The Lancaster Environment Centre

Annual Report for 2009 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 2009 quarter 1(Q1), quarter 2 (Q2) quarter 3 (Q3) and quarter 4 (Q4) 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 2009, 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, Manchester, Hazelrigg (Lancashire), High Muffles (North Yorkshire), 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.

TABLE OF CONTENTS

		Page
1.	Introduction	4
2.	Background to PCBs, PCDDs and PCDFs	4
3.	TOMPs sites in 2009	6
4.	Network sampling operations	8
5.	Extraction and clean-up procedures	9
6.	Data storage	11
7.	Results for year 2009	12
	7.1. Network operation	
	7.2. PCDD/Fs	
	7.3. PCBs	
8.	References	28
	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 and the devolved administrations 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 is bulked to provide quarterly data. These data are reported to Defra and published on the air quality data website www.airquality.co.uk. Three sites are maintained via sub-contracts; London AEA Technology, 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 furans') and PCBs. Polycyclic aromatic hydrocarbons (PAHs) are quantified and reported separately under another monitoring programme currently run by AEA Technology.

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).



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 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 2009

In 2009 the TOMPs programme operated 6 sites:

London (LON)	urban site established in 1991
Manchester (MAN)	urban site established in 1991
Hazelrigg (HR)	semi-rural site established in 1992
High Muffles (North Yorkshire) (HM)	rural site established in 1999
Auchencorth Moss (AC)	rural site established in 2008
Weybourne (WE)	Rural site established at the end of 2008

The sites consist of two urban locations in London (LON), Manchester (MAN), three rural sites at High Muffles (HM, North Yorkshire), Auchencorth Moss (AC, Mid Lothian) and Weybourne (Norfolk), 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.

Data from two new sites are available for year 2009: Auchencorth Moss and Weybourne. Auchencorth Moss was established in October 2008, 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 (European Monitoring and Evaluation Programme) 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. Weybourne was established at the University of East Anglia's field station, and is 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 °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 AEA Technology 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 (°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 ¹³C₁₂-labeled PCB congeners (¹³C₁₂ PCB 28, 52, 101, 138, 153, 180, 209) and an isotope dilution/recovery standard containing ¹³C₁₂-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 rotaevaporation 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 inner diameter (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 μ L. 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 $\begin{bmatrix} {}^{13}C_{12} \end{bmatrix}$ PCB 141 and $\begin{bmatrix} {}^{13}C_{12} \end{bmatrix}$ 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 ³⁷Cl-labeled 2,3,7,8-TCDDwas added to both the PCDD/F. Analysis is performed on a Micromass Autospec Ultima high resolution-mass spectrometry (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 coplanar 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.

<u>QA/QC</u> 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 (<u>http://www.airquality.co.uk</u>). 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 2009

<u>7.1</u> <u>Network Operations</u>: 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 2009. The bulked air volume is obtained by summing the volume (in m^3) obtained from each sample taken during the quarter (usually 6-7 samples depending on the sampling schedule). The aim is to obtain an average volume of 500-700m³ 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 can be analytically detected. Consequently, the total volume per quarter (bulked volume for 6-7 samples normally collected per each quarter) is approximately 4500-7000 m³ (see Table 1).

Samplers at all sites were calibrated once a year in the period April-June, 2009, with the exception of Auchencorth Moss that was calibrated in January 2009 by Lancaster personnel because of problems with sampler. High Muffles, Manchester and Hazelrigg were calibrated during normal visits for sample collection; Weybourne was calibrated by Lancaster in spring 2009. Auchencorth Moss and Weybourne were visited by Lancaster personnel 3 times in 2009 for equipment servicing and sample collection. Samples in Auchencorth Moss and Weybourne are stored in a freezer at -30 C at the sampling site until collection by Lancaster personnel. In general, Lancaster personnel collect the samples 3-5 months.

		QUARTER 1 (Q1) 2009				
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m ³	6934	4678	4840	3243	2979	1540
Number of samples	7	7	7	5	4	2
		QUARTER 2 (Q2) 2009				
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m3	5854	4268	4353	1448	5227	3852
Number of samples	6	6	6	2	7	5
		QUARTI	E R 3 (Q	3) 2009		
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m3	5351	5011	4968	709	4444	5402
Number of samples	7	7	7	1	6	6
		QUARTI	ER 4 (Q			
	London	Manchester	Hazelrigg	High Muffles	Auchencorth	Weybourne
Bulked Air volume m3	5031	3511	4500	2129	5223	4678
Number of samples	7	5	6	2	7	4

Table 1. Summary of the bulked air volumes and number of samples for each quarter at all sites in 2009.

High Muffles presents the least number of samples because of repeated electrical faults at the site since the end of March 2009. The electrical problem was resolved at the end of 2009. This did not cause the loss of data for the affected quarters, as the bulked volume was sufficiently large to enable the detection of PCBs, co-planar PCBs and PCDD/Fs within quarterly samples (see Appendix 1 and 2). Each quarter represents an integrated average of the 3 month sampling period. However, information on short-term fluctuations in atmospheric concentrations can be masked when bulking 6-7 samples in each quarter. For the High Muffles site during parts of 2009, fewer samples were collected for some quarters which means that individual samples may exert a stronger influence on quarterly averages, although this effect is likely to be minimal as the collected air volumes for each sample are high. For example, if in a quarter there is a sample with relatively high concentration and the other 5-6 have lower concentration, the information of the high concentration we get for each quarter is only an average of 6-7 samples. However, if the high concentrated sample is bulked with 1 or 2 that have lower concentration then the dilution of the high concentrated sample would be less and the influence greater. In the case of High Muffles,

the total sampling time for Q2, and Q4 only represents an average over a period of a month per quarter, or 15 days in the case of Q3. Although, a quarter would ordinarily constitute a 3 month sampling period (with 6-7 biweekly samples taken during this time), the samples collected will still enable the provision of time-trend data that can be used to provide information on year on year changes in pollutant levels at this site, and will therefore not have a great effect in the estimation of the mean annual concentrations for each compound class, and the interpretation of time trends. Currently, the site is running smoothly and we expect to retrieve all the samples for year 2010.

