

The Lancaster Environment Centre

Annual Report for 2004 on the UK Toxic Organic Micro-pollutants (TOMPs) Air Monitoring and Analysis Network

Dr Rosalinda Gioia

Dr Andy Sweetman

Professor Kevin Jones

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ

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

LANCASTER
UNIVERSITY



Executive Summary.

This report contains the 2004 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 2004, 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 2004	6
4. Network sampling operations	7
5. Extraction and clean-up procedures	8
6. Data storage	10
7. Results for year 2004	11
7.1. PCDD/Fs	
7.2. PCBs	
8. References	24
I. Appendix 1. PCDD/Fs and 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. Three sites are maintained via sub-contracts; London AEA Energy and Environment, Auchincorth 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. PAHs are quantified and reported separately under another monitoring programme currently run by AEA Energy and Environment.

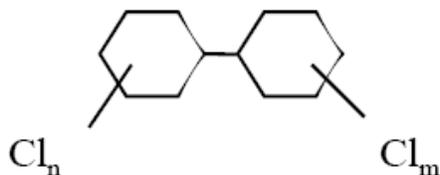
This annual report for polychlorinated biphenyls (PCBs) polychlorinated-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) includes:

- 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,

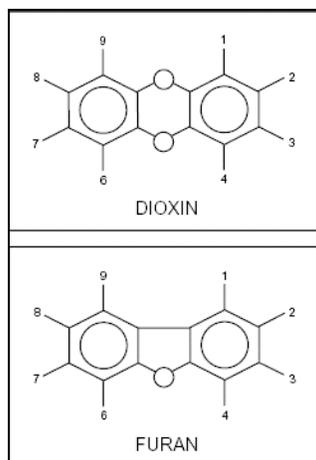
sealants and surface coatings (Eduljee, 1988; de Voogt and Brinkman, 1989; Harrad et al., 1994). Their basic structure is a biphenyl backbone with one to ten chlorine substituents and a general structure of $C_{12}H_{10-n}Cl_n$ ($n=1-10$) (Figure 2).



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 2004

In 2004 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 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 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*). Up to 2004 only seven PCB congeners were constantly measured in all samples: 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-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 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 $^{13}\text{C}_{12}$ -labelled PCBs standards and they ranged between 70-110%. Recoveries are monitored by quantifying 20 $^{13}\text{C}_{12}$ -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:

7. RESULTS FOR YEAR 2004

Table 1 contains information on the bulked air volume (in m³) and the number of samples bulked for each site and each quarter in 2004. The bulked air volume is obtained by summing the volume (in m³) 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 500-700m³ 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 (i.e. that can be analytically detected). Consequently, this leads to a total volume per quarter (bulk volume) of approximately 4500-6000 m³ (see Table 1). Samplers at all sites were calibrated once a year in the period (April-June).

Table 1. Summary of the bulked air volumes and number of samples for each quarter at all sites in 2004

		LON	MAN	MID	HM	SF	HR
Bulked Air Volumes m³	Q1	5781	4575	5389	4966	5873	4756
No. of samples		7	7	7	7	7	7
Bulked Air Volumes m³	Q2	4658	4789	4896	4896	4879	5000
No. of samples		6	6	6	6	6	6
Bulked Air Volumes m³	Q3	4478	4575	4917	4966	4758	4785
No. of samples		6	6	6	6	6	6
Bulked Air Volumes m³	Q4	5278	5057	4955	4919	5012	5550
No. of samples		7	7	7	7	7	7

PCBs

The urban sites of London and Manchester continue to display the highest concentrations of PCBs (107 pg/m³ and 220 pg/m³, respectively). The lowest average concentrations were observed at the rural site of Stoke Ferry (2.3 pg/m³), whereas at all the other sites, the average concentrations were around 10 -20 pg/m³. The highest concentration was observed in Q3 at all

sites while the lowest was observed in Q1 at all sites with the exception of Stoke Ferry which displays similar concentration to Q3 in Q1. 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 and 3).

