

BSAFs for freshwater fish and derivation of a sediment quality guideline for PCBs in the Rhone basin, France

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Received: 16 March 2011 / Accepted: 5 November 2011 / Published online: 6 December 2011
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Abstract

Purpose Since 2005, freshwater fish contamination by polychlorobiphenyls (PCBs), polychlorodibenzodioxins, and polychlorodibenzofurans has been assessed in the Rhone River basin (France). A large database of surface sediment contamination by PCBs is also available, opening the way to the study of biota-to-sediment accumulation factor (BSAF) distribution throughout this basin. The ultimate goal of the study was to determine a sediment quality guideline (SQG) corresponding to the regulatory fish consumption limit.

Materials and methods A bootstrapping procedure for determining BSAFs was applied to a data set matching the available databases of sediment and fish contamination

by PCBs in the Rhone River basin. The SQG was obtained by combining the current tissue-based regulatory threshold with a characteristic BSAF value, for a species particularly prone to accumulating these compounds. As the current regulatory threshold refers to dioxins and related compounds, while most available sediment data deal with non-dioxin-like PCBs, a set of correlations was used to derive an SQG for the sum of seven indicator PCBs. To assess the reliability of these SQG pairs, actual fish and sediment concentrations were classified into four categories, according to a comparison with the regulatory threshold for fish data and the calculated SQG.

Results and discussion BSAFs were determined for 11 species. The barbel and European eel had the highest BSAFs. The common carp, a benthic species, had surprisingly low BSAFs, as low as pelagic and omnivorous species such as chub. The data set was also split into two parts, one comprising fish samples at or above the regulatory limit and the other samples below this threshold. Sediment concentrations and BSAFs were higher in the former group. An SQG was derived on the basis of the 75th percentile of barbel's BSAF, equaling 26.6 ng g⁻¹ dry weight (range 15.6–38.6 ng g⁻¹) for the sum of seven indicator PCBs. When tested against the same database, this SQG displayed an overall efficiency of about 60% resulting from the limited reliability of sediment data and the factors influencing PCB bioavailability.

Conclusions From the perspective of regulatory frameworks such as the European Water Framework Directive, a tiered monitoring strategy combining sediments (first tier) and biota (second tier) could be more relevant than a single-compartment approach. In this context, an SQG such as the one determined herein would trigger the second tier.

Keywords BSAF · Fish · PCB · River · Sediment · SQG

Responsible editor: Arnold Hallare

Electronic supplementary material The online version of this article (doi:10.1007/s11368-011-0448-y) contains supplementary material, which is available to authorized users.

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1 Introduction

The publication of guidelines for dioxins and related compounds in foodstuffs by the European Commission (E.C.) in 2006 (E.C. 2006a, b) prompted in France an extensive assessment of dioxin, furan, and polychlorobiphenyl (PCB) contamination of freshwater fishes in rivers and lakes. Fish consumption advisories were promulgated accordingly. Since bottom sediments are an important source of fish exposure to these contaminants, Sediment Quality Guidelines (SQGs), accounting for bioaccumulation or biomagnification of these compounds at the basin scale, are required as an essential component of appropriate sediment management regulations. A distinction is made here between “guideline” and “standard”, in line with the recommendations of a SETAC workshop on SQGs (Wenning et al. 2005): a standard is legally binding, exceeding it would trigger remediation actions. A guideline can be used more flexibly; exceeding it could lead to a refined assessment, prior to management measures.

Currently, no SQGs for PCBs exist in France. Moreover, most of the SQGs for PCBs available in other regions or jurisdictions deal with the protection of benthic invertebrates from the direct effects of contamination (Babut et al. 2005; Moore et al. 2005; Apitz et al. 2007). Therefore, their reliability for the protection of top predators, including fish consumers, is questionable. The transfer of contaminants from sediment to biota is not addressed in either of the chapters on biota or sediments in the implementation of Environmental Quality Standards within the Water Framework Directive (E.C. 2010).

The biota-to-sediment accumulation factor (BSAF) is generally defined as the ratio of a chemical concentration in an organism normalized by its lipid content to that in sediment normalized to the organic carbon content (Ankley 1992; Burkhard 2006):

$$\text{BSAF} = C_{\text{lip}}/C_{\text{SOC}} \quad (1)$$

with C_{lip} as the concentration of pollutant in lipids in biota, which is equivalent to $C_{\text{org}}/f_{\text{lip}}$, with C_{org} as the concentration in the organism [in micrograms per kilogram wet weight (ww)], and f_{lip} the lipid content (in grams lipid per gram ww). C_{SOC} is the concentration of the pollutant in sediment organic carbon, equivalent to $C_{\text{sed}}/f_{\text{OC}}$, with C_{sed} as the concentration in bulk sediment [in micrograms per kilogram dry weight (dw)] and f_{OC} the organic fraction of sediment (in grams organic carbon per gram dw).

The BSAF can be combined with tissue concentrations associated with the adverse effects of this contamination to calculate sediment concentrations that would be expected to

produce these effects (Meador et al. 2002), as shown in Eq. 2:

$$C_{\text{SOC}} = \frac{\text{RT}}{\text{BSAF}} \quad (2)$$

Replacing the tissue concentration (C_{lip}) with a residue effect threshold or a tissue-based regulatory threshold (RT) makes it possible to determine a concentration in sediment organic carbon that corresponds to the tissue or the regulatory threshold.

In the above-mentioned study, Meador et al. (2002) determined BSAFs for different areas in the Duwamish River estuary (Washington State, USA) on the basis of the mean or 95th percentile of sediment PCB concentrations. They suggested using this approach in cases where bioaccumulation has been characterized, but raised concerns about sediment concentration variability and the relationships between sediment and fish tissue concentrations.