Q1 and Q4 in Weybourne include only 2 and 4 samples respectively because of difficulty in accessing the site during adverse weather conditions. Manchester has a sample less than anticipated in Q4 because the motor stopped working during sampling. Since the time of motor malfunction cannot be known, as the counter continued working (measuring time) during the sample period, this sample was not included in the analysis. The filter paper that collects particles appeared white when this sample was collected, therefore we assumed that sampling stopped at the beginning of the sampling period. This has not affected the integrity of the analytical procedure for Q4.

Sampling at Auchencorth Moss started in late 2008 (Q4). There were problems at the beginning of the sampling period with the calibration of the sampler, therefore the first two samples in Q1 were not suitable for analysis. This has not affected the integrity of the analysis as the other 4 samples collected for Q1 in 2009 were used for data analysis. The two new sites are running smoothly at the moment and we expect to retrieve all samples in 2010.

In this report data for Q1, Q2, Q3 and Q4 2009 are presented for PCBs, co-planar PCBs and PCDDs and PCDFs.

<u>7.2 PCDD/Fs: Results and discussion.</u> The measured PCDD/Fs concentrations were in general at very low levels, and similar to the ones we have reported for last 10 years. The highest concentrations were observed in LON (Q1 and Q2: 108 and 52 fg TEQ/m³ respectively) and WE

(Q1: 80 fg TEQ/m³). In 2009 the PCDD/F levels in AC were the lowest in the range of 0.05-3 fg TEQ/m³. The semirural and rural areas exhibited concentrations that ranged between 5 and 15 fg TEQ/m³. Figure 2 summarizes the occurrence of PCDD/Fs in the six sampling sites during 2009.

However, there are exceptions, such as Q2 in 2009 at High Muffles , which displays a relatively high concentration compared to the other rural/semi-rural TOMPs sites ($\sum TEQ PCDD/Fs = 29$ fg TEQ/m³). As demonstrated for PCBs, Weybourne displays a relatively high average concentration of PCDD/Fs in Q1 of 79 fg TEQ/m³, which is similar to what is measured in London, but a relatively low concentration 3.8 fg TEQ/m³ in Q2, Q3 and Q4. It is well known from the monitoring of other atmospheric contaminants (i.e. NOx) that this site receives "polluted air" from the London area from time to time, and so this could explain the higher levels of pollutants observed at WE in Q1. High levels in Q1 and Q2 may also reflect winter usage of heating.



Figure 2. Sum of PCDD/Fs in fg TEQ/m^3 at all sites and quarters in 2007.

Figure 3 shows the temporal trends for PCDD/Fs at London, Manchester, High Muffles and Hazelrigg. At Auchencorth Moss and Weybourne the data sets are too short (ca. 1 year) to observe a temporal trend. Comparing to 2008, all three urban sites had decreased average

PCDD/F concentrations, and so did HR, while HM exhibited a small increase, but rather insignificant. The increase in concentration of PCDD/Fs in Q2 at Hazelrigg has already been observed in Q2 2006 where the concentration was about 60 fg TEQ/m³. With concentrations relatively low, a small scale event/source can cause a relatively increase in concentration. In the long-term trends (Figure 3) there will always be points with relatively high concentration every now and then due to local sources or events.





Figure 3. Temporal trends at the urban and rural sites.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) constitute two classes of chemicals that are formed unintentionally during combustion (e.g. waste incineration, burning of coal, wood etc.), the refining of petroleum, several metal treatment processes and during the synthesis of certain chlorinated chemicals (e.g. pentachlorophenol). PCDD/Fs are classified as Persistent Organic Pollutants (POPs) under the 1998 UNECE Protocol and the 2001 Stockholm UNEP Convention. They are persistent in the environment, able to bioaccumulate and to undergo long-range atmospheric transport. PCDD/Fs are not new to the environment. They have been shown to occur in UK environmental samples archived since the 1860s (*Hassanin et al.,2006*; Alcock et al., 1996, 1998). Kjeller et al. (*1996*) clearly demonstrated that PCDD/F levels similar to the present ones existed even before the boom of the chlorine industry. Processes known now to be sources of PCDD/Fs to the atmosphere, such as coal and wood burning and metal smelting, will have been prevalent for centuries, indeed millennia.

Although the TOMPS program started in 1990 and shows air concentrations generally falling since that time, there is good evidence that this is actually part of a longer and more systematic decline. Media which are broadly reflective of trends in air – such as herbage and milk – show higher levels in the 1980s than 1990s (*Hassanin et al., 2006*; Alcock et al., 1996, 1998, Kjeller et al., *1996*), and higher levels still in the 1960s and 1970s. Human dietary intakes of PCDD/Fs are estimated to have declined 4-5 fold between 1982 and 1992 (Van der Gon et al., 2005) and to have declined still further since (UKFSA et al., 2006).

UK PCDD/F emission estimates are only available through the National Atmospheric Emission Inventory for the years 1990 – 2007. Therefore, it could not be possible to compare measurements with emissions inventories.

7.3 PCBs: Results and discussions

On average, the measured concentrations continue to be proportional with the population density (i.e. greater for urban sites (20-114 pg/m³)) and therefore the remoteness of the sampling site (i.e. rural sites have lower levels (3-44 pg/m³)). In 2009 the highest \sum_7 PCBs concentrations were observed in London, Manchester and surprisingly in High Muffles with an average of 49, 64 and 52 pg/m³ respectively (Figure 4). Auchencorth showed the lowest concentrations with an average

of 15.9 pg/m³. Hazelrigg and Weybourne show average concentrations of 29 and 34 pg/m³ respectively. The 2009 data set shows high variation between different quarters for all sites with the exception of Weybourne. The most extreme differences were monitored for High Muffles with 0.39 pg/m³ for Q1 and 130 pg/m³ for Q3. It is not known why High Muffles displays a high concentration in Q3 (as well as Q2) given also its remote location; however, these are the most warm periods of the year. Therefore, revolatilization of PCBs from surfaces such as soil may be an important process leading to a higher concentration in the atmosphere (see Figure 5). Higher levels can also be attributed to long-range atmospheric transport from 'dirty regions' (e.g.

