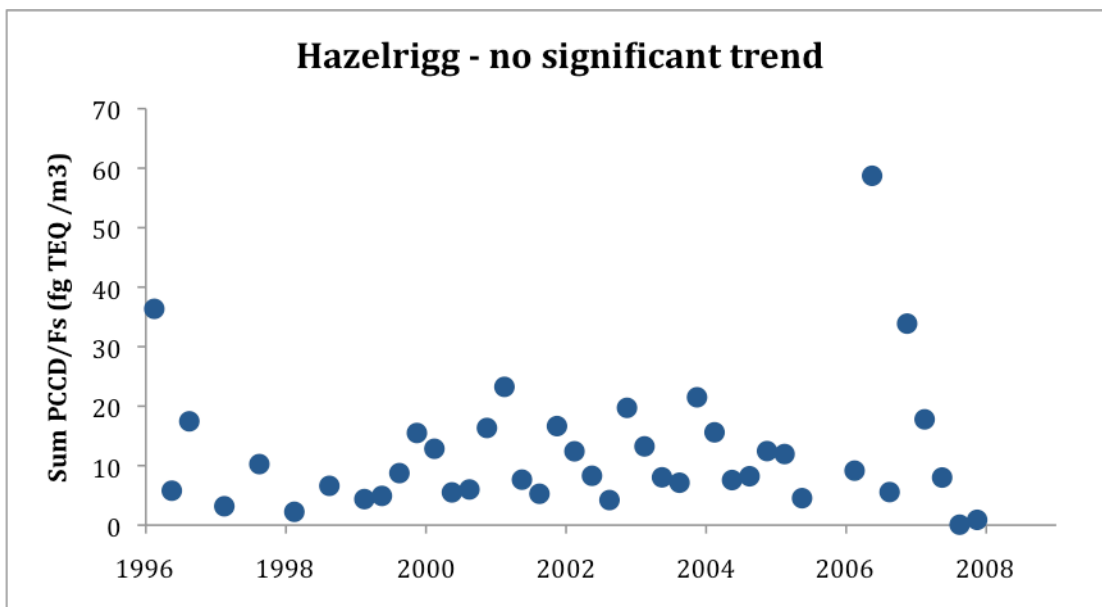


Figure 2f. PCDD/F data for the Hazelrigg TOMPs site

PCDD/Fs were also measured at the Auchencorth Moss site only for Q4 2008. The ∑PCDD/Fs was 6.4 fg TEQ/m$^3$. Results for this site are in line with what values measured at the High Muffles and Hazelrigg.

PCBs. The concentration data for 2008 are contained in Appendix 2. These data show that ambient PCB concentrations continued to decline for all measured congeners including the major congeners 28/31, 52, 90/101, 118, 138, 153/132 and 180 and respectively their sum $\sum_7 PCB$[1] (Figure 3a to e). In general, measured concentrations are proportional to local population density or alternatively the remoteness of the sampling site. In 2008 the highest $\sum_7 PCBs$ concentrations were observed in London and Manchester with an average of 62 and 49 pg/m$^3$ respectively. High Muffles and Hazelrigg showed the lowest concentrations with an average of 17 and 6.6 pg/m$^3$ respectively.
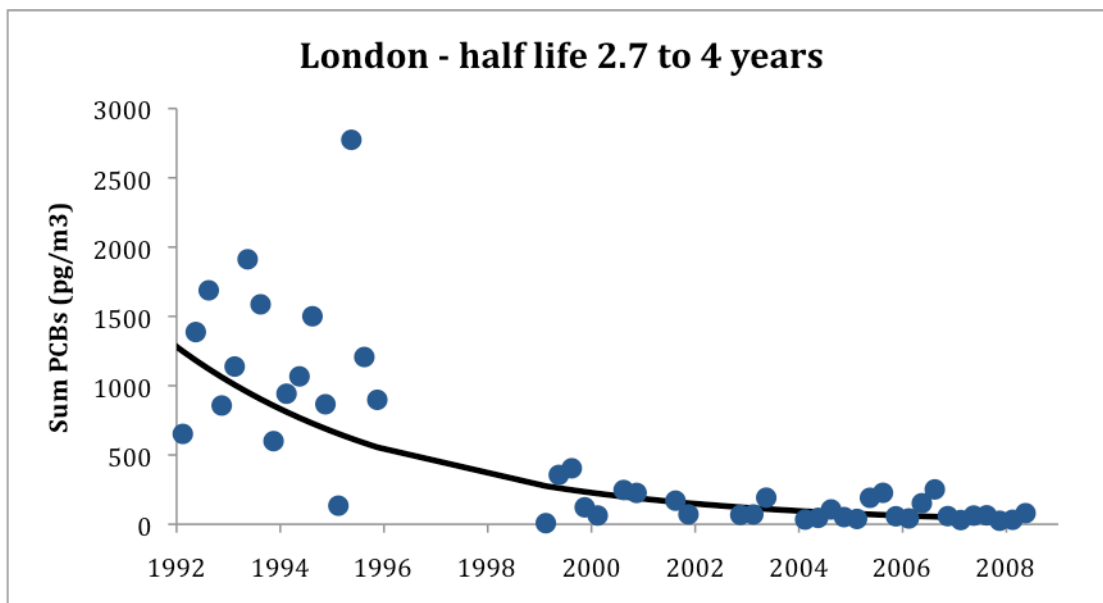