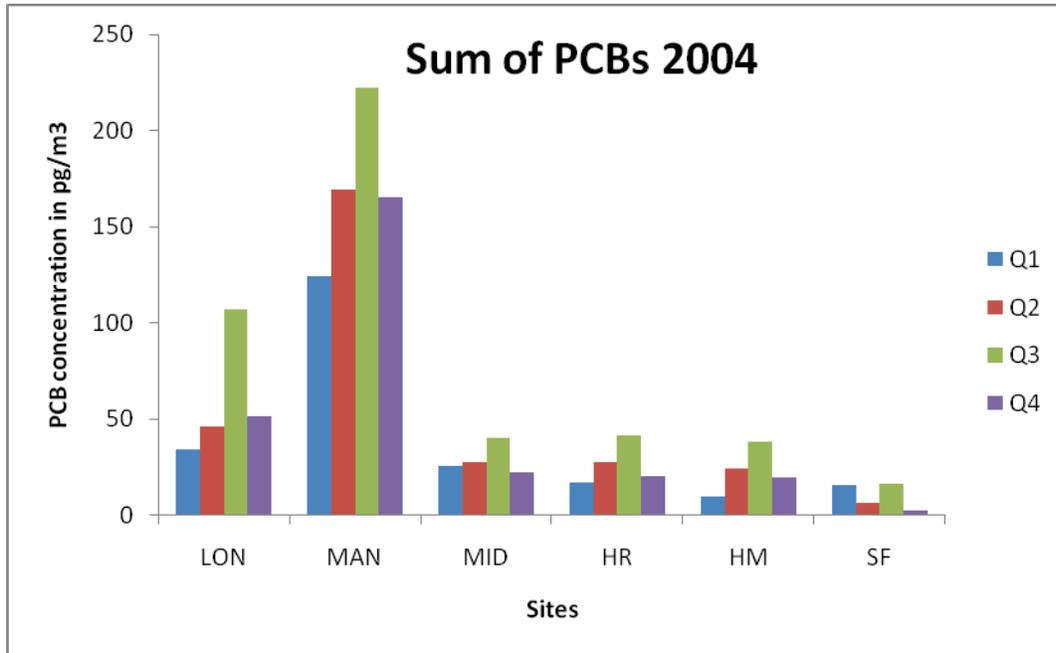


Figure 2. Sum of PCB concentrations at all sites for all quarters in 2004

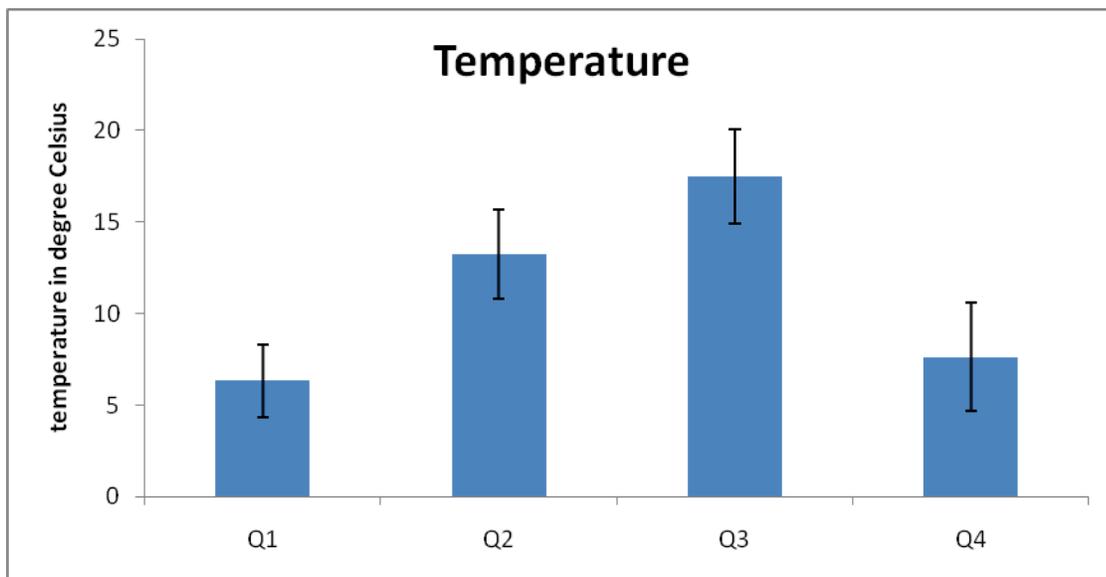


Figure 3. Average temperature for all quarters in 2004.

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 2004 the average half-life is 6.2 years with values spanning from 1.4 to 422 years. The observed half-lives for the rural sampling sites range from 1.5 – 422 years at Stoke Ferry and 3.9 – 7.6 years at Hazelrigg. For the urban sites the ranges are 3.3 – 6 years at Middlesbrough, 5.5 - 14 years at Manchester and 2.1 – 3.5 years at London. 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 fairly constant. Therefore concentrations measured in 2004 are not significantly different from those measured in 2003. The half-life calculations for High Muffles yielded no significant results.

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 HZ, LON, MAN and MID 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 such as industrial processes (including use of HFC, N₂O, NH₃, PFC & SF₆) and metal production