In comparison with PCB data from 2008, London shows slightly lower annual average (50 pg/m³) in 2009, but it still statistically similar (95% confidence) to that of 2008. At Manchester, the PCB annual mean is slightly higher than 2008, but not statistically different (95% confidence level). At High Muffles and Hazelrigg the 2009 PCB annual average is higher by a factor 10 and 5 respectively. These high annual averages are due to relatively high concentrations in Q2 and Q3 in High Muffles (see page 13) and Q3 and Q4 at Hazelrigg. We hope the results of 2010 will help to shed light on this issue.



Figure 4.Sum of PCB concentrations at all sites for all quarters in 2009

south, south-east) as there are no local sources at the site.



Figure 5. Average temperature for all quarters in 2009.



Figure 6a. \sum_7 PCB data for the London TOMPs site



Figure 6b. \sum_7 PCB data for the Manchester TOMPs site



Figure 6c. \sum_7 PCB data for the Hazelrigg TOMPs site



Figure 6d. \sum_7 PCB data for the High Muffles TOMPs site



Figure 6e. \sum_7 PCB data for the Weybourne TOMPs site.



Figure 6f. \sum_{7} PCB data for the Auchencorth TOMPs site

PCBs are classified as Persistent Organic Pollutants (POPs) under the 1998 UNECE Protocol and the 2001 Stockholm UNEP Convention. They are therefore subject to international restrictions on production and use, and efforts to identify and reduce ongoing sources. However, they have been the subject of restrictions in the UK for much longer. A voluntary ban on production was agreed with manufacturers in the late 1960s/early 1970s. Limits on emissions from incinerators, the handling of PCB-containing wastes etc were being applied from the late 1970/80s onwards, all before reliable routine environmental monitoring was possible or began. Estimates have been made of the burdens of PCBs in the UK environment (Harrad et al., 1994; Diamond et al., 2008). Key compartments are believed to be the stocks from past use in transformers, capacitors, buildings/sealants etc (all potential diffusive primary sources to atmosphere if they volatilise) (Harrad et al., 1993; Alcock et al., 1993), together with a burden of previously emitted PCBs in surface soils and sediments (potential secondary sources to atmosphere if they volatilize (Diamond et al., 2008; Robinson et al., 2004). An important issue, which relates to whether possible further source reductions can be made, is whether primary or secondary sources control ambient levels now, some 40 years after production and fresh use in the UK ceased.

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 for PCBs cannot be considered significantly different between sites or between congeners. For the data set up to the end of 2009 the average half-live is 4.2 years with values spanning from 2.4 to 8.6 years. The observed half-lives for the rural sampling sites range from 2.4 - 8.6 years at High Muffles and 3.2 - 5.4 years at Hazelrigg. For the urban sites the ranges are 4.9 - 7.4 years at Manchester and 2.8 - 4 years at London. Sampling at Stoke Ferry and Middlesbrough was stopped in 2008, but the last reported half-lives spanned from 2.2 - 6.7 years and 4.2 - 6.6 years respectively.

<u>Sources and emissions</u>. The PCB emission data contained in the NAEI broadly agrees with the time trends observed in the TOMPs datasets. Figure 7 shows a comparison between the PCB data provided by the NAEI and the Hazelrigg, London and Manchester data for the Σ_7 PCBs. This agreement holds for the other TOMPs datasets and suggests that the NAEI captures the main ongoing PCB sources including Industrial Processes (including use of HFC, N₂O, NH₃, PFC & SF₆) and metal production. As an additional exercise, we estimated emissions over time at the three TOMPs urban/semi-rural sites (London, Manchester, Hazelrigg) from the *Breivik et al.*

(2007) inventory. In this the total emission for a given country are distributed on a longitudelatitude 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 7 the grid square and the subsequent emission data were chosen closest to the geographical position of the sampling site. For Auchencorth Moss, Weybourne and High Muffles the data sets are not comprehensive enough to yield significant results.

PCB levels in the UK have undergone a sustained and consistent decline over the last 40 years. Declines started around the time of *voluntary* restrictions in PCB production and use, long before regulations and routine monitoring came into force. These voluntary restrictions happened because high levels of PCBs had been observed in birds of prey in the 1960s, causing concerns (Erickson et al., 1997) Pressure applied as a direct result of this biological monitoring work resulted in a timely intervention on production and highlights the critical role that prospective biomonitoring has had in alerting regulators and industry to potential problems (Giacomello et al., 2006).

The steady rate of decline since that time suggests that no specific regulatory action or intervention – apart from the ban in production and use – has helped dissipate PCBs from the environment any more quickly over time. Measures which *might* have been expected to hasten rates of decline include: destruction of PCB stocks via high temperature incineration, particularly through the 1980s; limits on disposal to landfills; and the International Conventions which are designed to identify sources and reduce them. However, their apparent lack of influence on trends suggests that slow volatilisation releases from the large stocks of PCBs which already existed by the 1970s in widely dissipated source materials (e.g. building materials, window sealants, capacitors and other electrical equipment) and 'reservoirs' has controlled levels and trends over the last 40 years.



