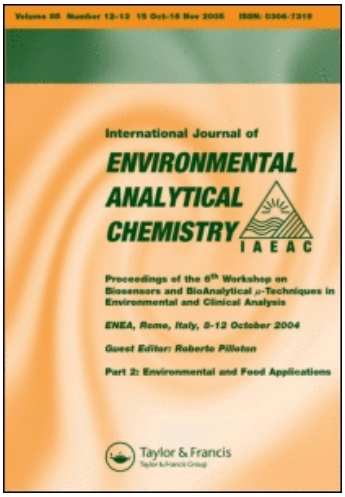

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A Comparison of Distributions of PCB Congeners and Other Chlorinated Compounds in Fishes from Coastal Areas and Remote Lakes

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To cite this Article Sánchez, J. , Solé, M. and Albaigés, J.(1993) 'A Comparison of Distributions of PCB Congeners and Other Chlorinated Compounds in Fishes from Coastal Areas and Remote Lakes', International Journal of Environmental Analytical Chemistry, 50: 4, 269 — 284
To link to this Article: DOI: 10.1080/03067319308027603
URL: http://dx.doi.org/10.1080/03067319308027603

Intern. J. Environ. Anal. Chem., Vol. 50, pp. 269-284
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A COMPARISON OF DISTRIBUTIONS OF PCB CONGENERS AND OTHER CHLORINATED COMPOUNDS IN FISHES FROM COASTAL AREAS AND REMOTE LAKES

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(Received, 8 January 1992; in final form, 15 June 1992)

A total of 28 PCB congeners, p,p'-DDE, p,p'-DDD, p,p'-DDT, HCB and γ-HCH were determined in lake trouts (*Salmo trutta*) from two isolated lakes in the Pyrenees and in red mullets (*Mullus barbatus*) from the Mediterranean coast. The lower concentrations, in the range of 1.9–6.0 ng g^{-1} (wet wt) for p,p'-DDE and 0.1–0.8 ng g^{-1} (wet wt) for the other individual compounds (2.6–7.2 ng g^{-1} for the sum of PCB congeners), were found in the remote lake samples, where the atmosphere was the only source for these anthropogenic compounds. These samples were also relatively enriched in γ-HCH, consistently with the predominant atmospheric transport pathway of this compound.

The PCB congener patterns exhibited substantial differences between both sets of samples. The trouts were enriched in the tri- to pentachlorobiphenyl congeners whereas the mullets were dominated by the hexachlorobiphenyl isomers, reflecting the predominance of atmospheric and aquatic point-source inputs, respectively. On the other hand, the congeners with adjacent unsubstituted positions were clearly depleted in the marine fishes, indicating a relatively enhanced metabolic activity of these chronically exposed organisms. All these features illustrate the advantage of the analysis of individual PCBs for a better understanding of their environmental transport and fate.

KEY WORDS: PCB congeners, HCB, HCH, DDTs, fishes, remote lakes, coastal waters, Mediterranean.

INTRODUCTION

Polychlorobiphenyls (PCBs) and chlorinated pesticides are ubiquitous contaminants in the aquatic environment as a result of uncontrolled spillages and surface run-off from application or dumping sites. Coastal areas and estuaries, in particular, are usually the major sinks for these pollutants[1,2]. However, they may also occur in remote areas, such as the open sea waters or isolated lakes, as a result of their long range atmospheric transport and deposition[3,4]. Remote lakes may be used as early warning systems of global or regional environmental changes.

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The various routes by which these compounds enter the aquatic environment, namely lakes, rivers, coastal areas and open sea, may originate different distributions in the corresponding ecosystems, because their occurrence in a certain compartment is controlled by physicochemical properties such as the vapor pressure, water solubility, K_{ow}, etc., which exhibit a large variability among them. For example, the vapor pressure varies, at 25°C, from 2.3×10^{-3} Torr for hexachlorobenzene (HCB) or dichlorinated PCBs to 9.8×10^{-7} Torr for the heptasubstituted PCB congeners[5,6]. γ-HCH (lindane) and the other isomers have intermediate vapor pressures (from 1.9×10^{-3} to 4.1×10^{-4} Torr), but they are more soluble in water (7–8 mg l^{-1}, at 25°C) than PCBs (1.1 to 0.009 mg l^{-1} for di- to pentachlorinated congeners)[5–7]. On the other hand, the log K_{ow} values for γ-HCH and HCB are, respectively, 3.85 and 5.5[8,9], whereas for the di- to heptachlorobiphenyls range, respectively, from 4.65 to 7.71[10]. Therefore, the determination of the distribution of individual components and particularly of PCB congeners in selected aquatic compartments will contribute to the understanding of their transport pathways in the environment.

The analysis of water, which could be the preferred approach for this study has, however, several limitations. First, it is not easy because of the very low concentrations of the components of concern and, then, because it may not even reflect the real situation of the compartment due to the large variability of those concentrations over time and space. The aquatic biota (e.g. fishes), which are able to accumulate in their tissues hydrophobic pollutants from water and food, constitute a useful alternative, particularly for components recalcitrant to degradation, and may also provide a more integrated picture of the contamination[11]. In this respect, the comparison of contaminant body burdens of representative species from contrasting habitats may give useful information on the significance of the different routes of transport and exposure of these contaminants. Biota from remote or isolated lakes will be able to speciate atmospheric inputs of pollutants.

