The Lancaster
Environment Centre

Annual Report for 2005 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network

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**Report to the Department for Environment, Food
and Rural Affairs, the Northern Ireland
Department of Environment, the Scottish
Government and the Welsh Assembly**

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Executive Summary.

This report contains the 2005 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) and the Devolved Administrations. In 2005, 37 PCBs congeners, 4 co-planar PCB congeners, 10 furans congeners and 7 dioxin congeners were the chemicals of interest for each sample. The TOMPs network includes sites in London, Manchester, Hazelrigg (Lancashire), High Muffles (North Yorkshire), Stoke Ferry (Norfolk) and Middlesbrough (North Yorkshire). The aim of the TOMPs network, which initiated in 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.

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1. Introduction

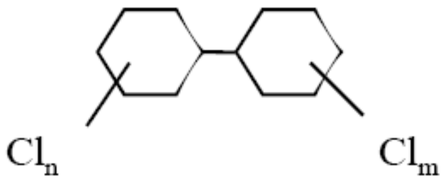
Lancaster University (LU) has been involved in the TOMPs programme since its inception in 1990. LU currently manages the programme on behalf of Defra which operates six sites, three urban, two rural and one semi-rural. Atmospheric sampling is carried out at each site, collecting a biweekly sample which 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.

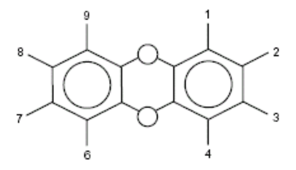
PCBs were first synthesized in 1881 by Schmidt and Schulz but their commercial production only began in 1929 in USA (*Danse et al.,* 1997). They were marked as mixed products under various trade names depending on the country where they were produced such as Aroclor (Monosanto, USA), Phenochlor and Clophen (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; *Harrad 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).



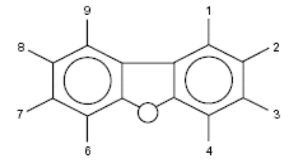
There are 209 different congeners with one to ten chlorines atoms attached. The International Council for the Exploration of the Seas (ICES) 7 PCB congeners generally reported in environmental samples are PCB 28 (2,4,4'-triPCB), PCB 52 (2,2',5,5'-tetraCB), PCB 101 (2,2',4,5,5'-pentaCB), PCB 118 (2,3',4,4',5-heptaCB), 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.



DIOXIN



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3. TOMPs sites operating in 2005

In 2005 the TOMPs programme operated 6 sites:

London	urban site established in 1991
Manchester	urban site established in 1991
Hazelrigg	semi-rural site established in 1992
High Muffles (North Yorkshire)	rural site established in 1999
Stoke Ferry	rural site established in 1997
Middlesbrough	urban site established in 1991

The sites consist of three urban locations in London (LON), Manchester (MAN), and Middlesbrough (MB), three rural-semi rural sites at High Muffles (HM, North Yorkshire), Stoke Ferry (SF, Norfolk) and 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. Some of the locations of the current samplers in the network are shown in Figure 1.

Figure 1. Sampling sites of the TOMPs program.

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 foam 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 manages the London 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. A sampler calibration is performed once a year at each site.

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 or 7 hexane fractions (depending on the length of each quarter) 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 FOR YEAR 2005

Table 1 contains information on the bulked air volume (in m^3) and the number of samples bulked for each site and each quarter in 2005. The bulked air volume is obtained by summing the volume (in m^3) obtained from each biweekly sample taken during the quarter (usually 6-7 samples, depending on the sampling schedule). The aim is to obtain an average volume of 500-700m^3 for every two week sampling period to avoid breakthrough of chemicals during sampling and to ensure the collection of a sufficient level of chemicals within the samples that canbe analytically detected. Consequently, this leads to a total volume per quarter (bulked volume) of approximately 4500-6000 m^3 (see Table 1). Samplers at all sites were calibrated once a year in the period (April-June).

Middlesbrough has less samples (5) for Q3 2005 because the motor stopped during the biweekly sampling period and the air volume could not be retrieved. Therefore, the sample was not considered suitable for analysis.

Table 1. Summary of the bulked air volumes and number of samples for each quarter at all sites in 2005.

		LON	MAN	MID	HM	SF	HR
Bulked Air Volumes m^3	**Q1**	4856	4522.1	5358.5	4320.8	4896	4728.6
N$_o$ of samples		7	6	7	6	7	6
Bulked Air Volumes m^3	**Q2**	4956	4791.0	4967.1	4977.6	4561	5068.1
N$_o$ of samples		6	6	6	6	6	6
Bulked Air Volumes m^3	**Q3**	4562	4796.9	4853.2	4918.4	4561	5004.5
N$_o$ of samples		6	6	5	6	6	6
Bulked Air Volumes m^3	**Q4**	5123	5109.7	4584.3	5359.0	5236	5271.9
N$_o$ of samples		7	7	6	7	7	7

PCBs

The urban sites of London and Manchester continue to display the highest concentrations of PCBs (50.49 pg/m^3 and 47.68 pg/m^3, respectively). The lowest average concentrations were observed at Stoke Ferry (2.7 pg/m^3), whereas at all the other sites, the average concentrations were at around 10 pg/m^3. All urban sampling sites and at the Stoke Ferry, the highest concentrations were observed at the third trimester, while at the other two sites, the highest levels were for the 4th quarter. As in 2004, the highest concentration was observed in Q3 at all the urban sites with the exception of the rural sites such as Hazelrigg, Stoke Ferry, High Muffles and Stoke Ferry where Q4 also displayed relatively ghigh concentration of PCBs. The lowest was observed in Q1 at all sites with the exception of Stoke Ferry which displays similar concentration for all quarters. Q3 is usually high This is possibly because higher temperature drives revolatilization of PCBs from surfaces (soil, vegetation and waters) causing an increase in the atmospheric concentrations (Figure 2, 3). Long-range atmospheric transport can be another explanation and an analysis with air mass back trajectories (wind direction) could shed the light on this; however, this is difficult to do with bulked samples like the TOMPs samples.

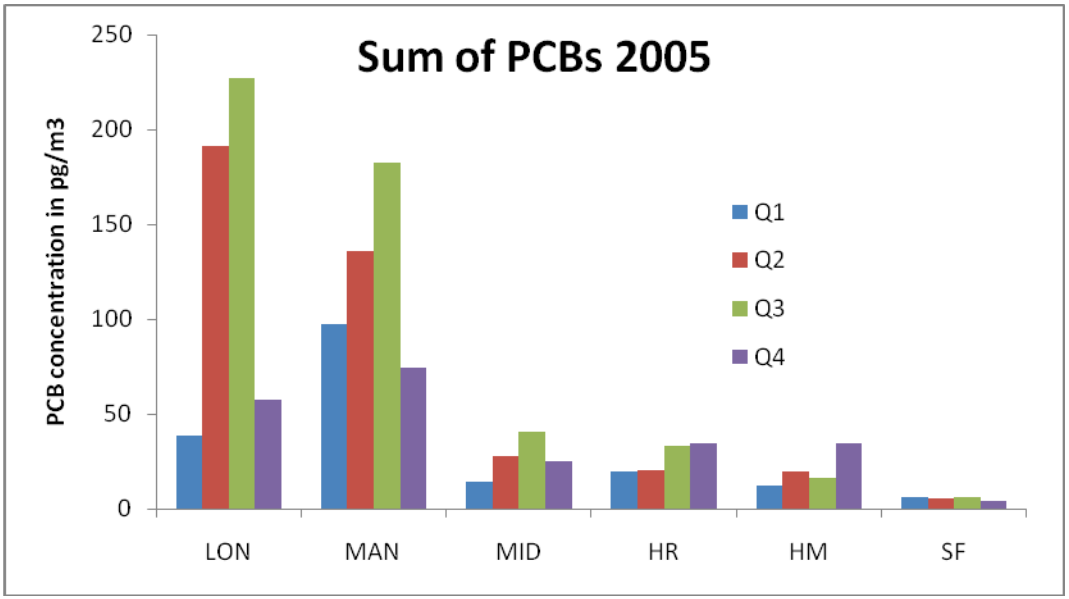


Figure 2.Sum of PCB concentrations at all sites for all quarters in 2005.