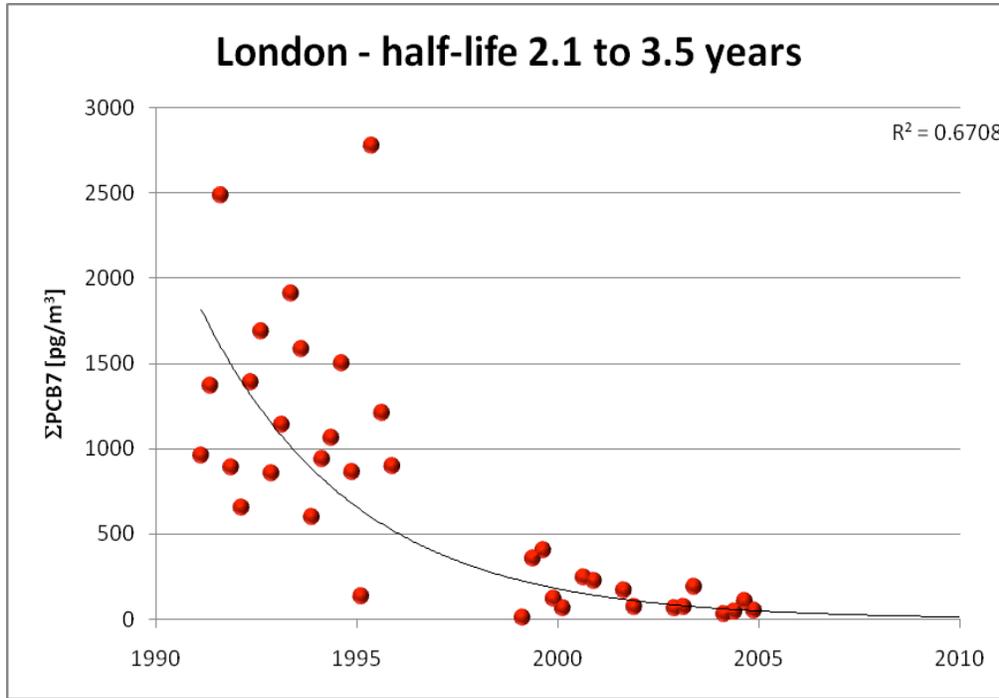


Figure 4a. Σ₇PCB data for the London TOMPs site

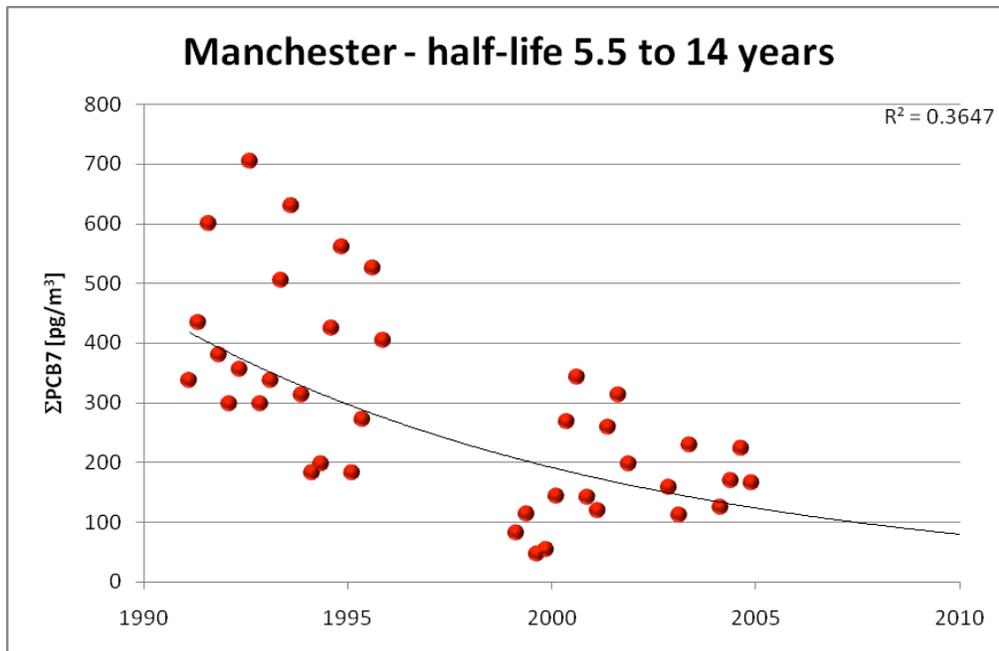


Figure 4b. $\Sigma_7\text{PCB}$ data for the Manchester TOMPs site

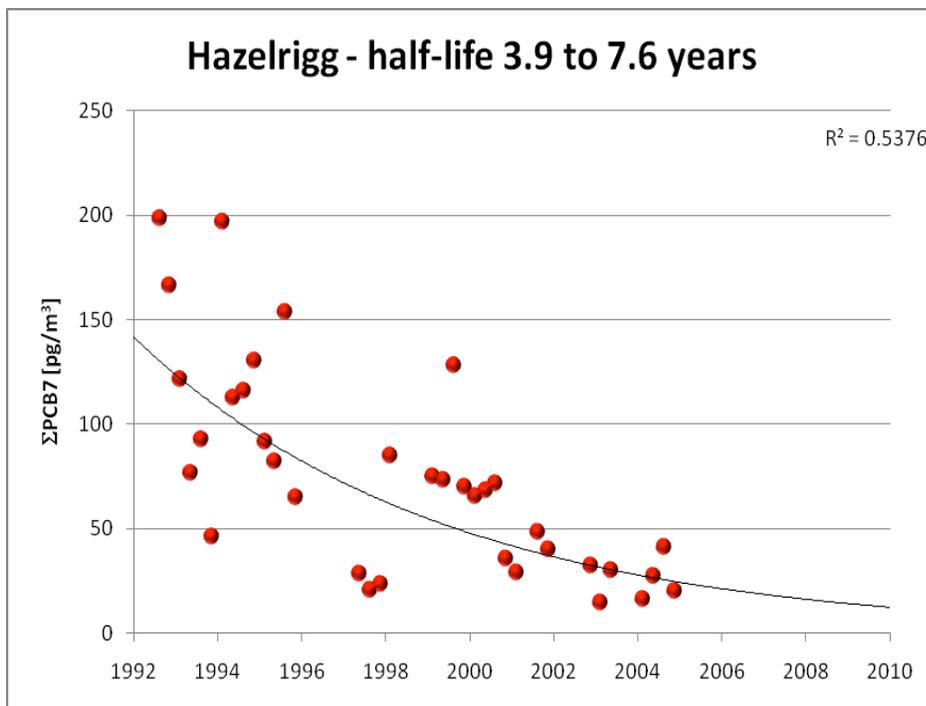


Figure 4c. $\Sigma_7\text{PCB}$ data for the Hazelrigg TOMPs site