In the present paper, we compare the distributions and concentrations of HCB, γ-HCH, DDTs and PCBs in trouts (*Salmo trutta*) from two isolated lakes, at 2.200 m of altitude, in the Sant Maurici National Park (Espot, Catalonia, Spain) and in several specimens of red mullet (*Mullus barbatus*) from the Mediterranean coast, near the Ebro Delta (Catalonia, Spain) (Figure 1), with the aim of assessing the overall spreading of these compounds and the relative importance of their transport pathways in this Southwestern region of Europe.

EXPERIMENTAL

Materials

All solvents (*n*-hexane, dichloromethane and diethyl ether from Merck, Darmstadt, Germany) were glass distilled before use. Alumina (70–230 mesh, neutral) was obtained from Merck (Darmstadt, Germany). Analytical reagent grade PCB congeners were purchased from Promochem (Wesel, Germany). The chemical structures of these congeners is indicated in Table 1.

Biota samples (fishes) of a similar size (15–20 cm) were collected by manual fishing

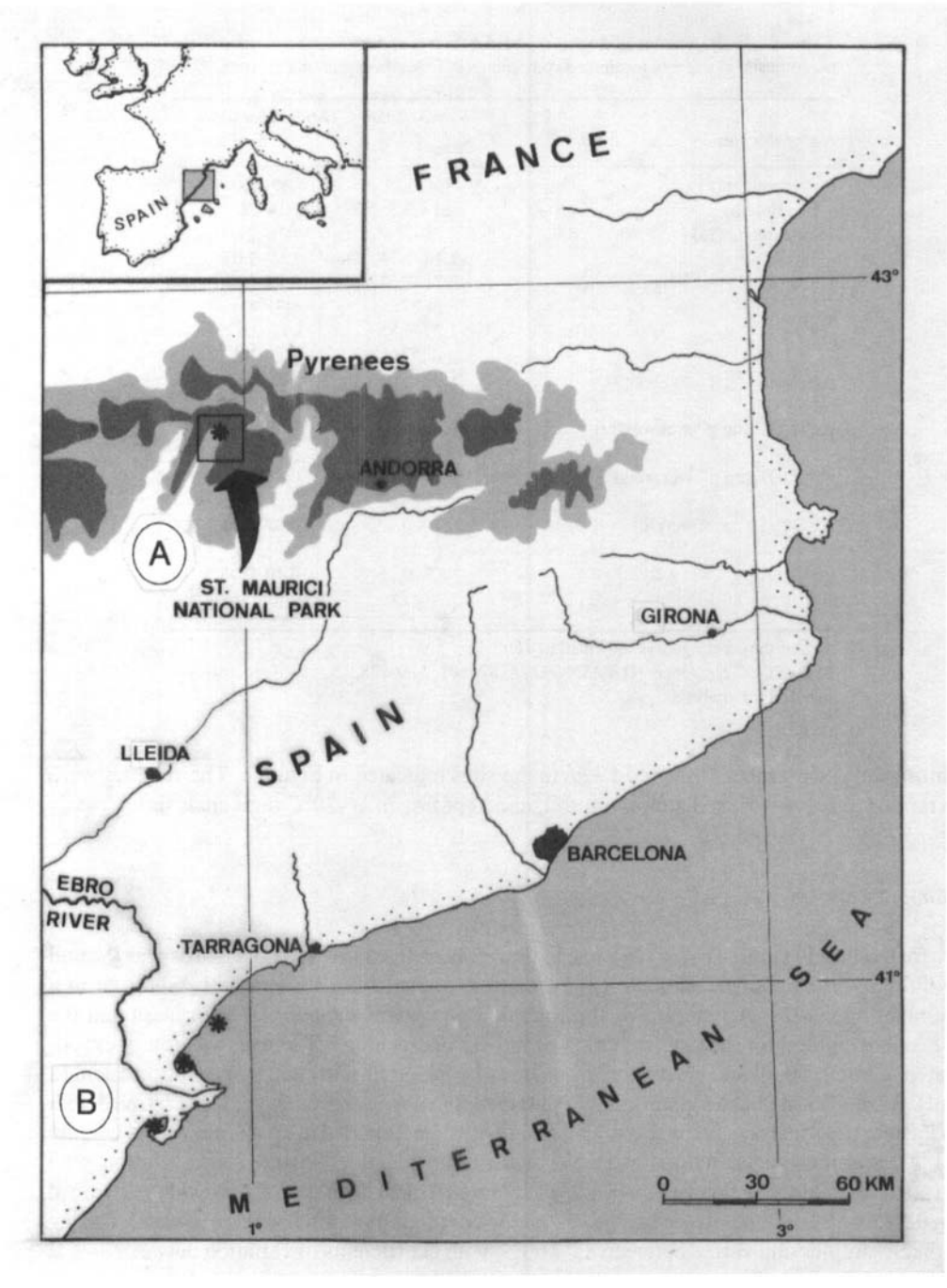


Figure 1 Geographical situation of the collected samples (*). A: *Salmo trutta*. B: *Mullus barbatus*.

Table 1 Body weights and lengths, lipid contents and mean concentrations (in parenthesis) of organochlorinated compounds in fishes from the studied sites.