Figure 3a. $\Sigma_7 PCB$ data for the London TOMPs site

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[1] Note: PCB congeners 28, 101 and 153 co-elute with other minor congeners and hence are reported as pairs; (28/31), (90/101), (153/132) which are included in the total
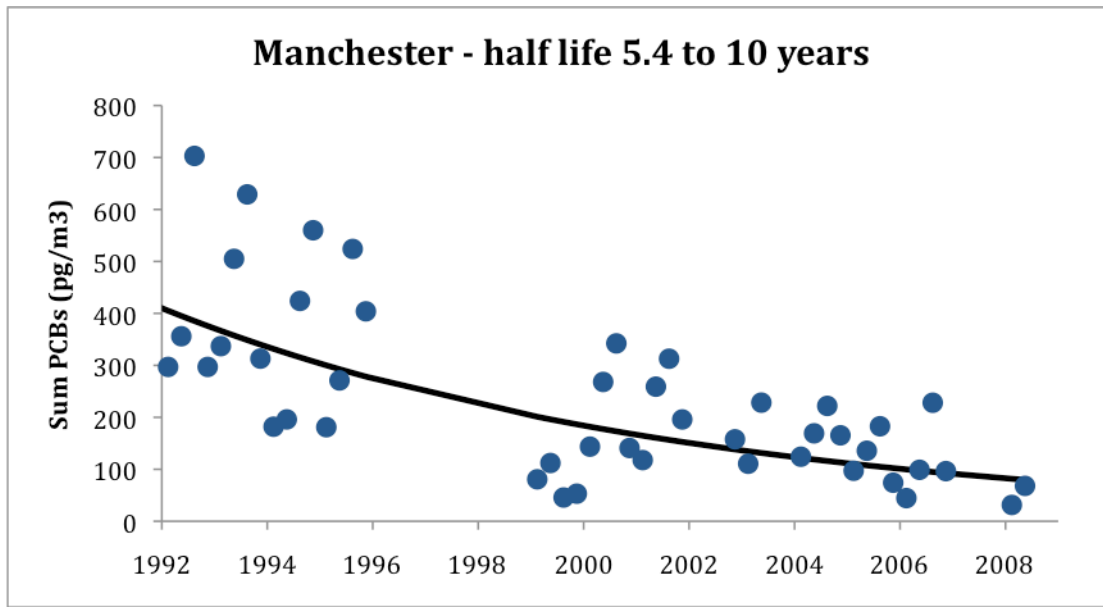
Figure 3b. $\Sigma_7$PCB data for the Manchester TOMPs site
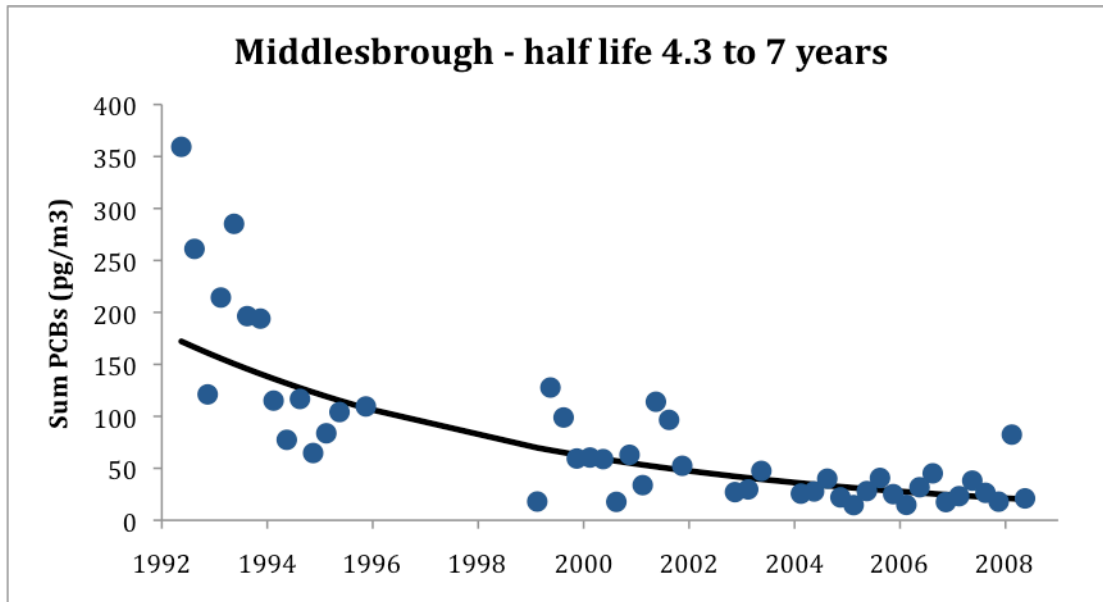


Figure 3c. $\Sigma_7$PCB data for the Middlesbrough TOMPs site
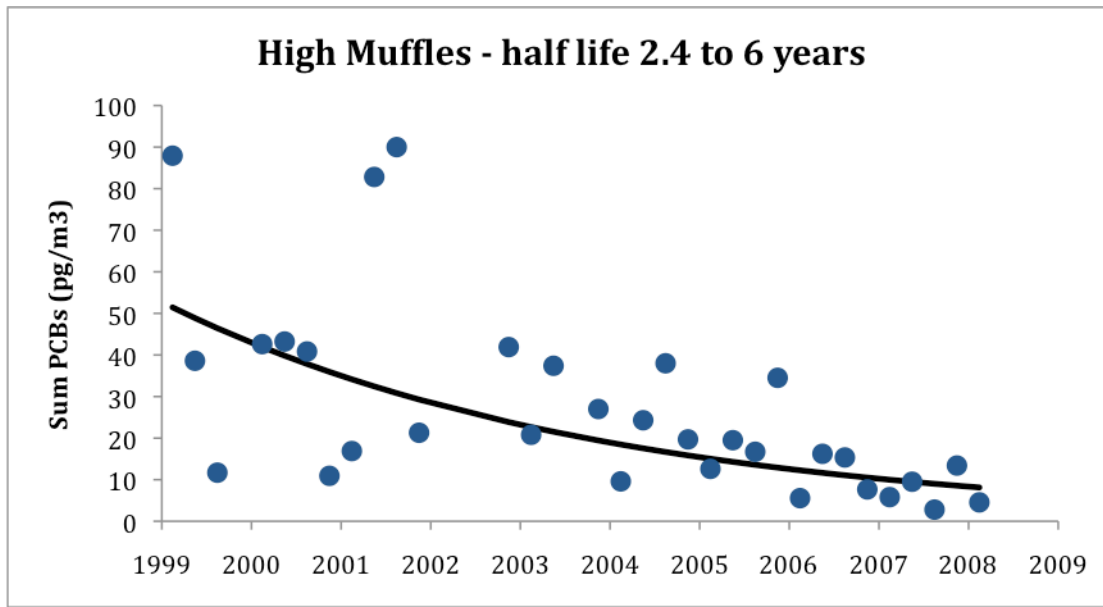
Figure 3d. $\Sigma_7$PCB data for the High Muffles TOMPs site
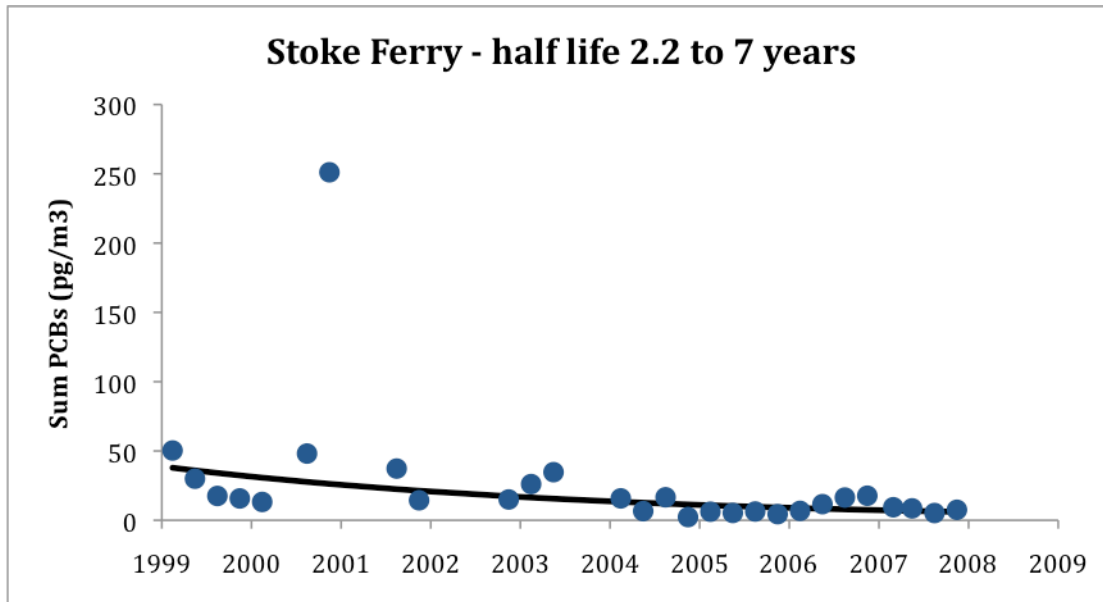


