

AN ENVIRONMENTAL ASSESSMENT OF CONTAMINANTS IN THE FIRTH OF CLYDE (1992 – 2005)

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Introduction

Due to its industrial legacy, the Clyde is arguably Scotland's most heavily contaminated water body. Effluent and accidental discharges from engineering works, military bases (Holy Loch), and textile and paper industries have all resulted in environmental contamination of the area. One of the most concentrated inputs of contaminants into the Firth of Clyde was as a result of sewage sludge (Garroch Head) and dredge spoil (Cloch Point) dumping. Sewage sludge was disposed of annually at Garroch Head, south of the Isle of Bute, from 1904 up to 1998 when disposal ceased to meet the UKs' obligations under the EC Urban Waste Water Treatment Directive 91/271/EEC. Dumped sewage sludge contains significant quantities of contaminants such as polychlorinated biphenyls (CBs) and polycyclic aromatic hydrocarbons (PAHs).

Commercial formulations of CBs have been widely used in transformers, capacitors, hydraulic fluids and as plasticisers. Due to concerns about the environmental impact of CBs, production in the UK ceased in the 1970s although use in closed systems continued until 1986 when sales of CB formulations finally stopped. However, CBs can still enter the marine environment following the destruction and disposal of industrial plants and equipment or as a result of emissions from old electrical equipment and landfill sites. Polycyclic aromatic hydrocarbons (PAHs) are another group of widespread chemical pollutants and can be of pyrolytic or petrogenic origin. PAHs enter the marine environment through atmospheric deposition, road run-off, and industrial discharges and as a result of oil spills. Both PAHs and CBs are of concern due to their toxicity and persistence in the environment and have the potential for long-range atmospheric transport. Hydrophobic compounds such as PAHs and CBs will accumulate in sediment and both have the potential to bioaccumulate, although PAHs tend to be metabolised rather effectively by fish but bioaccumulate in shellfish.

CBs have been monitored in plaice liver from Garroch Head since 1992 and a further four test sites (Holy Loch, Hunterston, Skelmorlie and Irvine Bay) since 1999. Three reference sites have also been monitored; Pladda since 1992 and two reference sites outwith the Firth of Clyde (Colonsay and Broad Bay) since 1999 (Fig. 1). CBs were monitored in fish liver and sediment and PAHs in sediment, from both the Clyde test and reference sites.

Materials and Methods

Determination of chlorobiphenyls (CBs) in sediment and liver: Freeze dried ground sediment (< 2 mm fraction; 10 - 100 g), or liver samples (0.5 - 3.0 g) ground with anhydrous sodium sulphate, were transferred into a cellulose thimbles and extracted by soxhlet using methyl *t*-butyl ether (MTBE). For sediment, activated copper powder was added to each flask. A recovery standard, containing CB35, 53, 112, 151, 198 and 209, was added prior to extraction. The sediment was extracted with at least 180 ml of MTBE for 12-16 hours. The extract was transferred into hexane before passing through alumina and silica columns. The internal standards (2,4-dichlorobenzyl alkyl hexyl ether with C₆ and C₁₆ alkyl chains) were added to the extract before concentrating using a TurboVap system. The concentration and composition of 23 CB congeners (CB31, 28, 52, 44, 49, 70, 74, 110, 101, 149, **118**, 153, **105**, **157**, 138, 158, 128, **156**, 180, 187, **189**, 170, 194)ⁱ were determined by gas chromatography with electron capture detection (GC-ECD) using a Varian 3500 GC fitted with a cool on-column injector. A medium polarity column was used for the analyses (HP 5, 60 m x 0.25 mm, 0.25 µm film thickness).

