ACCUMULATION OF PCBS IN THREE FISH SPECIES FROM RIA DE AVEIRO, PORTUGAL

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Introduction

Polychlorinated biphenyls (PCBs) are known for their persistence in the environment and accumulation in organisms. The partitioning of PCB congeners among water, sediment and aquatic organisms is linked to their physicochemical properties being bioconcentration factors (BCF) correlated to octanol-water partition coefficient (K_{ow}) [1, 2, 3]. However, the partition ratio between trophic levels and K_{ow} is not always correlated [4]. Bioaccumulation of PCBs is also related to physiological and biochemical processes within the organisms and is species dependent.

Ria de Aveiro is a coastal lagoon located in the northern of Portugal permanently connected to the sea that receives inputs from agriculture, urban and industrial activities. In this study eighteen PCB congeners were quantified in water and suspended matter and in eel (*Anguilla anguilla*), mullet (*Liza aurata*), common sole (*Solea vulgaris*) and senegalese sole (*Solea senegalensis*) and relationships with K_{ow} were examined.

Materials and Methods

Sampling

Surface water was sampled in high- and low tide in July and September 1998 at seven stations of Ria de Aveiro. Samples were filtered through pre-washed (hexane) and pre-combusted (350 ºC, 10 h) Gelman A/E filters to separate dissolved and particulate fractions. The dissolved fraction was collected in glass flasks and analysed within two days. The filters were stored frozen until analysis.

Samples of four different fish species were collected during 1998 in Ria de Aveiro. Length and weight were measured (Table 1), individuals dissected and muscle and liver taken for chemical analysis. Samples were prepared individually or in composite samples for the smaller individuals. In senegalese sole only muscle was analysed. Sample tissues were freeze-dried.

Table 1. Length (cm) and weight (g) ranges of individuals of each species, collected in Ria de Aveiro during 1998.

Species	Current name	n	Lenght (cm)	Weight (g)
Anguilla anguilla	Eel	31	22 - 50	20 - 208
Liza aurata	Mullet	98	12 - 31	11 - 284
Solea vulgaris	Common sole	34	10 - 22	10 - 122
Solea senegalensis	Senegalese sole	24	15 - 27	33 - 263

Chemical Analyses

Water samples were extracted with hexane. Filters and sample tissues were Soxhlet extracted with hexane respectively for 16 h and 6 h. The samples extracted were cleaned-up with Florisil and

sulphuric acid. Fat content was determined gravimetrically from aliquots of tissue extracts. After concentration each sample was injected into a Hewlett-Packard 5890 series II gas chromatograph equipped with an electron capture detector. A DB-5 (J&W Scientific) capillary column (60 m ´ 0.25 mm i.d.) was used for the quantification. The column was held at 60 ºC for 1 min, then programmed in three levels: at a rate of 20 ºC min^{-1} to 210 ºC (8 min); 2 ºC min^{-1} to 250 ºC (17 min) and 4 ºC min^{-1} to a final temperature of 260 ºC (15 min). The injector temperature was kept at 270 ºC and the detector was maintained at 320 ºC. Helium and argon:methane 90:10 were used as the carrier and the makeup gases, respectively. A mixture of individual CBs (18, 26, 52, 49, 44, 101, 151, 149, 118, 153, 105, 138, 187, 183, 128, 180, 170 and 194) was used as external standard for quantification. Recovery of the Florisil column was evaluated with a standard solution and more than 85% of each compound was obtained. For an injection of 2 ml the detection limits ranged from 0.3 pg for CB 194 to 0.6 pg for CB18.

One way analysis of variance with Scheffé's paired comparison procedure was used for compare concentrations [5]. A statistic test to compare more than two slopes and elevations were performed. A 5% significance level was used for all statistical tests.

Results and discussion

PCB congeners in water

Concentrations of PCB congeners in both water and suspended particulate matter (SPM) were not significantly different ($p<0.05$) among sampling stations, and between high- and low tide of April and September surveys. This suggests that spatial and temporal variations on PCB concentrations in water and suspended particles are poorly defined, due to the larger water volume exchanged with the sea. Mean levels are presented in Table 2. The most abundant components in the dissolved fraction were the tetra- to hexa- chlorinated congeners and in suspended matter the hexachlorinated biphenyls.

Table 2. Mean concentrations of tri- to octachlorobiphenyl congeners in water (ng L^{-1}) and in suspended particulate matter (ng g^{-1}) of samples collected in high- and low tide in 1998 in Ria de Aveiro.

	n	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-
Water (ng L^{-1})	28	0.78	1.56	1.27	1.49	0.34	0.01
SPM (ng g^{-1})	28	1.47	2.03	2.14	3.29	1.86	0.09

PCBs and lipids in fish

The eighteen analysed congeners were detected in most samples of muscle and liver of eel, mullet and sole. Concentrations of tPCB (calculated as the sum of individual CB levels) are compared in fish samples in Figure 1. Muscle of eel showed the highest level of tPCB (26 ng g^{-1}), followed by mullet (18 ng g^{-1}) and the soles (5.6 and 5.8 ng g^{-1}) (ANOVA, $p<0.05$). Mullet liver showed higher concentration (48 ng g^{-1}) than common sole (23 ng g^{-1}) but is not statistically different from eel (41 ng g^{-1}).