Figure 3e. $\Sigma_7$PCB data for the Stoke Ferry TOMPs site
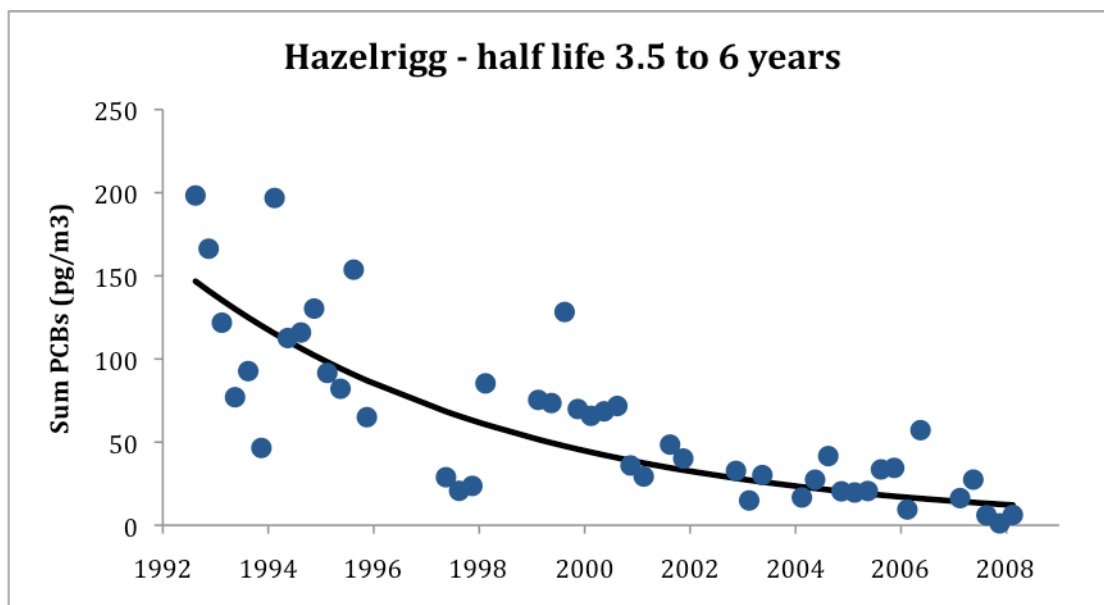
Figure 2f. $\Sigma_7$PCB data for the Hazelrigg TOMPs site

The concentration of PCBs in the atmosphere is controlled by a range of factors. First and foremost the proximity of sources has an important influence. PCB sources are differentiated into primary and secondary sources. Primary sources of PCBs are mainly open systems where they were added to articles or preparations such as plasticisers, paints and oils among others. Considering the application pattern for PCBs in domestic environments, the primary sources are mostly found in areas with high population density. Emission from secondary sources describes the process of re-emission or re-volatilisation of PCBs from environmental compartments like soil and sediments. The elimination of PCBs from the atmosphere is controlled by processes like the chemical degradation by reaction with OH-radicals or physical elimination via adsorption to particles followed by deposition. For long-term measurements these processes can be considered constant at each sampling site.

The calculated half-lives cannot be considered significantly different between sites or between congeners. The average half-live is 4.9 years with values spanning from 2.2 to 9.8 years. The observed half-lives for the rural sampling sites range from 2.2 – 6.7 years at Stoke Ferry, 2.4 - 5.8 years at High Muffles and 3.5 – 5.7 years at Hazelrigg. For the urban sites the ranges are 4.2 – 6.6 years at Middlesbrough, 5.4 – 9.8 years at Manchester and 2.7 – 4 years at London. Even though there seems to be a trend towards longer half-lives in urban areas, presumably a reflection

of on-going primary diffuse sources, no significant difference between the sites was observed. The PCB emission data contained in the NAEI broadly agrees with the time trends observed in the TOMPs datasets. Figure 4 shows a comparison between the PCB data provided by the NAEI and the Hazelrigg data for the $\Sigma_7$PCBs. This agreement holds for the other TOMPs datasets and suggests that the NAEI captures the main on-going PCB sources.
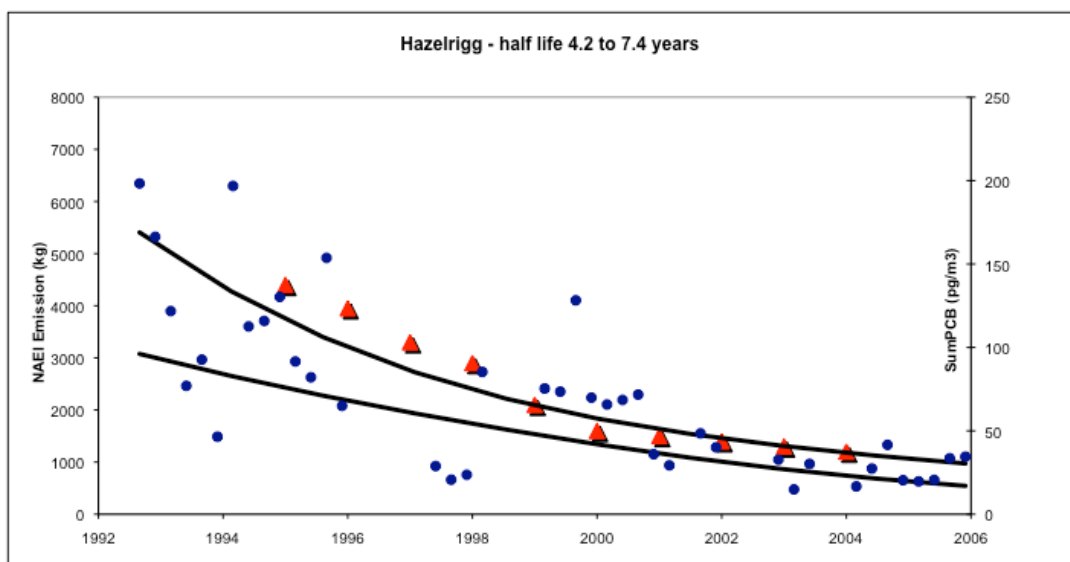


Figure 4 – Comparison of temporal trends in Hazelrigg air concentrations and emissions for $\Sigma_7$PCB

## 8.    CONCLUSIONS

This report presents the 2008 annual data report for polychlorinated biphenyls (PCBs) polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) monitoring and analysis network as part as of the Toxic Organic Micropollutants Monitoring Network (TOMPs) funded by the Department for Environment, Food and Rural Affairs (Defra).