A similar approach has recently been applied to the Canadian Great Lakes, where SQGs were calculated on the basis of BSAFs and tissue-based regulatory thresholds so as to prevent restrictions on fish consumption (Bhavsar et al. 2010). In this study, sediment and fish data originated from two independent surveys, so sediment data were selected on the basis of deposition rates to match the fish exposure timeframe. Fish and sediment measurements were pooled to provide lake-wide fish and average sediment concentrations. They studied various options, depending on the chemicals included in the SQG [polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs), total PCBs] and depending on the restrictions required by the regulatory fish advisory level determining the tissue residue level. They also derived site-specific SQGs for a harbor, but they did not attempt to assess the uncertainty associated with the whole-lake BSAFs or SQGs.

The variability of environmental conditions found in a large river basin is expected to be even greater than in a lake. In addition to natural settings (e.g., slope and flow regime), dams and other structures for navigation purposes influence sediment deposition and accordingly fish exposure to contaminants in sediment. Deriving SQGs incorporating bioaccumulation at such a large spatial scale entails capturing BSAF variability, so as to determine the SQGs that are actually protective in terms of fish consumption throughout the basin. A BSAF quantile such as the 95th percentile would afford this level of protection (Meador et al. 2002). Wong et al. (2001) attempted to study BSAF variability throughout the USA, with paired observations on sediments and either fishes or invertebrates from the US National Water-Quality Assessment program. These measurements were taken on biota composite samples paired with sediment samples collected at the same sites and on

the same dates. While this approach can yield realistic BSAFs for invertebrates, it seems more uncertain for fishes, which are exposed for longer periods of time than invertebrates. Moreover, the number of paired measurements above the reporting limits for most fish species was very limited, indicating that BSAF variability could not be estimated in this study.

Large individual fish data sets along with numerous sediment data could provide a good estimation of BSAF variability and thus derive sound characteristic BSAFs for various fish species in a large basin such as the Rhone basin in France. A PCB contamination inventory has been carried out in this basin since 2006, yielding a large database of fish contamination by PCBs and dioxins or furans. Furthermore, an extended sediment database from regular monitoring programs is also available. Nevertheless, for most sites available, sediment data are restricted to a set of seven PCB congeners (designated as indicator congeners, iPCBs). Our first objective was to match fish and sediment sampling sites in these two databases and develop an approach using a bootstrapping method for studying BSAF variability. The second objective was to derive a set of robust BSAF values, and the third objective was to apply these BSAFs to determine an SQG for fish consumption in the Rhone basin.

2 Methods

We used PCB contamination data from two main sources, accessible through a single web portal (SIE 2010). For fish contamination data, we referred to the database from the fish contamination studies started in 2006 in the Rhone basin. For sediments, we used data from the Rhone basin monitoring program database. Data obtained from these two databases refer to the whole set of data based on measurements, including limits of quantification (LQ). For sediments, the subcontracting laboratory reports constant “reporting limits” (Helsel 2005), instead of actual but variable LQ. For fish data, LQ are determined for a series of samples and may vary accordingly.

2.1 Fish sampling and analysis

Fish were sampled by local professional fishermen or technicians from ONEMA (the French National Agency for Water and Aquatic Environments) with nets and electrofishing. Fish size and weight were recorded on-site.

Lipid contents, PCBs, and dioxin-like compounds were analyzed by subcontracting laboratories. Details are provided in Appendix A (Electronic Supplementary Material). Uncertainties on PCB concentration results were evaluated by the laboratories at 15–20%.

2.2 Sediment sampling and analysis

Organic carbon (OC) is not currently measured in the Rhone basin sediment monitoring program. OC data were therefore sought from specific studies; 157 OC data were obtained from five data sets gathered in specific and recent studies in which total OC was analyzed following the NF ISO 14235 standard (Table A1 in Appendix A of Electronic Supplementary Material).

PCBs were measured in surface sediments as part of an extensive monitoring program managed by the Rhone-Mediterranean Water Agency. Sediments were collected with a grab sampler and transferred to an accredited subcontracting laboratory. Indicator PCBs (congeners 28, 52, 101, 118, 138, 153, and 180) have been analyzed most frequently since 1987. In most samples, reporting limits are set at $10 \mu\text{g kg}^{-1}$ (dw) for the congener concerned and $5 \mu\text{g kg}^{-1}$ (dw) in a few instances. No information on analytical uncertainty was available in the sediment database.