No. of samples		*Salmo trutta* 4	*Mullus barbatus* 6
Body: weight (g)		105–125	40–100
length (cm)		21–22.5	16–20
Tissue: water (%)		75–77	76–77
lipid (%)		1.40–1.74	1.67–2.07
PCBs (ng g^{-1} wet weight):	a)	2.71–7.52 (4.87)	15.52–61.37 (38.41)
	b)	1.27–3.85 (2.52)	7.43–33.25 (21.24)
p,p'-DDE (ng g^{-1} wet weight)		1.92–6.04 (3.39)	12.6–31.6 (19.10)
p,p'-DDD (ng g^{-1} wet weight)		0.09–0.25 (0.18)	0.25–0.77 (0.50)
p,p'-DDT (ng g^{-1} wet weight)		0.10–0.37 (0.24)	0.85–1.25 (1.12)
HCB (ng g^{-1} wet weight)		0.10–0.22 (0.15)	0.32–0.95 (0.68)
γ-HCH (ng g^{-1} wet weight)		0.08–0.25 (0.17)	0.10–0.55 (0.25)

a) Σ of the 28 congeners indicated in Table 2.
b) Σ of the 7 congeners (IUPAC Nos. 28, 52, 101, 118, 138, 153, 180) recommended for analysis.

during July-September 1989 and 1990, in the sites indicated in Figure 1. The samples were wrapped in solvent-rinsed aluminum foil, and kept frozen at -20°C until analysis.

Sample work-up

A freeze-dried sample (1–2 g) of muscle tissue taken from the fish dorsal area was ground with anhydrous sodium sulphate (2–5 g) and extracted for 12 hours with *n*-hexane in a Soxhlet apparatus. An aliquot of the organic extract was evaporated to dryness and the residue weighted for the determination of the lipid percentage. The rest, was rotary evaporated to about 10 ml and cleaned up by vigorous shaking (3 min) with conc. sulfuric acid (2 ml). After a good phase separation was obtained, the upper organic layer was removed with a Pasteur pipette, reduced to about 1 ml and further fractionated in an alumina short column (1 g), previously deactivated with 5% water. The solution obtained after elution with *n*-hexane-dichloromethane (90:10) was evaporated to near dryness and the residue dissolved in 0.5 ml of *iso*-octane. Recovery values for the compounds of interest were calculated using spiked samples and varied between 85–100%, with coefficients of variation between 4–9%, provided that solutions never reached to complete dryness.

Chromatographic analysis

Sample fractions (in *iso*-octane) were injected in the splitless mode (gas hold time = 35 s) in a Hewlett-Packard 8590 capillary gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) equipped with a Ni^{63} ECD and a 50 m × 0.25 mm ID fused silica capillary column coated with 0.25 μm of chemically immobilized DB-5 (J & W Scientific, Folsom, CA, USA). The column was temperature programmed from 80°C to 290°C at 6°C min^{-1}, lasting 10 min at isothermal conditions. The carrier gas was helium with a flow velocity of 30 cm s^{-1}. High purity N_2 was used as make up gas with a flow rate of 50 ml min^{-1}. The injector and detector temperatures were kept at 280°C and 310°C, respectively.

Identifications were based on co-injection of pure standards and further confirmation by GC-MS, using negative ion chemical ionization[12].

Quantitative analysis

Quantitation was performed on tissue wet weight basis using an external standard calibration mixture. An *iso*-octane solution containing 10-50 pg μl^{-1} of individual components, including PCB congeners, was prepared. Internal standard quantitation using 1,2,3,4-tetrachloronaphthalene (TCN) was also performed. The variance between both, external and internal, methods of quantitation was ca. 5%.

The solvents were analyzed for potentially interfering components (after a 100-fold concentration) and all dilutions were related to mass and not to volume. The linearity of the detection was determined by injecting a series of PCBs at 10 different concentrations and plotting the ratio of the peak height response to the mass, determined against the mass injected.

RESULTS AND DISCUSSION

The organochlorinated compounds monitored in the two fish species are shown in Table 1. In fact, these were the dominant peaks in the GC-ECD profiles, with p,p'-DDE being the most abundant among them. Although the samples were collected in two different periods (summer 1989 and 1990) and in different stations (Figure 1) the results are pooled together for each species because they were qualitatively very similar with no indication of any temporal variation. Moreover, the pollutants pattern exhibited by the red mullet samples was consistent with data available from the ongoing monitoring programs in the region[13].

Concentrations are reported on wet weight basis. Huckins *et al.*[14] found that the current practice of lipid-normalization of concentrations of organochlorine compounds in fishes increased variability among samples instead of reducing it. More recently, Schmitt *et al.*[15] have also found that little or no precision was gained by this adjustment and that differences among freshwater fish samples collected from a given site could not be explained solely on the basis of this factor. Nevertheless, we give in Table 1 the water and lipid contents of the sample tissues. In this way, concentrations can be easily converted into dry wt or lipid wt basis for comparison with literature data, if required.

The concentration ranges reported in Table 1 clearly indicate that the levels are significantly higher in the marine samples. This difference can only be explained by the vicinity and direct influence of contaminant point-sources in the coastal area because the body sizes of the two species and the lipid contents of the respective tissues are rather similar. This influence is reflected in the larger span of values exhibited by the red mullets, the higher values being found in samples collected in sites influenced by the Ebro river discharges (Figure 1). Although it is well known that organochlorinated pollutants are ubiquitous in the marine environment, recent studies have already shown that the Ebro river constitute a source of them in the coastal environment[16,17]. The discussion of the spatial distribution of this coastal pollution is, however, beyond the scope of the present paper. On the other hand, the very low concentrations in the trouts result from the unique contribution of atmospheric inputs of pollutants in the remote lakes. Indeed, these compounds have also been identified as the major organochlorinated pollutants in the European atmosphere[18].

The levels are, in general, at the lower end of the ranges found in similar samples from coastal areas of the Northern Hemisphere, including the Mediterranean[19–22], and from remote lakes, were the only source for these compounds was the atmosphere.[23–25] It appears, therefore, that despite the widespread occurrence of these pollutants in the two aquatic environments, the region is mainly dominated by low chronic inputs. In the last case, however, it should be considered that the trouts analysed by Swackhamer and Hites[23] from the Siskiwit Lake and by Macdonald and Metcalfe[24] from isolated Ontario Lakes, were much larger (1.2–3.0 kg in weight and 53–58 cm size range) and consequently with a higher bioaccumulation potential.