In 2008 the PCB monitoring network consisted of 37 PCBs congeners, 4 co-planar PCB congeners and 17 PCDD/Fs at 6 sites including London, Manchester, Middlesbrough, High Muffles, Hazelrigg and Auchencorth Moss. An additional site at University of East Anglia's Weybourne field station started in December 2008, but no data are reported for this site in this report. Data for this site will be available from Q1 2009.

*PCDD/Fs*

The TOMPs ambient air concentration data for PCDD/Fs over the period from the early to late nineties shows significant decreases for the urban sites such as London, Manchester and Middlesbrough with first order half lives ranging from approximately 3 to 8 years. However, for the rural and semi rural sites, such as Hazelrigg and High Muffles, no statistically significant trend was observed throughout the whole sampling period. A comparison of the ambient air data at the three urban sites with the National Atmospheric Emissions Inventory (NAEI) shows a strong correlation between the measurements and the inventory data. This correlation is particularly strong during the nineties when the contribution from waste incineration accounted for up to 50% of the emissions. After 1997, however, the contribution from incineration decreased and a number of more diffuse combustion sources started to dominate, along with a reduction in the total amount of PCDD/Fs released. When examining the ambient air data from the year 2000 onwards there is no discernable correlation with emission data for any sites including the urban locations. These data suggest that in the past a few sources of PCDD/Fs dominated and their reduction was reflected in the ambient air data, especially for the urban sites. However, the current data suggests that a larger number of smaller diffuse sources control the levels we now measure. These are, of course, by their very nature harder to quantify and control.

*PCBs*

Concentrations of the seven congeners routinely quantified ($\Sigma_7$PCBs) over the whole dataset, which include congeners 28/31, 52, 90/101, 118, 138, 153/132 and 180, ranged from 8 to 2700 pg m$^{-3}$ at the urban sites London, Manchester and Middlesbrough, from 1.1 to 72 pg m$^{-3}$ at the suburban site of Hazelrigg and from 2.3 to 90 pg m$^{-3}$ at the rural sites of High Muffles and Stoke Ferry. The highest concentrations were determined for PCB 28/31 and 52 at all sites which contributed 30-50% to $\Sigma_7$PCBs. PCB 90/101 contributed 10-15 % to the $\Sigma_7$PCBs, while PCB 118, 138 and 153/132 contributed 5-10% to $\Sigma_7$PCBs. PCB 180 was detected in 80% of the total samples analyzed and contributed 0.4-3 % to the $\Sigma_7$PCBs. The PCB congener profile did not change over time or between the six sites. The observed half-lives for the rural sampling sites ranged from 2.2 – 6.7 years at Stoke Ferry, 2.4 - 5.8 years at High Muffles and 3.5 – 5.7 years at

Hazelrigg. For the urban sites the ranges are 4.2 – 6.6 years at Middlesbrough, 5.4 – 9.8 years at Manchester and 2.7 – 4.0 years at London.

Air concentrations are controlled by many factors many including inputs from possible primary emission (first release sources) and secondary sources (recycling), advection and losses via deposition and atmospheric reactions. Over long sampling periods, as represented by this data set, advection, deposition and reaction processes can be discounted as the underlying causes 'controlling' the observed declines. That is not to say that these factors do not influence air concentrations, rather the systematic declines suggest that source reductions control the measurement data. We can take this a step further and use the data presented here to distinguish whether primary or secondary sources control the observations. In a primary sources controlled scenario over long time intervals, site by site differences in the rate of congener loss would not be expected. It is clear that the data presented here support a primary source controlled world where there has not been a change in sources profile over time at all six sites. This does not mean that re-emissions and recycling of PCBs are not important, because there are many studies showing that temperature dependent air-surface exchange of PCBs occurs above vegetated, bare soil and oceanic surfaces. However, we interpret this time trend in PCB concentrations as reflecting continued diffusive primary source control.

*The future of the TOMPs network*

The TOMPs network has run continuously since the early 1990's and represents an invaluable air quality dataset for a range of POPs in the UK. However, it is apparent that ambient air concentrations of PCBs and PCDD/Fs have responded to emission controls and are decreasing or stable at very low levels. For PCDD/Fs at some locations this represents a challenge as we will have to improve the detection limits to continue to confidently measured ambient concentrations. This can be achieved by collecting larger samples or improving the laboratory methods. Over the next few years, however, new 'candidate POPs' will need to be evaluated and a judgment reached as to their environmental significance and regulatory needs. Currently the UN/ECE are discussing the POP characteristics five substances, namely; hexabromocyclododecane (HBCD), pentachlorophenol (PCP), dicofol, trifluralin and endosulfan, whilst the Stockholm Convention

has added a number of substances during the 4th Conference of Parties in May 2009 which include;

α hexachlorocyclohexane
β hexachlorocyclohexane
chlordecone
hexabromobiphenyl
hexabromodiphenyl ether and heptabromodiphenyl ether
lindane
pentachlorobenzene
perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride
tetrabromodiphenyl ether and pentabromodiphenyl ether

It would be useful, therefore, to consider reducing the number of sites recording ambient air concentrations of PCDD/Fs and PCBs, or by reducing the sampling intervals, which would free the necessary resources to consider including some of the above substances, for example the tetra, penta, hexa and heptaBDEs, in the TOMPs network. The inclusion of some of these substances would be timely as we could establish baseline levels from which it will be possible to observe the effectiveness of any regulatory controls. The inclusion of additional substances to the programme will require appropriate checks on sampling efficiencies using the current air sampling methodologies and some development of the analytical methodologies currently used.