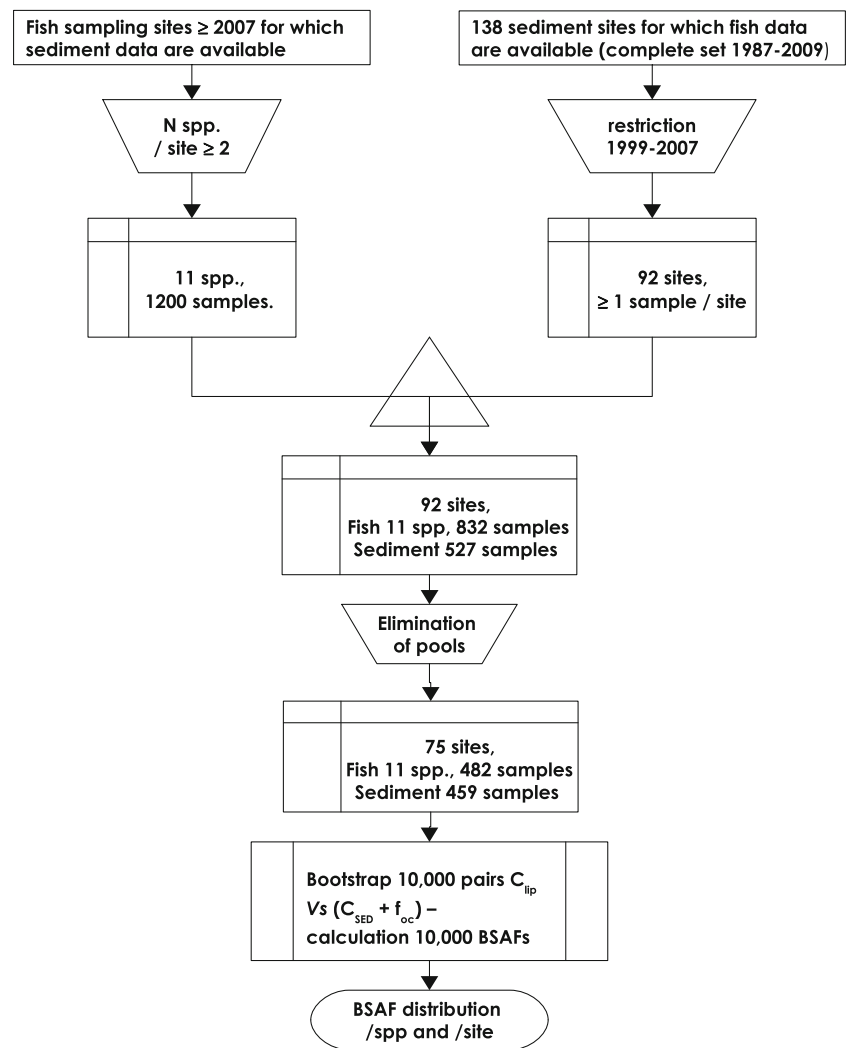
2.3 Fish and sediment sample selection

The selection process is summarized in Fig. 1. Matching fish sampling sites for the years 2007–2009 with sediment sampling sites in the fish database yielded 1,510 samples from 40 species at 140 sites. The concept of “site” covers different areas for sediment and fish; nevertheless, we assumed that the sediment sites were included in the fish sites when the site code was identical. Not all of the 1,510 records were relevant, with some species rarely found. As a rule of thumb, only species present at 10 sites or more with at least two individuals were selected first, yielding 1,200 samples of 11 species at 139 sites [Table A2 in Appendix A (step 1) of Electronic Supplementary Material].

From the current Rhone basin sediment monitoring program database, PCB data are available at 138 sites matching the fish database, from 1987 to 2009. Acknowledging that sediment contamination has decreased as a consequence of most contaminants being banned in 1987, we considered only the 1999–2007 period. We assumed that during this period, most direct sources, such as industrial wastewater discharges, were under control, so the sediment contamination did not vary substantially. This selection yielded 92 sites and accordingly reduced the number of fish samples available to 832 samples of 11 species [Table A2 in Appendix A (step 2) of Electronic Supplementary Material].

A number of these fish samples are pools, while others are individuals. Most pooled samples were purposely composed of fish of various sizes. Consequently, the last step of the selection process eliminated all the pooled samples except a few for which the number of individuals in the pool was two

Fig. 1 Flowchart of the sediment and fish data selection process



individuals of similar length. This further reduced the fish data set to 482 fish samples from 11 species [Table A2 in Appendix A (step 3) of [Electronic Supplementary Material](#)] and 459 sediment samples from 75 sites.

2.4 BSAF calculation

As mentioned above, the BSAF is generally defined as the ratio of a chemical concentration in an organism normalized by its lipid content to that in sediment normalized to the organic carbon content (Ankley 1992; Burkhard 2006) (Eq. 1). BSAFs are sometimes proposed for total PCBs or Aroclors; as different chemicals have different properties, it seems more appropriate to derive BSAFs for single congeners (Burkhard 2006). Given that the fish and sediment sets were constituted independently, there is no obvious way to obtain fish–sediment data pairs other than site-by-site random bootstrapping in the respective sets. As the numbers of samples of either fish or sediment differ among sites and the respective concentration distributions are unknown, it

would not be appropriate to use mean concentrations. A bootstrapping method allowing us to calculate BSAFs and draw their distribution was developed with R software (R) (R Development Core Team 2010). The code is provided in Appendix B ([Electronic Supplementary Material](#)). For each fish species at each site, we took 10^4 bootstrap samples of fish PCB concentration-to-lipid fraction ratios, combined with the ratio of 10^4 sediment concentration samples to 10^4 TOC values sampled from the global TOC distribution. In this way, BSAF variability for each species at each site was obtained. Sediment concentrations below the reporting limits were set at the reporting limit. When all the sediment concentrations at a site were below the reporting limit, the calculated BSAFs were not considered further.

2.5 SQG derivation

The current guidelines for fish consumption in Europe target PCDDs and related compounds, such as dioxin-like PCBs (DL-PCBs). For all species but eel, a limit of

8 pg g⁻¹ (ww) is set for the toxicity equivalent concentration (TEQ, calculated on the basis of 1998 WHO toxic equivalent factors) of PCDDs and similar compounds (E.C. 2006b). For eels, the threshold is set at 12 pg TEQ g⁻¹ (ww). It has been shown that in most cases DL-PCBs account for about 80% of the TEQ. Either the TEQ for DL-PCBs or the overall TEQ is generally correlated to the sum of indicator PCBs (iPCBs, i.e., congeners #28, 52, 101, 118, 138, 153, and 180) (Babut et al. 2009) or to estimates of the total PCB concentration (Bhavsar et al. 2007a, b). Therefore, the RTs can be replaced by the corresponding sums of iPCB (ΣiPCB) concentrations according to Babut et al. (2009) if individual congeners including the set of iPCBs are measured.