The relative distributions of compounds in the two species deserve additional comments which are given below.

HCH and HCB

In general, and refered to the major individual component p,p'-DDE, the lake trouts contain more lindane and less PCBs than the red mullets (Table 1). As it is known, the main pathway of global distribution of HCHs is through atmospheric transport[26] and their high solubility in water supports an enrichment in the aquatic environment through atmospheric wash out by rain[27]. The bioaccumulation of HCHs in aquatic biota, however, is not easy to predict by the complexity of their environmental fate. The isomeric distribution in the different compartments depends on the formulations used, which may contain different proportions of the active γ-isomer (lindane), and on the length of time since its application at the source, the α-isomer being the more refractory to degradation[28]. It appears, also, that a rapid transfer of HCHs isomers occurs between wet deposition and plankton with little alteration in the isomeric composition[29,30]. However, food chain effects are not significant for compounds exhibiting log $K_{ow} < 5$[31], as in the present case.

Most atmospheric measurements in Northern Hemisphere background areas have shown a large prevalence of the α- over the γ-isomer[26,32], while in precipitation the ratio approaches 1 or even decreases below[33]. Conversely, air and snow samples collected in Central Europe exhibited ratios lower than 1[18]. A predominance of the γ-isomer was also observed in the German Bight waters[34], possibly reflecting that the major input of HCHs in Western Europe derives from lindane.

Although in this study the values for the α-isomer are not reported, they were always lower than those of the γ-isomer, especially in the marine samples. Isomeric ratios (α/γ) below 1 have already been reported for Mediterranean surface waters[35] and benthic fishes (Ligurian[36] and Aegean[21]). Therefore, this seems to be the current pattern of HCHs in the region.

Due to their vapor pressures and water solubilities, the concentrations of HCHs in air and water usually exceed those of HCB[3,4,18,30], but the concentrations in aquatic biota are rather similar[23,30]. This also occurs in our samples, indicating that HCB appears to bioconcentrate to a higher extent than HCHs. HCB also partitions more strongly into suspended particles and sediments, so that benthic fishes can be relatively more exposed to this contaminant. In this respect, Oliver and Niimi[30] have suggested that the HCHs/HCB ratios can be used to differentiate between samples containing mainly sediment and those which contain significant amounts of biologically generated material.

In the present case, the HCHs/HCB ratios found in red mullets are three times lower than those in the lake trouts (Table 1). Although this may be attributed to the above mentioned processes, it may also originate in the occurrence of particular inputs of HCB in the coastal environment, the Ebro River being recognized as a source of this compound in the area.[16,17]

DDTs

Among the different components of this family, p,p′-DDE was the most abundant in all samples, and also the most abundant among the other organochlorinated species. p,p′-DDE is a degradation product of p,p′-DDT, that can be formed either by UV-irradiation in the atmosphere or by the metabolism of organisms.

Larsson and Okla[37] have demonstrated "ageing" of DDT during transport from southern to northern Sweden, giving rise to an increase of the DDE/DDT ratio up to 2.5. Aerosols collected in rural stations of central Europe and United States have also shown DDE/DDT ratios higher than 3.[18,38]

The metabolism of DDT in fish generally gives DDE through dehydrochlorination. Reductive dechlorination to DDD may also occur but to a lesser extent[39]. Consequently, a predominance of p,p′-DDE has currently been observed in lake and marine fishes from areas distant of recent DDT sources.[19,21–23,40–42]

The proportional composition of the DDT mixture typically encountered in fish exceeds 70% of DDE[15,42] in the absence of recent or continued inputs of DDT to the aquatic environment. In our case the values range from 82–92%, indicating a significant weathering of the DDT present. The concentration profiles found in the present samples (Table 1) are consistent with an uptake of DDT deposited from the atmosphere after long range transport, in the case of lake trouts, or with a chronic uptake from rather old sources, including contaminated sediments, in the case of mullets, together with an active fish metabolic process.

Interestingly, the concentrations of DDT, DDD and DDE in lake trouts and in red mullets are very similar to those reported, respectively, for Alpian lake salmonids[25] and for red mullets from coastal Aegean Sea waters[21]. A relative increase of p,p′-DDE in bivalves and coastal benthic fishes from the Western Mediterranean has been observed during the last 10

years,[13,43,44] probably reflecting the progressive phasing out of DDT in the region during the late 70s and early 80s.

Although the p,p'-DDE/p,p'-DDT ratio may be used as an indication of DDT degradation, since DDE is practically absent from technical DDT, this ratio should be interpreted with some caution because the known DDT metabolites, DDE and DDD, may also originate from other sources like the pesticides Kelthane[45] and Rhothane[46], respectively.

PCBs

Besides the HCB, γ-HCH and DDT components, a total of 40 peaks corresponding to 51 PCB congeners were clearly recognized in the GC-ECD chromatogram. From these, the 26 indicated in Table 2, corresponding to 28 major congeners, covering the range of tri-to octachlorinated species, were selected for analysis.

Most of recent studies on PCBs in aquatic biota based on individual congeners have focused the attention on these ones because of their potential toxicity, their abundance in the samples and persistence in the environment[23,24,30,42,47–50]. They also include the set of seven congeners recommended for analysis by ICES[51] and later extended to twelve in the BCR certification programme[52].