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## I. Appendix 1. PCDD/Fs data.

| London 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| DIOXINS & FURANS | fgTEQ/m3 | fg TEQ/m3 | fg TEQ/m3 | fg TEQ/m3 |
| 2,3,7,8-TCDF | 1.28 | 1.24 | 0.72 | 0.48 |
| 1,2,3,7,8-PeCDF | 0.23 | nd | nd | 0.18 |
| 2,3,4,7,8-PeCDF | 4.42 | 2.99 | nd | 4.19 |
| 1,2,3,4,7,8-HxCDF | 0.66 | 0.62 | nd | nd |
| 1,2,3,6,7,8-HxCDF | 0.56 | nd | nd | 0.59 |
| 2,3,4,6,7,8-HxCDF | 0.70 | 0.51 | nd | 0.48 |
| 1,2,3,7,8,9-HxCDF | nd | nd | 1.34 | nd |
| 1,2,3,4,6,7,8-HpCDF | 0.29 | 0.21 | nd | nd |
| 1,2,3,4,7,8,9-HpCDF | 0.04 | nd | nd | nd |
| OCDF | 0.0022 | 0.0024 | 0.00048 | 0.0021 |
| 2,3,7,8-TCDD | nd | nd | nd | nd |
| 1,2,3,7,8-PeCDD | 3.51 | nd | 4.89 | 2.84 |
| 1,2,3,4,7,8-HxCDD | 0.37 | nd | 0.71 | nd |
| 1,2,3,6,7,8-HxCDD | 0.70 | 0.65 | 1.40 | 0.44 |
| 1,2,3,4,7,8-HxCDD | 1.03 | nd | 1.29 | 0.49 |
| 1,2,3,4,6,7,8-HpCDD | 0.97 | 0.65 | 1.32 | 0.57 |
| OCDD | 0.03 | 0.03 | 0.14 | 0.14 |
| ΣTEQ dioxins and furans | 14.80 | 6.90 | 11.81 | 10.26 |
| COPLANAR PCBs | fg/m3 | fg/m3 | fg/m3 | fg/m3 |
| 3,3',4,5-TetraCB | nd | nd | nd | nd |
| 3,3',4,4'-TetraCB | 0.1 | 0.048 | 0.13 | 0.02 |
| 3,3',4,4',5-PentaCB | 0.0 | 0.005 | 2.8 | 0.33 |
| 3,3',4,4',5,5'-HexaCB | 0.0033 | nd | nd | nd |

## Manchester 2008

| DIOXINS & FURANS | Q1.08 fg TEQ/m3 | Q2.08 fg TEQ/m3 | Q3.08 fg TEQ/m3 | Q4.08 fg TEQ/m3 |
|---|---|---|---|---|
| 2,3,7,8-TCDF | 6.80 | 1.33 | 0.53 | 2.02 |
| 1,2,3,7,8-PeCDF | 0.85 | 0.17 | 0.23 | 0.56 |
| 2,3,4,7,8-PeCDF | 11.50 | 2.42 | nd | 4.49 |
| 1,2,3,4,7,8-HxCDF | 5.48 | 0.70 | 0.46 | 1.72 |
| 1,2,3,6,7,8-HxCDF | 3.37 | 0.59 | 0.46 | 1.28 |
| 2,3,4,6,7,8-HxCDF | 4.14 | 0.66 | 0.62 | 1.89 |
| 1,2,3,7,8,9-HxCDF | nd | nd | nd | nd |
| 1,2,3,4,6,7,8-HpCDF | 2.00 | 0.26 | 0.15 | 0.50 |
| 1,2,3,4,7,8,9-HpCDF | 0.21 | 0.04 | nd | 0.04 |
| OCDF | 0.01 | 0.00 | 0.00 | 0.00 |
| 2,3,7,8-TCDD | nd | nd | nd | nd |
| 1,2,3,7,8-PeCDD | 8.39 | nd | nd | 3.93 |
| 1,2,3,4,7,8-HxCDD | 0.78 | nd | nd | 0.34 |
| 1,2,3,6,7,8-HxCDD | 1.78 | nd | nd | 0.35 |
| 1,2,3,4,7,8-HxCDD | 1.52 | 0.40 | nd | nd |
| 1,2,3,4,6,7,8-HpCDD | 1.49 | 0.32 | 0.25 | 0.92 |
| OCDD | 0.03 | 0.01 | 0.07 | 0.32 |
| | | | | |
| ΣTEQ dioxins and furans | 48.32 | 6.88 | 2.71 | 18.05 |
| | | | | |
| COPLANAR PCBs | fg/m3 | fg/m3 | fg/m3 | fg/m3 |
| | | | | |
| 3,3',4,5-TetraCB | nd | nd | nd | nd |
| 3,3',4,4'-TetraCB | 0.224 | 0.126 | 0.078 | 0.019 |
| 3,3',4,4',5-PentaCB | 0.032 | 0.018 | 2.9 | 1.8 |
| 3,3',4,4',5,5'-HexaCB | 0.013 | 0.007 | nd | nd |

| Middlesbrough 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| Site closed Q3 2008 | | | | |
| | | | | |
| DIOXINS & FURANS | fgTEQ/m3 | fg TEQ/m3 | fg TEQ/m3 | fg TEQ/m3 |
| | | | | |
| 2,3,7,8-TCDF | 4.50 | 2.95 | | |
| 1,2,3,7,8-PeCDF | 0.55 | 0.35 | | |
| 2,3,4,7,8-PeCDF | 7.27 | 6.33 | | |
| 1,2,3,4,7,8-HxCDF | 2.02 | 1.42 | | |
| 1,2,3,6,7,8-HxCDF | 1.49 | 1.05 | | |
| 2,3,4,6,7,8-HxCDF | 1.75 | 1.19 | | |
| 1,2,3,7,8,9-HxCDF | nd | nd | | |
| 1,2,3,4,6,7,8-HpCDF | 0.61 | 0.43 | | |
| 1,2,3,4,7,8,9-HpCDF | 0.09 | 0.06 | | |
| OCDF | 0.00 | 0.00 | | |
| 2,3,7,8-TCDD | nd | nd | | |
| 1,2,3,7,8-PeCDD | 7.67 | nd | | |
| 1,2,3,4,7,8-HxCDD | 0.77 | nd | | |
| 1,2,3,6,7,8-HxCDD | 1.40 | 0.71 | | |
| 1,2,3,4,7,8-HxCDD | 2.35 | 1.03 | | |
| 1,2,3,4,6,7,8-HpCDD | 1.31 | 0.61 | | |
| OCDD | 0.03 | 0.02 | | |
| | | | | |
| ΣTEQ dioxins and furans | 31.82 | 16.14 | | |
| | | | | |
| COPLANAR PCBs | fg/m3 | fg/m3 | fg/m3 | fg/m3 |
| | | | | |
| 3,3',4,5-TetraCB | nd | nd | | |
| 3,3',4,4'-TetraCB | 0.685 | 0.177 | | |
| 3,3',4,4',5-PentaCB | 0.019 | 0.014 | | |
| 3,3',4,4',5,5'-HexaCB | 0.006 | 0.041 | | |