From Eqs. 1 and 2 and replacing C_{org} with the sum of iPCB concentrations corresponding to the regulatory threshold (ΣiPCB ~ RT), it stands that:

$$\sum iPCB_{sed} = \frac{\sum iPCB \sim RT / f_{lip}}{BSAF / f_{oc}} \quad (3)$$

where ΣiPCB_{sed} is an SQG allowing fish consumption, expressed as the sum of the concentrations of indicator congeners (dry weight in bulk sediment). As stated above, BSAFs are more robust if determined for single congeners. The most chlorinated congeners in the set of iPCBs usually account for the majority of ΣiPCBs (e.g., Kannan et al. 1992; De Boer et al. 1993; Atuma et al. 1996). The correlation between one of these more chlorinated congeners, such as PCB153 and ΣiPCBs, can therefore be used to calculate a concentration of a specific congener equivalent to the regulatory thresholds in fish. Accordingly, the sediment concentration derived in Eq. 3 would stand for the same congener in sediment. Then the ΣiPCB_{sed} in sediment can be back calculated from the regression between this congener and the sum of indicator congeners in sediments (Fig. 2; Table A3 in Appendix A of Electronic Supplementary Material).

The third quartiles of barbel’s f_{lip} and BSAFs and the first quartile of f_{oc} were used to obtain a more protective SQG. We used the third quartile of BSAFs and not the 95th percentile because the quartile seemed more robust, in particular according to the uncertainty in sediment concentration distribution. We used the third quartile of f_{lip} to be consistent with the choice of BSAF quartile.

2.6 Statistics

Statistical tests such as Kolmogorov–Smirnov, ANOVA, and linear regression were performed with XLStat 2008®. Quartiles for series including non-detects were calculated with the KMStats Excel worksheet (Practical Stats 2010). To assess the reliability of SQGs, pairs of actual fish and

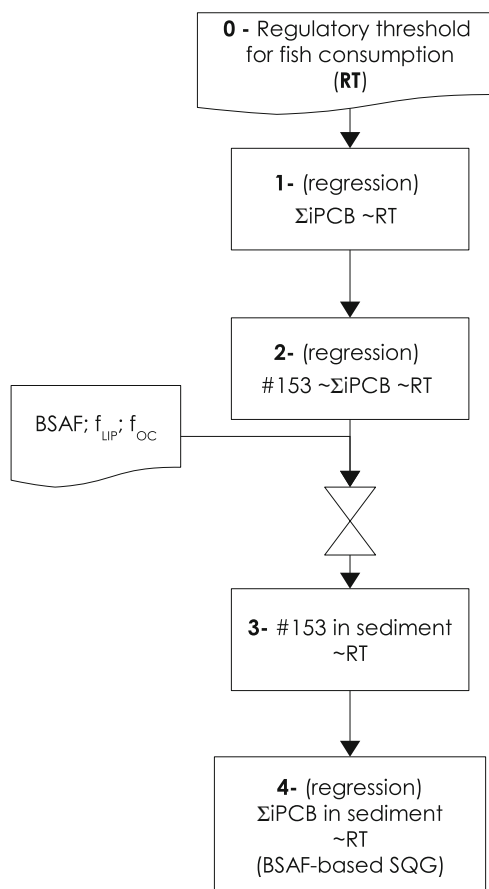


Fig. 2 Flowchart of SQG derivation

sediment concentrations were classified into four categories, according to a comparison with the RT (for fish data) and the calculated SQG (for sediment data). Fish are expected to exceed RT when the maximum sediment concentration at the considered site exceeds the SQG; in other words, fish are predicted to fall above RT. The four categories are as follows: *A*, individuals predicted to fall below the limit but that actually exceed it; *B* and *C*, samples correctly predicted above or below the threshold, respectively; and *D*, individuals predicted to exceed the limit that are actually below it. Based on these categories, we calculated the sensitivity [i.e., the ratio of $B/(A + B)$], the specificity [i.e., the $C/(C + D)$ ratio], and the overall efficiency [which is the ratio of $(B + C)/(A + B + C + D)$] (Shine et al. 2003). Sensitivity is the extent to which the SQG correctly predicts fish contamination as exceeding the regulatory threshold, while specificity is the rate at which the SQG correctly predicts fish contamination as not exceeding this threshold. These measures are complementary type I $[D/(D + B) \times 100]$ and II $[A/(A + C) \times 100]$ error rates.

3 Results

3.1 Fish contamination

The number of species sampled at each site ranged from 1 to 7, and the number of samples analyzed from 1 to 36. Two species, tench (*Tinca tinca*) and nose carp (*Chondrostoma nasus*), were found at four sites only; the most widespread species were chub (*Squalius cephalus*) and barbel (*Barbus barbus*), which were found at 39 and 25 sites, respectively. Considering iPCBs, there were not more than two non-detects for all PCB congeners, except for #28 ($n=23$). Nevertheless, all Σ iPCBs could be calculated and ranged from 1.5 to 6,624 ng g⁻¹ (ww) in the entire database, while lipid contents ranged from 0.0009 to 0.393 g g⁻¹ (ww). Overall, 143 samples exceeded the regulatory threshold for fish consumption. Pike-perch (*Sander lucioperca*) and tench never exceeded this threshold ($n=27$ and 8, respectively), while eel (*Anguilla anguilla*; 15/19), common bream (*Abramis brama*, 24/37), and barbel (35/72) did so frequently. Congeners #101, 118, 138, 153, and 180 were all correlated to Σ iPCBs (Table A4 in Appendix A of [Electronic Supplementary Material](#)). Congener PCB153 in particular was strongly correlated to Σ iPCBs (adjusted $R^2=0.951$; $p<0.0001$), with a slope of 2.73 (± 0.029) and an intercept of 3.38 (± 5.53).