Determination of polycyclic aromatic hydrocarbons in sediment: To an aliquot of sediment (10 - 20 g) was added deuterated aromatic standards (d₈-naphthalene, d₁₀-biphenyl, d₈-dibenzothiophene, d₁₀-anthracene, d₁₀-pyrene and d₁₂-benzo[*a*]pyrene). The hydrocarbons were extracted using

ⁱ Those in bold are the dioxin-like mono-*ortho* CBs; these CBs are more toxic than those with more than one chlorine in the ortho position

dichloromethane/methanol with sonication. The halogenated solvent was isolated and dried over anhydrous Na₂SO₄ and solvent exchange to *iso*-hexane was performed. The aliphatic and aromatic hydrocarbons were separated by isocratic, normal phase high performance liquid chromatography (HPLC). The concentration of the PAHs (2- to 6-ring parent and branched) was determined by gas chromatography – electron impact mass spectroscopy (GC-EIMS) using an HP6890 Series gas chromatograph interfaced with an HP5973 MS and fitted with a cool on-column injector and a HP5 MS column (30 m x 0.25 mm id, 0.25 µm film thickness). A total of 29 ions plus the six internal standard ions were measured using selective ion monitoring (SIM). The analysis incorporated 2- to 6-ring, parent and branched PAHs. All methods are accredited to ISO 17025 by the United Kingdom Accreditation Service (UKAS).

Results and Discussion

Chlorobiphenyls (CBs) in plaice liver

At all Clyde test sites concentrations for the ΣICES7ⁱⁱ CBs in plaice liver were > 500 µg/kg lipid weight, except at Hunterston in 1999 and Irvine Bay in 2005 (Fig. 2). Highest CB concentrations were determined in areas where greater impact of contaminants would be expected; Holy Loch and Garroch Head. As expected, CB concentrations in plaice liver at the three reference sites were significantly lower, with concentrations < 500 µg/kg lipid weight for the ΣICES7 CBs at Broad Bay and Colonsay. At Pladda, concentrations were < 500 µg/kg lipid weight in 2001, 2004 and 2005 (and also 1996). No temporal trends in concentration were detected at any of the test sites.

Background Assessment Concentrations (BACs) were established by OSPAR to assess whether concentrations of contaminants were near background, for naturally occurring substances such as PAHs, or close to zero for xenobiotic substances such as CBs¹. CB concentrations at all sites, with the exception of CB180 at Broad Bay, were above the BACs for CBs in fish liver. Toxic Equivalent (TEQs) concentrations in fish liver were calculated using the five mono-*ortho* (dioxin-like) CBs measured in this study. TEQs were also estimated using published models to predict the overall TEQ using total CB^{2, 3} or indicator CB (CB153, CB138 and CB118)³ concentrations. The estimated TEQs from the models were similar to each other and were approximately double the TEQs calculated using the five mono-*ortho* CBs. The model TEQs were plotted against the TEQs calculated using the five dioxin-like CBs analysed as part of this study (Fig. 3). There was a strong linear correlation with correlation coefficients of 0.98 for all three (p < 0.001). Highest TEQs were at Garroch Head and Holy Loch. TEQs are normally used to assess if fish or fishery products are safe to eat, with the Commission Regulation (199/2006/EC) setting a maximum TEQ concentration for the sum of dioxins and dioxin-like CBs of 8 pg/g wet weight in the muscle meat of fish and fishery products. Both estimated and calculated TEQs indicated that the CB concentrations found in fish from the Clyde are unlikely to represent a risk to human health.

Sediment

CBs and PAHs were measured in sediment collected from the fish sites. Concentrations for both contaminants were significantly higher at Holy Loch and Garroch Head compared to all other sites (Fig. 4). Lowest CB and PAH concentrations were found furthest from the estuary, with Irvine Bay having the lowest CB and PAH concentrations of the five Clyde test sites. There was a marginal downward trend in both PAH and CB (normalised to TOC) concentrations at Holy Loch between 2002 and 2005. Concentrations were significantly lower at the reference sites.