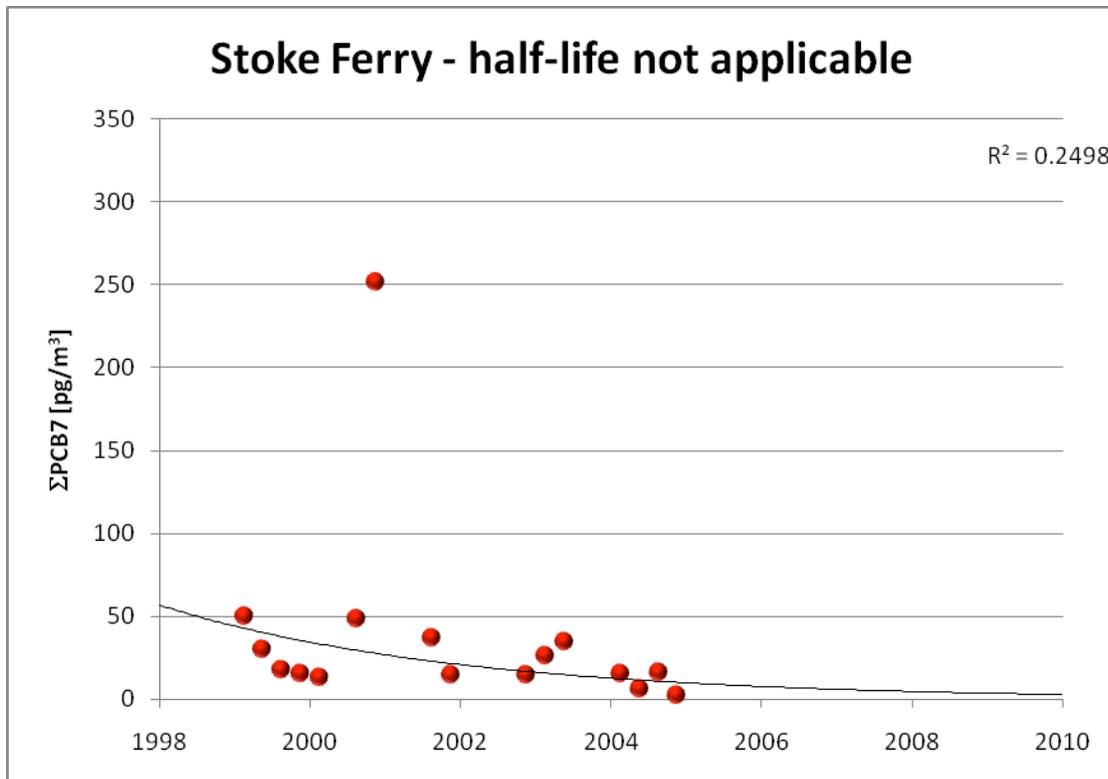


Figure 4f. Σ_7 PCB data for the Stoke Ferry TOMPs site

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 (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 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.