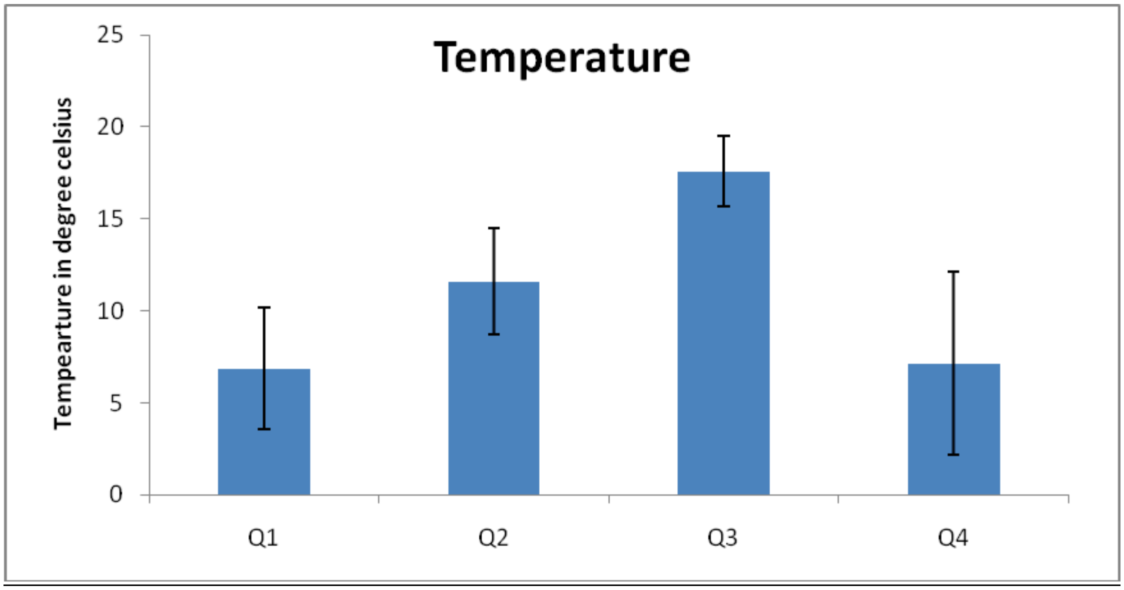


Figure 3. Average temperature for all quarters in 2005.