Figure 7. Correlation of observed PCB air concentrations^{\otimes} [pg/m³] to emission estimates [tonnes] for the sampling areas of London (LON), Manchester MAN) and Hazelrigg (HZ) (*Breivik et al.* 2007)^{\otimes} (\blacktriangle) and to emission inventory estimates [tonnes] by the National Atmospheric Emissions Inventory (NAEI)^{\otimes} for the whole of the UK (\bullet)

[®] sum of PCB congeners 28, 52, 90/101, 118, 138, 153/132, 180

 $^{\otimes\otimes}$ total sum of PCB congeners.

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Appendix 1. PCDD/Fs data.

LONDON 2009	Q1.09	Q2.09	Q3.09	Q4.09	2009
					AVERAGE
DIOXINS & FURANS	fgTEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3
2,3,7,8-TCDF	1.25	0.77	0.32	0.39	0.68
1,2,3,7,8-PeCDF	0.65	nd	nd	nd	0.65
2,3,4,7,8-PeCDF	5.23	1.47	nd	1.87	2.86
1,2,3,4,7,8-HxCDF	27.37	10.26	nd	0.44	12.69
1,2,3,6,7,8-HxCDF	24.69	12.56	nd	0.35	12.54
2,3,4,6,7,8-HxCDF	30.04	25.32	nd	0.47	18.61
1,2,3,7,8,9-HxCDF	9.08	nd	nd	nd	9.08
1,2,3,4,6,7,8-HpCDF	nd	0.11	0.07	0.15	0.11
1,2,3,4,7,8,9-HpCDF	0.67	nd	nd	nd	0.67
OCDF	0.0427	nd	0.0004	0.0010	0.01
2,3,7,8-TCDD	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDD	4.18	nd	nd	nd	4.18
1,2,3,4,7,8-HxCDD	0.25	nd	nd	nd	0.25
1,2,3,6,7,8-HxCDD	1.65	0.29	nd	0.59	0.85
1,2,3,4,7,8-HxCDD	1.79	0.30	nd	0.40	0.83
1,2,3,4,6,7,8-HpCDD	1.45	0.22	0.15	0.57	0.60
OCDD	0.30	0.01	0.05	0.16	0.13
ΣTEQ dioxins and furans	108.65	51.32	0.55	5.23	41.44
COPLANAR PCBs	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3
3,3',4,5-TetraCB	nd	nd	nd	nd	nd
3,3',4,4'-TetraCB	0.015	0.033	0.02	0.02	0.02
3,3',4,4',5-PentaCB	1.8	1.5	0.8	0.57	1.16
3,3',4,4',5,5'-HexaCB	0.084	0.032	0.031	nd	0.05

MANCHESTER 2009	Q1.09	Q2.09	Q3.09	Q4.09	2009 AVERAGE
DIOXINS & FURANS	fgTEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3
2,3,7,8-TCDF	0.45	0.46	0.43	2.40	0.93
1,2,3,7,8-PeCDF	0.22	0.28	nd	nd	0.25
2,3,4,7,8-PeCDF	3.73	nd	2.21	8.11	4.68
1,2,3,4,7,8-HxCDF	nd	0.66	0.31	4.44	1.80
1,2,3,6,7,8-HxCDF	0.65	0.78	0.55	6.88	2.22
2,3,4,6,7,8-HxCDF	0.96	nd	0.64	3.41	1.67
1,2,3,7,8,9-HxCDF	nd	3.52	nd	nd	3.52
1,2,3,4,6,7,8-HpCDF	nd	0.07	0.23	0.92	0.41
1,2,3,4,7,8,9-HpCDF	0.04	0.49	nd	0.10	0.21
OCDF	0.0023	0.0010	0.0009	0.0045	0.00
2,3,7,8-TCDD	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDD	nd	nd	nd	8.13	8.13
1,2,3,4,7,8-HxCDD	nd	nd	nd	nd	nd
1,2,3,6,7,8-HxCDD	0.36	nd	nd	2.18	1.27
1,2,3,4,7,8-HxCDD	0.43	0.39	nd	1.69	0.84
1,2,3,4,6,7,8-HpCDD	0.41	0.26	0.20	1.48	0.59
OCDD	0.01	0.01	0.04	0.44	0.13
ΣTEQ dioxins and furans	7.27	6.92	4.37	38.28	14.21
COPLANAR PCBs	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3
3,3',4,5-TetraCB	nd	nd	nd	nd	ND
3,3',4,4'-TetraCB	0.016	0.049	0.034	0.031	0.03
3,3',4,4',5-PentaCB	1.3	2.3	2.014	3.6	2.29
3,3',4,4',5,5'-HexaCB	0.164	0.051	0.041	nd	0.09

AUCHENCORTH 2009	Q1.09	Q2.09	Q3.09	Q4.09	2009 AVERAGE
fgTEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m4	fg TEQ/m3
2,3,7,8-TCDF	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDF	0.303246	nd	nd	nd	0.30
2,3,4,7,8-PeCDF	9.283025	nd	nd	nd	9.28
1,2,3,4,7,8-HxCDF	nd	nd	nd	nd	nd
1,2,3,6,7,8-HxCDF	nd	nd	nd	nd	nd
2,3,4,6,7,8-HxCDF	nd	nd	nd	nd	nd
1,2,3,7,8,9-HxCDF	nd	0.437662	nd	nd	0.44
1,2,3,4,6,7,8-HpCDF	nd	nd	nd	0.03	0.03
1,2,3,4,7,8,9-HpCDF	nd	0.054964	nd	nd	0.05
OCDF	0.000967	0.000409	nd	nd	0.00
2,3,7,8-TCDD	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDD	nd	nd	nd	nd	nd
1,2,3,4,7,8-HxCDD	2.422203	nd	nd	nd	2.42
1,2,3,6,7,8-HxCDD	nd	nd	nd	nd	nd
1,2,3,4,7,8-HxCDD	nd	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDD	0.388797	0.041848	nd	0.10	0.18
OCDD	0.008361	0.001755	0.009842	0.03	0.01
ΣTEQ dioxins and furans	2.067766	0.107328	0.009842	0.052385	0.56
COPLANAR PCBs	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3
3,3',4,5-TetraCB	nd	nd	nd	nd	nd
3,3',4,4'-TetraCB	0.0052	0.0059	0.0043	0.00	0.00
3,3',4,4',5-PentaCB	nd	nd	nd	nd	nd
3,3',4,4',5,5'-HexaCB	nd	nd	nd	nd	nd