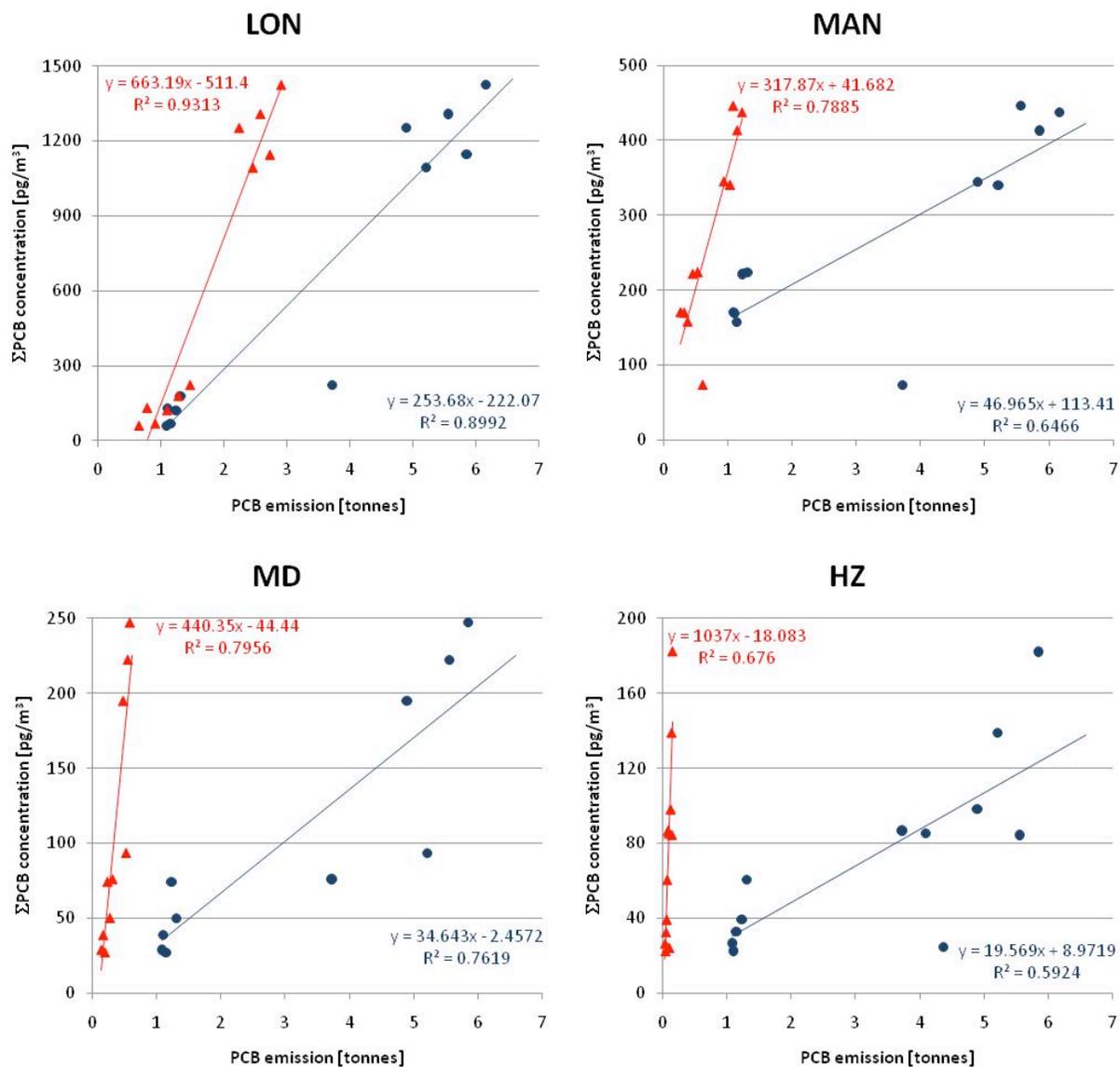


Figure 5. Correlation of observed PCB air concentrations* [pg/m^3] to emission estimates [tonnes] for the sampling areas of London (LON), Manchester (MAN), Middlesbrough (MD) and Hazelrigg (HZ) (Breivik et al. 2007) (▲) and to emission inventory estimates [tonnes] by the National Atmospheric Emissions 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 measured PCDD/Fs concentrations were in general at low levels. Manchester was the site where the highest concentration was observed (Q4: 104.29 fg TEQ/m³) followed by Middlesbrough (Q4: 56.68 (fg TEQ/m³) and London (Q4: 34.95 (fg TEQ/m³). At High Muffles the highest concentration was also observed at the fourth quarter (14.55 (fg TEQ/m³), whereas for Hazelrigg and Stoke Ferry, the highest concentrations were observed during the first quarter of the year (15.59 and 21.56 fg TEQ/m³, respectively). The highest concentrations during winter is something observed in almost all scientific studies and reports (e.g. Coutinho et al., 2007) and it is attributed to emissions during heating. Therefore, this explains why Q1 and Q4 may display the highest concentrations.

In summary, the results of this report are in line with what is considered as typical levels by Lohmann and Jones (1998), with a remote, rural and urban-industrial gradient of typically <10, 10-100 and 100~500 fg TEQ m⁻³, respectively. Typical background concentrations of PCDD/Fs for rural areas are considered to be within a range of 6-15 fg m⁻³, while the mean background concentrations in ambient air in remote areas ranges from 0.1 to 3 fg m⁻³ (Cleverly et al., 2007).

Figure 5 shows how the PCDD/F values varied between the various sites and the various quarters in 2004 (Y axis is in fg TEQ m⁻³).

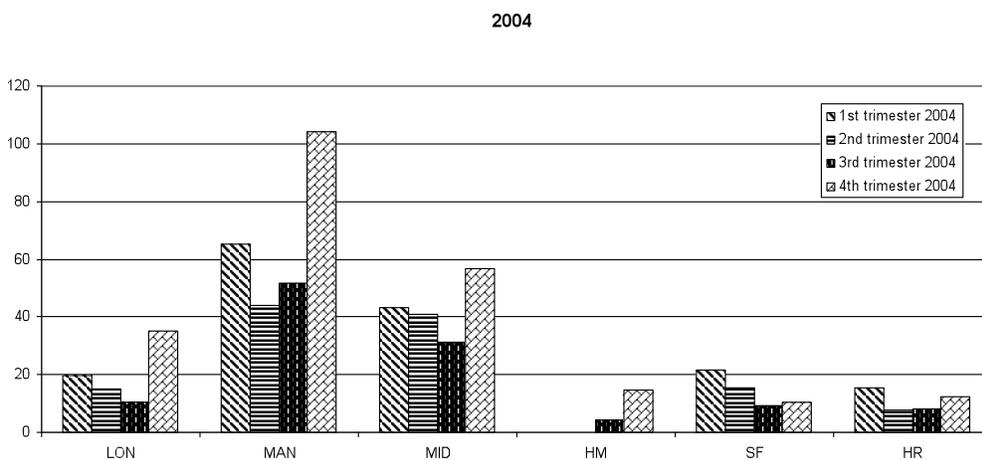
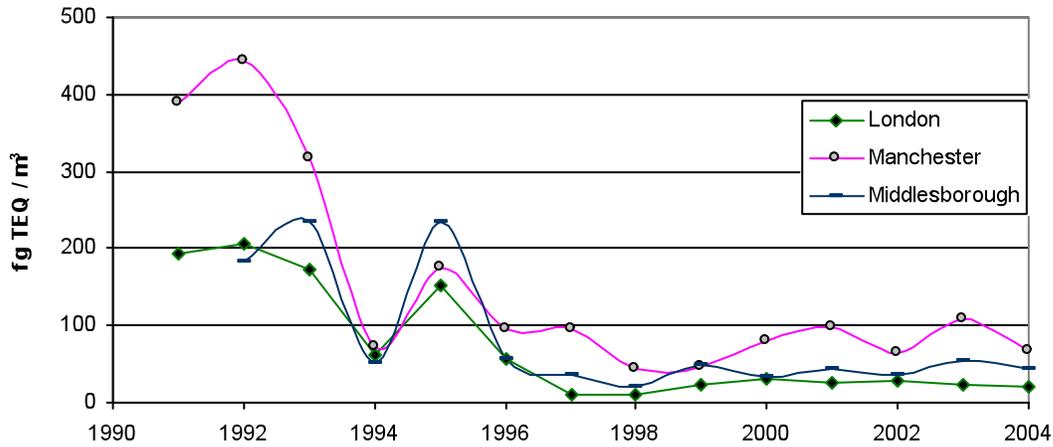


Figure 5. Sum of PCDD/Fs in fg TEQ/m³ at all sites and quarters in 2004.

We can observe that in all cases, Q1 and Q4 were the periods with the highest PCDD/F concentrations, suggesting the seasonality that exists in PCDD/F occurrence. We can also note that in general, urban areas exhibit higher concentrations than the rural ones, however the London site exhibits the same level of PCDD/Fs as Stoke Ferry. This was not expected since in a big city like London, would expect to have much higher concentrations than a semi-rural site, suggesting probably that the sources that used to exist in London or in its proximity have been reduced. In any case, the concentrations of PCDD/Fs in the UK have been decreasing (see Figure 6) 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.