3.2 Sediment characteristics: organic carbon

A total of 157 sediment samples were analyzed for OC from five subsets (Table A1 in Appendix A of [Electronic Supplementary Material](#)). Eighteen were non-detects. Although the subsets may be statistically different, they all belong to a single hydrographic system, which is heterogeneous by nature. Moreover, the overall distribution of detects was very close to a Gaussian distribution (data not shown). Therefore, we considered it appropriate to merge these sets. Following the Kaplan–Meier procedure adapted to left-censored data (Helsel 2005), the first and third quartiles equaled 0.013 and 0.019 g g⁻¹ (dw), respectively, and the median was 0.015 g g⁻¹ (dw).

3.3 Sediment contamination by PCBs

A total of 459 sediment samples were collected in the sediment data set; all had complete measurements of iPCBs, while dioxin-like congeners (DL-PCBs), dioxins, and furans were not found in the majority of the samples. The number of results available for the 1999–2007 period ranged from one to 10 per site. Rather than quantification or detection limits, non-detects were identified with reference to reporting limits, i.e., constant values equaling 10 μ g kg⁻¹ (dw) for the congener concerned in most cases and

5 μ g kg⁻¹ (dw) in a few instances. Concentrations were highly variable throughout the period of time considered, with no detectable pattern. For 34 sites out of 75, there were no PCB congeners detected for the entire period, whatever the number of samples taken. When considering Σ iPCBs, the proportion of non-detects remained high (362/459). Not surprisingly, the proportion of detects increased with the amount of chlorine per congener, from 1.1% for #28 to 19.6% for PCB153.

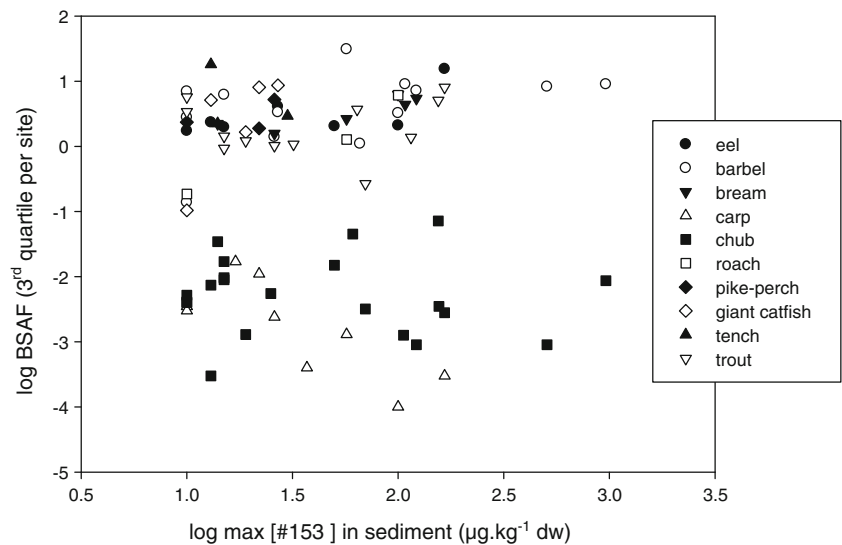
Considering only measurable concentrations, congeners 101, 138, 153, and 180 were correlated to Σ iPCBs. Congener PCB153 was correlated to Σ iPCBs ($R^2=0.95$; $p<0.0001$) and accounted for 10–59% of Σ iPCBs, and even 100% in a few samples with low concentrations. The concentrations of congeners #101, 138, and 180 were also correlated to the concentration of PCB153. Details on these correlations are provided in Table A5 in Appendix A of [Electronic Supplementary Material](#).

3.4 BSAF calculation

When determined, fish age ranged between 2–3 years and approximately 10 years. BSAFs could be determined for 10 out of 11 species at 40 sites where PCB153 concentrations in sediments were measured. For some samples, due to a change in the analytical method, the reporting limit was 5 μ g kg⁻¹ (dw), lower than the standard value of 10 μ g kg⁻¹ (dw). Unfortunately, other samples at the same sites were simply reported as below the usual reporting limit of 10 μ g kg⁻¹ (dw). Consequently, for five sites, some concentrations were measured at, for example, 7 μ g kg⁻¹ (dw), while for other years, the limit at the same sites was set at 10 μ g kg⁻¹ (dw) and samples were reported as non-detects. In these cases, the BSAFs were considered to be workable, and the minimum concentration of PCB153 was set at 10 μ g kg⁻¹ (dw), i.e., one of the reporting limits. Plotting the third quartiles of BSAFs versus the maximum concentration of congener PCB153 measured in sediments did not reveal consistent variations in these factors as a function of sediment concentration (Fig. 3). There are clearly two groups of species, i.e., eel, barbel, bream, giant catfish (*Silurus glanis*), roach (*Rutilus rutilus*), tench, and trout (*Salmo trutta fario*) which display medium to high BSAFs, while carp (*Cyprinus carpio*) and chub have low BSAFs. Due to the limited number of sites with measurable sediment concentrations, roach and tench cannot be compared to other species; nonetheless, their maximum BSAFs fall within the range of the values for barbels, breams, etc.