These congeners represent more than 85% of the total PCBs present in the samples and approximately 60% of the total congener composition of Aroclors 1254 and 1260[53]. They elute as baseline peaks on a 50m DB-5 (5% phenyl-methyl siloxane) column, except the pairs 31/28 and 149/118, which are not well resolved. However, they can still be quantitated and, therefore, they are indicated separately. The rest of the peaks, reported as homogeneous in numerous studies, have been found to contain coeluting components, some of them only resolved by multidimensional (MD) GC[53] or by NICI mass fragmentography in GC-MS[54].

Schulz *et al.*[53] carried out a complete characterization by MDGC of the 87 peaks, containing 123 congeners, of the GC-ECD profile of two commercial PCB mixtures. Larsen *et al.*[54] have recently reviewed the chromatographic behaviour of 140 congeners on five capillary columns with stationary phases representing a wide range of polarities. A general discussion on key chlorobiphenyl separations that are required for monitoring and ecotoxicological programs has also been reported[55].

Based on these grounds we have indicated in Table 2 the main composition of each GC peak considered. Those congeners indicated in parenthesis represent less than 10% of the peak, so that not affecting significantly the quantitation of the major component.

There are, however, three cases where the situation is more complicated. Congeners 82 and 151 constitute an almost 1:1 mixture in Aroclor 1254 (or Clophen A50), although the former is absent in Aroclor 1260 (or Clophen A60)[53]. Therefore, the concentration has been calculated with reference to the latter. Congeners 132 and 105 coelute immediately after the congener 153, the former being slightly more abundant in a commercial Aroclor mixture[53]. However, the concentrations are reported with respect to congener 105, which exhibits the higher relative response factor[56]. Finally, the peak corresponding to congener 138 includes several other isomers, although in rather low concentrations. Larsen *et al.*[54] indicated that the coeluting compounds were congeners 163 and 160, whereas Schulz *et al.*[53] reported congeners 158 and 160 as the main interferences. The peak has been quantitated as 138,

Table 2 Structures and concentration ranges of PCB congeners determined in fish tissues from the studied sites

IUPAC No[a]	*Chlorine substitution*		*Conc. ranges (ng g^{-1} wet weight)*	
	ring 1	*ring 2*	*Salmo trutta*	*Mullus barbatus*
18	2	2,4	0.07–0.20	0.02–0.14
31	4	2,4	0.08–0.38	0.07–0.44
28	4	2,5	0.06–0.40	0.08–0.36
52	2,5	2,5	0.15–0.68	0.16–1.75
44	2,5	2,3	0.09–0.60	0.10–0.84
101	2,5	2,4,5	0.17–0.35	0.32–2.18
(90)	(2,4)	(2,3,5)		
99	2,4	2,4,5	0.10–0.17	0.37–1.50
97	2,3	2,4,5	0.15–0.25	0.00–0.02
110	3,4	2,3,6	0.18–0.35	0.30–1.50
(77)	(3,4)	(3,4)		
82/	2,3	2,3,4		
/151	2,5	2,3,5,6	0.05–0.17	0.39–1.34
149	2,3,6	2,4,5	0.10–0.34	0.30–2.05
(123)	(2,4)	(3,4,5)		
118	3,4	2,4,5	0.13–0.36	0.63–4.83
134	2,3	2,3,5,6	0.03–0.09	0.00–0.02
146	2,3,5	2,4,5	0.04–0.12	0.37–2.02
153	2,4,5	2,4,5	0.23–0.86	2.67–8.92
132/	2,3,4	2,3,6		
/105	3,4	2,3,4	0.09–0.25	0.44–1.65
138	2,3,4	2,4,5	0.25–0.78	2.23–10.52
(163/	(3,4/	2,3,5,6,/		
/158)	/3,4)	/2,3,4,6)		
187	2,4,5	2,3,5,6	0.07–0.29	2.12–5.48
183	2,4,5	2,3,4,6	0.02–0.12	0.60–1.85
128	2,3,4	2,3,4	0.09–0.19	0.62–1.65
174	2,3,6	2,3,4,5	0.02–0.16	0.58–1.82
177	2,3,4	2,3,5,6	0.06–0.15	0.67–1.80
180	2,4,5	2,3,4,5	0.16–0.32	1.28–5.32
170	2,3,4	2,3,4,5	0.09–0.22	0.85–4.18
(190)	(3,4)	(2,3,4,5,6)		
201	2,3,5,6	2,3,4,5	0.02–0.07	0.32–0.96
194	2,3,4,5	2,3,4,5	0.01–0.05	0.12–0.82

(a) in order of elution on a DB-5 column.

although Wells *et al.*[52] have pointed out that most estimates of this congener are likely to produce in some matrices an over-estimate of the true value by some 20–30%.

The comparison of these concentrations with others from the literature is not easy, because many data on PCBs, particularly the old ones, have been reported in equivalents of commercial mixtures (e.g. Aroclor) and not on individual components and, even in this case, the congeners analysed were not always the same. However, taking into account the contribution of the present components to commercial PCB mixtures[53] and the correlation established between these and the seven congeners recommended for analysis in marine biota samples[57] (see Table 1, footnote b), it can be concluded that the concentrations found in both species are generally lower than those reported in similar areas of the Northern Hemisphere[19–25,49,50], thus indicating their relative distance from PCB point-sources.