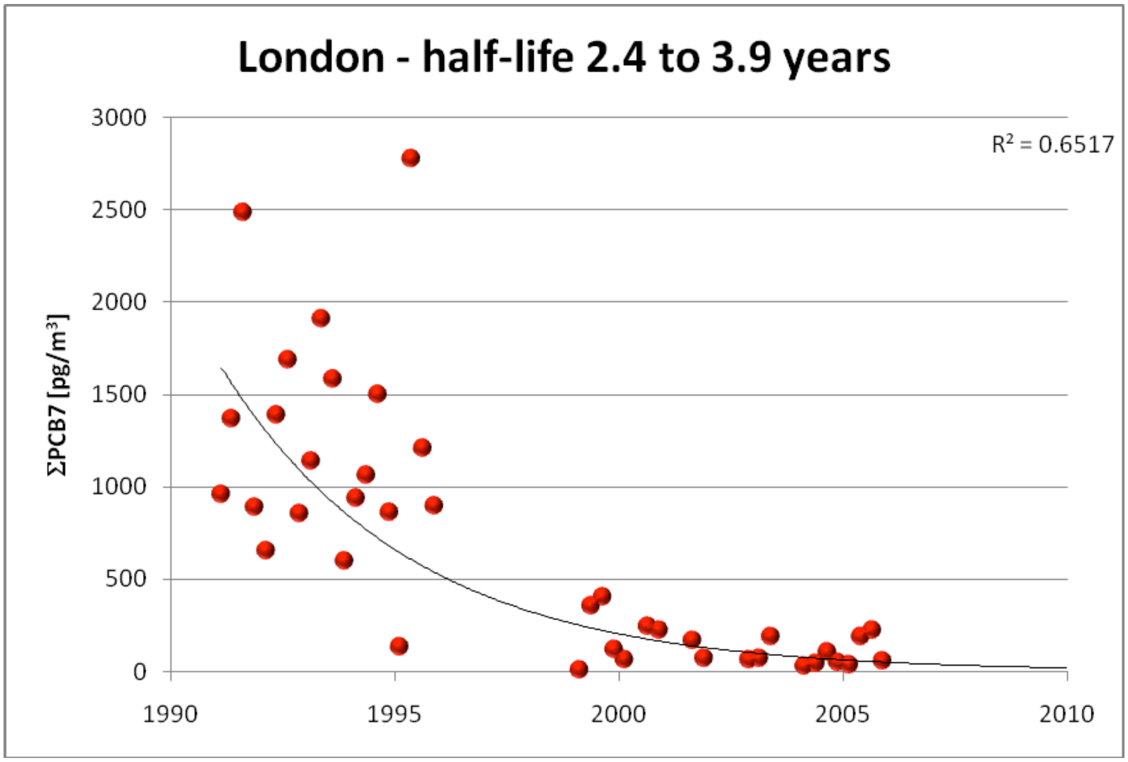


Figure 4a. $\sum_7$PCB data for the London TOMPs site

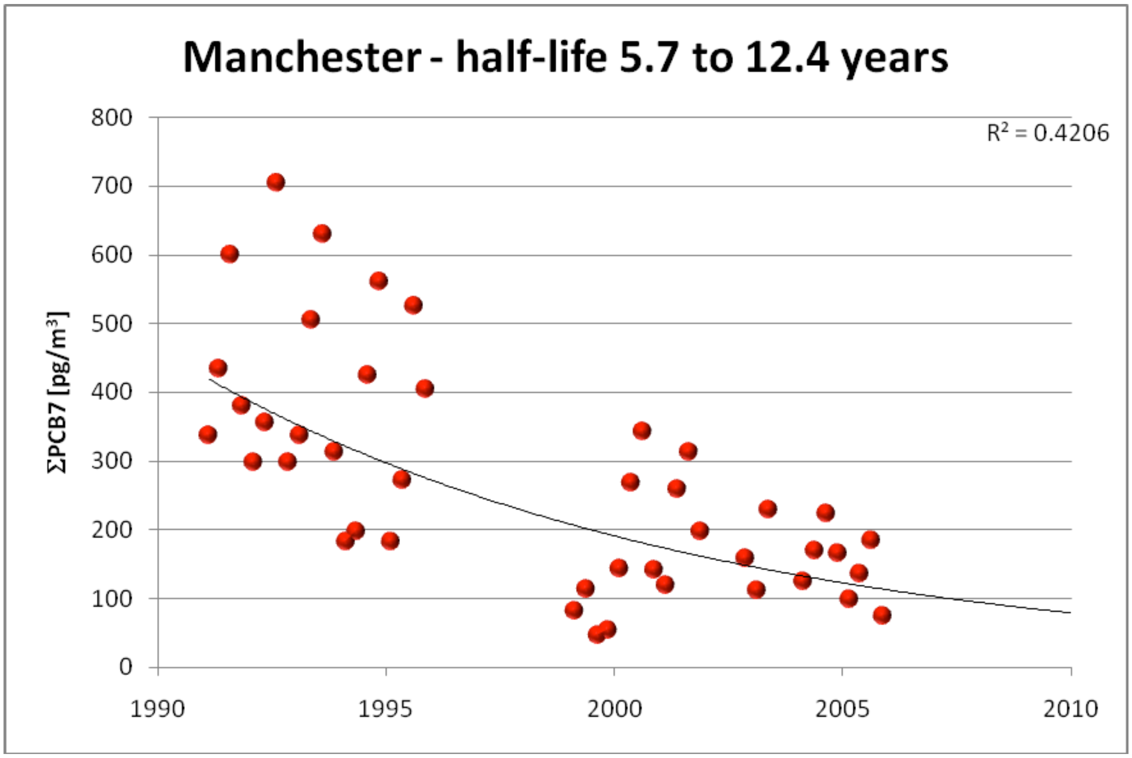


Figure 4b. $\sum_7$PCB data for the Manchester TOMPs site

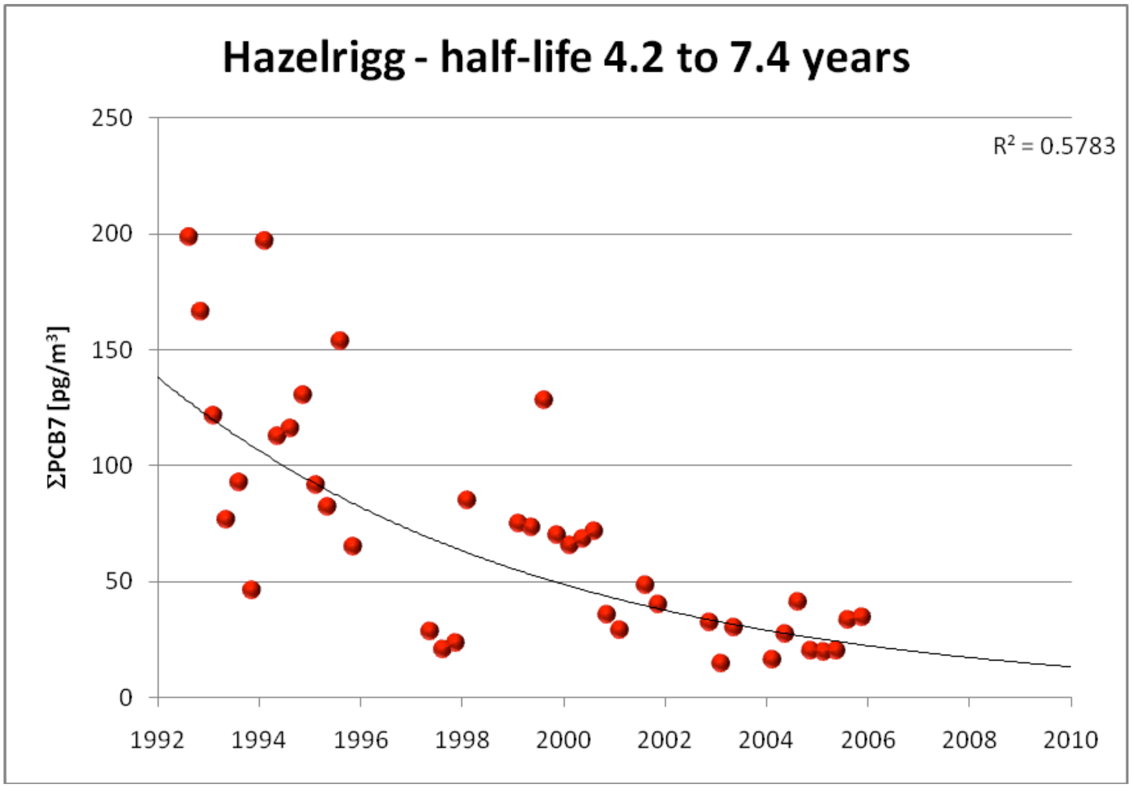


Figure 4c. $\sum_7$PCB data for the Hazelrigg TOMPs site

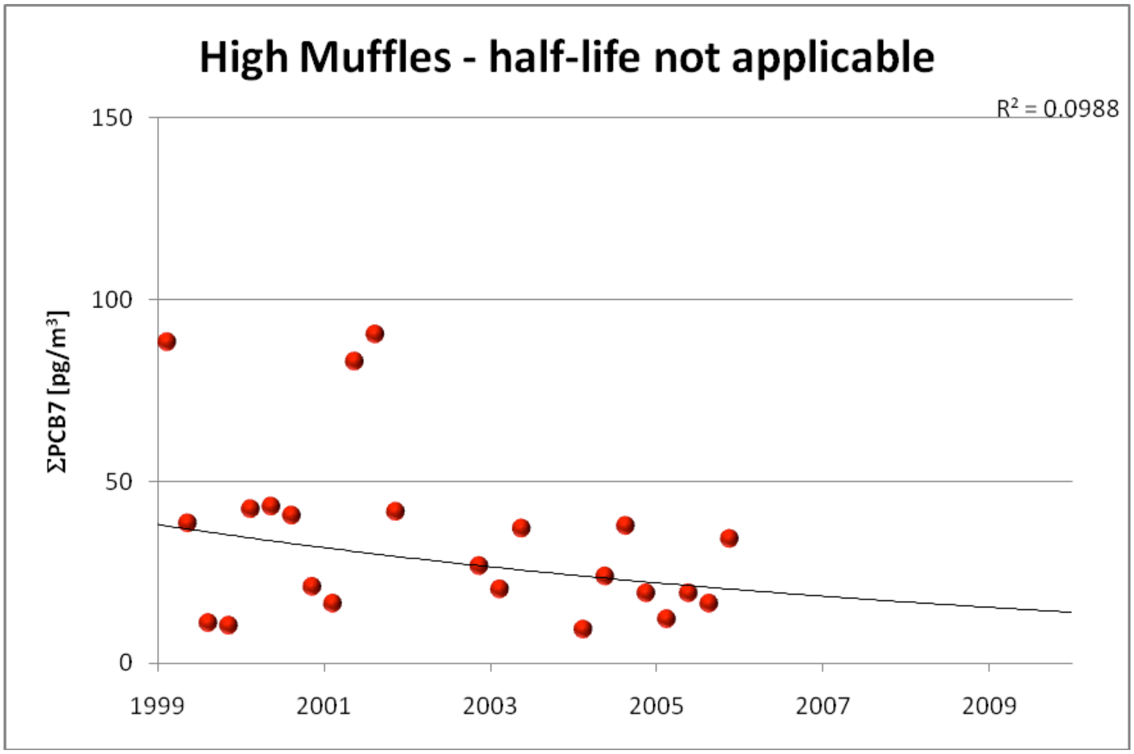


Figure 4d. $\sum_7$PCB data for the High Muffles TOMPs site

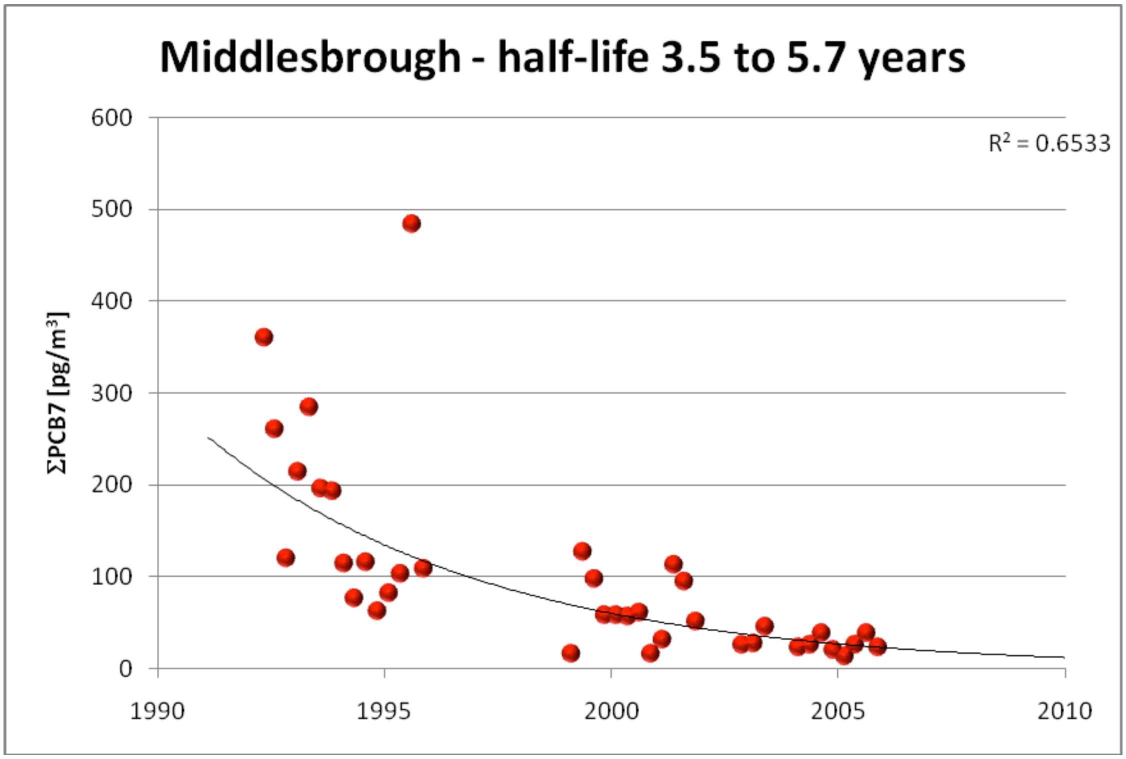


Figure 4e. $\sum_7$PCB data for the Middlesbrough TOMPs site

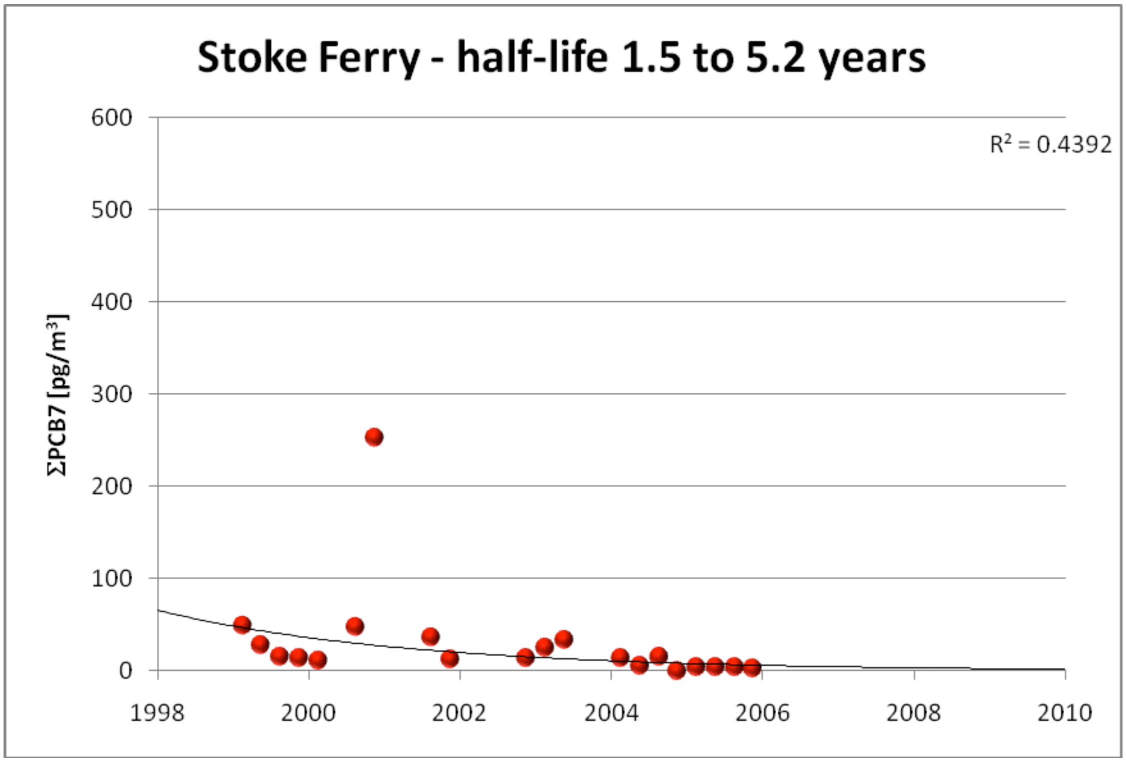


Figure 4f. $\sum_7$PCB data for the Stoke Ferry TOMPs site

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.

Although the urban sites of London, Manchester and Middlesbrough always display the highest concentration, the temporal trends show that PCBs dramatically declined at these sites from 1990 to year 2000 (Figure 4). Since then PCB concentrations measured at the urban sites has always been pretty much constant. Therefore concentrations measured in 2005 are not significantly different from those measured in 2004. The calculated half-lives cannot be considered significantly different between sites or between congeners. For the data set up to the end of 2005 the average half-live is 5.9 years with values spanning from 1.5 to 12 years. The observed half-lives for the rural sampling sites range from 1.5 – 5.2 years at Stoke Ferry and 4.2 – 7.4 years at Hazelrigg. For the urban sites the ranges are 3.5 – 5.7 years at Middlesbrough, 5.7 - 12 years at Manchester and 2.4 – 3.9 years at London.. The half-life calculations for High Muffles yielded no significant results. 