

The Lancaster Environment Centre

Annual Report for 2007 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**



Executive Summary.

This report contains the 2007 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 2007, 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.

TABLE OF CONTENTS

	Page
1. Introduction	4
2. Background to PCBs, PCDDs and PCDFs	4
3. TOMPs sites in 2007	6
4. Network sampling operations	7
5. Extraction and clean-up procedures	8
6. Data storage	10
7. Results for year 2007	11
7.1. PCDD/Fs	
7.2. PCBs	
8. References	24
I. Appendix 1. PCDD/Fs data	
II. Appendix 2. PCBs data	

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.

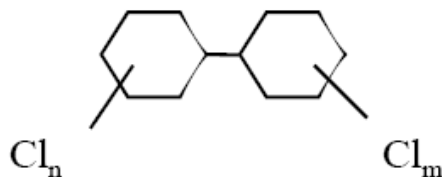
This annual report for polychlorinated biphenyls (PCBs) polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) includes:

- 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 marketed as mixed products under various trade names depending on the country where they were produced such as Aroclor (Monosanto, USA), Pheno-chlor 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,

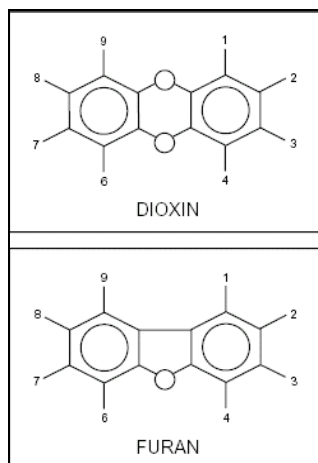
sealants and surface coatings (Eduljee, 1988; de Voogt and Brinkman, 1989; Harrad et al., 1994). Their basic structure is a biphenyl backbone with one to ten chlorine substituents and a general structure of $C_{12}H_{10-n}Cl_n$ ($n=1-10$) (Figure 2).



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 were 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 2007

In 2007 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) 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. The locations of the current samplers in the network are shown in Figure 1.



Figure 1. Locations of the sampling sites.

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 °C 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 (°C). 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 °C overnight following established procedures. Each sample (gas + particle) was spiked with a recovery standard of $^{13}\text{C}_{12}$ -labeled PCB congeners ($^{13}\text{C}_{12}$ PCB 28, 52, 101, 138, 153, 180, 209) and an isotope dilution/recovery standard containing $^{13}\text{C}_{12}$ -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 rotary 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 m³ 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 H₂SO₄, 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 [¹³C₁₂] PCB 141 and [¹³C₁₂] 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. 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 ³⁷Cl-labeled 2,3,7,8-TCDD was 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 fg m⁻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 ¹³C₁₂-labelled PCBs standards and they ranged between 70-110%. Recoveries are monitored by quantifying 20 ¹³C₁₂-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 2007

During the sampling campaigns, 5-7 samples were bulked from each site during each trimester and the total air volume bulked ranged between 2700 and 5000 m³.

Problems with analytical interferences occurred for the LON site during the 2nd quarter and for MID during the 4th quarter, which led to non calculation of the PCDD/F concentrations for the afore-mentioned periods. A number of additional steps to remove these interferences were attempted but were not successful.

Table 1. Summary of the bulked air volumes and number of samples for each quarter at all sites in 2007.

		LON	MAN	MID	HM	SF	HR
Bulked Air Volumes m3	Q1	4788	3910	2680	4057	3831	3319
No of samples		6	6	6	6	6	6
Bulked Air Volumes m3	Q2	5593	5266	2292	3565	4236	5351
No of samples		7	7	7	7	7	7
Bulked Air Volumes m3	Q3	3845	5681	3103	4626	4703	5226
No of samples		7	7	7	7	7	7
Bulked Air Volumes m3	Q4	5593	4416	2712	3985	4236	4239
No of samples		6	6	6	6	6	6

PCBs

The measured concentrations in the two urban sites of London and Manchester continue to be higher comparing to the remote ones (max concentrations 64.7 and 77.4 pg/m³, respectively). However, the average concentrations at the two urban sites of London and Manchester has declined since 2006 for all quarters by a factor of 2 (see Figure 2 and Figure 2 in report 2006). The three suburban - rural sites values in the levels of 10 – 20 of pg/m³; these PCB concentrations remain similar to those measured in 2006.

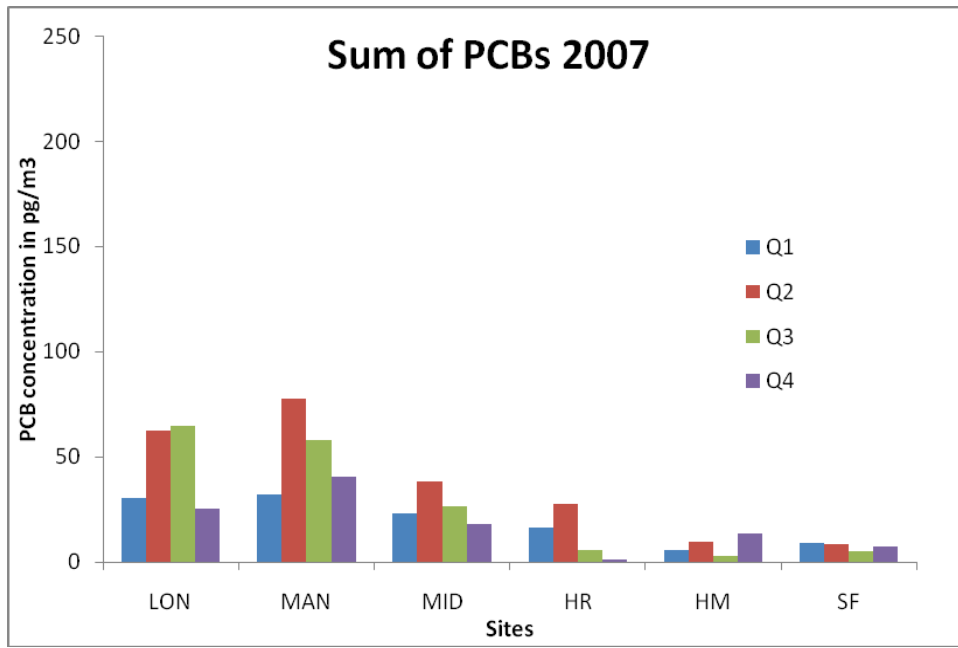


Figure 2. Sum of PCB concentrations at all sites for all quarters in 2007.

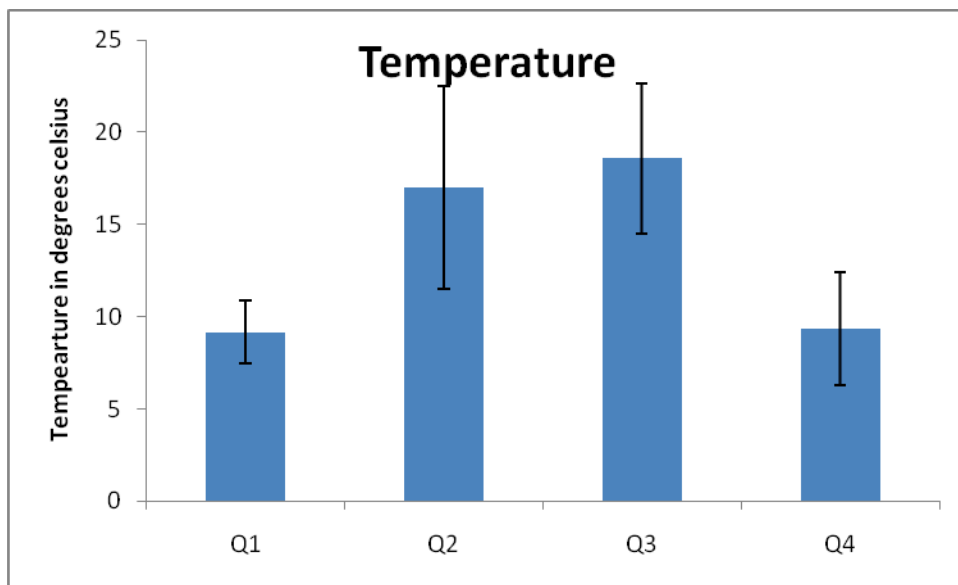


Figure 3. Average temperature for all quarters in 2007.

