DECLINING LEVELS OF PERSISTENT ORGANIC POLLUTANTS IN SCOTTISH FRESHWATERS

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Introduction

Persistent Organic Pollutants (POPs) are chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife when present at sufficient concentrations [1]. SEPA therefore has a responsibility to assess the significance of POPs in the Scottish environment and this paper provides an overview of the freshwater biota sampling and analysis for a range organochlorine pesticides (OCP) polychlorinated biphenyls (PCB) and polybromodiphenyl ethers (PBDEs) carried out between 2004 and 2006.

Due to the physical chemical properties of POPs, SEPA has adopted a biological monitoring approach to these chemicals, by using the freshwater eel, *Anguilla anguilla* as an indicator organism. The eel was selected because it lives between 7 and 50 years within Scottish rivers [2, 3], it has a high fat content of between 8 and 30% and remains in the same river stretch for long periods. The contaminant body burden can therefore be considered to be related to the particular stretch of river in which the eel lives. Whilst the spatial distributions of POPs in Scotland is investigated, previous research carried out on Scottish eels [4, 5] also provides the opportunity to compare current levels of chemicals with those found 21 years ago.

Materials and Methods

29 freshwater sites in Scotland were sampled to monitor for the presence of POPs. Sampling was carried out by SEPA ecologists using electro fishing. Physical properties of each sample were noted and samples were stored at -20^{o}C until analysis was carried out.

Critical issues in the survey were to ensure that the eels selected for final analysis were of a consistent size (size was used as a surrogate for age in this study) and to ensure that spatial and temporal comparisons of the levels of contamination of eel tissue with PCB and OCPs were valid, particularly for the historical comparison. The main criterion was that eels greater than 30cm in length were the most representative size for comparison to be made. Once mature samples from each of the sites were selected, each site had 5 individual eels analysed for PCB and OCPs.

The PCB/OCP and PBDEs were extracted from the eel tissue using automated Accelerated Solvent Extraction (ASE) technology with final analysis and quantification by a Varian triple quad 1200L and GC-ECD. Table 1 shows how the analysis was split up over the 3 year period. The solvent extraction was carried out by taking a 1g aliquot of freeze-dried homogenized eel tissue and extracting using the ASE with a solvent ratio of 33:66 Acetone:Hexane. The raw tissue solvent extract was then cleaned up using an acid-silica and alumina column absorption chromatography. The clean extract was then analysed using Varian triple quad 1200L or GC-ECD.

Table 1: Analysis techniques and compound suites used over the 3 year sampling period.

Year sampled	Number of sites sampled this year	Analytical technique used to quantify with	Compound suite for each site
2004	7	GC –ECD	9 OCPs / 9 PCBs
2005	10	GC-ECD	9 OCPs / 9 PCBs
2006	12	GC-MSMS	10 OCPs / 32 PCBs / 13PBDEs

To ensure that the results were reproducible and accurate the method underwent extensive validation and routine analytical quality control protocols. Furthermore, all analysis was carried out in a UKAS accredited laboratory in which in-house accredited methods were used in component quantification of the extract. Using the methods

outlined above, recoveries ranged from 63.4% for PCB 101 to 96.2% for op-DDT with GC-ECD method detection limits of 1.0µg/kg for all compounds. GC-MSMS method detection limits ranged from 1.0µg/kg for PCB 101 to 2.7µg/kg for PCB 183.

Results

The mean sample results for the 2004-2005 sampling program can be seen in table 2.

As this is an ongoing project the data generated from 12 sites sampled in 2006 has still to be completed.

Discussion

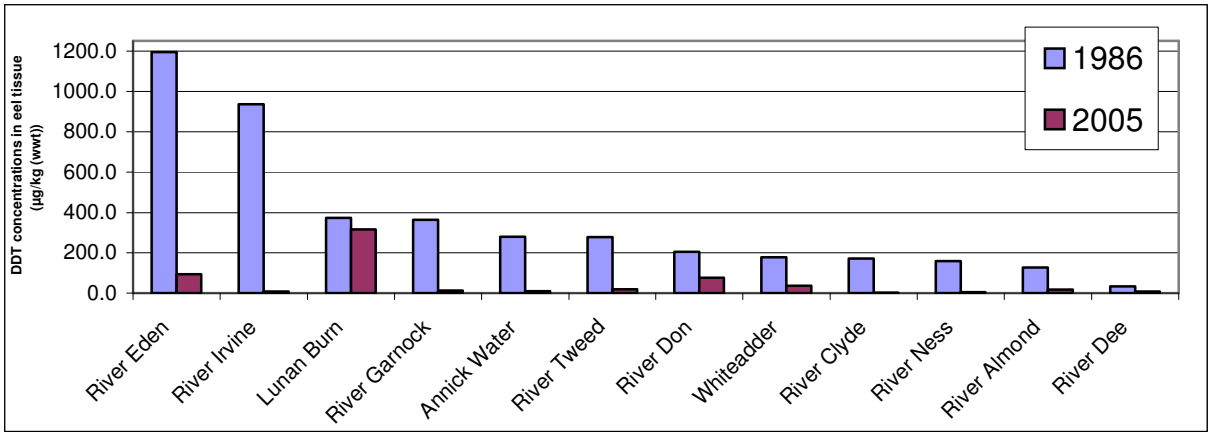
Of the seventeen Scottish river sites studied, concentrations of a selected range of OCP and PCBs in eel tissue were generally low and broadly similar, albeit with the exception of the River Clyde. Moreover the distribution of POPs was seen to correlate with expected pressures i.e. agricultural or urban/industrial as discussed below.