Temporal trends for urban sites (1992-2004)



Temporal trends for rural and semi-rural sites (1996-2004)

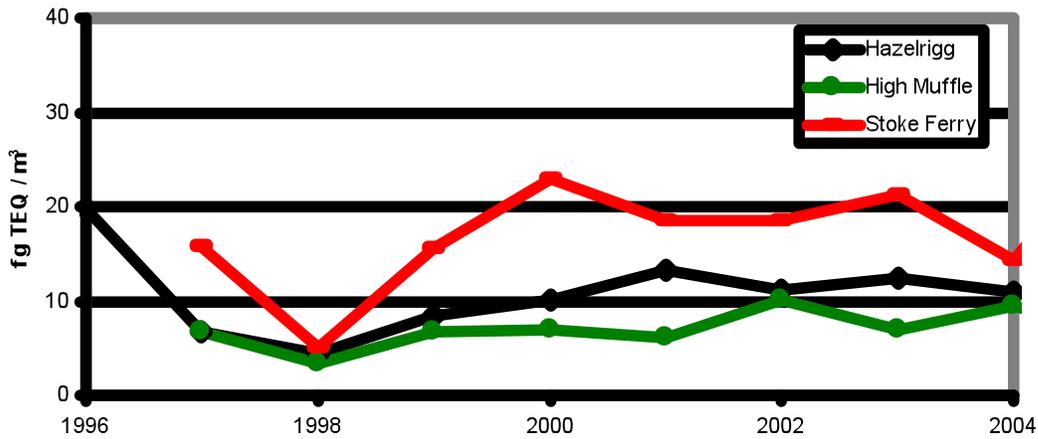


Figure 6. Temporal trends at the urban and rural sites.

The decrease at the 3 urban sites can be plotted as following first order kinetics (5), using the formula:

$$C = C_0 e^{-kT} \text{ or } C = \ln C_0 - kT$$

where C is the concentration of the chemical in air (fg m⁻³), k is the rate constant and T is the time in years.

By applying this formula, the $T_{1/2}$ for PCDD/Fs at LON ranged between 3.2 and 5.9 years ($p < 0.001$), between 4.1 and 5.9 years ($p < 0.001$) at MAN and between 3.9 to 11.1 years ($p = 0.001$) at MID. In contrast, there has been no statistically significant decline at the rural and semi-rural sites, so $T_{1/2}$ for PCDD/Fs was not calculated.

The decrease in the emissions of PCDD/Fs can be observed in figure 7, extracted by data extracted by the website <http://www.naei.org.uk>.

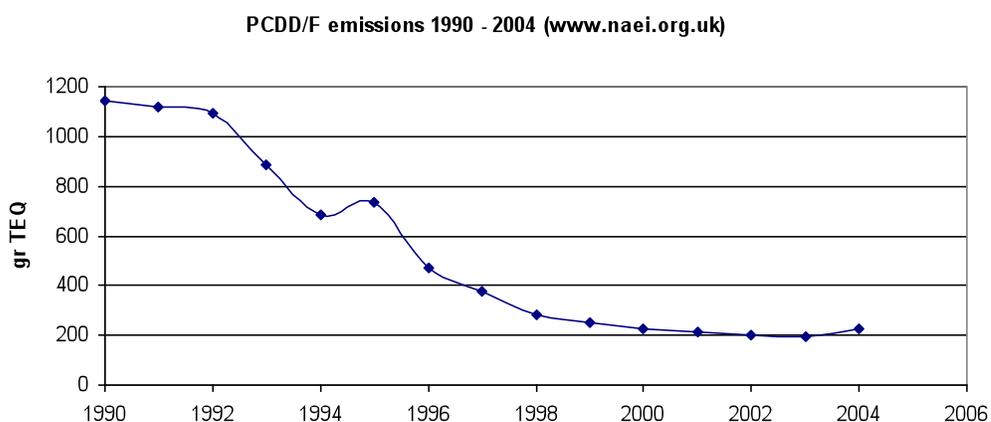


Figure 7. PCDD/F emissions 1990-2004.

A correlation analysis between the overall UK emissions and the overall average of PCDD/F concentrations suggests that emissions and concentrations correlate very strongly ($R^2 = 0.90$) (Figure 8), therefore we can safely say that the decline in the Atmospheric concentrations in the UK is a result of the reduced emissions.

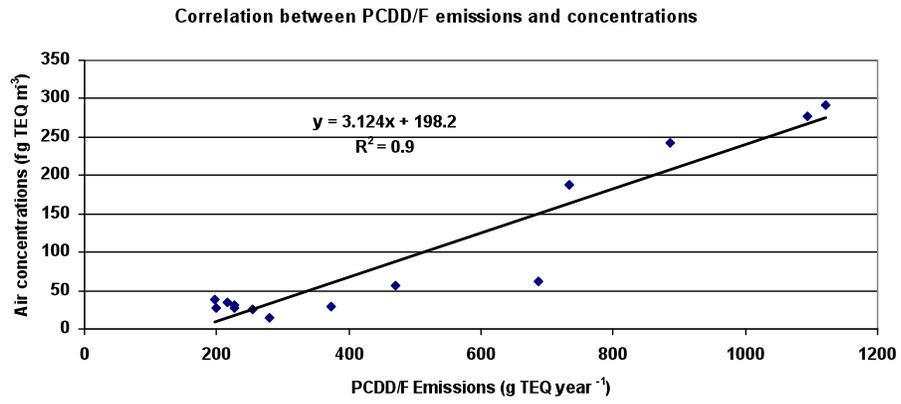


Figure 8. Correlation between PCDD/Fs emissions and concentrations

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.; Kriebich, 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.
- Lohmann, R.; and Jones, K.C. Dioxins and furans in air and deposition: a review of levels, behavior and processes. *Sci. Total Environ.* **1998**, 219, 53-81.
- Coutinho, M.; Pereira, M.; Borrego, C. Monitoring of ambient air PCDD/F levels in Portugal. *Chemosphere* **2007**, 67, 1715-1721.
- Cleverly, D.; Ferrario, J.; Byrne, C.; Riggs, K.; Joseph, D.; Hartford, P. A general indication of the contemporary background levels of PCDDs, PCDFs, and coplanar PCBs in the ambient air over rural and remote areas of the United States. *Environ. Sci. Technol.* **2007**, 41, 1537-1544.