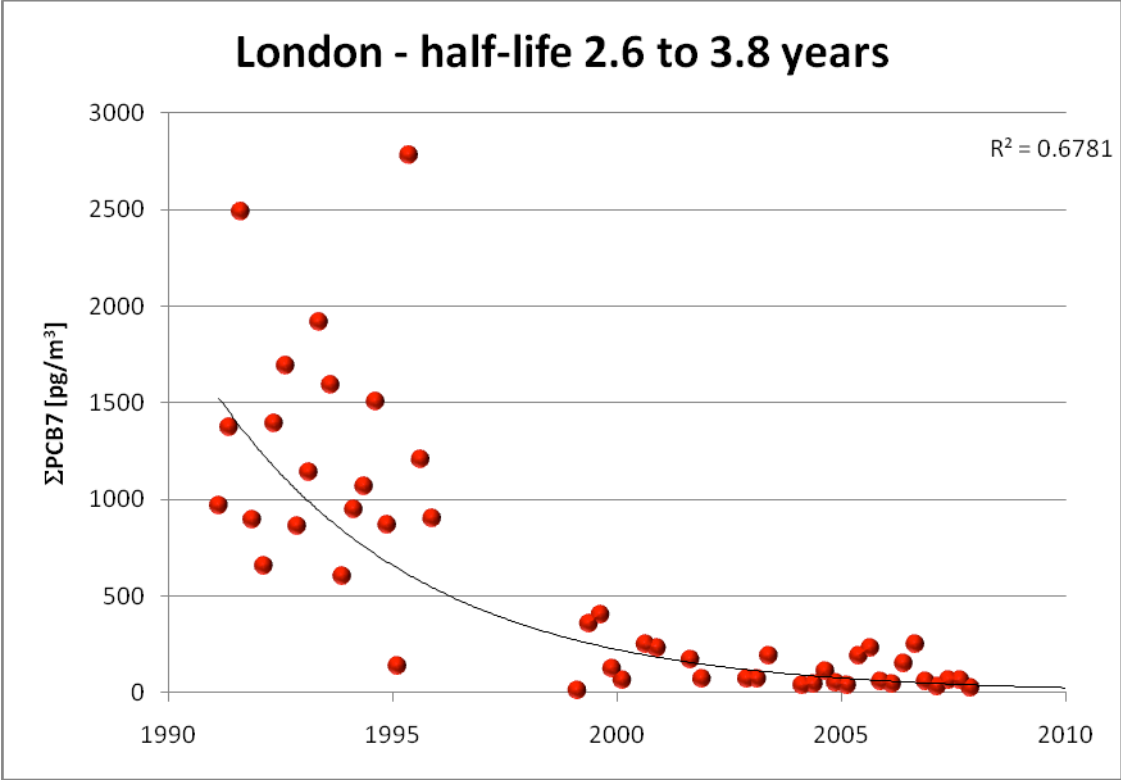


Figure 4a. $\Sigma_7\text{PCB}$ data for the London TOMPs site

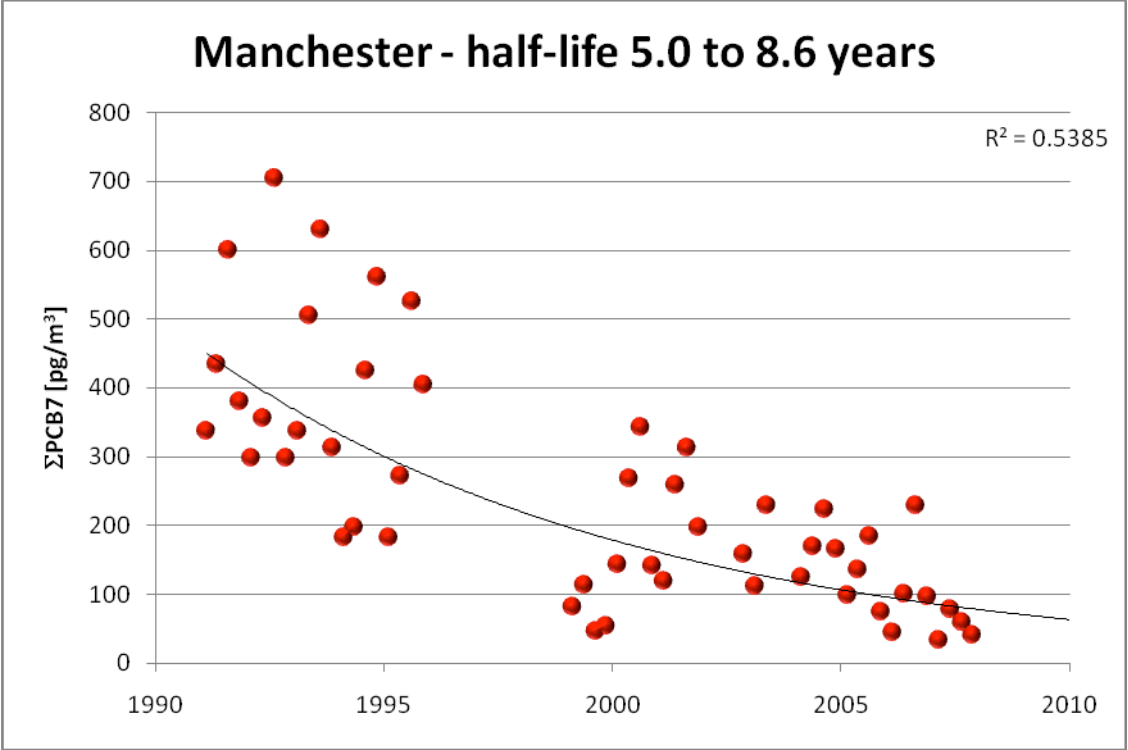


Figure 4b. $\Sigma_7\text{PCB}$ data for the Manchester TOMPs site

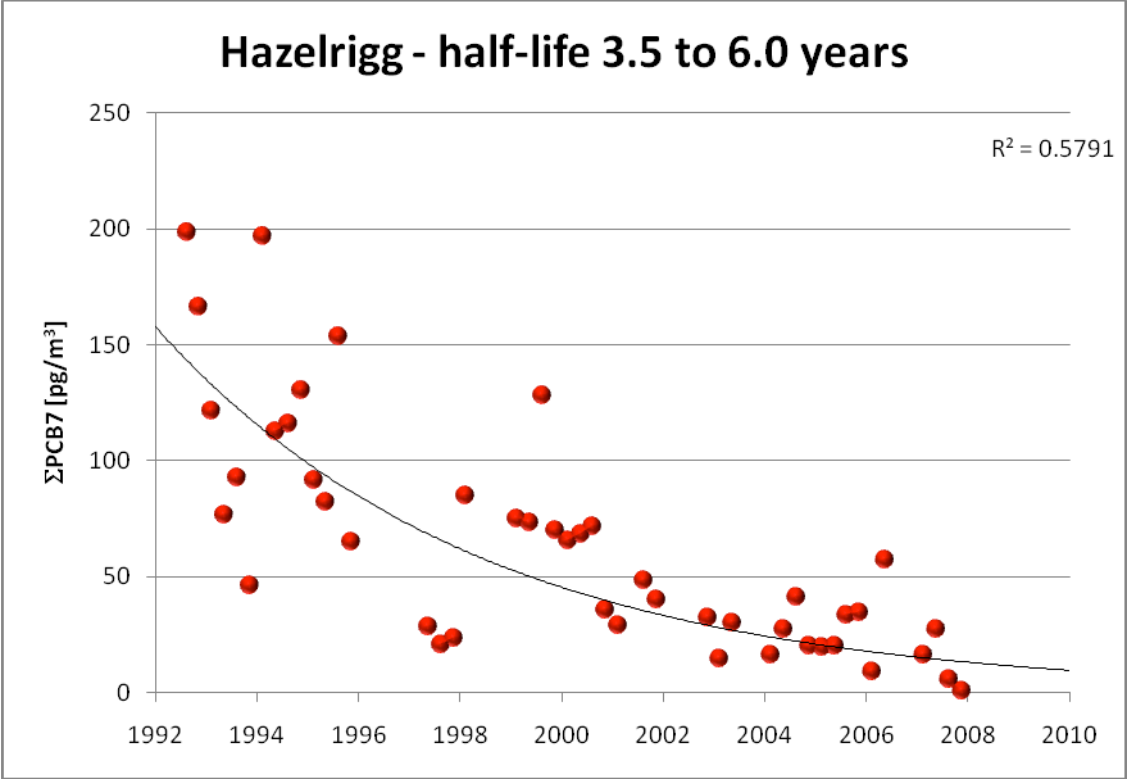


Figure 4c. Σ₇PCB data for the Hazelrigg TOMPs site

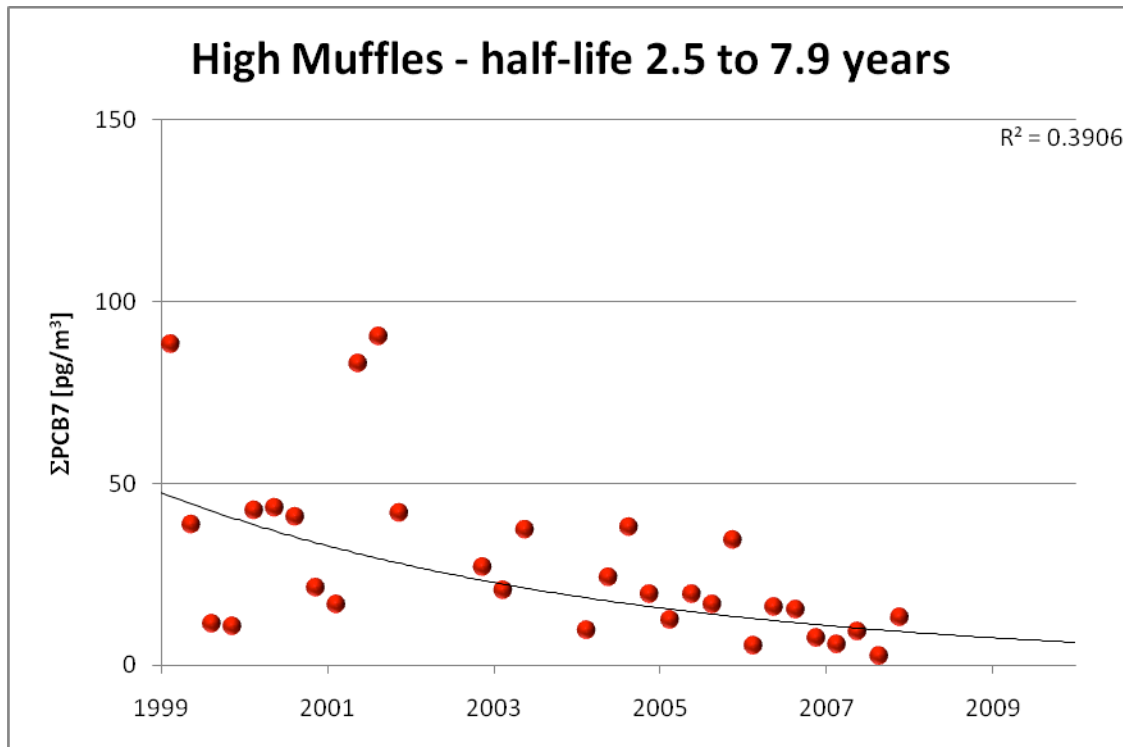


Figure 4d. $\Sigma_7\text{PCB}$ data for the High Muffles TOMPs site

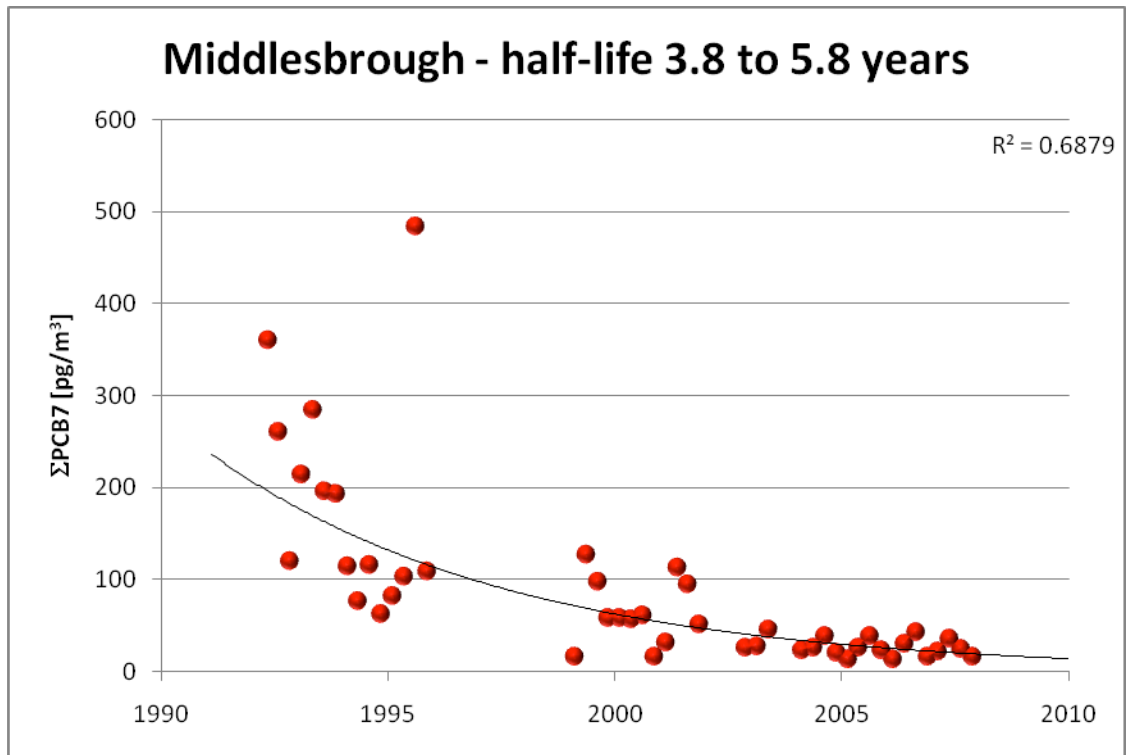


Figure 4e. $\Sigma_7\text{PCB}$ data for the Middlesbrough TOMPs site

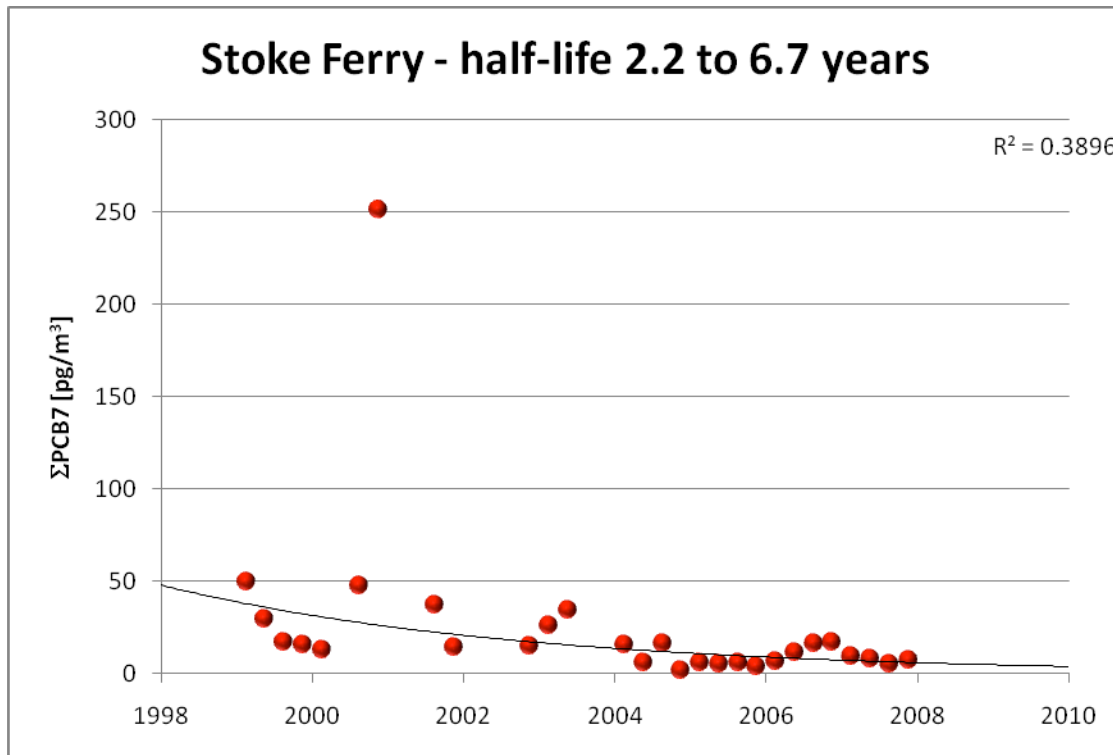


Figure 4f. Σ_7 PCB data for the Stoke Ferry TOMPs site

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.

The calculated half-lives cannot be considered significantly different between sites or between congeners. For the data set up to the end of 2007 the average half-life is 4.4 years with values spanning from 2.2 to 8.6 years. The observed half-lives for the rural