The calculation process was undertaken a second time, in order to check whether exceedance of the regulatory limit for fish consumption was associated with higher sediment concentrations or higher BSAFs. BSAFs were

Fig. 3 Log-transformed third quartiles of PCB153 BSAFs plotted versus log-transformed maximum PCB153 concentrations in sediment. BSAFs were not determined for sites where all PCB measurements in sediment yielded non-detects. Each dot represents the third quartile of BSAFs for one species at one site versus the corresponding concentration in sediment



calculated separately for fish samples at or above the regulatory limit (group 1; G1) and for samples below this threshold (group 2; G2). Note that some sites may belong to both groups. PCBs are more often measurable in sediments from the G1 sites; the median and upper quantiles of sediment PCB concentrations calculated according to the Kaplan–Meier method are higher for sites in G1 than those in G2 (Table 1). Though it is impossible to compare BSAF values in these two groups using a classical hypothesis test, they also appear higher in G1 than in G2 (Table 2).

3.5 SQG calculation

BSAF distributions for 10 sites or more are available for European eel, barbel, carp, chub, and trout (see Table 2). Barbels display higher BSAF values, either when fishes exceeded the regulatory threshold or when they did not.

Table 1 Distribution of PCB153 sediment concentrations according to RT exceedance in fish samples (concentrations in micrograms per kilogram dw) and in the entire set of selected data

	G1	G2	Overall
Number of sites	33	69	75
Number of sites \geq LQ/number of sites	64%	48%	53%
1st quartile	10	10	10
Median	15	10	10
Mean	80.1	29.74	46.1
Standard deviation	32.4	8.2	14.9
3rd quartile	66	22	32
Maximum	963	507	963

Twenty-six sites belong to both groups, as some fishes caught at these sites are above RT, while others are below. G1: Fishes displaying TEQ values \geq RT; G2: fishes displaying TEQ values $<$ RT

G1 group 1, G2 group 2

Moreover, eels have a higher regulatory limit than barbels. Therefore, an SQG determination based on barbel BSAFs will provide better protection against the risk of exceeding any regulatory threshold.

The regulatory threshold of 8 pg TEQ g⁻¹ (ww) is equivalent to 154 ng g⁻¹ ww Σ iPCBs (Babut et al. 2009), the confidence interval ranging from 120 to 200 ng g⁻¹ (ww). Based on the correlations noted above, this is equivalent to 37.4 ng g⁻¹ ww (9.8–72.5) of congener PCB153 in barbel filets. The third quartile of barbel BSAFs for the entire set of sites equals 12.6. Applying Eq. 2 with f_{OC} set at 0.013 (first quartile of OC set) and f_{lip} at 0.03 (third quartile of barbel f_{lip} distribution) yields a PCB153 concentration in sediments of 1.13 ng g⁻¹ (dw) (range, 0.30–2.20) or 26.6 ng g⁻¹ (dw) for Σ iPCBs (range, 15.6–38.6). Details on interval calculation are provided in Appendix D (Electronic Supplementary Material).

Ideally, the reliability of these values should be tested against an independent data. This was not feasible, due to the current availability of data. Therefore, we plotted the actual data selected in the Rhone database for this study on a graph showing how they compare with the calculated SQGs (Fig. 4).

A total of 298 out of 482 fish specimens (62%) were correctly classified by the BSAF-based SQG (i.e., their TEQ values were equal to or above RT), while they were caught at sites where the sediment maximum concentration was measured equal to or above the proposed SQG, or conversely both TEQ and Σ iPCB sediment concentrations were below the respective criteria. The sensitivity, specificity, and overall efficiency calculated on the basis of Σ iPCBs \sim RT equal 0.50, 0.71, and 0.65, respectively. The overall efficiency was only slightly improved (0.68) when the SQG was set at the upper bound and Σ iPCBs \sim RT at the lower bound of their respective confidence intervals.

Table 2 Median and third quartile ranges of congener PCB153 BSAFs depending on regulatory threshold exceedance: G1: fishes displaying TEQ values \geq RT; G2: fishes displaying TEQ values $<$ RT

	Eel	Barbel	Bream	Carp	Chub	Trout
G1						
Number of fishes	15	35	24	14	29	5
Number of sites	9	13	6	9	13	4
Number of sites \geq LQ	5	10	3	5	9	4
Median range	1.04–6.87	1.89–15.5	2.40–2.47	0.0001–0.0007	0.0003–0.011	0.72–5.34
3rd quartile range	1.935–15.9	3.31–32.5	4.38–5.40	0.0001–0.0017	0.0007–0.024	1.21–7.94
G2						
Number of fishes	4	37	13	40	92	44
Number of sites	4	16	6	14	35	18
Number of sites \geq LQ	2	6	4	5	18	8
Median range	0.27–1.26	0.54–8.39	0.83–4.19	0.0015–0.014	0.0002–0.032	0.19–3.65
3rd quartile range	0.41–1.73	0.8–11.99	1.58–6.57	0.0024–0.021	0.0003–0.067	0.271–5.08