| High Muffles 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| DIOXINS & FURANS | fgTEQ/m3 | fg TEQ/m3 | fg TEQ/m3 | fg TEQ/m3 |
| 2,3,7,8-TCDF | nd | 0.47 | nd | nd |
| 1,2,3,7,8-PeCDF | nd | nd | nd | 0.31 |
| 2,3,4,7,8-PeCDF | nd | 1.36 | nd | 1.87 |
| 1,2,3,4,7,8-HxCDF | nd | 0.27 | nd | nd |
| 1,2,3,6,7,8-HxCDF | nd | nd | nd | nd |
| 2,3,4,6,7,8-HxCDF | nd | 0.27 | nd | nd |
| 1,2,3,7,8,9-HxCDF | nd | nd | nd | nd |
| 1,2,3,4,6,7,8-HpCDF | 0.04 | 0.08 | 0.09 | nd |
| 1,2,3,4,7,8,9-HpCDF | nd | nd | nd | nd |
| OCDF | 0.00 | 0.00 | nd | 0.0006 |
| 2,3,7,8-TCDD | nd | nd | nd | nd |
| 1,2,3,7,8-PeCDD | nd | nd | nd | nd |
| 1,2,3,4,7,8-HxCDD | nd | nd | nd | nd |
| 1,2,3,6,7,8-HxCDD | nd | nd | nd | 0.54 |
| 1,2,3,4,7,8-HxCDD | nd | 0.33 | nd | 0.70 |
| 1,2,3,4,6,7,8-HpCDD | 0.09 | 0.17 | 0.094 | 0.22 |
| OCDD | 0.0026 | 0.0048 | 0.021 | 0.07 |
| ΣTEQ dioxins and furans | 0.13 | 2.97 | 0.18 | 3.64 |
| COPLANAR PCBs | fg/m3 | fg/m3 | fg/m3 | fg/m3 |
| 3,3',4,5-TetraCB | nd | nd | nd | nd |
| 3,3',4,4'-TetraCB | 0.081 | 0.032 | 0.020 | 0 |
| 3,3',4,4',5-PentaCB | 0.005 | nd | nd | 0.5 |
| 3,3',4,4',5,5'-HexaCB | nd | nd | nd | nd |

| Hazelrigg 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| DIOXINS & FURANS | fgTEQ/m3 | fg TEQ/m3 | fg TEQ/m3 | fg TEQ/m3 |
| 2,3,7,8-TCDF | 0.86 | 0.57 | 0.44 | 0.58 |
| 1,2,3,7,8-PeCDF | nd | nd | nd | 0.29 |
| 2,3,4,7,8-PeCDF | 3.72 | nd | nd | nd |
| 1,2,3,4,7,8-HxCDF | 0.51 | nd | nd | 0.83 |
| 1,2,3,6,7,8-HxCDF | nd | nd | nd | 0.50 |
| 2,3,4,6,7,8-HxCDF | nd | nd | nd | 0.43 |
| 1,2,3,7,8,9-HxCDF | nd | nd | nd | nd |
| 1,2,3,4,6,7,8-HpCDF | 0.17 | 0.08 | 0.07 | 0.12 |
| 1,2,3,4,7,8,9-HpCDF | nd | nd | nd | nd |
| OCDF | 0.0010 | 0.0006 | 0.0008 | 0.0016 |
| 2,3,7,8-TCDD | nd | nd | nd | nd |
| 1,2,3,7,8-PeCDD | nd | nd | nd | nd |
| 1,2,3,4,7,8-HxCDD | 0.42 | nd | 0.37 | nd |
| 1,2,3,6,7,8-HxCDD | 0.43 | nd | 0.42 | nd |
| 1,2,3,4,7,8-HxCDD | 0.63 | nd | 0.74 | 0.38 |
| 1,2,3,4,6,7,8-HpCDD | 0.44 | 0.14 | 0.85 | 0.69 |
| OCDD | 0.01 | 0.0036 | 0.10 | 0.11 |
| ΣTEQ dioxins and furans | 7.18 | 0.79 | 2.89 | 3.81 |
| COPLANAR PCBs | fg/m3 | fg/m3 | fg/m3 | fg/m3 |
| 3,3',4,5-TetraCB | nd | nd | nd | nd |
| 3,3',4,4'-TetraCB | 0.086 | 0.0894 | 0.011 | 0.009 |
| 3,3',4,4',5-PentaCB | nd | 0.0063 | 1.17 | 1.05 |
| 3,3',4,4',5,5'-HexaCB | nd | nd | nd | nd |

| Auchencorth 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| Sampling commenced Q4 2008 | | | | |
| | | | | |
| fgTEQ/m3 | fg TEQ/m3 | fg TEQ/m3 | fg TEQ/m3 | fg TEQ/m3 |
| | | | | |
| 2,3,7,8-TCDF | | | | nd |
| 1,2,3,7,8-PeCDF | | | | 0.21 |
| 2,3,4,7,8-PeCDF | | | | 4.76 |
| 1,2,3,4,7,8-HxCDF | | | | nd |
| 1,2,3,6,7,8-HxCDF | | | | nd |
| 2,3,4,6,7,8-HxCDF | | | | nd |
| 1,2,3,7,8,9-HxCDF | | | | nd |
| 1,2,3,4,6,7,8-HpCDF | | | | nd |
| 1,2,3,4,7,8,9-HpCDF | | | | nd |
| OCDF | | | | 0.0008 |
| 2,3,7,8-TCDD | | | | nd |
| 1,2,3,7,8-PeCDD | | | | nd |
| 1,2,3,4,7,8-HxCDD | | | | 1.20 |
| 1,2,3,6,7,8-HxCDD | | | | nd |
| 1,2,3,4,7,8-HxCDD | | | | nd |
| 1,2,3,4,6,7,8-HpCDD | | | | 0.22 |
| OCDD | | | | 0.05 |
| | | | | |
| ΣTEQ dioxins and furans | | | | 6.44 |
| | | | | |
| COPLANAR PCBs | | | | |
| | | | | |
| 3,3',4,5-TetraCB | | | | nd |
| 3,3',4,4'-TetraCB | | | | 0.01 |
| 3,3',4,4',5-PentaCB | | | | nd |
| 3,3',4,4',5,5'-HexaCB | | | | nd |