Appendix 1. PCDD/Fs (fg TEQ/m³).

London 2004	Q1	Q2	Q3	Q4
2,3,7,8-TCDF	0.99	0.91	1	2.2
2,3,4,7,8-PeCDF	4.85	3.5	1.65	8
1,2,3,4,7,8-HxCDF	1.1	0.99	0.57	2.1
1,2,3,6,7,8-HxCDF	1.1	0.82	0.49	1.5
2,3,4,6,7,8-HxCDF	0.11	0.15	0.75	1.9
1,2,3,7,8,9-HxCDF	1	0.87	0.04	0.12
1,2,3,4,6,7,8-HpCDF	0.38	0.37	0.28	0.7
1,2,3,4,7,8,9-HpCDF	0.053	0.039	0.028	0.074
OCDF	0.003	0.0029	0.0015	0.0046
2,3,7,8-TCDD	2.1	2.1	1.3	1.3
1,2,3,7,8-PeCDD	4.7	2.2	2	8
1,2,3,4,7,8-HxCDD	0.47	0.55	0.2	0.89
1,2,3,6,7,8-HxCDD	1.2	0.87	0.44	2.3
1,2,3,7,8,9-HxCDD	0	0	0.78	3
1,2,3,4,6,7,8-HpCDD	1.2	1.2	0.53	2.2
OCDD	0.033	0.03	0.016	0.064
ΣTEQ dioxins and furans	19.65	14.93	10.32	34.95

Manchester 2004	Q1	Q2	Q3	Q4
2,3,7,8-TCDF	4.1	3	3.4	7.8
1,2,3,7,8-PeCDF	1.55	0.85	1.35	2.3
2,3,4,7,8-PeCDF	19.5	13.5	15	33.5
1,2,3,4,7,8-HxCDF	5.5	4.1	4.1	7.9
1,2,3,6,7,8-HxCDF	2.6	1.7	2	4.2
2,3,4,6,7,8-HxCDF	0.42	0.24	5.1	8
1,2,3,7,8,9-HxCDF	5.8	4.4	0.27	0.46
1,2,3,4,6,7,8-HpCDF	1.8	1.2	1.6	2.3
1,2,3,4,7,8,9-HpCDF	0.22	0.17	0.19	0.31
OCDF	0.011	0.0072	0.0085	0.015
2,3,7,8-TCDD	2.1	2.1	1.3	2.3
1,2,3,7,8-PeCDD	13	7.9	8.8	18
1,2,3,4,7,8-HxCDD	1.3	0.88	0.83	1.9
1,2,3,6,7,8-HxCDD	2.6	1.7	2	4.2
1,2,3,7,8,9-HxCDD	0	0	2.7	6
1,2,3,4,6,7,8-HpCDD	2	1.3	1.6	3.6
OCDD	0.054	0.032	0.047	0.11
ΣTEQ dioxins and furans	65.15	44.17	51.69	104.29

Middlesbrough	Q1	Q2	Q3	Q4	
2,3,7,8-TCDF		3	2.6	2.2	3.3
1,2,3,7,8-PeCDF		1	0.85	0.75	1.25
2,3,4,7,8-PeCDF		11	11	9	14.5
1,2,3,4,7,8-HxCDF		3.5	3.3	2.5	4.1
1,2,3,6,7,8-HxCDF		2.6	2.8	1.8	3.5
2,3,4,6,7,8-HxCDF		0.23	0.3	2.6	5.3
1,2,3,7,8,9-HxCDF		3.4	3.9	0.12	0.33
1,2,3,4,6,7,8-HpCDF		1	0.98	0.72	1.7
1,2,3,4,7,8,9-HpCDF		0.15	0.15	0.11	0.24
OCDF		0.0072	0.0046	0.0049	0.012
2,3,7,8-TCDD		2.1	2.1	1.3	1.5
1,2,3,7,8-PeCDD		11	8	5.6	11
1,2,3,4,7,8-HxCDD		0.78	1	0.58	1.1
1,2,3,6,7,8-HxCDD		2	2.3	1.3	3
1,2,3,7,8,9-HxCDD		0	0	1.8	3.8
1,2,3,4,6,7,8-HpCDD		1.5	1.5	0.93	2
OCDD		0.039	0.037	0.021	0.049
ΣTEQ dioxins and furans		43.30	40.82	31.33	56.68

Stoke Ferry 2004	Q1	Q2	Q3	Q4	
2,3,7,8-TCDF		0.82	0.93	0.61	0.84
1,2,3,7,8-PeCDF		0.375	0.33	0.095	0.11
2,3,4,7,8-PeCDF		4.85	3.55	2.15	2.7
1,2,3,4,7,8-HxCDF		1.5	1	0.76	0.86
1,2,3,6,7,8-HxCDF		1.3	0.73	0.64	0.6
2,3,4,6,7,8-HxCDF		0.15	0.11	0.77	0.83
1,2,3,7,8,9-HxCDF		1.6	1.1	0.04	0.04
1,2,3,4,6,7,8-HpCDF		0.57	0.31	0.24	0.25
1,2,3,4,7,8,9-HpCDF		0.092	0.038	0.012	0.029
OCDF		0.0039	0.00174	0.0012	0.0016
2,3,7,8-TCDD		2.1	2.1	1.3	1.3
1,2,3,7,8-PeCDD		5.2	3.8	1.3	0.6
1,2,3,4,7,8-HxCDD		0.57	0.35	0.15	0.2
1,2,3,6,7,8-HxCDD		1.2	0.59	0.41	0.51
1,2,3,7,8,9-HxCDD		0	0	0.56	1
1,2,3,4,6,7,8-HpCDD		1.2	0.54	0.34	0.64
OCDD		0.035	0.016	0.0089	0.018
ΣTEQ dioxins and furans		21.56	15.49	9.38	10.52