sampling sites range from 2.2 – 6.7 years at Stoke Ferry, 2.5 – 7.9 years at High Muffles and 3.5 – 6.0 years at Hazelrigg. For the urban sites the ranges are 3.8 – 5.8 years at Middlesbrough, 5.0 – 8.6 years at Manchester and 2.6 – 3.8 years at London. 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_7 PCBs. This agreement holds for the other TOMPs datasets and suggests that the NAEI captures the main on-going PCB sources.

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* inventory. 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 km² 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.

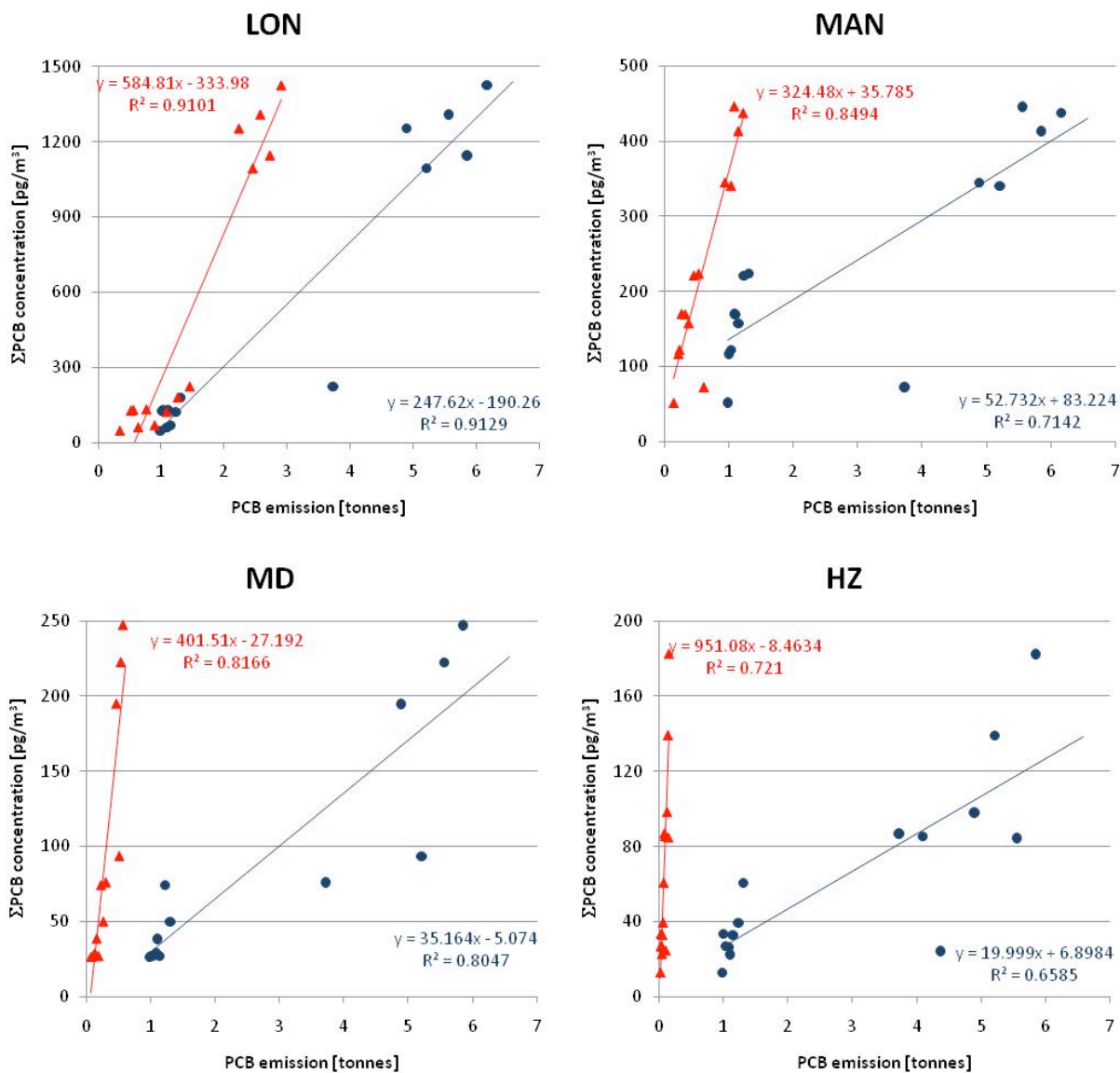


Figure 5. Correlation of observed PCB air concentrations^o [pg/m^3] to emission estimates [tonnes] for the sampling areas of London (LON), Manchester (MAN), Middlesbrough (MD) and Hazelrigg (HZ) (*Brevik et al.* 2007)^o (▲) and to emission inventory estimates [tonnes] by the National Atmospheric Emissions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

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

^{oo} total sum of PCB congeners

PCDD/Fs

The measured PCDD/Fs concentrations were in general at very low levels, similar to the ones we have reported for the previous years. The highest concentrations were observed in MAN (Q2: 32.78 fg TEQ/m³) and MID (Q1: 24.77 fg TEQ/m³). The PCDD/F levels in LON were very low (highest at the Q4: 11.59 fg TEQ/m³), confirming the results of the previous 2-3 years, which were suggesting that there has been an important decrease in the sources of PCDD/Fs at the London area. The semirural – rural areas exhibited concentrations that ranged between 0.015 and 17.78 fg TEQ/m³. Q2 in London and Q4 in Middlesbrough were not quantifiable for dioxins and furans because of possible interferences in the samples. The following figure summarizes the occurrence of PCDD/Fs in the six sampling sites during 2007.