Hexachlorobenzene and hexachlorocyclohexanes were only detected at very low levels and it is likely that concentrations of these substances in the environment are now low throughout the majority of Scotland.

The pesticide DDT and its metabolites were found in eels from all sites, with the highest concentrations being detected in eels from agricultural catchments such as the River Eden and Lunan Burn. Comparing the ratio of the concentrations of pp-DDT to pp-DDE in the eel tissue may provide an indication of whether new inputs of pp DDT have occurred. In this study mean concentrations of DDE were notably higher than DDT at all sites, indicating that no significant new inputs are present and that the breakdown of DDT to DDE has occurred over time.

Figure 1 shows a comparison of historical DDT concentrations monitored in eels and those found in the 2005 study, for sites where data are available from both studies. The sites that show the most significant decrease in DDT levels are the River Eden and River Irvine. The Lunan Burn, however, has not shown any significant decrease in DDT levels present in eel tissue over the last 20 years.

Figure 1: DDT Levels in eel tissue

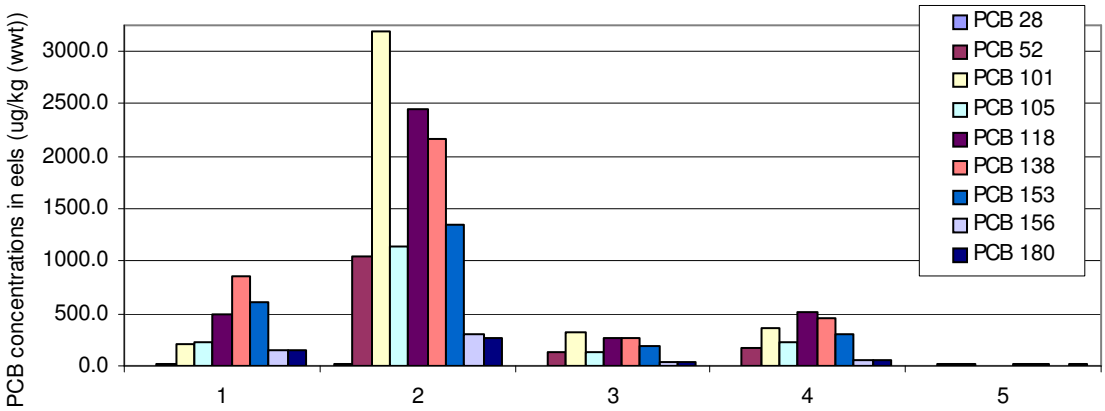


The levels of total-DDT were significantly lower in those rivers potentially impacted by urban or industrial pressures, with PCBs more prevalent at some of these locations. The River Clyde, exhibited the highest levels of PCBs in eel tissue, a legacy of its industrial past. Due to levels found at this site individual congener and eel results were then broken down and plotted to see if a specific Aroclor mix for the River Clyde could be identified (see figure 2).

The general variation in PCB congeners may be attributed to different degradation patterns and availability of PCBs within the watercourse, although the congener profile for eels from the River Clyde is similar to that of a sample of Aroclor 1245 reported [6].

However, whilst significant concentrations have been detected in this study, the levels of contamination of eel tissue are comparable with those found in eels from other fresh and tidal European waters [7, 8].

Figure 2 PCB congener concentrations for individual eels from the River Clyde.



With the exception of the River Devon sites, which were only sampled after 2005, a decreasing trend is evident in POPs concentrations found in eels for Scottish rivers in Table 2. This decline in OCPs and PCBs in eels is believed to reflect reductions in inputs to the aquatic environment over the last 20 years and is not unexpected given the considerable restrictions on the production, use and disposal of these compounds. The levels found in the freshwater sites should continue to reduce but traces are likely to persist in the aquatic environment for several more decades. With the exception of eels from the River Clyde, which contained high levels of PCBs, there is not expected to be any significant risk to eel consumers from the levels of POPs identified in eel tissue during this study.