HIGH MUFFLES 2009	Q1.09	Q2.09	Q3.09	Q4.09	2009
					AVERAGE
DIOXINS & FURANS	fgTEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3
2,3,7,8-TCDF	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDF	nd	0.96	nd	nd	nd
2,3,4,7,8-PeCDF	nd	20.78	nd	nd	nd
1,2,3,4,7,8-HxCDF	nd	1.12	3.38	nd	nd
1,2,3,6,7,8-HxCDF	nd	2.88	nd	nd	nd
2,3,4,6,7,8-HxCDF	nd	2.40	3.13	0.99	nd
1,2,3,7,8,9-HxCDF	nd	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDF	nd	0.13	0.76	0.13	0.34
1,2,3,4,7,8,9-HpCDF	nd	0.11	nd	nd	nd
OCDF	nd	0.00	0.01	0.0009	0.00
2,3,7,8-TCDD	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDD	nd	nd	nd	nd	nd
1,2,3,4,7,8-HxCDD	nd	nd	nd	nd	nd
1,2,3,6,7,8-HxCDD	nd	nd	nd	nd	nd
1,2,3,4,7,8-HxCDD	nd	nd	nd	nd	nd
1,2,3,4,6,7,8-HpCDD	nd	0.70	0.512	0.40	0.54
OCDD	0.002	0.027	0.155	0.128	0.08
ΣTEQ dioxins and furans	0.00168	29.10813	7.29	1.13	9.38
COPLANAR PCBs	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3
3,3',4,5-TetraCB	nd	nd	nd	nd	nd
3,3',4,4'-TetraCB	0.007	0.044	0.338	0	0.10
3,3',4,4',5-PentaCB	nd	1.2	16.9	nd	9.07
3,3',4,4',5,5'-HexaCB	nd	nd	nd	nd	nd

HAZELRIGG 2009	Q1.09	Q2.09	Q3.09	Q4.09	2009 AVERAGE
DIOXINS & FURANS	fgTEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3
2,3,7,8-TCDF	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDF	0.62	nd	nd	nd	0.62
2,3,4,7,8-PeCDF	14.35	5.32	nd	nd	9.83
1,2,3,4,7,8-HxCDF	nd	2.87	0.51	0.56	1.31
1,2,3,6,7,8-HxCDF	nd	4.79	0.33	0.37	1.83
2,3,4,6,7,8-HxCDF	0.45	5.64	0.36	0.40	1.71
1,2,3,7,8,9-HxCDF	nd	nd	2.09	2.31	nd
1,2,3,4,6,7,8-HpCDF	nd	nd	0.47	0.52	0.49
1,2,3,4,7,8,9-HpCDF	nd	0.21	0.24	0.26	nd
OCDF	0.0007	0.0138	0.0018	0.0020	0.0046
2,3,7,8-TCDD	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDD	nd	6.06	nd	nd	nd
1,2,3,4,7,8-HxCDD	nd	0.43	nd	nd	0.43
1,2,3,6,7,8-HxCDD	nd	1.70	0.31	0.34	0.78
1,2,3,4,7,8-HxCDD	nd	2.23	nd	nd	2.23
1,2,3,4,6,7,8-HpCDD	nd	0.2127	0.38	0.41	0.33
OCDD	nd	0.06	0.05	0.05	0.05
ΣTEQ dioxins and furans	15.42	29.48	4.31	4.76	13.49
	faTEQ/m3	faTEQ/m3	faTEQ/m3	faTEQ/m3	faTEQ/m3
	.g g/mo	.9 3/110	.9	.9 6/110	.9 3, 110
3,3',4,5-TetraCB	nd	nd	nd	nd	nd
3,3',4,4'-TetraCB	0.0073	0.011	nd	nd	0.01
3,3',4,4',5-PentaCB	0.69	0.63	0.47	0.67	0.62
3,3',4,4',5,5'-HexaCB	0.11	nd	nd	nd	0.11

WEYBOURNE 2009	Q1.09	Q2.09	Q3.09	Q4.09	2009 AVERAGE
fgTEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m3	fg TEQ/m4	fg TEQ/m3
2,3,7,8-TCDF	3.5	0.57	nd	0.65	1.59
1,2,3,7,8-PeCDF	1.3	nd	nd	nd	1.28
2,3,4,7,8-PeCDF	28.5	2.2	nd	2.69	11.12
1,2,3,4,7,8-HxCDF	5.7	0.40	nd	0.60	2.23
1,2,3,6,7,8-HxCDF	5.1	nd	nd	0.65	2.85
2,3,4,6,7,8-HxCDF	2.8	n d	nd	0.91	1.85
1,2,3,7,8,9-HxCDF	2.7	nd	nd	nd	2.71
1,2,3,4,6,7,8-HpCDF	nd	0.11	0.056974	0.23	0.13
1,2,3,4,7,8,9-HpCDF	nd	nd	nd	0.04	nd
OCDF	0.0016	0.00060	0.000334	0.0013	0.0010
2,3,7,8-TCDD	nd	nd	nd	nd	nd
1,2,3,7,8-PeCDD	17.1	nd	nd	nd	17.10
1,2,3,4,7,8-HxCDD	3.0	nd	nd	nd	3.05
1,2,3,6,7,8-HxCDD	3.1	nd	nd	0.76	1.92
1,2,3,4,7,8-HxCDD	3.3	nd	nd	0.64	1.96
1,2,3,4,6,7,8-HpCDD	2.7	0.19	0.091633	0.78	0.93
OCDD	0.68	0.047	0.028037	0.21	0.24
ΣTEQ dioxins and furans	79.435261	3.508713	0.176978	8.168261	22.82
COPLANAR PCBs	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3	fgTEQ/m3
3,3',4,5-TetraCB	nd	nd	nd	nd	nd
3,3',4,4'-TetraCB	0.2695689	0.079992	0.014	0.01	0.09
3,3',4,4',5-PentaCB	5.7256494	2.985775	0.422	0.61	2.44
3,3',4,4',5,5'-HexaCB	nd	nd	nd	0.07	nd