Fish lipid content can influence the bioaccumulation of organochlorines. However, in this study, only muscle concentrations of the analysed species were correlated ($p<0.001$) with lipid content ($r^2=0.60$). In liver, the concentrations were independent of lipids.

The composition of PCBs, determined as the concentration ratios between individual congener and tPCB, in the analysed fish species showed some differences. CBs 153, 138 (hexa-) and 180 (heptachlorobiphenyl) were predominant in the muscle of mullet and eel and CBs 18 (tri-), 153 and 138

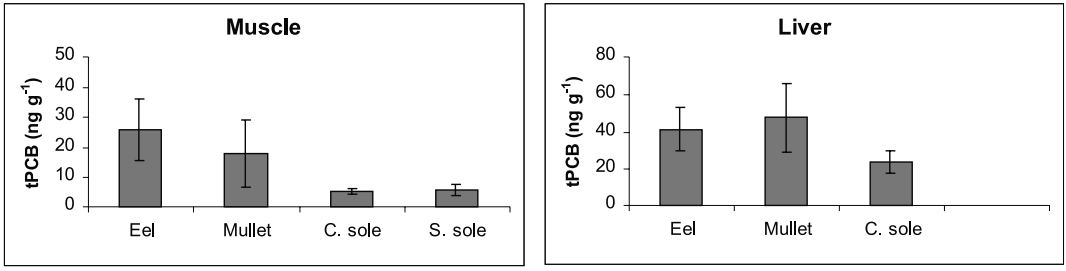

Figure 1. Concentrations of tPCB (ng g^{-1} dry weight) in muscle and liver of eel, mullet, common sole (C. sole) and senegalese sole (S. sole) from Ria de Aveiro. Different letters represent significant differences ($p<0.05$) according to ANOVA followed by Scheffé test.

(hexachlorobiphenyl) in the muscle of sole. In livers the differences between the species were not evident.

Bioconcentration and bioaccumulation factors

Several works showed that the chemical properties of pollutants are important in determining fish body burden, with a good correlation being found between bioconcentration factors and chemical's octanol-water partition coefficient (K_{ow}) [1, 2, 6]. In order to examine whether water and suspended particles are important vehicles for the transport of PCBs in Ria de Aveiro, [fish]:[water] (BCF) and [fish]:[SPM] (BSAF) ratios were calculated and values plotted against K_{ow}. A positive linear correlation of BCF with log K_{ow} was found in muscle and liver of the four species (Fig. 2). However, the values of CB 18 (log K_{ow}=5.2) were greater than the expected from their log K_{ow}. This suggests that the bioconcentration of this congener was favoured by their water solubility and inefficient metabolism in the studied species. The slopes were identical ($p<0.05$) except for muscle of eel and mullet which

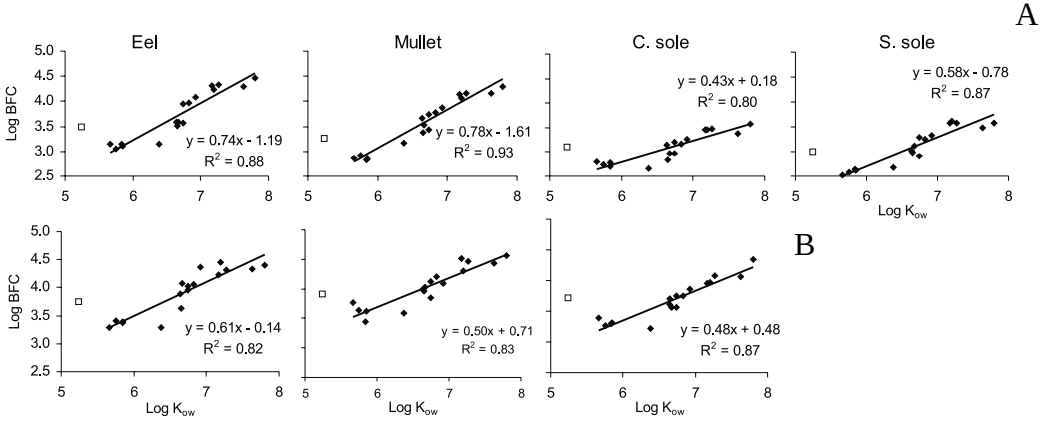

Figure 2. Relationship between bioconcentration factors and K_{ow} in the muscle (A) and liver (B) of eel, mullet, common sole (C. sole) and senegalese sole (S. sole) from Ria de Aveiro. The value corresponding to CB 18 (•) was excluded from the regression.

slopes were similar with each other. This suggests that bioconcentration of these compounds with respect to their K_{ow} was similar in some of the analysed species. Statistical differences were observed in line elevations reflecting accumulation differences between the species and between the analysed tissues. Only muscle of soles showed similar elevations.

No relationships of [fish]:[SPM] ratios (BSAF) versus K_{ow} were observed. Kucklick and Backer [4] interpret the lack of relationships between log BSAF and log K_{ow} as evidence that particle/biota partitioning is a major source of PCBs to the organism. A similar interpretation appears to be valid for eel, mullet and sole in Ria de Aveiro.

Acknowledgements

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