Total PAH concentrations at the Colonsay and Broad Bay reference sites would be classed as low (<150 µg/kg dry weight) and at Pladda as medium (150 – 750 µg/kg dry weight). Concentrations at all Clyde test sites were classed as high (>750 µg/kg dry weight). OSPAR BACs were exceeded for all individual PAHs at the Clyde test sites, and at Pladda for all except the 6-ring PAHs. Colonsay (for all PAHs except naphthalene) and Broad Bay were below BACs. To assess the environmental significance of these concentrations comparisons were made to Effects Range (ER) values. ER values can be used to predict adverse biological effects on organisms. Absolute PAH concentrations were above ER-Low (ERL) values for all the specified PAHs at Holy Loch and for 5 of the 10 PAHs at Garroch Head. Three of the PAHs were above ERLs at Skelmorlie and one at Irvine Bay and Hunterston. Furthermore concentrations for

ⁱⁱ Seven CB congeners selected by the International Council for the Exploration of the Seas (ICES) as indicators due to their relatively high concentrations in technical mixtures and wide chlorination range.

benzoperylene exceeded ER-Medium (ERM) values at Holy Loch, Garroch Head and Skelmorlie. Only the reference sites were below ERLs for all PAHs. BACs were exceeded for all ICES7 CBs (normalised to 2.5% organic carbon) at all sites, except Irvine Bay for CB28, 118 and 138. Although CB concentrations at the reference sites were typical of remote areas ($< 2 \mu\text{g}/\text{kg}$ dry weight), due to the low organic carbon content at of these sediments, normalising to 2.5% TOC resulted in concentrations above BACs. Absolute total CB (sum of all congeners) concentrations were above the ERL ($23 \mu\text{g}/\text{kg}$ dry weight) at Garroch Head and Holy Loch in all years and Huntleston and Skelmorlie in 2003. All other sites gave concentrations below the ERL. Therefore, adverse biological effects on organisms would be likely at Garroch Head and Holy Loch since ERLs were exceeded for both PAHs and CBs.

References

1. C.F Moffat, J. Pijnenburg and T. Trass (eds), Report of the joint OSPAR/ICES Workshop, The Hague, Netherlands 9-13 February 2004.
2. S. P. Bhavsar, A. Hayton, E. J. Reiner and D. A. Jackson, *Environ. Toxicol. Chem*, 2007; 26: 1622.
3. J. A. Lasrado, C. R. Santerre and G. P. McCabe, *Journal of Food Protection*, 2005; 68: 2679.

Figure 1 Map showing the locations of the five Clyde test sites and three reference sites, including the two reference sites outwith the Clyde. The dump site at Cloch Point (X) is included for reference.

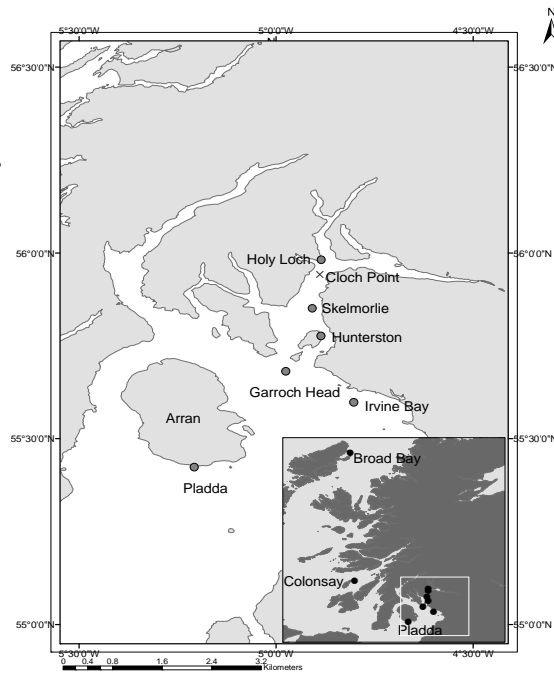


Figure 2 Mean Σ ICES7 CB concentration ($\mu\text{g}/\text{kg}$ lipid weight) in plaice liver from the Clyde test (open symbols) and reference (filled symbols) sites.