High Muffles 2004	Q3	Q4
2,3,7,8-TCDF	0.31	1.5
1,2,3,7,8-PeCDF	0.05	0.255
2,3,4,7,8-PeCDF	0.65	3.1
1,2,3,4,7,8-HxCDF	0.28	1.1
1,2,3,6,7,8-HxCDF	0.21	0.74
2,3,4,6,7,8-HxCDF	0.23	0.93
1,2,3,7,8,9-HxCDF	0.1	0.96
1,2,3,4,6,7,8-HpCDF	0.092	0.27
1,2,3,4,7,8,9-HpCDF	0.012	0.036
OCDF	0.00072	0.0018
2,3,7,8-TCDD	1.3	1.3
1,2,3,7,8-PeCDD	0.5	2.1
1,2,3,4,7,8-HxCDD	0.06	0.24
1,2,3,6,7,8-HxCDD	0.4	0.47
1,2,3,7,8,9-HxCDD	0.1	0.96
1,2,3,4,6,7,8-HpCDD	0.1	0.58
OCDD	0.0034	0.017
ΣTEQ dioxins and furans	4.39	14.55

Hazelrigg 2004	Q1	Q2	Q3	Q4
2,3,7,8-TCDF	0.25	0.55	0.54	0.69
1,2,3,7,8-PeCDF	0.24	0.06	0.18	0.245
2,3,4,7,8-PeCDF	3.55	1.35	1.95	3.05
1,2,3,4,7,8-HxCDF	0.89	0.39	0.88	0.98
1,2,3,6,7,8-HxCDF	0.71	0.28	0.43	0.7
2,3,4,6,7,8-HxCDF	0.11	0.11	0.48	0.82
1,2,3,7,8,9-HxCDF	0.8	0.4	0.04	0.06
1,2,3,4,6,7,8-HpCDF	0.26	0.13	0.2	0.27
1,2,3,4,7,8,9-HpCDF	0.038	0.02	0.018	0.032
OCDF	0.0019	0.00083	0.0012	0.002
2,3,7,8-TCDD	2.1	2.1	1.3	1.3
1,2,3,7,8-PeCDD	4.9	1.2	1	1.9
1,2,3,4,7,8-HxCDD	0.43	0.14	0.12	0.21
1,2,3,6,7,8-HxCDD	0.65	0.59	0.4	0.6
1,2,3,7,8,9-HxCDD	0	0	0.4	0.94
1,2,3,4,6,7,8-HpCDD	0.65	0.25	0.27	0.63
OCDD	0.018	0.0069	0.0073	0.016
ΣTEQ dioxins and furans	15.59	7.57	8.21	12.44

Appendix 2. PCBs data in pg/m³

<i>London 2004</i>				
	Q1	Q2	Q3	Q4
PCBs	pg/m ³	pg/m ³	pg/m ³	pg/m ³
28	12	11	33	19
52	8.2	13	34	16
101(90/101)	4.6	8.2	4.4	2
118	2	3.1	9.3	3.9
138	2.7	3.7	12	4.9
153	1	5.6	9.7	3.9
180	3.5	1.6	4.4	2
sum	34	46.2	106.8	51.7

<i>Manchester 2004</i>				
	Q1	Q2	Q3	Q4
PCBs	pg/m ³	pg/m ³	pg/m ³	pg/m ³
28	22	42	58	47
52	30.5	41	68	44
101(90/101)	28	36	11	7.4
118	7.1	8.7	19	13
138	12	14	29	24
153	19	22	26	19
180	5.6	5.5	11	11
sum	124.2	169.2	222	165.4

<i>Middlesbrough 2004</i>				
	Q1	Q2	Q3	Q4
PCBs	pg/m ³	pg/m ³	pg/m ³	pg/m ³
28	11	12	21	13
52	6.2	6.9	11	5.4
101(90/101)	3.3	3.6	1.1	0.6
118	1.3	1.2	1.8	0.8
138	1.5	1.4	2.5	1
153	1.9	2.2	2	0.9
180	0.4	0.4	0.6	0.3
sum	25.6	27.7	40	22

<u>Stoke Ferry 2004</u>				
	Q1	Q2	Q3	Q4
PCBs	pg/m ³	pg/m ³	pg/m ³	pg/m ³
28	7.5	3.3	7.2	1.7
52	4	<1.96	4.4	<1.25
101(90/101)	1.5	1.4	0.9	<0.39
118	<1.01	<1.01	1.1	<0.79
138	1.1	0.7	1.5	0.3
153	0.3	1	1.1	0.2
180	1.4	0.2	0.4	0.1
sum	15.8	6.6	16.6	2.3

<u>High Muffles 2004</u>				
	Q1	Q2	Q3	Q4
PCBs	pg/m ³	pg/m ³	pg/m ³	pg/m ³
28	5.6	15	19	11
52	2.5	6.4	14	6.9
101(90/101)	1.2	2.6	1.2	0.7
118	<1.01	<1.01	1.4	<0.79
138	0.2	0.2	2.1	1
153	<0.04	<0.04	<0.04	<0.04
180	0.1	0.1	0.3	0.1
sum	9.6	24.3	38	19.7

<u>Hazelrigg 2004</u>				
	Q1	Q2	Q3	Q4
PCBs	pg/m ³	pg/m ³	pg/m ³	pg/m ³
28	7.5	13	21	9.7
52	4.1	5.3	11	6.6
101(90/101)	2.4	4.1	2	0.7
118	<1.01	1.5	2.4	1.1
138	1.1	1.2	2.5	1.1
153	1.4	2	2.2	1
180	0.2	0.3	0.5	0.2
sum	16.7	27.4	41.6	20.4