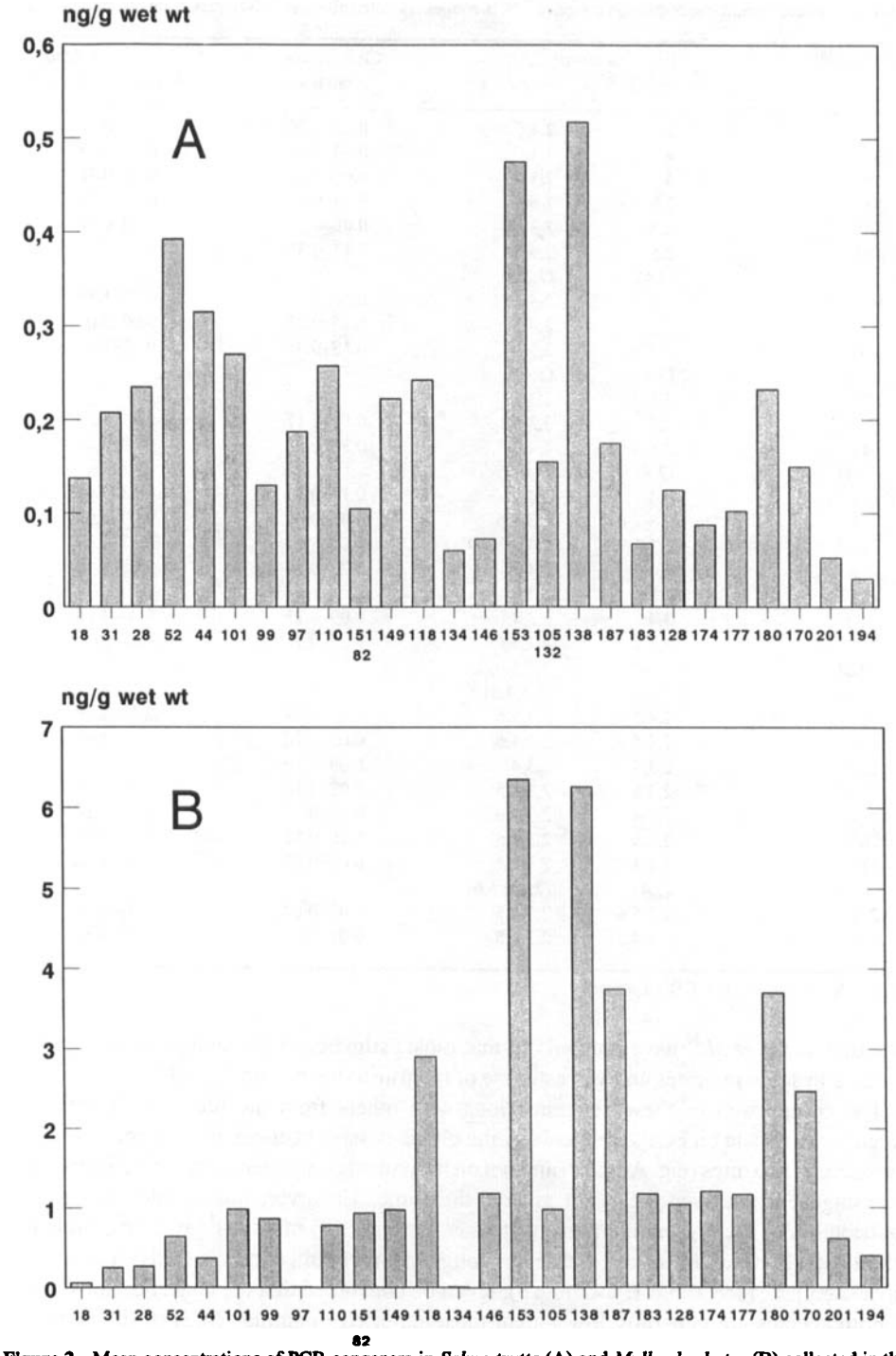


Figure 2 Mean concentrations of PCB congeners in *Salmo trutta* (A) and *Mullus barbatus* (B) collected in the sites indicated in Figure 1.

The bioaccumulation pattern of these PCB components exhibited significant differences between both sets of samples, as it is schematically shown in Figure 2. The trouts were enriched in the tri- to pentachlorobiphenyl congeners whereas the mullets were relatively depleted in these components.

Previous studies have indicated that percentages of highly chlorinated congeners increase with the trophic levels in marine biota. A phenomenon which is related to an increased lipid content in larger fishes and lower depuration rates of highly chlorinated homologs[30,47,58]. The observed distributions, however, cannot be attributed to biomagnification factors, because both species are similar in terms of their lipid contents (Table 1) and position in the food chain. They should mainly be originated by differences in the occurrence of these congeners in the respective aquatic environments.

In fact, the PCB profiles exhibited by the red mullets (Figure 2B), commonly found in freshwater and marine fishes[30,42,48–50], resemble a commercial PCB mixture with a modal distribution of tri- to octachlorinated congeners centered at the hexachlorinated species, so with 50–60% chlorination. Therefore, they most likely derive from a PCB point source with this chlorine composition. In this respect, it is interesting to note that similar profiles were found in coastal Mediterranean waters, with a clear predominance of the hexa- and hepta-chlorinated isomers in the dissolved and particulate phases, respectively (Figure 3a)[16,59]. Consistently with these features several bioaccumulation models have indicated that the fish uptake of lipophilic pollutants with log $K_{ow} < 5$ takes place essentially through a partitioning process between fish lipids and the components dissolved in the water[30,31,60]. Swackhamer and Hites[23], however, indicated that these models have some limitations for interpreting field data because bioconcentration of PCBs depends on several structural features of the components that determine selective metabolism of different congeners, as will be illustrated later, or affect membrane transport and therefore their uptake and depuration rates.