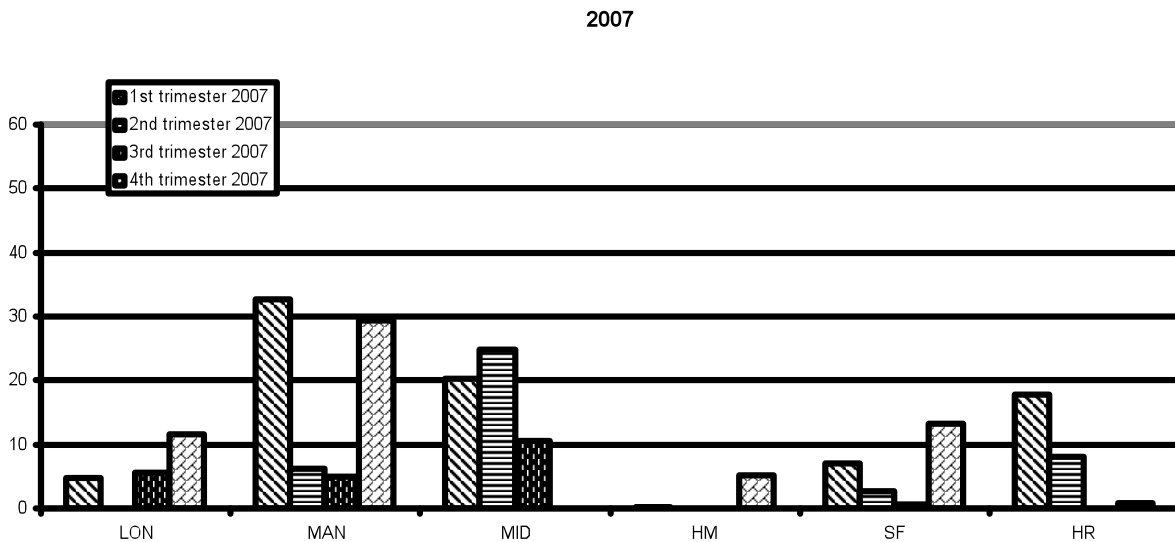


Figure 6. Sum of PCDD/Fs in fg TEQ/m³ at all sites and quarters in 2007.

We can see that Manchester exhibited the typical seasonal profile with high Q1, Q4 concentrations and low Q2, Q3, lower than Middlesbrough's ones. Among the semirural-rural areas, Q1 from HR was considerably high and the same with the Q4 from Stoke Ferry.

Comparing to 2006, following figure, all three urban sites had decreased average PCDD/F concentrations, and so did two out of the three semirural sites (SF and HR), while HM exhibited a small increase, but rather insignificant.

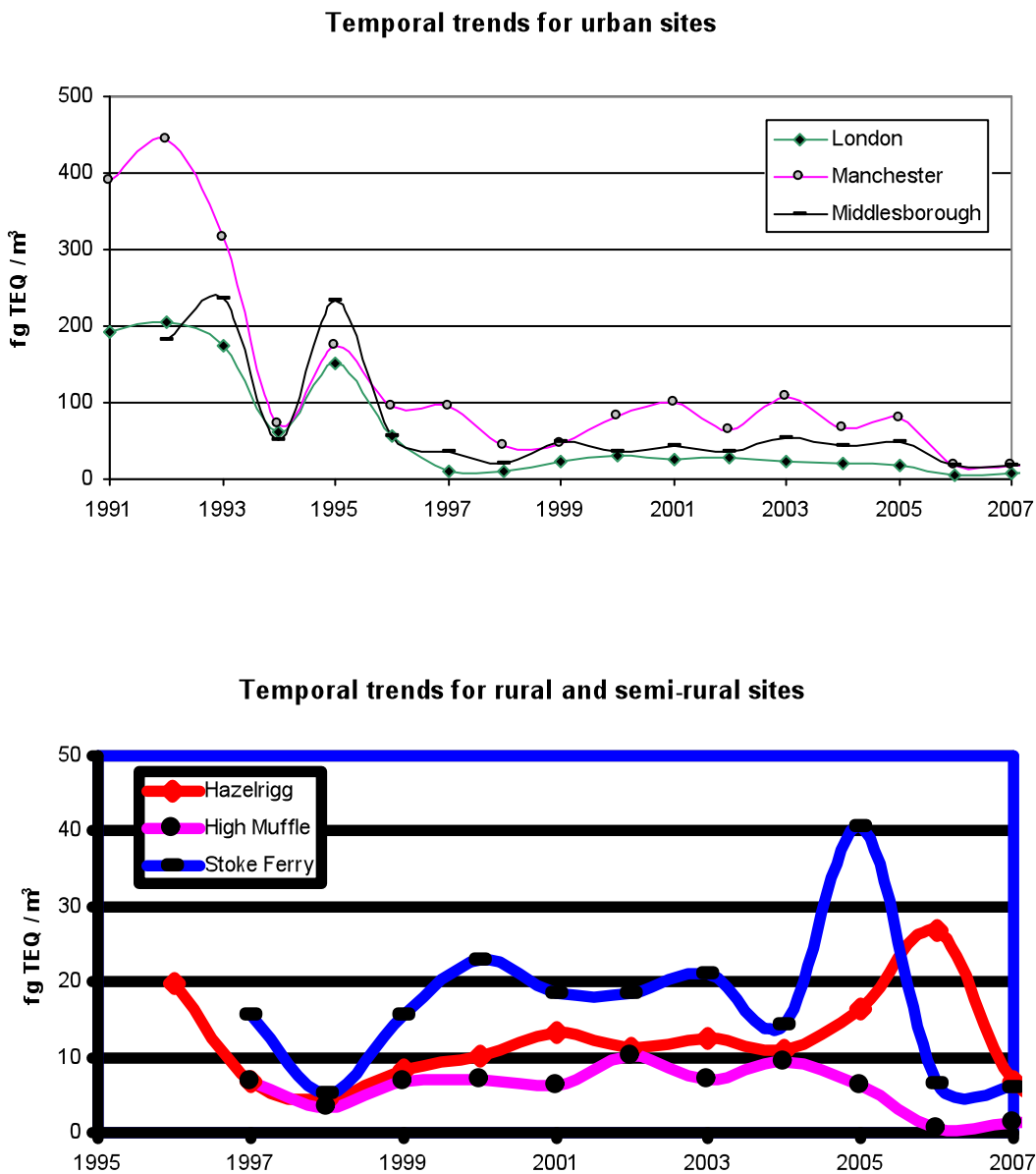


Figure 7. Temporal trends at the urban and rural sites.

The lower concentrations in all sites show that there have not been in 2007 new and/or uncontrolled sources of PCDD/Fs in the UK. This is supported also by the annual PCDD/Fs emissions inventory (<http://www.naei.org.uk>), which is slightly decreased comparing to 2006 (from ~197 to ~189 g TEQ).

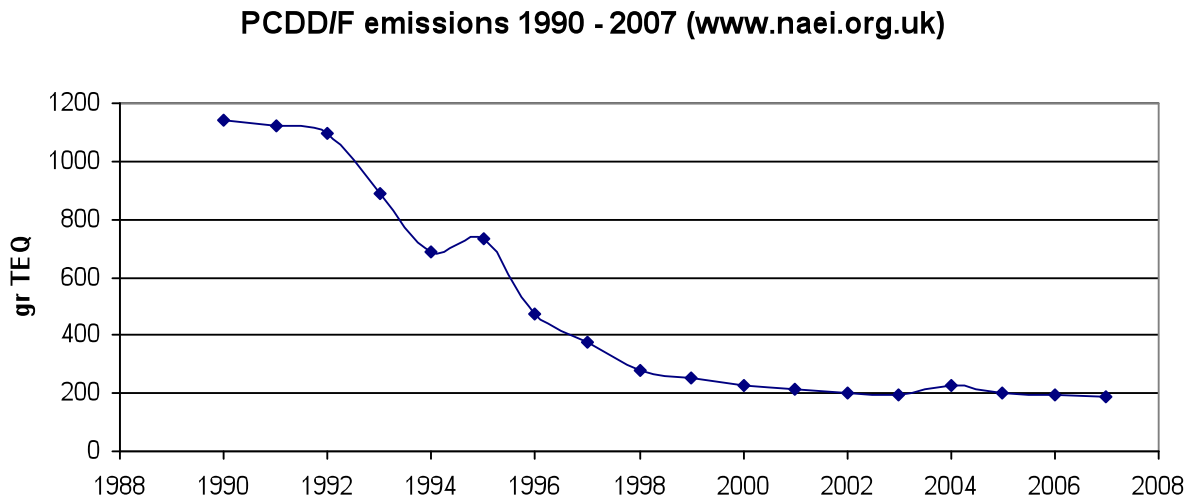


Figure 8. PCDD/F emissions 1990-2004.