G1 group 1, G2 group 2

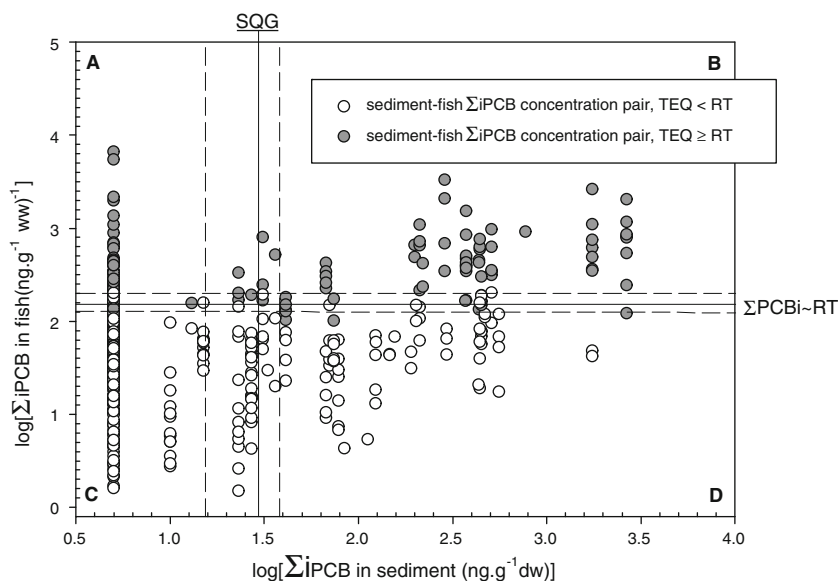
4 Discussion

BSAF distributions were estimated for 10 fish species at 40 sites throughout the Rhone basin. This may appear disappointing based on the number of sites initially selected (75), and the representativeness of the results could be questioned. There are very few other studies of this type at such a large scale. Wong et al. (2001) obtained BSAFs for 12 species, but for most of them, the number of samples was not higher than in the present study, although they worked at a larger scale. Therefore, the representativeness of these results is the best that can be afforded in the current state of available data.

BSAFs may vary across ecosystems (Burkhard et al. 2005), possibly by one order of magnitude or more, so comparing the BSAF values obtained in this study to previously

published ones is of limited value. Nevertheless, if the differences were over several orders of magnitude, either our approach or the published studies’ protocol could be questionable. Comparison is difficult, however, because many published BSAFs were calculated for total PCBs rather than for single congeners. Moreover, the few BSAFs available for congener PCB153 are often expressed as mean values of several pairs of fish and sediment samples. Ankley (1992) estimated a BSAF for hexachlorobiphenyls of 3.37 ± 0.59 for black bullhead (*Amiurus melas*) in the Fox River (USA). The mean BSAF values for congener PCB153 of 10.1 and 9.84 were determined for eel and pike, respectively, at a site in the River Severn (UK) (Harrad and Smith 1997). In their nationwide US study that encompassed an array of benthic and pelagic species (common carp, various suckers,

Fig. 4 Reliability of a BSAF-based SQG. The vertical solid and dashed lines represent the calculated SQG and its confidence interval. The horizontal solid and dashed lines correspond to Σ iPCBs \sim RT and its confidence interval. Sediment concentrations below the LQ are arbitrarily set at $5 \mu\text{g kg}^{-1}$ (dw)



sculpins and channel catfish, rainbow and brown trout, two types of bass, and mosquitofish), Wong et al. (2001) determined a median BSAF value of 2.4 ($n=11$, all species included) for total PCBs, with mosquitofish and bass displaying higher values than the other species. In their study on Lake Michigan trout, Burkhard et al. (2004) obtained mean PCB153 BSAFs ranging from 3.82 (2-year-old fishes) to 5.69 (9-year-old fishes). The USEPA database on fish tissue residues (USEPA PCBres Database. http://www.epa.gov/med/Prods_Pubs/pcbres.htm) displays a single PCB153 BSAF value of ≈ 1.80 (± 1.28) for the largemouth bass (*Micropterus salmoides*). Since in these studies the fish component of the pairs is most often made of composite samples, standard deviations do not provide the same information on BSAF variability as in our approach. With these methodological differences in mind, median BSAF values in fishes from the Rhone basin (Table 2) appear comparable to the published studies.

A challenging point when determining BSAFs on the basis of measured pairs is the connection between fish and sediment samples (Burkhard et al. 2005). One aspect of this issue is the extent to which the sediment measurements correspond to the fish exposure window. The selected period (1999–2007) may be deemed too long in this respect, according to the PCB depuration ability of some fish species. Half-lives of 1–4 months in rainbow trout (Niimi and Oliver 1983), 6–7 months in juvenile rainbow trout (Fisk et al. 1998; Buckman et al. 2004), and 12–24 months in guppy (*Poecilia reticulata*) (Sijm et al. 1992) have been reported. Nevertheless, these experiments were conducted on young fish at constant (and optimal) temperatures, for relatively short periods of time. In a 1-year experiment on yellow perch (*Perca flavescens*) from three size classes at ambient temperature, Paterson et al. (2007b) did not observe any elimination of congeners of $\log K_{OW} > 6.5$ in the two larger size classes. There was virtually no elimination over the cold months, i.e., approximately 8 months, for most congeners of $\log K_{OW} \leq 5.7$, which contribute partially to the understanding of biomagnification mechanisms (Paterson et al. 2007a). Moreover, in the field, PCB loss by depuration (if any) is more or less continuously balanced with uptake through food consumption. A second aspect is the extent to which sporadic composite surface sediment samples accurately represent the mean exposure of several-year-old fishes. By randomly extracting sediment data within the entire period delimited by fish ages, we expect to estimate the probable exposure of adult fishes more accurately. The selection of sediment data would have been different had we been able to assume or detect PCB contamination trends in this compartment.