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 Σ_7PCBs. This agreement holds for the other TOMPs datasets and suggests that the NAEI captures the main on-going PCB sources such as industrial processes (including use of HFC, N2O, NH3, PFC & SF6) and metal production. As an additional exercise, we estimated emissions over time around the three TOMPS urban/semi-rural sites (London, Manchester, Middlesbrough, Hazelrigg) from the *Breivik et al. (2007)* inventory (Figure 5). In this the total emission for a given country are distributed on a longitude-latitude grid based on population density within the grid square. The area described by each grid square varies from 7300-7700 km^2 for the areas surrounding the TOMPS sites. For the correlations presented in Figure 4 the grid square and the subsequent emission data were chosen closest to the geographical position of the sampling site. For Stoke Ferry and High Muffles the data sets are not comprehensive enough to yield significant results.

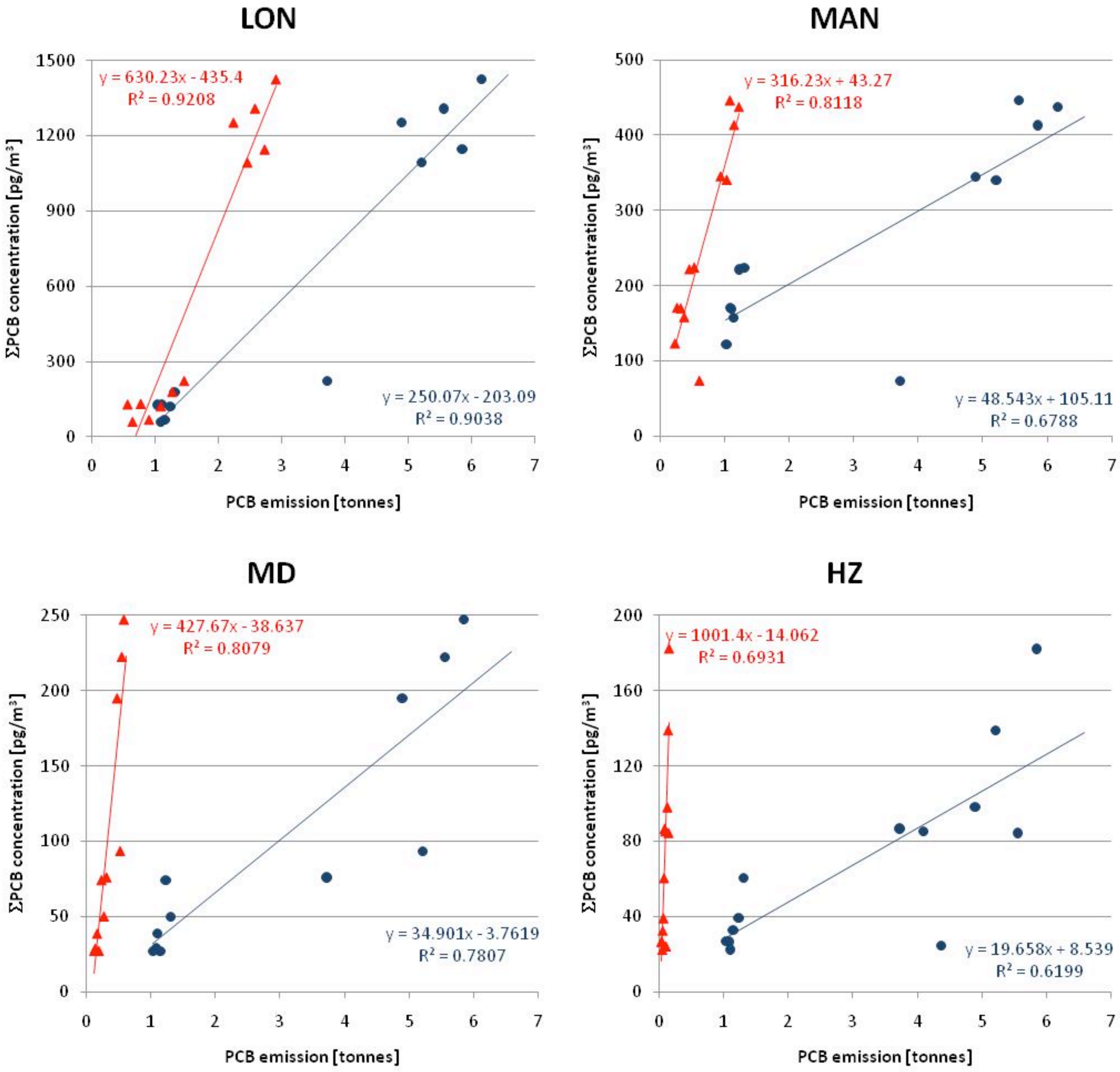


Figure 5. Correlation of observed PCB air concentrations◦ [pg/m^3] to emission estimates [tonnes] for the sampling areas of London (LON), Manchester MAN) Middlesbrough (MD) and Hazelrigg (HZ) (*Breivik et al.* 2007)◦ (▲) and to emission inventory estimates [tonnes] by the National Atmospheric Emissions Inventory (NAEI)◦◦ for the whole of the UK (●)

◦ sum of PCB congeners 28, 52, 90/101, 118, 138, 153/132, 180

◦◦ total sum of PCB congeners

PCDD/Fs

The highest average concentrations of dioxins and furans was observed in Manchester (79.44 fgTEQ/m^3), followed by Middlesbrough (47.79 fgTEQ/m^3) and Stoke Ferry (40.59 fgTEQ/m^3). Surprisingly, the concentrations of PCDD/Fs in London (18.49 fgTEQ/m^3) were at the levels of the semirural areas Hazelrigg (16.47 fgTEQ/m^3) and High Muffles (10.92 fgTEQ/m^3). It can be seen from the following figure that in general the Q1 and Q4 at all sites are the most polluted periods of the year by PCDD/Fs.