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Appendix 1. PCDD/Fs and PCBs data.

a) PCDD/Fs

LONDON 2007	Q1.07	Q2.07	Q3.07	Q4.07
DIOXINS & FURANS	fgTEQ/m³	Not Available	fgTEQ/m³	fgTEQ/m³
2,3,7,8-TCDF	0.78		ND	0.99
1,2,3,7,8-PeCDF	ND		ND	0.20
2,3,4,7,8-PeCDF	1.68		2.51	2.48
1,2,3,4,7,8-HxCDF	0.43		ND	0.88
1,2,3,6,7,8-HxCDF	0.33		ND	0.55
2,3,4,6,7,8-HxCDF	0.34		0.57	0.74
1,2,3,7,8,9-HxCDF	ND		ND	ND
1,2,3,4,6,7,8-HpCDF	0.16		0.13	0.27
1,2,3,4,7,8,9-HpCDF	ND		ND	ND
OCDF	0.0009		ND	0.0017
2,3,7,8-TCDD	ND		ND	ND
1,2,3,7,8-PeCDD	ND		ND	3.08
1,2,3,4,7,8-HxCDD	ND		0.39	ND
1,2,3,6,7,8-HxCDD	0.49		0.61	0.71
1,2,3,4,7,8-HxCDD	ND		ND	0.70
1,2,3,4,6,7,8-HpCDD	0.45		0.62	0.78
OCDD	0.01		0.67	0.20
ΣTEQ dioxins and furans	4.66		5.50	11.59

Sample Q2 was not quantifiable for dioxins and furans

COPLANAR PCBs	fg/m³	fg/m³	fg/m³	fg/m³
3,3',4,5-TetraCB	ND	nd	nd	nd
3,3',4,4'-TetraCB	1155.1	1109	0.038	0.017
3,3',4,4',5-PentaCB	0.7	0.71	2.0100759	1.0012851
3,3',4,4',5,5'-HexaCB	ND	ND	ND	ND

MANCHESTER 2007	Q1.07	Q2.07	Q3.07	Q4.07
DIOXINS & FURANS	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³
2,3,7,8-TCDF	4.31	1.15	1.02	3.83
1,2,3,7,8-PeCDF	0.57	0.15	ND	0.51
2,3,4,7,8-PeCDF	8.27	2.63	1.98	7.34
1,2,3,4,7,8-HxCDF	2.87	0.52	0.55	2.54
1,2,3,6,7,8-HxCDF	1.83	0.45	0.40	1.64
2,3,4,6,7,8-HxCDF	2.50	0.55	0.46	2.22
1,2,3,7,8,9-HxCDF	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDF	0.73	0.19	0.21	0.65
1,2,3,4,7,8,9-HpCDF	0.10	ND	ND	0.09
OCDF	0.01	0.00	0.00	0.00
2,3,7,8-TCDD	ND	ND	ND	ND
1,2,3,7,8-PeCDD	5.89	ND	ND	5.30
1,2,3,4,7,8-HxCDD	0.76	ND	ND	0.69
1,2,3,6,7,8-HxCDD	1.91	0.31	ND	1.71
1,2,3,4,7,8-HxCDD	1.82	ND	ND	1.61
1,2,3,4,6,7,8-HpCDD	1.20	0.21	0.20	1.06
OCDD	0.0314	0.005	0.052	0.278
ΣTEQ dioxins and furans	32.78	6.17	4.89	29.47

COPLANAR PCBs	fg/m³	fg/m³	fg/m³	fg/m³
3,3',4,5-TetraCB	ND	nd	nd	nd
3,3',4,4'-TetraCB	2244	3361	0.032	0.025
3,3',4,4',5-PentaCB	1.5	1.7	1.9	2.3
3,3',4,4',5,5'-HexaCB	ND	ND	ND	ND

MIDDLESBROUGH 2007	Q1.07	Q2.07	Q3.07	Q4.07
DIOXINS & FURANS	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³	Not available
2,3,7,8-TCDF	2.36	4.61	1.88	
1,2,3,7,8-PeCDF	0.49	0.64	nd	
2,3,4,7,8-PeCDF	7.28	7.80	3.37	
1,2,3,4,7,8-HxCDF	2.58	2.99	1.05	
1,2,3,6,7,8-HxCDF	1.39	1.97	0.68	
2,3,4,6,7,8-HxCDF	2.16	2.83	0.93	
1,2,3,7,8,9-HxCDF	nd	nd	nd	
1,2,3,4,6,7,8-HpCDF	0.80	0.99	0.38	
1,2,3,4,7,8,9-HpCDF	0.08	0.14	nd	
OCDF	0.00	0.01	0.00	
2,3,7,8-TCDD	nd	nd	nd	
1,2,3,7,8-PeCDD	nd	nd	nd	
1,2,3,4,7,8-HxCDD	nd	nd	nd	
1,2,3,6,7,8-HxCDD	1.03	0.95	0.62	
1,2,3,4,7,8-HxCDD	1.24	1.20	0.97	
1,2,3,4,6,7,8-HpCDD	0.76	0.63	0.53	
OCDD	0.01721	0.01327	0.112568	
ΣTEQ dioxins and furans	20.18	24.77	10.52	
Q4 was unquantifiable for dioxins and furans				
COPLANAR PCBs	fg/m³	fg/m³	fg/m³	fg/m³
3,3',4,5-TetraCB	nd	nd	nd	nd
3,3',4,4'-TetraCB	1593	3708	0.031	0.020
3,3',4,4',5-PentaCB	1	1.7	0.7	1.6
3,3',4,4',5,5'-HexaCB	nd	nd	nd	nd

HIGH MUFFLES 2007	Q1.07	Q2.07	Q3.07	Q4.07
DIOXINS & FURANS	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³
2,3,7,8-TCDF	nd	nd	nd	nd
1,2,3,7,8-PeCDF	nd	nd	nd	nd
2,3,4,7,8-PeCDF	nd	nd	nd	3.6439
1,2,3,4,7,8-HxCDF	nd	nd	nd	nd
1,2,3,6,7,8-HxCDF	nd	nd	nd	0.5256
2,3,4,6,7,8-HxCDF	nd	nd	nd	nd
1,2,3,7,8,9-HxCDF	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDF	nd	nd	nd	0.6926
1,2,3,4,7,8,9-HpCDF	nd	nd	nd	nd
OCDF	nd	nd	nd	0.0017
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	nd
1,2,3,4,7,8-HxCDD	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDD	0.12	0.04	nd	0.3307
OCDD	0.003	0.0014	0.015	0.04
ΣTEQ dioxins and furans	0.12	0.05	0.015	5.23
COPLANAR PCBs	fg/m³	fg/m³	fg/m³	fg/m³
3,3',4,5-TetraCB	nd	nd	nd	nd
3,3',4,4'-TetraCB	459	1508	0	0
3,3',4,4',5-PentaCB	nd	0.6	nd	nd
3,3',4,4',5,5'-HexaCB	nd	nd	nd	nd