Acknowledgements
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Table 2: Eel Monitoring Results for the2004-2005 sampling year.

		Organochlorine Pesticide Results in wet wt (µg/kg)									Polychlorinated Biphenyl Results in wet wt (µg/kg)									TOTAL
SITE	**NGR**	**HCBD**	**HCB**	**α-HCH**	**β-HCH**	**γ-HCH**	**pp-DDT**	**op-DDT**	**pp-DDD**	**pp-DDE**	**PCB 28**	**PCB 52**	**PCB 101**	**PCB 105**	**PCB 118**	**PCB 138**	**PCB 153**	**PCB 156**	**PCB 180**	**PCB**
Annick Water	NS331383	<1.0	1.6	<1.0	1.2	1.7	9.2	<1.0	19.7	91.6	<1.0	4.4	10.6	7.6	20.7	24.3	21.7	2.8	5.0	97.1
River Clyde	NS595645	<1.0	1.0	<1.0	1.3	2.2	1.4	<1.0	53.3	4.4	5.6	275	819	348	745	755	495	113	109	3660
River Clyde @ Garnock	NS308427	<1.0	1.5	<1.0	1.8	<1.0	12.5	2.5	16.4	85.9	<1.0	11.1	9.4	5.9	17.3	25.4	28.2	2.6	10.9	111
River Irvine	NS325375	<1.0	1.3	<1.0	1.4	<1.0	7.9	<1.0	11.9	47.5	<1.0	3.5	7.0	6.5	16.2	28.6	26.6	3.1	8.7	100
White Cart @ Hammils	NS486638	<1.0	1.6	<1.0	<1.0	<1.0	5.9	<1.0	10.1	68.2	1.2	6.4	9.6	7.6	9.8	25.4	17.7	2.7	7.9	216
White Cart @ Pollock	NS548617	<1.0	2.3	<1.0	2.5	1.7	27.6	<1.0	48.5	91.7	1.6	21.0	33.2	14.3	48.5	44.8	44.0	3.1	5.5	88.2
River Tweed	NT898477	<1.0	<1.0	<1.0	3.7	<1.0	19	<1.0	21.8	93.9	<1.0	2.1	1.8	1.3	2.4	3.6	4.5	<1.0	1.8	17.5
U/S River Devon	NS985979	<1.0	<1.0	<1.0	1.6	<1.0	22.7	<1.0	10.6	69.7	<1.0	<1.0	1.1	1.2	3.4	10.0	5.3	<1.0	1.4	22.4
D/S River Devon	NS985979	<1.0	1.4	<1.0	2.7	1.7	20.1	1.5	12.8	57.0	<1.0	2.6	3.1	4.9	9.5	10.9	10.6	1.7	2.8	46.2
Whiteadder	NT939536	<1.0	1.1	<1.0	1.8	<1.0	37.1	3.3	43.2	408	1.6	1.1	2.3	2.5	7.2	8.9	11.6	1.4	3.9	40.6
River Almond	NT165752	<1.0	1.7	<1.0	2.2	5.5	17.1	2.5	9.1	35.9	1.1	15.1	23.8	17.1	48.6	54.2	46.8	4.8	8.9	220
River Eden	NO415158	<1.0	1.5	<1.0	3.7	3.1	93.3	5.7	75.1	169	<1.0	2.5	3.1	2.2	4.7	7.0	8.2	1.2	2.7	31.7
Monikie Burn	NO579353	<1.0	1.6	<1.0	<1.0	<1.0	70.6	5.2	24.6	126	<1.0	4.5	2.4	1.1	3.2	5.4	7.1	<1.0	2.5	26.1
Lunan Burn	NO133445	<1.0	1.4	<1.0	3.0	<1.0	317	13.9	72.8	463	<1.0	<1.0	<1.0	<1.0	<1.0	2.5	3.1	<1.0	<1.0	5.6
River Dee	NJ 858003	<1.0	<1.0	<1.0	6.3	<1.0	7.8	<1.0	4.4	14.0	<1.0	<1.0	<1.0	1.5	1.5	2.8	4.5	<1.0	1.9	12.2
River Don	NJ 924093	<1.0	2.3	<1.0	<1.0	1.9	76.8	11.5	49.4	227	2.4	31.5	27.5	74.0	156	157	146	23.7	71.1	690
Ness (H'land)	NH665445	<1.0	<1.0	<1.0	<1.0	<1.0	4.5	<1.0	2.4	11.2	<1.0	1.7	<1.0	<1.0	2.0	3.6	4.7	<1.0	2.2	14.2

NOTE: The results shown in table 2 are from the mean of 5 eels caught at each of the freshwater sites during 2004-2005