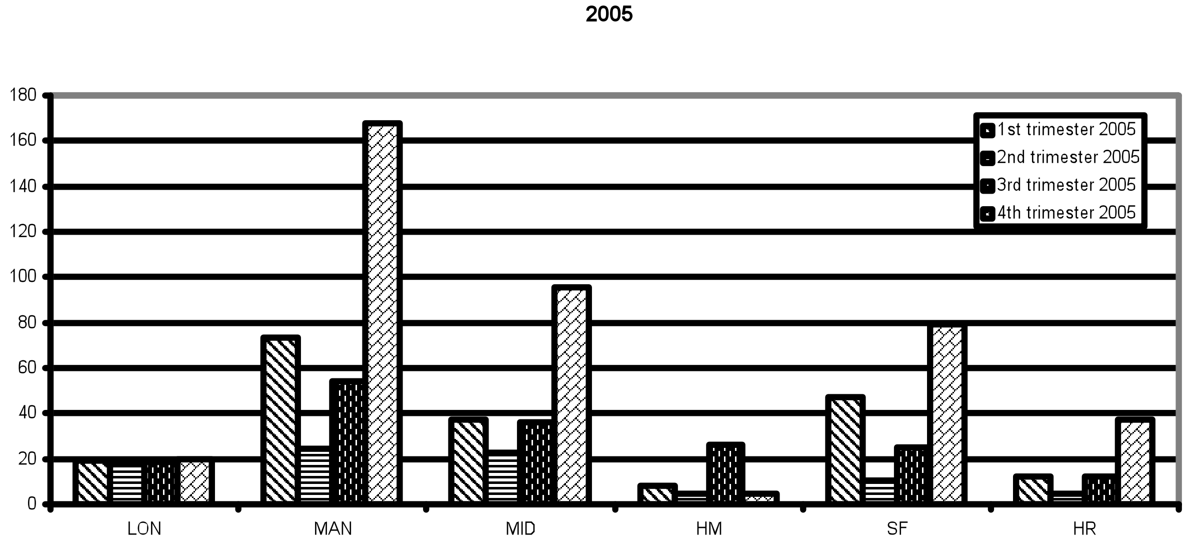
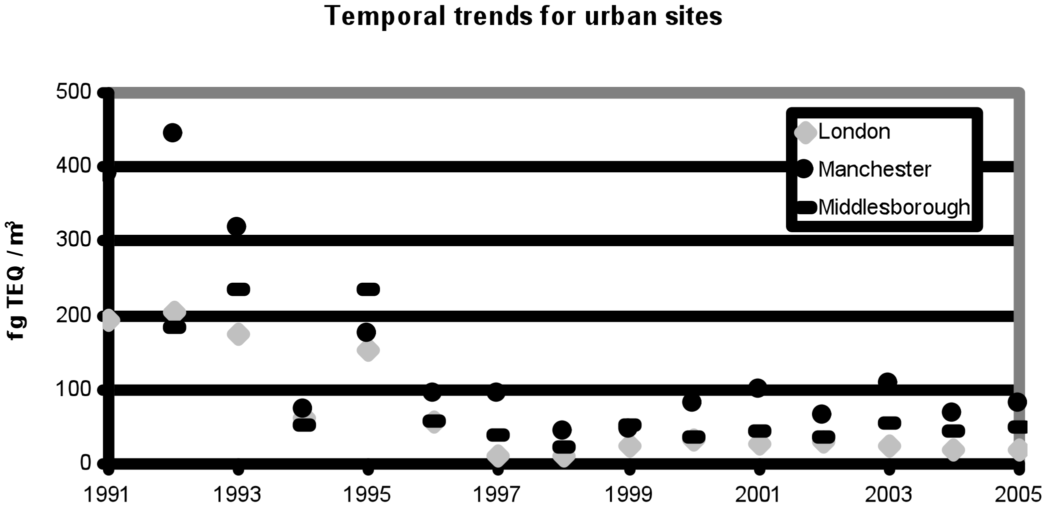


Figure 6. Sum of PCDD/Fs in fg TEQ/m^3 at all sites and quarters in 2005.

This was observed in 2004, is stated in many scientific papers and is widely known as "seasonality of PCDD/Fs". The obvious reason for that is that a big percent of the PCDD/F emissions comes from combustion for heating needs. The low concentrations in London and the fact that there is no seasonality, suggests that in that area, people become very much concern about environmental problems and avoid burning wood or plastic for heating purposes.

In general, the concentrations of PCDD/Fs are showing a continuous decline, something that is in line with the decrease in the emissions of PCDD/Fs and was reported also at the respective report of 2004. Comparing the average values with the respective of 2004, we see that MID and LON are at the same levels and MAN increased (from 66.3 to 79.9 fgTEQ/m^3).



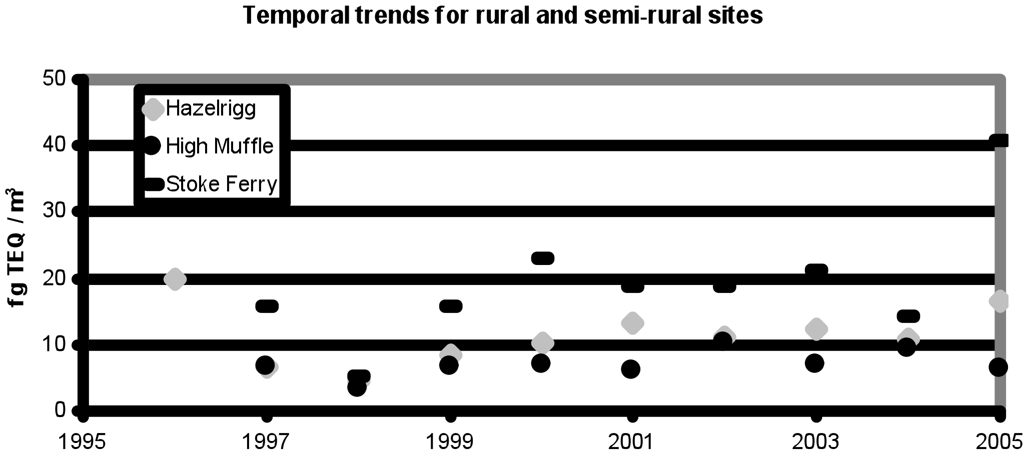


Figure 7. Temporal trends at the urban and rural sites.

As far as the semirural areas are concerned, we can note an increase in the average concentrations of PCDD/Fs in SF, where it was more than doubled compared to 2004 (from 14.4 to 41 fgTEQ/m^3), while HM and HR exhibited a small decrease and increase, respectively. In any case, the concentrations of PCDD/Fs in the UK have been decreasing (see Figure 7) from 1990 to 1997 reflecting that way the decrease that has taken place in the emissions of PCDD/Fs. Since 1997 the PCDD/Fs concentrations measured at all sites has been significantly similar.

The concentrations of PCDD/Fs in 2005 were in same or higher levels than in 2004, although the emissions were slightly decreased, as we can see from the following figure (emissions of PCDD/Fs in the UK, according to https://www.naei.org.uk). The uncertainties that exist while emissions inventories are created, or the existence of local sources which are not included in the inventories, as well as the long range atmpspheric transport by other countries can explain this small discrepancy between emissions and measured concentrations.