STOKE FERRY 2007	Q1.07	Q2.07	Q3.07	Q4.07
DIOXINS & FURANS	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³
2,3,7,8-TCDF	1.02	0.69	0.339175	1.06
1,2,3,7,8-PeCDF	ND	ND	ND	0.20
2,3,4,7,8-PeCDF	2.44	ND	ND	3.56
1,2,3,4,7,8-HxCDF	0.58	0.45	ND	0.81
1,2,3,6,7,8-HxCDF	0.49	0.40	ND	0.66
2,3,4,6,7,8-HxCDF	0.69	0.39	ND	0.98
1,2,3,7,8,9-HxCDF	ND	ND	ND	ND
1,2,3,4,6,7,8-HpCDF	0.24	0.17	0.095	0.29
1,2,3,4,7,8,9-HpCDF	ND	ND	ND	0.04
OCDF	0.00	0.00	ND	0.00
2,3,7,8-TCDD	ND	ND	ND	ND
1,2,3,7,8-PeCDD	ND	ND	ND	3.02
1,2,3,4,7,8-HxCDD	ND	ND	ND	0.32
1,2,3,6,7,8-HxCDD	0.42	ND	ND	0.70
1,2,3,4,7,8-HxCDD	0.65	0.45	ND	0.82
1,2,3,4,6,7,8-HpCDD	0.46	0.19	0.143	0.64
OCDD	0.011	0.0047	0.035	0.150
ΣTEQ dioxins and furans	7.00	2.74	0.61	13.27

COPLANAR PCBs	fg/m ³	fg/m ³	fg/m ³	fg/m ³
3,3',4,5-TetraCB	nd	nd	nd	nd
3,3',4,4'-TetraCB	320	1059	0	0
3,3',4,4',5-PentaCB	nd	0.6	nd	1
3,3',4,4',5,5'-HexaCB	ND	ND	nd	ND

HAZELRIGG 2007	Q1.07	Q2.07	Q3.07	Q4.07
DIOXINS & FURANS	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³	fgTEQ/m³
2,3,7,8-TCDF	3.10	1.89	nd	nd
1,2,3,7,8-PeCDF	0.34	0.19	nd	nd
2,3,4,7,8-PeCDF	2.93	2.13	nd	nd
1,2,3,4,7,8-HxCDF	1.07	0.93	nd	nd
1,2,3,6,7,8-HxCDF	0.78	0.52	nd	nd
2,3,4,6,7,8-HxCDF	1.21	0.76	nd	0.43
1,2,3,7,8,9-HxCDF	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDF	0.39	0.26	nd	0.14
1,2,3,4,7,8,9-HpCDF	nd	0.03	nd	nd
OCDF	0.00	0.00	nd	0.00
2,3,7,8-TCDD	nd	nd	nd	nd
1,2,3,7,8-PeCDD	4.11	nd	nd	nd
1,2,3,4,7,8-HxCDD	0.43	nd	nd	nd
1,2,3,6,7,8-HxCDD	0.80	0.44	nd	nd
1,2,3,4,7,8-HxCDD	1.75	0.51	nd	nd
1,2,3,4,6,7,8-HpCDD	0.86	0.33	0.05	0.25
OCDD	0.019	0.008	0.019	0.064
ΣTEQ dioxins and furans	17.78	8.00	0.07	0.89

COPLANAR PCBs	fg/m³	fg/m³	fg/m³	fg/m³
3,3',4,5-TetraCB	nd	nd	nd	nd
3,3',4,4'-TetraCB	1706.2	2132	0.009	0.007
3,3',4,4',5-PentaCB	1.041715	1.049625	nd	nd
3,3',4,4',5,5'-HexaCB	nd	nd	nd	nd

b) PCBs

LONDON 2007	Q1.07	Q2.07	Q3.07	Q4.07
PCB/OC	pg/m³	pg/m³	pg/m³	pg/m³
18	8.2	12.7	16.5	2.2
22	3.0	5.5	7.6	4.6
44	3.4	11.5	8.7	14.2
49	2.8	12.8	7.6	23.6
52	6.1	13.3	<0.04	7.1
70	2.9	8.3	6.3	3.4
74	1.31	3.55	3.91	<0.04
87	1.4	4.4	3.5	1.2
95	4.1	11.7	11.2	3.2
99	1.1	3.4	3.3	0.9
104	<0.04	<0.04	<0.04	<0.04
105	nd	1.25	nd	0.7
110	2.7	8.3	7.5	2.1
114	<0.04	0.1	<0.04	<0.04
118	1.5	4.2	3.8	1.1
123	<0.04	0.11	0.2	0.1
138	1.7	5.5	4.0	1.5
141	0.41	1.7	0.7	0.19
149	2.6	9.4	5.7	2.3
151	1.1	4.4	2.1	1.0
155	<0.04	<0.04	1.0	0.0
156	<0.04	0.3	<0.04	<0.04
157	<0.04	<0.04	<0.04	<0.04
158	0.1	0.7	0.2	0.1
167	<0.04	0.58	<0.04	<0.04
170	<0.04	0.87	<0.04	0.22
174	0.50	1.70	0.59	0.37
180	0.77	2.4	0.6	0.80
183	0.34	1.39	0.26	0.30
187	0.82	3.5	0.8	0.72
188	<0.04	<0.04	<0.04	<0.04
189	<0.04	0.0	<0.04	<0.04
194	<0.04	0.3	<0.04	<0.04
199	<0.04	0.2	<0.04	<0.04
203	<0.04	0.8	<0.04	<0.04
153+132	2.5	10.56	4.32	3.6
31+28	13.72	13.63	42.4	7.98
41/64	3.11	6.72	5.04	5.27
60/56	1.19	2.3	3.2	0.8
90/101	4.1	13.2	9.6	3.4
Σ₇PCB	30.4	62.7	64.7	25.4

MANCHESTER 2007	Q1.07	Q2.07	Q3.07	Q4.07
PCB/OC	pg/m ³	pg/m ³	pg/m ³	pg/m ³
18	<0.04	22.8	16.5	4.8
22	2.6	11.9	6.3	<0.04
44	27.7	32.0	60.0	43.2
49	58.8	62.0	75.3	70.4
52	10.5	17.7	16.1	11.4
70	0.9	2.5	<0.04	0.9
74	<0.04	4.93	<0.04	3.26
87	2.1	7.6	4.2	3.1
95	6.4	18.3	11.4	7.5
99	1.7	4.7	3.0	2.7
104	0.0	nd	0.0	0.0
105	1.3	3.8	1.1	2.6
110	3.5	12.0	8.2	5.1
114	0.2	<0.04	<0.04	<0.04
118	2.2	5.8	3.8	2.7
123	0.45	<0.04	<0.04	<0.04
138	2.3	6.2	3.7	2.4
141	0.79	1.62	0.3	0.16
149	3.7	8.5	5.0	3.1
151	1.6	3.5	1.9	1.0
155	<0.04	<0.04	<0.04	<0.04
156	0.6	<0.04	<0.04	0.5
157	0.2	nd	0.1	nd
158	0.3	0.9	0.5	0.3
167	<0.04	<0.04	<0.04	<0.04
170	0.46	1.24	nd	0.46
174	0.65	1.33	0.63	0.25
180	1.29	1.80	1.1	0.6
183	0.31	0.83	0.41	0.27
187	1.07	2.00	0.9	0.3
188	<0.04	<0.04	<0.04	<0.04
189	<0.04	<0.04	<0.04	0.1
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	4.00	9.9	5.87	6.6
31+28	10.14	18.66	16.87	9.09
41/64	nd	12.51	20.64	19.12
60/56	2.53	3.64	nd	1.6
90/101	1.4	17.3	10.6	7.7
Σ₇PCB	31.9	77.4	58.0	40.5