## II. Appendix 2. PCB data

| LONDON 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| PCB | $pg/m^3$ | $pg/m^3$ | $pg/m^3$ | $pg/m^3$ |
| 18 | 7.9 | 14.7 | 28.4 | 15.9 |
| 22 | 2.3 | 4.9 | 8.7 | 5.8 |
| 44 | 3.9 | 10.2 | 7.3 | 6.9 |
| 49 | 3.1 | 6.4 | 7.4 | 7.9 |
| 52 | 7.1 | 18.9 | 13.4 | 15.0 |
| 70 | 3.77 | 9.99 | 7.97 | 9.0 |
| 74 | 1.1 | 3.4 | 8.7 | 3.6 |
| 87 | <0.04 | 6.3 | 4.2 | 3.3 |
| 95 | 5.2 | 17.7 | 2.5 | 5.9 |
| 99 | 1.5 | 4.63 | 0.6 | 4.0 |
| 104 | <0.04 | <0.04 | <0.04 | <0.04 |
| 105 | 0.6 | 2.1 | 1.8 | 3.0 |
| 110 | 3.7 | 11.7 | 8.2 | 10.0 |
| 114 | 0.0 | 0.0 | <0.04 | <0.04 |
| 118 | 1.88 | 5.34 | 4.1 | 5.0 |
| 123 | 0.4 | 1.0 | 0.5 | 0.5 |
| 138 | 3.35 | 8.0 | 4.8 | 7.0 |
| 141 | 0.6 | 2.3 | 1.2 | 2.30 |
| 149 | 4.3 | 14.8 | 7.4 | 17.9 |
| 151 | 1.7 | 7.7 | 2.5 | 3.2 |
| 155 | <0.04 | <0.04 | <0.04 | <0.04 |
| 156 | <0.04 | <0.04 | <0.04 | <0.04 |
| 157 | <0.04 | <0.04 | <0.04 | <0.04 |
| 158 | 0.23 | 0.68 | 0.64 | 0.3 |
| 167 | 0.23 | <0.04 | <0.04 | <0.05 |
| 170 | 1.06 | 0.92 | 0.85 | 0.98 |
| 174 | 1.78 | 2.4 | 1.4 | 1.20 |
| 180 | 3.41 | 3.10 | 1.42 | 3.10 |
| 183 | 0.96 | 1.7 | <0.04 | <0.04 |
| 187 | 2.5 | 4.4 | 1.9 | 2.10 |
| 188 | <0.04 | <0.04 | <0.04 | <0.04 |
| 189 | <0.04 | <0.04 | <0.04 | <0.04 |
| 194 | <0.04 | <0.04 | <0.04 | <0.04 |
| 199 | <0.04 | <0.04 | <0.04 | <0.04 |
| 203 | <0.04 | <0.04 | <0.04 | <0.04 |
| 153+132 | 5.26 | 14.20 | 5.0 | 5.9 |
| 31+28 | 7.97 | 15.14 | 45.40 | 12.90 |
| 41/64 | 3.14 | 5.3 | 7.8 | 6.90 |
| 60/56 | <0.04 | <0.04 | 4.2 | <0.04 |
| 90/101 | 3.3 | 15.3 | 2.6 | 10.8 |
| $\Sigma_7 PCB$ | 32.2 | 80.0 | 76.6 | 59.7 |

| MANCHESTER 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| PCB | pg/m$^3$ | pg/m$^3$ | pg/m$^3$ | pg/m$^3$ |
| 18 | 9.0 | 17.4 | 14.0 | 4.9 |
| 22 | 2.2 | 6.1 | 5.0 | 1.7 |
| 44 | 5.1 | 9.1 | 9.5 | 3.1 |
| 49 | 2.8 | 6.0 | 5.8 | 2.1 |
| 52 | 9.1 | 19.4 | 19.8 | 5.9 |
| 70 | 4.94 | 9.24 | 10.39 | 3.74 |
| 74 | 1.2 | 2.9 | 4.1 | 1.2 |
| 87 | 2.9 | 6.8 | 10.7 | 4.3 |
| 95 | 8.7 | 17.8 | 6.4 | 2.9 |
| 99 | 2.4 | 5.0 | 1.7 | 0.8 |
| 104 | <0.04 | <0.04 | <0.04 | <0.04 |
| 105 | <0.04 | 1.7 | 3.7 | 1.5 |
| 110 | 5.7 | 12.4 | 21.7 | 8.5 |
| 114 | <0.04 | <0.04 | <0.04 | <0.04 |
| 118 | 2.68 | 5.94 | 10.19 | 3.8 |
| 123 | 0.2 | 0.4 | 0.7 | 0.3 |
| 138 | 2.90 | 5.43 | 7.3 | 2.94 |
| 141 | 0.2 | 1.0 | 1.4 | 0.5 |
| 149 | 3.4 | 7.1 | 10.2 | 4.3 |
| 151 | 1.1 | 3.0 | 2.9 | 1.2 |
| 155 | <0.04 | <0.04 | <0.04 | <0.04 |
| 156 | <0.04 | <0.04 | <0.04 | <0.04 |
| 157 | <0.04 | <0.04 | <0.04 | <0.04 |
| 158 | 0.28 | 0.57 | 0.75 | 0.3 |
| 167 | <0.04 | <0.04 | <0.04 | <0.04 |
| 170 | <0.05 | 0.52 | 0.76 | <0.04 |
| 174 | 0.51 | 0.83 | 1.1 | 0.4 |
| 180 | 0.62 | 1.20 | 0.36 | 0.07 |
| 183 | 0.26 | 0.31 | <0.04 | <0.04 |
| 187 | 0.63 | 1.0 | 0.5 | 0.3 |
| 188 | <0.04 | <0.04 | <0.04 | <0.04 |
| 189 | <0.04 | <0.04 | <0.04 | <0.04 |
| 194 | <0.04 | <0.04 | <0.04 | <0.04 |
| 199 | <0.04 | <0.04 | <0.04 | <0.04 |
| 203 | <0.04 | <0.04 | <0.04 | <0.04 |
| 153+132 | 3.87 | 7.22 | 3.90 | 1.65 |
| 31+28 | 7.31 | 13.53 | 27.04 | 8.28 |
| 41/64 | 2.64 | 4.66 | 6.8 | 2.4 |
| 60/56 | nd | 0.9 | 3.6 | 1.3 |
| 90/101 | 4.9 | 15.4 | 4.6 | 2.0 |
| | | | | |
| $\Sigma_7$PCB | 31 | 68 | 73 | 25 |