On the other hand, the profiles shown by the remote lake trouts (Figure 2A) parallel those reported for PCBs in aerosols[37,61–65] and suggests the atmospheric deposition as the sole source of contamination in these lakes. Very similar profiles were also found in previous studies on salmonids from other remote lakes[23,24]. Considering the lower contribution of aerosols to the total concentration of PCBs in atmospheric samples (less than 5%)[62–65] this hypothesis requires further confirmation.

There are several ways by which atmospheric PCBs may get into these lakes and made available to biota. These include scavenging of organics on particles and gases by precipitation[61], dry deposition of particles[62] and gas deposition or exchange with surface waters[63]. The relative magnitude of each process is still unclear, but the congener distributions in the different atmospheric compartments may provide some insight into this question.

PCBs are largely found in the gas phase in the atmosphere[62–65], but their relatively high Henry's law constants indicate that they should be largely removed via particle-associated scavenging[65]. Wet deposition, however, is usually much greater than dry deposition, including rainout and snowfall of both particulate and vapor phases. Consistently, the congener distributions in rain and snow show an enrichment of the less chlorinated congeners and a close similarity with aerosol samples[62,64,65]. In Figure 3b the mean distribution of the different chlorinated PCB congeners in lake trouts is compared with those reported by Duinker and Bouchertall[64] for vapor, aerosol and rain, thus confirming that particle scavenging by rain (or snow) is the main contributor of pollutants to these high altitude lakes.

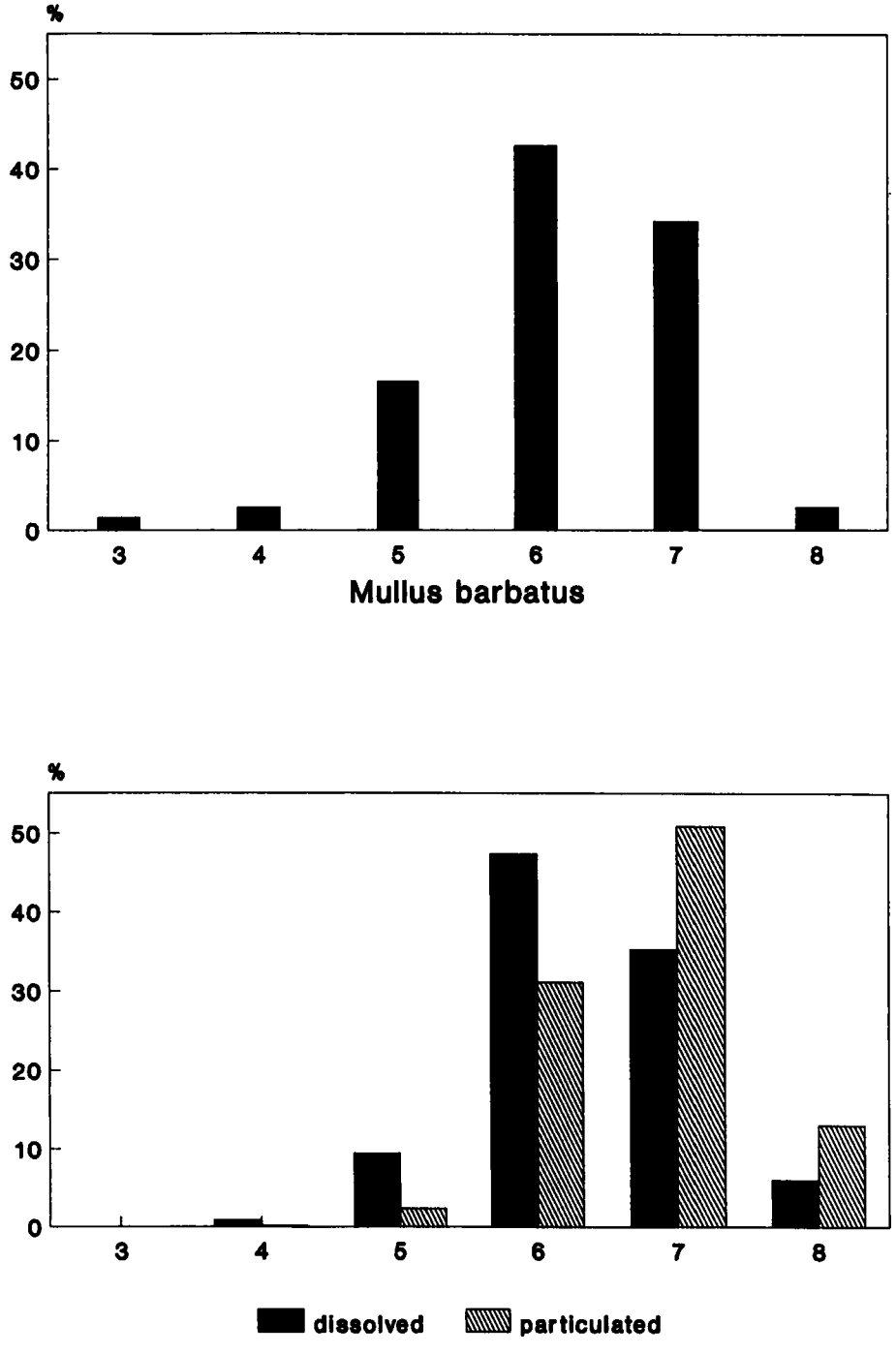
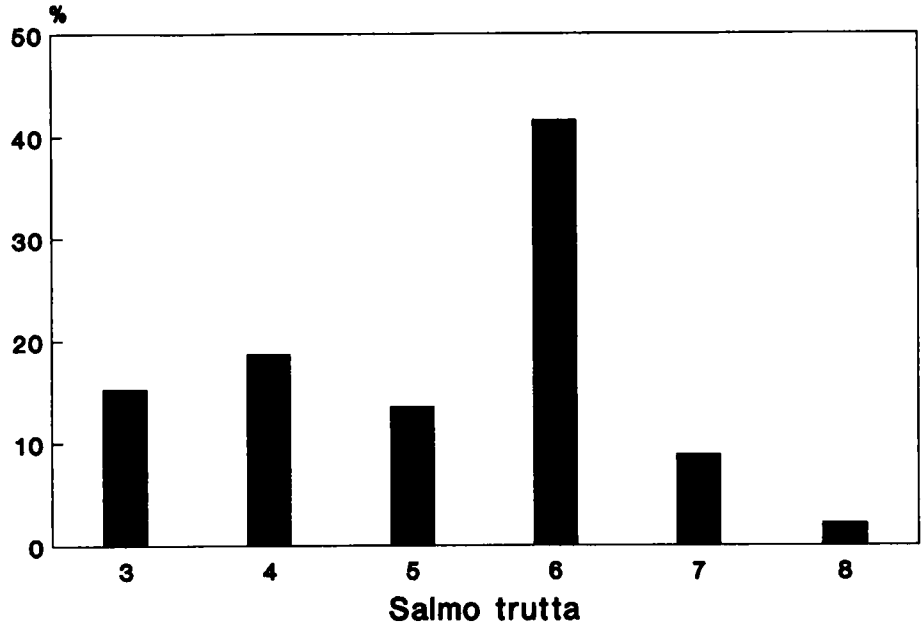