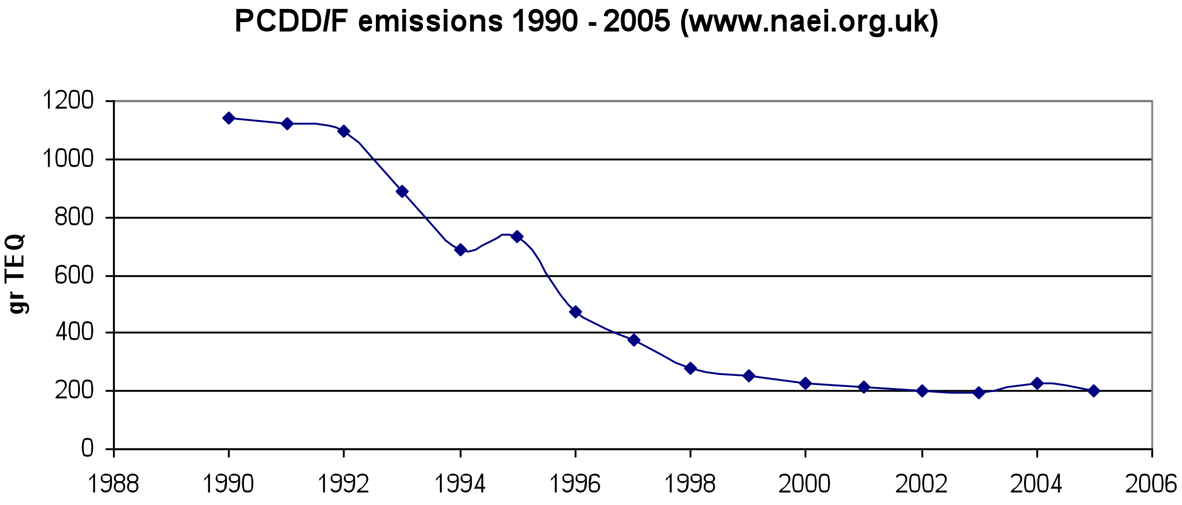


Figure 8. PCDD/F emissions 1990-2004.

8. REFERENCES

Danse, I. R., Jaeger, R. J., Kava, R., Kroger, M., London, W. M., Lu, F. C., Maickel, R. P., McKetta, J. J., Newwell, G. W., Shindell, S., Stare, F. J., Whelan, E. M. 1997. Position paper of the American Council on Science and Health: Public health concerns about environmental polychlorinated biphenyls (PCBs), Ecotoxicology and Environmental Safety, 38, 71-84.

Eduljee, G.H. 1988. PCBs in the environment. Chemistry in Britain, 24, 241-244.

de Voogt, P., Brinkman, U. A. T. 1989. Production, properties and usage of polychlorinated biphenyls. In: Kimbrough R. D., Jensen A A (Eds). Halogenated biphenyls, terphenyls, naphthalenes, debenzodioxins and related products. Elsevier-North, Amsterdam, Holland. Safety, 38, 71-84.

Harrad, S. J., Sewart, A. P., Alcock, R., Boumphrey, R., Burnett, V., Duarte-Davidson, R., Halsall, C., Sanders, G., Waterhouse, K., Wild, S. R., Jones, K. C. 1994. Polychlorinated biphenyls (PCBs) in the British environment: Sinks, sources and temporal trends. Environmental Pollution, 85, 131-146.

Breivik, K., Sweetman, A., Pacyna, J. M., Jones, K. C. 2002b. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach: 2. Emissions. Science of Total Environment 290, 199-224.

Thomas, G. O.; Sweetman, A. J.; Parker, C. A.; Kreibich, H.; Jones, K. C. Development and validation of methods for the trace determination of PCBs in biological matrices. Chemosphere, 1998, 36, 2447-2459.

Gouin T.; Thomas G. O.; Cousins I.; Barber J.; Mackay D. and Jones K. C. Air-surface exchange of polybrominated diphenyl ethers and polychlorinated biphenyls. Environ. Sci. Technol., 2002, 38, 1426-1434.

Appendix 1. PCDD/Fs data (fgTEQ/m^3).

London	Q1	Q2	Q3	Q4	Average
2378 TCDF	0.89	1.80	1.80	1.20	1.42
23478 PeCDF	4.85	4.80	4.80	6.00	5.11
123478 HxCDF	1.70	1.40	1.40	1.20	1.43
123678 HxCDF	1.40	0.90	0.90	0.93	1.03
234678 HxCDF	1.30	1.20	1.20	1.50	1.30
123789 HxCDF	0.04	0.03	0.03	0.07	0.04
1234678 HpCDF	0.42	0.34	0.34	0.41	0.38
1234789 HpCDF	0.04	0.05	0.05	0.05	0.05
OCDF	0.00	0.00	0.00	0.00	0.00
2378 TCDD	1.40	0.90	0.90	1.70	1.23
12378 PeCDD	1.40	3.20	3.20	3.00	2.70
123478 HxCDD	0.63	0.37	0.37	0.42	0.45
123678 HxCDD	1.40	0.83	0.83	1.20	1.07
123789 HxCDD	1.60	0.96	0.96	0.95	1.12
1234678 HpCDD	1.60	1.00	1.00	0.98	1.15
OCDD	0.04	0.03	0.03	0.03	0.03
WHO-TEQ	19.21	18.36	18.36	20.01	18.49

Manchester	Q1	Q2	Q3	Q4	Average
2378 TCDF	4.30	1.40	2.29	4.25	3.06
12378 PeCDF	1.75	0.50	1.16	2.61	1.51
23478 PeCDF	29.50	7.50	17.79	62.79	29.40
123478 HxCDF	6.10	2.20	4.43	11.05	5.94
123678 HxCDF	2.50	0.87	3.51	8.65	3.88
234678 HxCDF	5.40	1.90	4.95	15.46	6.93
123789 HxCDF	0.33	0.06	0.00	4.04	1.11
1234678 HpCDF	1.20	0.53	1.36	3.91	1.75
1234789 HpCDF	0.14	0.06	0.21	0.49	0.23
OCDF	0.01	0.00	0.01	0.03	0.01
2378 TCDD	1.70	1.00	1.73	7.00	2.86
12378 PeCDD	10.00	4.30	10.36	28.27	13.23
123478 HxCDD	1.30	0.35	0.97	2.94	1.39
123678 HxCDD	2.50	0.87	2.26	6.75	3.09
123789 HxCDD	2.70	1.30	1.71	4.14	2.46
1234678 HpCDD	2.70	0.79	1.34	5.32	2.54
OCDD	0.08	0.02	0.03	0.13	0.06
WHO-TEQ	73.31	24.59	54.10	167.81	79.44

Middlesbrough	Q1	Q2	Q3	Q4	Average
2378 TCDF	1.80	1.60	1.48	2.65	1.88
12378 PeCDF	0.85	0.55	0.80	1.36	0.89
23478 PeCDF	8.50	6.00	12.97	29.16	14.16
123478 HxCDF	2.10	1.80	2.60	6.06	3.14
123678 HxCDF	2.00	1.50	2.12	4.19	2.45
234678 HxCDF	2.10	1.50	2.80	7.36	3.44
123789 HxCDF	0.16	0.06	0.15	2.02	0.60
1234678 HpCDF	0.63	0.53	0.71	1.78	0.91
1234789 HpCDF	0.09	0.07	0.09	0.26	0.13
OCDF	0.01	0.00	0.00	0.01	0.01
2378 TCDD	2.90	1.40	0.00	3.94	2.06
12378 PeCDD	8.70	4.30	7.45	20.30	10.19
123478 HxCDD	0.93	0.44	0.74	2.24	1.09
123678 HxCDD	1.70	0.91	1.75	4.67	2.26
123789 HxCDD	2.60	1.30	1.19	4.38	2.37
1234678 HpCDD	1.90	0.88	1.00	4.93	2.18
OCDD	0.05	0.02	0.02	0.13	0.06
WHO-TEQ	37.01	22.87	35.85	95.44	47.79

Hazelrigg	Q1	Q2	Q3	Q4	Average
2378 TCDF	0.51	0.38	0.55	1.31	0.69
12378 PeCDF	0.28	0.11	0.24	0.56	0.30
23478 PeCDF	3.00	1.00	3.54	11.69	4.81
123478 HxCDF	1.00	0.17	0.80	2.40	1.09
123678 HxCDF	0.78	0.33	0.74	1.75	0.90
234678 HxCDF	0.69	0.27	1.15	2.53	1.16
123789 HxCDF	0.03	0.03	0.04	0.71	0.20
1234678 HpCDF	0.23	0.12	0.31	0.62	0.32
1234789 HpCDF	0.02	0.01	0.05	0.08	0.04
OCDF	0.00	0.00	0.00	0.01	0.00
2378 TCDD	1.00	1.00	1.18	2.93	1.53
12378 PeCDD	1.80	0.40	2.61	6.64	2.86
123478 HxCDD	0.28	0.04	0.11	0.77	0.30
123678 HxCDD	0.68	0.30	0.32	1.87	0.79
123789 HxCDD	0.87	0.15	0.17	1.68	0.72
1234678 HpCDD	0.76	0.22	0.40	1.62	0.75
OCDD	0.02	0.01	0.01	0.05	0.02
WHO-TEQ	11.95	4.53	12.22	37.20	16.47