MIDDLESBROUGH 2007	Q1.07	Q2.07	Q3.07	Q4.07
PCB/OC	pg/m ³	pg/m ³	pg/m ³	pg/m ³
18	4.8	7.4	6.7	3.8
22	3.6	10.6	3.7	2.1
44	3.5	5.7	11.2	9.3
49	5.1	10.5	17.1	5.6
52	5.6	8.9	6.2	4.3
70	3.2	4.6	4.5	3.1
74	1.83	3.74	3.7	1.5
87	nd	1.6	0.7	0.5
95	2.7	4.1	3.3	1.8
99	1.07	1.6	1.0	0.7
104	<0.04	<0.04	<0.04	<0.04
105	1.4	0.6	3.7	3.6
110	1.5	3.4	2.6	1.3
114	<0.04	<0.04	<0.04	<0.04
118	1.1	1.5	1.1	0.7
123	<0.04	0.19	<0.04	0.0
138	1.23	1.8	1.4	0.25
141	<0.04	0.73	0.20	<0.04
149	1.43	2.8	1.85	0.83
151	0.43	0.9	0.8	0.34
155	<0.04	<0.04	<0.04	<0.04
156	<0.04	<0.04	1.2	<0.04
157	<0.04	0.2	<0.04	<0.04
158	0.17	0.5	0.1	0.2
167	<0.04	<0.04	0.8	0.56
170	0.26	0.37	0.40	<0.04
174	0.20	0.43	0.2	<0.04
180	0.51	0.34	0.45	0.25
183	0.10	<0.04	0.18	0.26
187	0.16	0.69	0.36	0.25
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	1.69	4.85	2.5	1.2
31+28	10.59	16.46	11.51	9.35
41/64	4.0	10.58	7.92	4.91
60/56	1.88	3.39	2.50	1.77
90/101	2.5	4.3	3.2	1.8
Σ₇PCB	23.2	38.1	26.4	17.9

STOKE FERRY 2007	Q1.07	Q2.07	Q3.07	Q4.07
PCB/OC	pg/m ³	pg/m ³	pg/m ³	pg/m ³
18	2.6	3.2	nd	0.7
22	4.35	1.3	3.5	<0.02
44	12.5	0.9	10.1	16.4
49	29.3	0.8	22.5	48.0
52	2.7	1.3	1.5	1.3
70	2.0	0.7	1.0	<0.02
74	0.51	0.38	0.50	<0.02
87	0.34	0.2	0.2	<0.02
95	0.91	0.91	0.29	<0.02
99	0.30	0.23	0.17	0.03
104	<0.02	<0.02	<0.02	<0.02
105	0.22	nd	0.00	<0.02
110	0.59	0.53	0.47	0.21
114	<0.02	<0.02	<0.02	0.12
118	0.37	0.3	0.2	0.08
123	0.06	0.0	0.05	0.12
138	0.40	0.42	0.18	0.19
141	0.15	0.05	0.21	0.14
149	0.51	0.63	0.19	1.18
151	0.18	0.3	0.1	0.6
155	<0.02	0.29	0.020	0.02
156	<0.02	<0.02	<0.02	0.2
157	<0.02	<0.02	<0.02	0.2
158	<0.02	0.03	<0.02	0.4
167	<0.02	<0.02	<0.02	<0.02
170	0.12	<0.02	0.07	<0.02
174	0.06	0.06	0.05	0.14
180	0.18	0.10	0.00	0.20
183	0.08	0.04	<0.02	0.13
187	0.18	0.09	0.08	0.3
188	<0.02	<0.02	<0.02	<0.02
189	<0.02	<0.02	<0.02	0.6
194	<0.02	<0.02	<0.02	<0.02
199	<0.02	<0.02	<0.02	<0.02
203	<0.02	<0.02	<0.02	<0.02
153+132	1.33	0.53	0.58	1.76
31+28	3.66	5.07	2.30	3.0
41/64	7.06	0.48	6.85	9.14
60/56	0.72	0.39	0.48	1.4
90/101	0.80	0.8	0.4	1.0
Σ₇PCB	9.39	8.59	5.23	7.56

HIGH MUFFLES 2007

	Q1.07	Q2.07	Q3.07	Q4.07
PCB/OC	pg/m ³	pg/m ³	pg/m ³	pg/m ³
18	2.34	6.4	5.9	5.0
22	0.9	<0.02	<0.02	<0.02
44	0.6	45.7	7.6	4.9
49	0.8	<0.02	8.4	3.9
52	1.1	<0.02	1.8	0.8
70	0.5	14.2	<0.02	0.64
74	0.3	6.20	<0.02	0.3
87	0.1	0.6	<0.02	0.43
95	0.64	1.6	<0.02	1.32
99	0.16	0.91	0.29	0.32
104	<0.02	<0.02	0.023	<0.02
105	<0.02	1.87	<0.02	0.28
110	0.4	1.2	<0.02	1.0
114	<0.02	<0.02	0.77	0.2
118	0.13	0.4	<0.02	0.65
123	<0.02	<0.02	0.4	0.1
138	0.20	0.55	0.10	0.85
141	<0.02	0.07	0.14	0.22
149	0.38	1.38	0.03	1.35
151	0.15	1.25	0.03	0.54
155	0.45	<0.02	0.03	0.03
156	<0.02	<0.02	0.40	<0.02
157	<0.02	0.11	0.19	<0.02
158	<0.02	0.16	0.34	0.08
167	<0.02	0.51	0.8	<0.02
170	<0.02	<0.02	<0.02	<0.02
174	<0.02	0.14	0.0	0.2
180	0.06	0.19	0.06	0.22
183	0.04	0.13	0.1	0.1
187	0.06	0.23	0.11	0.28
188	<0.02	<0.02	0.00	<0.02
189	<0.02	<0.02	0.05	<0.02
194	<0.02	<0.02	<0.02	<0.02
199	<0.02	<0.02	<0.02	0.02
203	<0.02	<0.02	<0.02	<0.02
153+132	0.3	1.46	0.8	2.2
31+28	3.49	7.3	<0.02	7.2
41/64	0.5	9.3	<0.02	0.6
60/56	0.27	3.47	28.13	0.3
90/101	0.5	0.1	<0.02	1.6
Σ₇PCB	5.8	9.5	2.8	13.4

HAZELRIGG 2007	Q1.07	Q2.07	Q3.07	Q4.07
PCB/OC	pg/m ³	pg/m ³	pg/m ³	pg/m ³
18	7.1	5.9	1.43	4.75
22	<0.03	2.0	nd	nd
44	1.7	3.3	0.72	4.64
49	2.5	2.7	0.56	3.70
52	4.4	5.8	1.15	0.71
70	1.7	3.1	0.47	nd
74	1.07	1.23	0.24	nd
87	0.6	1.6	0.18	nd
95	2.4	4.4	0.63	nd
99	1.03	1.2	0.20	0.04
104	<0.03	<0.03	<0.03	nd
105	<0.03	<0.03	<0.03	nd
110	0.99	3.26	0.44	0.12
114	<0.03	<0.03	<0.03	0.16
118	0.83	1.7	0.19	
123	<0.03	0.18	<0.03	nd
138	1.10	2.13	0.25	0.09
141	0.17	0.51	0.03	0.06
149	1.63	3.0	0.32	0.29
151	0.65	1.2	0.14	0.02
155	0.40	0.27	0.16	0.01
156	<0.03	0.1	<0.03	0.29
157	<0.03	<0.03	<0.03	0.03
158	0.07	0.2	<0.03	0.13
167	<0.03	<0.03	<0.03	0.30
170	<0.03	<0.03	<0.03	nd
174	0.17	0.64	0.03	0.04
180	0.18	0.63	0.03	0.03
183	0.06	0.27	0.10	0.06
187	0.25	0.78	0.06	0.06
188	<0.03	<0.03	<0.03	nd
189	<0.03	<0.03	<0.03	nd
194	<0.03	0.08	<0.03	nd
199	<0.03	<0.03	<0.03	nd
203	<0.03	0.14	<0.03	nd
153+132	1.03	2.39	0.30	0.31
31+28	6.29	10.83	3.45	Nd
41/64	0.35	2.94	0.61	Nd
60/56	0.17	0.79	0.35	Nd
90/101	2.5	3.9	0.62	Nd
Σ₇PCB	16.33	27.47	5.99	1.14