| HIGH MUFFLES 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| PCB | pg/m$^3$ | pg/m$^3$ | pg/m$^3$ | pg/m$^3$ |
| 18 | 3.5 | nd | 2.4 | 1.4 |
| 22 | <0.02 | nd | 1.1 | 0.7 |
| 44 | 2.2 | nd | 1.5 | 0.7 |
| 49 | 8.7 | 0.2 | 1.0 | 0.5 |
| 52 | 2.2 | 0.6 | 2.6 | 0.9 |
| 70 | 1.6 | nd | 1.9 | 0.6 |
| 74 | 2.32 | nd | 0.61 | 0.27 |
| 87 | 0.44 | nd | 1.94 | 0.24 |
| 95 | 1.7 | nd | 0.91 | 0.12 |
| 99 | 0.35 | nd | 0.204 | 0.021 |
| 104 | <0.02 | nd | <0.02 | <0.02 |
| 105 | <0.02 | nd | 0.6 | 0.2 |
| 110 | <0.02 | nd | 4.12 | 0.5 |
| 114 | <0.02 | nd | <0.02 | <0.02 |
| 118 | 0.41 | nd | 1.8 | 0.2 |
| 123 | <0.02 | nd | 0.12 | 0.04 |
| 138 | 0.58 | nd | 1.41 | 0.25 |
| 141 | <0.02 | nd | 0.27 | 0.07 |
| 149 | 1.16 | nd | 1.91 | 0.46 |
| 151 | 0.57 | nd | 0.54 | 0.16 |
| 155 | <0.02 | nd | <0.02 | <0.02 |
| 156 | <0.02 | nd | <0.02 | <0.02 |
| 157 | <0.02 | nd | <0.02 | <0.02 |
| 158 | <0.02 | nd | 0.2 | <0.02 |
| 167 | <0.02 | nd | <0.02 | <0.02 |
| 170 | <0.02 | nd | <0.02 | <0.02 |
| 174 | 0.16 | nd | 0.24 | 0.07 |
| 180 | 0.12 | nd | 0.0 | 0.0 |
| 183 | 0.13 | nd | <0.02 | <0.02 |
| 187 | 0.26 | nd | 0.19 | 0.13 |
| 188 | <0.02 | nd | <0.02 | <0.02 |
| 189 | <0.02 | nd | <0.02 | <0.02 |
| 194 | <0.02 | nd | <0.02 | <0.02 |
| 199 | <0.02 | nd | <0.02 | <0.02 |
| 203 | <0.02 | nd | <0.02 | <0.02 |
| 153+132 | 1.2 | nd | 0.7 | 0.1 |
| 31+28 | 0.02 | nd | 4.3 | 2.6 |
| 41/64 | 7.1 | nd | 1.48 | 0.7 |
| 60/56 | <0.02 | nd | 0.7 | 0.4 |
| 90/101 | 0.0 | nd | 0.66 | 0.07 |
| | | | | |
| $\Sigma_7$PCB | 4.55 | | 11 | 4.1 |

<span style="color:red">Problem with sample intereferences. Not all congeners were quantifiable</span>

| HAZELRIGG 2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| PCB | $pg/m^3$ | $pg/m^3$ | $pg/m^3$ | $pg/m^3$ |
| 18 | 2.9 | nd | 2.65 | 0.11 |
| 22 | 2.8 | nd | 1.18 | 0.14 |
| 44 | 1.2 | nd | 1.34 | 0.11 |
| 49 | 0.9 | 0.2 | 1.01 | 0.19 |
| 52 | 1.6 | 0.7 | 2.24 | 0.20 |
| 70 | 1.00 | nd | 1.22 | 0.19 |
| 74 | 0.4 | nd | 0.51 | 0.15 |
| 87 | 0.4 | nd | 0.88 | 0.13 |
| 95 | 1.52 | nd | 0.91 | 0.16 |
| 99 | 0.3 | nd | 0.22 | 0.26 |
| 104 | <0.02 | nd | <0.02 | <0.02 |
| 105 | <0.02 | nd | 0.30 | <0.02 |
| 110 | 0.62 | nd | 1.94 | 0.10 |
| 114 | <0.02 | nd | <0.02 | <0.02 |
| 118 | 0.02 | nd | 0.83 | 0.15 |
| 123 | <0.02 | nd | 0.08 | 0.13 |
| 138 | 0.62 | nd | 1.08 | 0.11 |
| 141 | <0.02 | nd | 0.23 | 0.18 |
| 149 | 1.31 | nd | 1.63 | 0.11 |
| 151 | 0.89 | 0.14 | 0.56 | 0.16 |
| 155 | <0.02 | nd | <0.02 | <0.02 |
| 156 | <0.02 | nd | <0.02 | <0.02 |
| 157 | <0.02 | nd | <0.02 | <0.02 |
| 158 | <0.02 | nd | 0.11 | 0.11 |
| 167 | <0.02 | nd | <0.02 | <0.02 |
| 170 | <0.02 | nd | 0.18 | 0.12 |
| 174 | 0.20 | nd | 0.20 | 0.14 |
| 180 | 0.10 | nd | 0.06 | 0.12 |
| 183 | 0.06 | nd | 0.02 | 0.14 |
| 187 | 0.18 | nd | 0.23 | 0.18 |
| 188 | <0.02 | nd | <0.02 | <0.02 |
| 189 | <0.02 | nd | <0.02 | <0.02 |
| 194 | <0.02 | nd | <0.02 | <0.02 |
| 199 | <0.02 | nd | <0.02 | <0.02 |
| 203 | <0.02 | nd | <0.02 | <0.02 |
| 153+132 | 0.87 | nd | 0.71 | 0.22 |
| 31+28 | 2.99 | 0.08 | 6.52 | 0.17 |
| 41/64 | 1.21 | nd | 1.48 | 0.37 |
| 60/56 | <0.02 | nd | 0.78 | 0.36 |
| 90/101 | 0.0 | nd | 0.79 | 0.47 |
| | | | | |
| $\Sigma_7 PCB$ | 6.22 | | 12.23 | 1.44 |

Problem with sample intereferences. Not all congeners were quantifiable

| Auchencourt_2008 | Q1.08 | Q2.08 | Q3.08 | Q4.08 |
|---|---|---|---|---|
| PCB | pg/m3 | pg/m3 | pg/m3 | pg/m3 |
| 18 | | | | 7.7 |
| 22 | | | | 2.7 |
| 44 | | | | 2.0 |
| 49 | | | | 1.6 |
| 52 | | | | 2.0 |
| 70 | | | | 2.4 |
| 74 | | | | 1.1 |
| 87 | | | | 0.9 |
| 95 | | | | 1.3 |
| 99 | | | | 0.1 |
| 104 | | | | <0.02 |
| 105 | | | | 0.3 |
| 110 | | | | 1.6 |
| 114 | | | | <0.02 |
| 118 | | | | 0.6 |
| 123 | | | | 0.2 |
| 138 | | | | 1.66 |
| 141 | | | | 0.3 |
| 149 | | | | 3.0 |
| 151 | | | | 0.8 |
| 155 | | | | <0.02 |
| 156 | | | | <0.02 |
| 157 | | | | <0.02 |
| 158 | | | | 0.1 |
| 167 | | | | <0.02 |
| 170 | | | | <0.02 |
| 174 | | | | 0.46 |
| 180 | | | | 0.07 |
| 183 | | | | 0.02 |
| 187 | | | | 0.3 |
| 188 | | | | <0.02 |
| 189 | | | | <0.02 |
| 194 | | | | <0.02 |
| 199 | | | | <0.02 |
| 203 | | | | <0.02 |
| 153+132 | | | | 0.83 |
| 31+28 | | | | 11.72 |
| 41/64 | | | | 2.6 |
| 60/56 | | | | 1.6 |
| 90/101 | | | | 0.5 |
| | | | | |
| $\Sigma_7$PCB | | | | 17.4 |