High Muffles	Q1	Q2	Q3	Q4	Average
2378 TCDF	0.37	0.24	0.51	0.40	0.38
12378 PeCDF	0.14	0.05	0.39	0.13	0.18
23478 PeCDF	1.75	1.35	7.58	1.15	2.96
123478 HxCDF	0.59	0.19	1.67	0.43	0.72
123678 HxCDF	0.65	0.28	1.45	0.43	0.70
234678 HxCDF	0.57	0.20	2.33	0.44	0.89
123789 HxCDF	0.42	0.16	0.09	0.04	0.18
1234678 HpCDF	0.16	0.09	0.62	0.15	0.25
1234789 HpCDF	0.02	0.02	0.10	0.02	0.04
OCDF	0.00	0.00	0.00	0.00	0.00
2378 TCDD	1.00	1.00	0.50	0.09	0.65
12378 PeCDD	0.60	0.40	6.46	0.83	2.07
123478 HxCDD	0.22	0.04	0.69	0.12	0.27
123678 HxCDD	0.38	0.30	1.41	0.29	0.59
123789 HxCDD	0.42	0.16	1.13	0.14	0.46
1234678 HpCDD	0.71	0.15	1.18	0.24	0.57
OCDD	0.03	0.00	0.03	0.01	0.02
WHO-TEQ	8.03	4.63	26.14	4.87	10.92

Stoke Ferry	Q1	Q2	Q3	Q4	Average
2378 TCDF	2.50	0.65	0.72	1.77	1.41
12378 PeCDF	1.00	0.22	0.36	1.08	0.66
23478 PeCDF	12.50	2.90	6.95	20.97	10.83
123478 HxCDF	4.50	0.95	1.52	4.25	2.81
123678 HxCDF	3.40	0.70	1.48	2.69	2.07
234678 HxCDF	3.50	0.69	2.05	5.95	3.05
123789 HxCDF	0.17	0.03	0.57	1.50	0.57
1234678 HpCDF	1.30	0.23	0.51	1.33	0.84
1234789 HpCDF	0.19	0.01	0.09	0.19	0.12
OCDF	0.01	0.00	0.00	0.01	0.01
2378 TCDD	1.30	1.00	1.32	2.34	1.49
12378 PeCDD	7.90	1.50	5.59	18.33	8.33
123478 HxCDD	0.87	0.28	0.33	2.71	1.05
123678 HxCDD	2.50	0.47	1.30	4.44	2.18
123789 HxCDD	2.90	0.61	1.16	4.82	2.37
1234678 HpCDD	2.80	0.50	1.08	6.40	2.70
OCDD	0.12	0.01	0.03	0.30	0.12
WHO-TEQ	47.46	10.75	25.06	79.08	40.59

Appendix 2. PCBs data.

LONDON 2005	Q1.05	Q2.05	Q3.05	Q4.05
PCB/OC	pg/m^3	pg/m^3	pg/m^3	pg/m^3
18	12	28	48	17
22	2.7	7.1	17	5.5
28	11	29	54	16
31	12	37	43	15
44	6.3	24	31	8.4
49	5	18	23	5.9
52	11	39	52	14
54	<0.36	<0.36	0.097	0.028
70	6	24	27	6.9
74	2.6	11	11	3.1
87	2.2	11	15	3.7
95	5.8	26	38	9.7
99	1.7	7.3	10	2.5
104	<0.04	<0.05	<0.04	<0.03
105	0.6	2.9	5.1	1.1
110	3.9	21	28	6.7
114	<0.05	<0.05	0.31	0.085
118	2.2	13	16	3.6
123	0.4	3.2	1.4	0.24
132			17	3.1
138	3.1	25	26	5.3
141	1	9.7	7.3	1.4
149	3.8	34	36	7.1
151	2	19	16	3.1
153	2.8	25	23	6.3
155	<0.04	<0.05	<0.04	<0.03
156	<0.15	1	0.89	0.22
157	<0.14	1	0.72	0.13
158	0.3	2.3	2.2	0.5
167	<0.14	0.4	0.6	0.1
170	1	8.8	4.1	0.92
174	1.2	18	11	2
180	2.5	30	16	3
183	1	13	8	1.3
187	2.3	33	21	3.4
188	<0.09	<0.09	0.026	<0.03
189	<0.04	<0.05	0.053	<0.03
194	0.8	6.9	1.5	0.36
199	0.1	1.6	1.2	0.2
203	0.9	10	4.6	0.88
41/64	5.6	21	27	7.6
60/56	1.9	7.1	14	3.3
90/101	6	30	40	9.4
Σ_7PCBs	15.3	76.6	88.3	21.74

COPLANAR PCBs				
	fg/m3	fg/m3	fg/m3	fg/m3
3,3',4,5-TetraCB	12	50	61	16
3,3',4,4'-TetraCB	240	900	1620	380
3,3',4,4',5-PentaCB	18	61	90	22
3,3',4,4',5,5'-HexaCB	4	6	6.3	2.5

MANCHESTER 2005	**Q1.05**	**Q2.05**	**Q3.05**	**Q4.05**
PCB/OC	pg/m^3	pg/m^3	pg/m^3	pg/m^3
18	24	43	55	21
22	9	9.9	18	6.9
28	24	31	52	18
31	22	30	40	15
44	15	15	26	10
49	11	12	18	7
52	28	26	48	20
54	<0.36	<0.36	0.099	0.046
70	16	16	24	10
74	6.6	7.3	9.5	3.8
87	7.3	8.9	14	6.1
95	19	25	38	17
99	5.8	5.6	10	4.4
104	<0.04	<0.04	<0.03	<0.03
105	2.4	2.3	3.9	1.5
110	14	16	26	11
114	<0.05	<0.05	0.24	0.13
118	8.1	8.7	12	5.3
123	1.3	2.1	0.82	0.32
132			6.7	2.7
138	8.7	17	15	5.8
141	2.3	6.1	3.4	1.2
149	9.4	22	19	7.6
151	4	11	7	2.8
153	6.1	14	15	7.4
155	<0.04	<0.04	<0.03	<0.03
156	0.3	1	0.64	0.25
157	<0.14	0.6	0.22	0.092
158	0.9	1.6	1.1	0.51
167	0.2	0.4	0.31	0.17
170	1.1	5.7	1.9	0.71
174	1.8	7.4	3.4	1.1
180	2.3	12	4.8	1.7
183	1.5	4.7	2	0.7
187	3.2	11	4.7	1.5
188	<0.09	<0.09	0.016	<0.03
189	<0.04	<0.04	0.021	<0.03
194	0.2	3	0.39	0.18
199	0.1	0.4	0.25	0.1
203	0.5	3.2	0.94	0.36
41/64	12	14	20	7.7
60/56	5.4	6.4	12	4.6
90/101	20	27	36	16
Σ_7PCBs	38.2	54	69.58	28.94

COPLANAR PCBs				
	fg/m3	fg/m3	fg/m3	fg/m3
3,3',4,5-TetraCB	59	43	59	33
3,3',4,4'-TetraCB	950	920	1500	620
3,3',4,4',5-PentaCB	55	54	79	63
3,3',4,4',5,5'-HexaCB	11	6	5.2	14

MIDDLESBROUGH 2005	**Q1.05**	**Q2.05**	**Q3.05**	**Q4.05**
PCB/OC	pg/m^3	pg/m^3	pg/m^3	pg/m^3
18	6.6	12	16	11
22	2.1	4.2	6.6	3.8
28	6.2	13	19	12
31	7.3	14	17	8.8
44	3.3	6.5	8.4	4.5
49	3	5.2	6.5	3.7
52	4.2	7.8	10	6
54	<0.36	<0.36	0.03	0.032
70	3.1	5.8	7.8	3.9
74	1.7	3.4	4	2.1
87	0.7	1.3	2	1
95	1.8	3.2	5.3	3.1
99	0.5	0.9	1.4	0.86
104	<0.04	<0.04	<0.05	<0.03
105	<0.04	0.3	0.48	0.27
110	0.9	2.1	3.6	1.9
114	<0.05	<0.05	0.07	0.032
118	0.7	1.1	1.5	0.79
123	0.2	0.3	0.17	0.091
132			1.2	0.59
138	0.8	1.5	2	1.2
141	<0.04	0.5	0.52	0.34
149	1.4	2.1	3.1	2
151	0.6	0.9	1.2	0.9
153	0.6	1.1	2.7	1.7
155	<0.04	<0.04	<0.05	<0.03
156	<0.15	<0.15	0.074	0.069
157	<0.14	<0.14	0.057	0.025
158	<0.06	0.3	0.13	0.11
167	<0.14	<0.14	0.15	0.033
170	<0.07	<0.07	0.18	0.13
174	<0.04	0.2	0.35	0.22
180	0.2	0.3	0.43	0.34
183	0.3	0.2	0.3	0.19
187	0.4	0.7	0.62	0.38
188	<0.09	<0.09	<0.05	<0.03
189	<0.04	<0.04	<0.05	<0.03
194	<0.04	<0.04	<0.05	0.015
199	<0.04	<0.04	<0.05	0.013
203	<0.04	<0.04	0.11	0.095
41/64	3.7	7.7	8.7	4.8
60/56	1.4	3.1	5.4	2.8
90/101	1.9	3.3	5.1	3.1
Σ_7PCBs	7	14.1	19.31	10.823