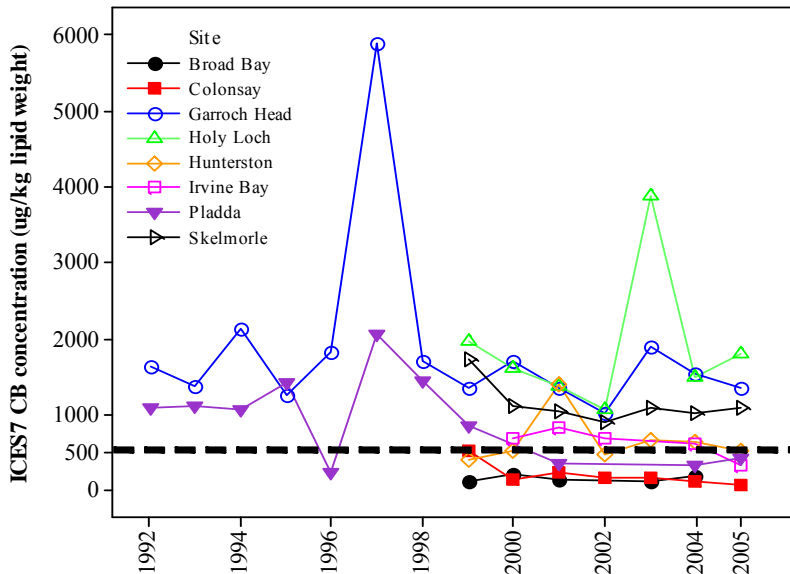


Figure 3 Plot showing the relationship between the calculated toxic equivalence (TEQ) concentrations from the five dioxin-like CBs measured in biota and the estimated TEQs derived from published models.

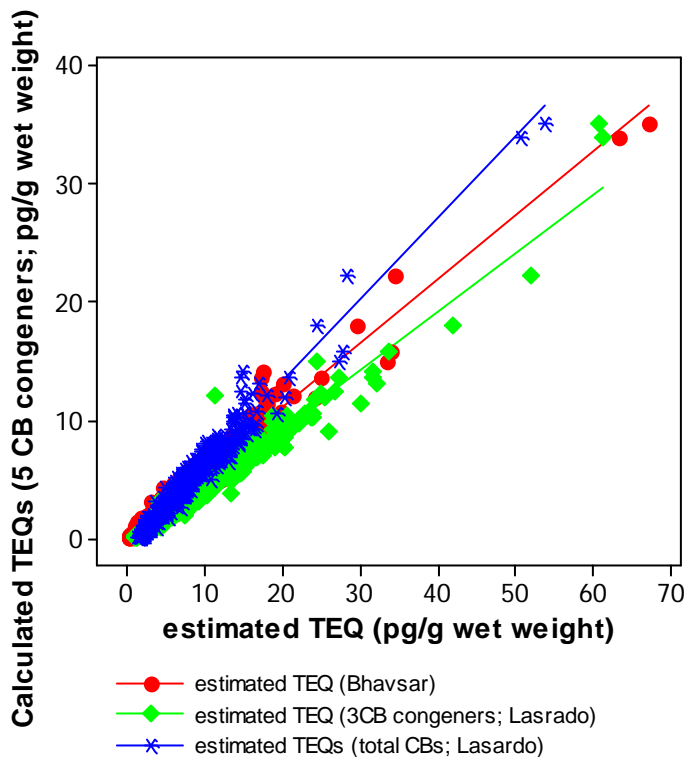


Figure 4 Mean PAH and Σ ICES7 CB concentration ($\mu\text{g}/\text{kg}$ dry weight) in sediment from the Clyde test (open symbols) and reference sites (filled symbols). The dashed line represents the ERL for total CBs in sediment.