LONDON 2009	Q1.09	Q2.09	Q3.09	Q4.09	
					2009
					AVERAGE
PCB/OC	pg/m ³				
18	1.7	12.2	124.2	5.9	36.0
22	1.2	0.7	686.5	3.6	173.0
44	0.1	0.6	24.0	4.2	7.2
49	1.1	6.3	<0.04	<0.04	3.7
52	4.5	23.4	34.2	2.1	16.0
70	0.7	4.0	26.2	1.5	8.1
74	0.8	4.4	19.9	1.2	6.5
87	<0.04	1.0	16.8	0.9	6.2
95	0.6	4.73	0.5	1.9	1.9
99	1.7	5.60	17.3	0.6	6.3
104	<0.04	<0.04	<0.04	<0.04	<0.04
105	<0.04	<0.04	2.9	1.5	2.2
110	<0.04	0.33	1.0	1.4	0.9
114	<0.04	<0.04	2.9	<0.04	2.9
118	0.6	3.6	7.2	0.8	3.0
123	0.09	0.6	4.6	<0.04	1.8
138	0.1	0.1	8.6	0.67	2.4
141	0.9	2.0	2.7	0.2	1.5
149	2.3	9.0	2.8	0.8	3.7
151	1.8	5.0	4.6	0.3	2.9
155	<0.04	<0.04	<0.04	<0.04	<0.04
156	<0.04	<0.04	<0.04	<0.04	<0.04
157	<0.04	<0.04	<0.04	<0.04	<0.04
158	0.22	0.19	0.58	0.13	0.3
167	<0.04	<0.04	3.05	0.39	1.7
170	<0.04	<0.04	<0.04	<0.04	<0.04
174	0.1	1.02	0.65	<0.04	0.6
180	1.66	1.9	2.4	0.3	1.6
183	0.7	0.7	1.3	<0.04	0.9
187	1.6	2.1	3.0	0.3	1.7
188	< 0.04	< 0.04	< 0.04	<0.04	< 0.04
189	<0.04	< 0.04	<0.04	<0.04	<0.04
194	<0.04	< 0.04	<0.04	<0.04	<0.04
199	<0.04	< 0.04	0.1	<0.04	0.1
203	< 0.04	< 0.04	0.5	0.1	0.3
153+132	5.09	5.52	12.89	1.36	6.2
31+28	1.24	9.8	21.9	9.40	10.6
41/64	0.5	1.1	22.4	4.8	1.2
60/56	<0.04	<0.04	<0.04	<0.04	< 0.04
90/101	9.6	22.1	3.2	1.8	9.3
$\Sigma_7 PCB$	23	67	90	16	49

Appendix 2. PCB data

 $\Sigma_7 PCB = Sum of PCB 28+31, PCB 52, PCB 90/101, PCB 118, PCB 138, PCB 153+132, PCB180$

MANCHESTER 2009	Q1.09	Q2.09	Q3.09	Q4.09	
					2009
	_	_	_	_	AVERAGE
PCB/OC	pg/m³	pg/m ³	pg/m ³	pg/m ³	pg/m ³
18	0.2	0.4	13.2	28.7	10.6
22	1.2	2.2	6.5	27.9	9.4
44	<0.04	0.1	22.8	39.6	20.8
49	0.3	0.2	35.0	68.3	25.9
52	2.6	0.8	18.1	29.3	12.7
70	<0.04	<0.04	5.2	15.6	10.4
74	0.3	<0.04	3.Z	11.0	4.8
05	<0.04	<0.04	4.7	11.9 29.6	0.3
95	0.1	<0.04	3.5	20.0	37
104	<0.04	<0.04	<0.04	<0.0	<0.04
104	<0.04	<0.04	<0.04	<0.04	<0.04
110	< 0.04	< 0.04	10.6	19.4	15.0
114	< 0.04	< 0.04	< 0.04	< 0.04	<0.04
118	0.43	0.24	5.2	9.3	3.8
123	<0.04	<0.04	<0.04	<0.04	<0.04
138	0.3	0.1	4.4	9.0	3.5
141	0.5	0.9	1.0	2.1	1.1
149	1.1	0.6	7.1	13.4	5.5
151	1.6	1.9	2.8	4.7	2.7
155	<0.04	<0.04	<0.04	<0.04	<0.04
156	<0.04	<0.04	<0.04	<0.04	<0.04
157	<0.04	<0.04	<0.04	<0.04	<0.04
158	0.12	0.10	0.32	0.93	0.4
167	< 0.04	<0.04	0.40	1.01	0.7
170	<0.04	<0.04	<0.04	< 0.04	<0.04
174	<0.04	< 0.04	0.49	1.21	0.9
180	1.24	2.7	0.8	2.3	1.8
183	0.3	1.2	0.3	0.7	0.7
107	-0.04	2.0 ~0.04	~0.01	2.0 ~0.04	<0.04
189	<0.04	<0.04	<0.04	<0.04	<0.04
194	<0.04	<0.04	0.2	<0.04	0.2
199	<0.04	< 0.04	< 0.04	0.1	0.1
203	< 0.04	< 0.04	< 0.04	0.45	0.5
153+132	5.30	15.40	7.01	14.29	10.5
31+28	0.2	0.6	28.9	41.9	17.9
41/64	0.3	0.8	1.6	20.6	5.8
60/56	<0.04	<0.04	<0.04	<0.04	<0.04
90/101	11	22	15.1	6.3	13.6
$\Sigma_7 PCB$	21	42	79	112	64
$\Sigma_7 PCB = Sum of PCB 28+3$	1, PCB 52, PC	B 90/101, PCB 1	18, PCB 138	8, PCB 153+	-132, PCB180