COPLANAR PCBs				
	fg/m3	fg/m3	fg/m3	fg/m3
3,3',4,5-TetraCB	19	18	31	19
3,3',4,4'-TetraCB	260	400	690	340
3,3',4,4',5-PentaCB	15	13	18	22
3,3',4,4',5,5'-HexaCB	4	4	3.2	11

STOKE FERRY 2005	**Q1.05**	**Q2.05**	**Q3.05**	**Q4.05**
PCB/OC	pg/m^3	pg/m^3	pg/m^3	pg/m^3
18	2.8	2.9	6.9	4
22	1.4	1.5	4.7	1.5
28	2	2.2	5.1	3.5
31	1.8	2.1	2.8	1.9
44	1	1	2.2	1.3
49	0.9	1.2	1.5	1.1
52	1.6	1.5	3.3	2.1
54	<0.36	<0.36	0.011	0.011
70	0.6	0.7	1.4	0.89
74	0.4	0.6	0.78	0.46
87	<0.4	<0.4	0.56	0.41
95	0.9	0.7	1.8	1.2
99	0.3	0.3	0.47	0.4
104	<0.05	<0.04	<0.01	<0.01
105	<0.05	<0.04	0.18	0.12
110	0.4	0.4	1.1	0.76
114	<0.05	<0.05	<0.01	<0.01
118	0.2	0.3	0.57	0.36
123	<0.05	<0.04	<0.01	0.037
132			0.4	0.26
138	0.6	0.3	0.77	0.6
141	<0.05	<0.04	0.18	0.11
149	0.6	0.5	1.1	0.76
151	0.3	<0.12	0.44	0.29
153	0.5	0.2	0.96	0.74
155	<0.05	<0.04	<0.01	0.023
156	<0.15	<0.15	0.028	0.024
157	<0.14	<0.14	0.023	0.017
158	0.4	<0.06	0.071	0.051
167	<0.14	<0.14	0.022	0.017
170	<0.07	<0.07	0.098	0.08
174	<0.05	<0.04	0.14	0.13
180	0.3	0.1	0.21	0.18
183	<0.06	<0.06	0.1	0.081
187	0.3	0.1	0.25	0.18
188	<0.09	<0.09	<0.01	<0.01
189	<0.05	<0.04	<0.01	<0.01
194	<0.05	<0.04	0.009	0.031
199	<0.05	<0.04	0.009	0.011
203	<0.05	<0.04	0.05	0.049
41/64	1.3	1.3	0.99	0.96
60/56	<0.42	0.5	0.7	0.45
90/101	1	0.7	1.6	1.2
Σ_7PCBs	2.3	2.5	3.358	2.701

COPLANAR PCBs				
	fg/m3	fg/m3	fg/m3	fg/m3
3,3',4,5-TetraCB	9	7	5.5	5.3
3,3',4,4'-TetraCB	46	63	85	57
3,3',4,4',5-PentaCB	17	6	6.1	8.2
3,3',4,4',5,5'-HexaCB	5	2	0.95	2

HIGH MUFFLES 2005	Q1.05	Q2.05	Q3.05	Q4.05
PCB/OC	pg/m^3	pg/m^3	pg/m^3	pg/m^3
18	4	6.5	7.1	10
22	3.1	5.4	3.5	8.4
28	6.7	9.7	8.1	19
31	6.1	9.5	7.4	9
44	3.1	5	3.4	6.9
49	2.9	4	2.8	4.7
52	3.3	5.4	4.1	7.3
54	<0.36	<0.36	0.012	0.018
70	2.9	4.4	3.4	6.5
74	1.9	2.7	1.9	3.6
87	0.5	0.6	0.6	1.3
95	1.7	2.8	2.3	3.5
99	0.4	0.5	0.5	0.91
104	<0.05	<0.04	<0.02	<0.02
105	<0.05	<0.04	0.17	0.29
110	0.8	1.4	1.1	2.2
114	<0.05	<0.05	0.023	<0.02
118	0.4	0.6	0.52	1.1
123	0.3	0.3	0.064	0.19
132			0.42	0.93
138	0.6	1	0.72	1.3
141	<0.05	0.4	0.2	0.38
149	0.9	1.7	1.5	2.5
151	0.5	0.7	0.71	1.2
153	<0.05	<0.04	1.1	1.8
155	<0.15	<0.15	<0.02	<0.02
156	<0.14	<0.14	0.032	0.037
157	<0.06	<0.06	0.019	0.04
158	<0.14	<0.14	0.053	0.11
167	<0.07	<0.07	0.045	0.037
170	<0.05	0.1	0.077	0.11
174	<0.05	0.2	0.16	0.27
180	<0.06	0.1	0.17	0.3
183	<0.05	0.4	0.11	0.18
187	<0.09	<0.09	0.26	0.44
188	<0.05	<0.04	<0.02	<0.02
189	<0.05	<0.04	<0.02	<0.02
194	<0.05	<0.04	<0.02	0.015
199	<0.05	<0.04	0.007	0.011
203	0.5	0.8	0.036	0.043
41/64	3.8	5.8	3.9	7.2
60/56	1.7	2.7	2.5	6.3
90/101	1.6	2.7	2	3.7
Σ_7PCBs	7.6	12	8.44	17.27

COPLANAR PCBs				
	fg/m3	fg/m3	fg/m3	fg/m3
3,3',4,5-TetraCB	11	19	16	33
3,3',4,4'-TetraCB	140	280	270	560
3,3',4,4',5-PentaCB	5.2	9	8.4	16
3,3',4,4',5,5'-HexaCB	1	0.7	<0.6	<0.6

HAZELRIGG 2005	Q1.05	Q2.05	Q3.05	Q4.05
PCB/OC	pg/m^3	pg/m^3	pg/m^3	pg/m^3
18	5.9	7.2	11	10
22	5.2	5.5	7.6	8.4
28	9.9	10	17	19
31	10	10	9.8	9
44	4.6	4.4	5.4	6.9
49	3.6	3.8	3.8	4.7
52	4.8	4.9	6.7	7.3
54	<0.36	<0.36	0.017	0.018
70	4.4	4.2	2.2	6.5
74	2.7	2.8	0.53	3.6
87	0.4	0.4	1.5	1.3
95	2.4	2.3	4.3	3.5
99	0.4	0.7	1.2	0.91
104	<0.04	<0.04	<0.02	<0.02
105	<0.04	<0.04	0.38	0.29
110	1.3	1.2	2.7	2.2
114	<0.05	<0.05	<0.02	<0.02
118	0.4	0.8	1.3	1.1
123	0.2	0.2	0.2	0.19
132			0.95	0.93
138	1	1.3	1.6	1.3
141	<0.04	0.3	0.42	0.38
149	1.8	1.7	3	2.5
151	0.7	0.5	1.3	1.2
153	0.9	1	2.5	1.8
155	<0.04	<0.04	<0.02	<0.02
156	<0.15	<0.15	0.055	0.037
157	<0.14	<0.14	0.022	0.04
158	<0.06	0.1	0.12	0.11
167	<0.14	<0.14	0.053	0.037
170	<0.07	<0.07	0.16	0.11
174	0.1	0.2	0.32	0.27
180	0.3	0.3	0.38	0.3
183	0.1	0.2	0.22	0.18
187	0.4	0.5	0.48	0.44
188	<0.09	<0.09	<0.02	<0.02
189	<0.04	<0.04	<0.02	<0.02
194	<0.04	<0.04	0.011	0.015
199	<0.04	<0.04	0.011	0.011
203	<0.04	<0.04	0.057	0.043
41/64	5.5	5.5	4.8	7.2
60/56	3.2	2.8	4.3	6.3
90/101	2.4	2.3	4.1	3.7
Σ_7PCBs	11.1	10.6	13.27	17.27

COPLANAR PCBs				
	fg/m3	fg/m3	fg/m3	fg/m3
3,3',4,5-TetraCB	9.6	12	20	11
3,3',4,4'-TetraCB	170	300	530	240
3,3',4,4',5-PentaCB	4.9	2.6	10	8.8
3,3',4,4',5,5'-HexaCB	1.6	1.6	<0.6	1.7