Surprisingly, the BSAFs for carp, a benthic species, are as low as for chub, an omnivorous pelagic species, much lower than those of the benthic giant catfish or bream,

another benthic species. Chubs live in various habitats (riffles and pools) and feed on a wide variety of aquatic and terrestrial animals as well as plants. Consequently, this variety of conditions may lower their exposure compared to benthic species. Carp and bream habitats seem to be comparable: breams inhabit ponds or lower stretches of slow-flowing rivers and feed on insects, small crustaceans, mollusks, and plants, while carps favor large water bodies with slow-flowing regimes and feed on benthic organisms and plants (Grandmottet 1980). Based on this habitat similarity, one could expect BSAFs for carps to be comparable to those for breams, but they differ by several orders of magnitude. Wong et al. (2001) found BSAFs for carps comparable to other benthic fish species, with a median of approximately 4; however, they analyzed PCBs in whole fish samples. In the present study, there were only three sites in which carp and bream BSAFs could be compared. At these sites, BSAFs for breams ranged between 0.04 and 14.6, and for carps between 0.00002 and 0.007. Growth dilution did not contribute much to the low BSAFs in carps because there were few juvenile specimens (Table A6 in Appendix A of [Electronic Supplementary Material](#)). This discrepancy could have a physiological cause, given that carps accumulate hydrophobic compounds such as dioxins more in brain, viscera, and mesenteric fat than in fillets (Kuehl et al. 1987) and therefore could have lower PCB concentrations in their fillets than other species accumulating preferably in muscles, even though they exploit the same habitats. Moreover, the common carp has a potamodromous behavior; that is it migrates potentially long distances within the same water body. Adults may therefore feed on larger habitats than juveniles and accordingly forage both contaminated and uncontaminated food. In our data set, the highest PCB concentrations were observed in carps weighing less than 830 g (Fig. A1 in Appendix A of [Electronic Supplementary Material](#)).

Moreover, barbels live in rather fast-flowing reaches, but feed mainly on benthic invertebrates. As a result, the habitat does not appear to be the main factor explaining the higher accumulation potential of barbels, as compared to breams. Nor can interspecies f_{lip} variations explain these differences, since most species display the same range of flip values (ANOVA). Other factors such as metabolism (Burkhard et al. 2004) or the proportion of detrital carbon in food (Villa et al. 2011) may also contribute to these interspecies differences in BSAFs. Furthermore, intraspecies f_{lip} differences can be pointed out at least for barbel, bream, carp, and chub (Kolmogorov–Smirnov test): for these species, specimens exceeding RT (group G1) are more fatty than those that do not (G2).

Sediment contamination is another factor involved in the accumulation potential, although this role is not unequiv-

ocal. BSAFs were higher for fishes exceeding RT (Table 2), and these fishes are exposed to higher PCB concentrations (Table 1). Nevertheless, BSAFs did not increase as a function of increasing sediment concentrations, and the Σ PCB concentration ranges in G1 and G2 sediments overlapped. This suggests differences in PCB availability at some sites. Such differences in availability have already been pointed out in a few studies and ascribed to black carbon (Burkhard et al. 2004; Moermond et al. 2005).

The SQG derivation approach relies on correlations between PCB153 and Σ PCBs either in sediment or in fish, which determines the overall uncertainty of the resulting SQG. Another important source of uncertainty is the reliability of sediment data, which cannot be assessed quantitatively. We argue that the bootstrap procedure we propose reduces uncertainty, in that the BSAF ranges found using this procedure arguably represent the potential distribution of BSAFs more accurately than mean BSAFs and their standard deviations determined from measured pairs, because in the latter case there is no certainty that the entire range of actual ratio values has been accounted for.

Beyond the uncertainty related to the standard calculation, the standard efficiency is important to consider and should be tested on other data sets. Nevertheless, as the sediment standard we derived is based on a single species (barbel), whereas the selected fish and sediment data set encompasses an array of 11 species, this efficiency assessment seems acceptable as a first attempt.

In their recent paper on a similar topic, Bhavsar et al. (2010) argue that it is easier to derive fish consumption advisory-based sediment quality thresholds (fca-SQT), conceptually identical to the standard we derived, on the basis of non-normalized BSAFs, because sediment OC contents are not systematically available, and guidelines are generally expressed on a non-normalized basis. In fact, using normalized or non-normalized BSAFs in a given system would yield the same result (Appendix C of [Electronic Supplementary Material](#)). However, they also acknowledge that the uncertainty on the fca-SQTs they have determined is important, due to the use of fish and sediment concentrations in whole-lake averages; they accordingly suggest using site-specific sediment and fish data for a better assessment. The approach we developed is entirely based on site-specific data; moreover, normalized BSAFs can be used to adjust the guideline we calculated to local conditions (OC content), if needed.

The tissue-based sediment guideline determined herein for the Rhone basin ($26.6 \text{ ng g}^{-1} \text{ dw}$) is fairly comparable to existing effect-based sediment guidelines, $22\text{--}23 \text{ ng g}^{-1} \text{ (dw)}$ (Apitz et al. 2007; Kwok et al. 2008) to $34.1 \text{ ng g}^{-1} \text{ (dw)}$ (EC 1999). Furthermore, it is far below the mechanistically based benchmarks reported elsewhere (e.g.,

Fuchsman et al. 2006), even though the latter are expressed as Aroclors. The Rhone SQG proposed is also comparable to the total PCBs fca-SQT ranging from 1 to $60 \text{ ng g}^{-1} \text{ (dw)}$ determined by Bhavsar et al. (2010) for several Great Lakes locations and four species. The most sensitive species in their study was lake trout, with an fca-SQT between 1 and $20 \text{ ng g}^{-1} \text{ (dw)}$ depending on the lake or location.

5 Conclusion: implications for monitoring and management

When actually determining whether biota are impaired or not by hydrophobic contaminants such as PCBs, a tiered approach based on sediment in the first step and fish or other biota in the second might be more appropriate than either an approach relying only on biota or only on sediments. An SQG related to a tissue-based threshold would trigger the second tier. In this perspective, the SQG we determined for the Rhone River on the basis of BSAF distributions for a range of species continues to have limited efficiency.

Acknowledgments This study was supported by a grant from DREAL Rhône-Alpes. We thank Thierry Meunier (TREDI, groupe Séché), Eric Doutriaux (Compagnie Nationale du Rhône), and Héléne Giot (Rhone Méditerranée Water Agency) for their help in gathering sediment data and Linda Northrup for editing the manuscript.

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