AUCHENCORTH					
2009	Q1.09	Q2.09	Q3.09	Q4.09	
					2009
					AVERAGE
PCB/OC	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3
18	0.3	0.4	23.0	2.5	6.5
22	0.1	<0.02	15.2	<0.02	7.6
44	0.0	<0.02	13.4	4.0	5.8
49	0.1	0.2	5.4	11.7	4.3
52	0.6	1.1	5.4	1.7	2.2
70	<0.02	<0.02	4.5	0.8	2.6
74	< 0.02	0.1	3.2	1.1	1.5
87	< 0.02	<0.02	0.6	0.1	0.4
95	< 0.02	0.08	1.4	0.5	0.7
99	0.1	0.27	<0.02	0.1	0.2
104	< 0.02	<0.02	<0.02	<0.02	<0.02
105	< 0.02	<0.02	3.1	<0.02	3.1
110	0.0	<0.02	1.0	0.4	0.5
114	< 0.02	<0.02	<0.02	<0.02	<0.02
118	< 0.02	<0.02	0.7	0.2	0.4
123	< 0.02	<0.02	<0.02	<0.02	<0.02
138	0.4	0.2	0.9	0.3	0.4
141	0.2	0.2	0.1	<0.02	0.2
149	0.4	0.6	1.0	0.3	0.6
151	0.2	0.4	0.3	0.1	0.3
155	<0.02	<0.02	<0.02	<0.02	<0.02
156	<0.02	<0.02	<0.02	<0.02	<0.02
157	<0.02	<0.02	<0.02	<0.02	<0.02
158	<0.02	0.04	0.24	<0.02	0.1
167	<0.02	<0.02	0.67	<0.02	0.7
170	<0.02	<0.02	<0.02	<0.02	<0.02
174	0.08	<0.02	0.17	<0.02	0.1
180	0.32	0.6	0.2	0.07	0.3
183	0.1	0.1	<0.02	0.0	0.1
187	0.2	0.4	0.2	0.1	0.3
188	< 0.02	<0.02	<0.02	<0.02	<0.02
189	< 0.02	<0.02	<0.02	<0.02	<0.02
194	< 0.02	<0.02	<0.02	<0.02	<0.02
199	< 0.02	<0.02	<0.02	<0.02	<0.02
203	<0.02	<0.02	0.0	<0.02	0.0
153+132	0.50	1.33	1.40	0.44	0.9
31+28	0.35	0.3	35.1	6.7	10.6
41/64	<0.02	<0.02	15.7	0.4	8.1
60/56	<0.02	<0.02	<0.02	<0.02	<0.02
90/101	0.8	1.7	1.0	0.5	1.0
S7PCB	2.9	5.3	44.7	9.9	15.9

 Σ_7 PCB = Sum of PCB 28+31, PCB 52, PCB 90/101, PCB 118, PCB 138, PCB 153+132, PCB180

HIGH MUFFLES 2009	Q1.09	Q2.09	Q3.09	Q4.09	
					2009
					AVERAGE
PCB/OC	pg/m ³				
18	<0.02	16.0	19.9	6.5	14.11
22	<0.02	1.2	12.6	2.5	5.42
44	<0.02	0.6	5.7	3.5	3.28
49	<0.02	3.4	23.1	11.5	12.68
52	0.0	8.6	31.2	0.8	10.18
70	<0.02	1.8	14.19	0.81	5.60
74	<0.02	1.9	6.79	0.54	3.06
87	<0.02	0.60	9.61	0.61	3.61
95	<0.02	1.765	26.587	1.907	10.09
99	0.0	1.02	7.61	<0.02	2.89
104	<0.02	<0.02	<0.02	<0.02	<0.02
105	<0.02	<0.02	<0.02	4.7	4.69
110	<0.02	<0.02	20.04	0.99	10.52
114	<0.02	<0.02	<0.02	0.5	0.51
118	<0.02	0.79	9.20	0.39	3.46
123	<0.02	0.44	<0.02	<0.02	0.44
138	0.23	0.48	9.16	<0.02	3.29
141	0.07	0.80	1.65	<0.02	0.84
149	<0.02	4.62	12.36	1.26	6.08
151	<0.02	3.8	4.05	0.44	2.78
155	<0.02	<0.02	<0.02	<0.02	<0.02
156	<0.02	<0.02	<0.02	<0.02	<0.02
157	<0.02	<0.02	<0.02	<0.02	<0.02
158	<0.02	0.19	0.56	<0.02	0.38
167	<0.02	<0.02	<0.02	0.58	0.58
170	<0.02	<0.02	<0.02	<0.02	<0.02
174	<0.02	0.60	0.9	<0.02	0.76
180	0.06	2.08	1.5	<0.02	1.22
183	<0.02	0.59	0.56	0.13	0.42
187	0.03	1.41	1.41	0.09	0.74
188	<0.02	<0.02	<0.02	<0.02	<0.02
189	<0.02	<0.02	<0.02	<0.02	<0.02
194	<0.02	<0.02	0.5	<0.02	0.50
199	<0.02	<0.02	<0.02	0.00	0.00
203	<0.02	<0.02	<0.02	<0.02	<0.02
153+132	<0.02	4.5	12.6	1.1	6.05
31+28	<0.02	10.54	38.69	6.7	18.64
41/64	<0.02	1.7	14.3	3.0	6.31
60/56	<0.02	<0.02	<0.02	<0.02	<0.02
90/101	0.057605	9.4	25.6	1.5	9.14
$\Sigma_7 PCB$	0.39	36	128	10	52
Σ ₇ PCB = Sum of PCB 28+31, PCB 52, PCB 90/101, PCB 118, PCB 138, PCB 153+132, PCB180					