Figure 3a Mean distribution of PCB congreners by number of chlorine atoms in red mullets (*Mullus barbatus*) from the Ebro Delta and in dissolved and particulate phases of coastal seawater (from ref. 59).



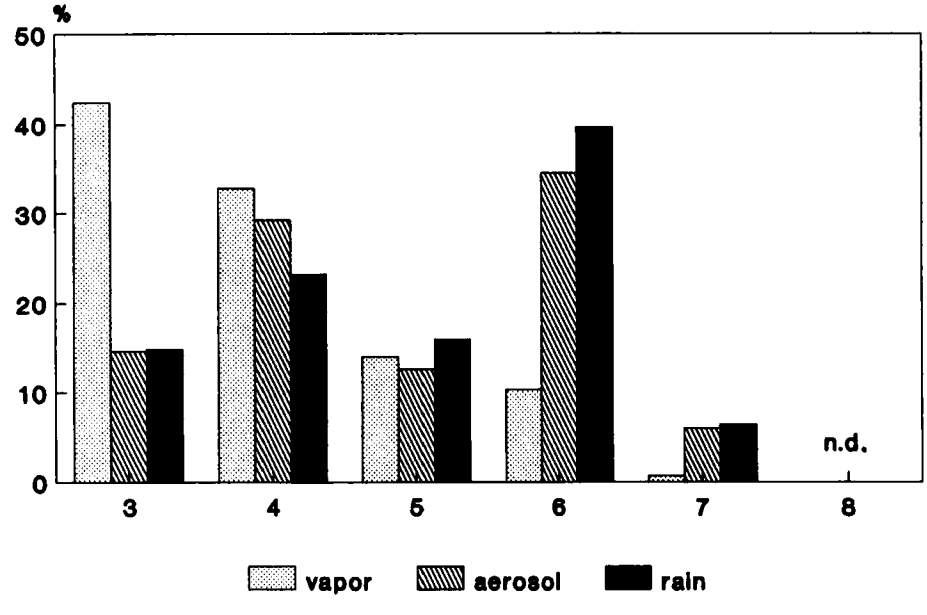


Figure 3b Mean distributions of PCB congeners by number of chlorine atoms in trouts (*Salmo trutta*) from the Pyrenees lakes and in vapor, aerosol and rain from central Europe (from ref. 64). n.d.: not determined.

Besides the above general differences in the PCB profiles of both sets of samples specific variations were observed within a certain domain of congeners (e.g. the pentachlorinated species). As shown in Figure 2, two congeners are almost absent in red mullets, namely 97 and 134, and some others (e.g. 44, 101, 110 and 149) are relatively depleted with respect to those in lake trouts.

Although fishes appear to be less capable of metabolizing PCBs than for example marine mammals[47,55] it has been shown that certain congeners can effectively be degraded, depending on their chlorine substitution pattern. Zell *et al.*[66] established that structures with substitutions in positions 2,3-, 2,5-, 2,6- or 2,3,6- were more readily degraded by marine fish, whereas substitutions 2,4-, 3,4-, 2,3,4-, 2,3,5- and 2,4,6- provided recalcitrance to degradation and, therefore, a higher abundance in the organisms.

This observation, supported by the conclusions of several authors[47,49,67,68], suggests that the presence of vicinal unsubstituted *m*- and *p*- positions in at least one aromatic ring facilitates the enzymatic oxidation by fish. In this respect, it should be noticed that all congeners mentioned above (nos. 44, 101, 97, 110, 149 and 134) belong to this family. Moreover, the more abundant congeners in the marine fish, that is 118, 153, 138, 187, 180 and 170 (Figure 2B), share the recalcitrant 4,4′-substitution or no vicinal H-atoms in both aromatic rings. These features may imply an increased metabolic capacity of marine fishes, usually exposed to higher concentrations of PCBs. The ability of organisms under chronic exposure to aryl pollutants to develop or induce their MFO enzymatic systems has been recognized[69].

In summary, it has been shown that due to the large pattern variations of PCBs in the environment an accurate understanding of their fate can only be obtained by the individual congener analytical approach.

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