HAZELRIGG 2009	Q1.09	Q2.09	Q3.09	Q4.09	
					2009
					AVERAGE
PCB/OC	pg/m ³				
18	0.1	0.6	13.06	12.03	6.5
22	0.5	<0.02	41.94	34.99	25.8
44	0.1	0.0	10.75	9.81	5.2
49	0.1	0.3	<0.02	<0.02	0.2
52	0.6	0.8	4.10	7.02	3.1
70	<0.02	0.4	36.52	10.62	15.8
74	<0.02	0.3	14.32	8.33	7.7
87	<0.02	0.1	6.52	1.06	2.6
95	0.1	0.2	6.21	3.53	2.5
99	0.27	0.1	3.10	0.79	1.1
104	<0.02	<0.02	<0.02	<0.02	<0.02
105	<0.02	<0.02	<0.02	4.58	4.6
110	<0.02	<0.02	0.73	0.33	0.5
114	<0.02	<0.02	0.07	<0.02	0.1
118	<0.02	0.14	<0.02	<0.02	0.1
123	<0.02	0.06	<0.02	<0.02	0.1
138	0.20	0.1	2.17	1.32	0.9
141	0.18	0.1	0.44	0.07	0.2
149	0.35	0.50	4.98	2.54	2.1
151	0.7	0.6	2.20	0.77	1.1
155	<0.02	<0.02	<0.02	<0.02	<0.02
156	<0.02	<0.02	<0.02	<0.02	<0.02
157	<0.02	<0.02	<0.02	<0.02	<0.02
158	0.05	0.08	0.22	0.21	0.1
167	<0.02	<0.02	0.70	<0.02	0.7
170	<0.02	<0.02	<0.02	<0.02	<0.02
174	<0.02	0.06	0.34	0.23	0.2
180	0.39	0.19	0.53	0.36	0.4
183	0.15	0.08	0.29	0.17	0.2
187	0.36	0.23	0.75	0.36	0.4
188	<0.02	<0.02	<0.02	<0.02	<0.02
189	<0.02	<0.02	<0.02	<0.02	<0.02
194	<0.02	<0.02	<0.02	<0.02	<0.02
199	<0.02	<0.02	<0.02	0.03	0.0
203	< 0.02	< 0.02	0.10	0.04	0.1
153+132	1.56	0.96	3.78	2.15	2.1
31+28	0.15	0.41	48.23	29.69	19.6
41/64	< 0.02	0.2	< 0.02	< 0.02	0.2
60/56	< 0.02	< 0.02	< 0.02	< 0.02	<0.02
90/101	2.6	1.6	3.51	3.61	2.8
$\Sigma_7 PCB$	5.5	4.2	62	44	29.1

 Σ_7 PCB = Sum of PCB 28+31, PCB 52, PCB 90/101, PCB 118, PCB 138, PCB 153+132, PCB180

WEYBOURNE 2009	Q1.09	Q2.09	Q3.09	Q4.09	
					2009
					AVERAGE
PCB/OC	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3
18	1.3	<0.02	7.95	4.25	4.5
22	17.1	8.2	4.11	<0.02	9.8
44	31.1	15.8	2.30	1.87	12.8
49	62.3	5.9	3.33	5.14	19.2
52	11.1	6.7	4.23	1.61	5.9
70	5.6	3.0	2.16	0.97	2.9
74	9.57	<0.02	1.06	0.56	3.7
87	1.4	0.5	0.56	0.27	0.7
95	3.95	1.9	1.42	0.72	2.0
99	2.34	0.78	0.55	0.33	1.0
104	<0.02	<0.02	<0.02	<0.02	<0.02
105	<0.02	<0.02	<0.02	<0.02	<0.02
110	3.52	1.26	1.14	0.42	1.6
114	<0.02	<0.02	<0.02	<0.02	<0.02
118			0.68	0.24	0.5
123	<0.02	<0.02	0.10	<0.02	0.1
138	4.13	1.4	0.96	0.41	1.7
141	1.40	0.27	0.23	0.11	0.5
149	4.3	1.5	1.15	0.52	1.9
151	0.97	0.2	0.43	0.14	0.4
155	<0.02	<0.02	<0.02	<0.02	<0.02
156	<0.02	<0.02	<0.02	<0.02	<0.02
157	<0.02	<0.02	<0.02	<0.02	<0.02
158	<0.02	<0.02	<0.02	0.04	0.0
167	<0.02	<0.02	<0.02	0.13	0.1
170	<0.02	<0.02	<0.02	<0.02	<0.02
174	2.00	<0.02	0.21	0.09	0.8
180	1.15	0.28	0.24	0.14	0.5
183	2.40	0.81	0.12	0.06	0.8
187	1.22	0.37	0.31	0.14	0.5
188	<0.02	<0.02	<0.02	<0.02	<0.02
189	<0.02	<0.02	<0.02	<0.02	<0.02
194	<0.02	<0.02	<0.02	0.07	0.1
199	<0.02	<0.02	<0.02	<0.02	<0.02
203	<0.02	<0.02	<0.02	<0.02	<0.02
153+132	5.22	1.93	1.55	0.64	2.3
31+28	21.9	37.4	23.17	7.16	22.4
41/64	21.8	<0.02	2.09	2.25	8.7
60/56	<0.02	<0.02	0.69	0.08	0.4
90/101	5.5	1.9	1.50	0.83	2.4
$\Sigma_7 PCB$	45	48	31	11	34

 $\overline{\Sigma_7 PCB}$ = Sum of PCB 28+31, PCB 52, PCB 90/101, PCB 118, PCB 138, PCB 153+132, PCB180