PCB DATA VALIDATION AND INTERPRETATION FOR ESTABLISHING FISH CONSUMPTION GUIDELINES IN THE USA – A TEXAS CASE STUDY

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Introduction

Ellison Creek Reservoir (ECR) is a 1,516 acre fresh-water lake in northeast Texas, USA. ECR is used for recreational activities including swimming, boating, water skiing, and catch and release fishing tournaments. The shores of ECR serve as a home to hundreds of residents and several industries including a marina, a steel mill, and an electrical power facility. In 2005, a state agency collected 34 fish from ECR by electroshock and gill nets for analysis of metals, pesticides, and PCBs in tissue. Split fillets of these fish were obtained and analyzed for PCBs by congener-specific and by Aroclor pattern analyses. Total PCBs were calculated and average PCB levels were compared to US EPA guidelines for fish consumption advisories on a per species basis. This paper presents an exercise of developing a fish consumption advisory based on these results and the guidance recommended by US EPA. Due to the conservative risk assessment guidance provided by the US EPA for PCBs in fish, very sensitive analytical techniques are required to accurately determine the total PCB level in fish tissues for comparison to the guidelines. Examples of analytical uncertainties and their effects on total PCB calculation for use in fish consumption advisories are presented as well as how the impact of consumption advisories can be affected by different interpretations and applications of US EPA guidance.

Materials and Methods

Fish samples were collected from ECR in May 2005 and consisted of a variety of species: hybrid striped bass (HSB, n=7), largemouth bass (LMB, n=9), channel catfish (CC, n=10), flathead catfish (FHCF, n=1, common carp (CARP, n=5) and white crappie (WC, n=2). All fish were weighed and length measured after sampling. All fish samples were analyzed by Analytical Perspectives (Wilmington, NC, USA). To prepare for chemical analysis, fish fillets were thawed, skin removed, homogenized and transferred to precleaned glass amber vials and re-frozen. For analysis, samples were thawed, approximately one gram of tissue removed and transferred to a mortar to commence the extraction method. The extraction. purification and analysis methodologies are proprietary to Analytical Perspectives but are similar to EPA method 1668A¹ with some improvements and modifications. Analysis was conducted for all 209 PCB congeners on 34 fish samples using gas chromatography coupled with high resolution mass spectrometry (HRMS). The laboratory reported the concentration of 173 distinct peaks which includes 36 peaks with one or more co-elutions. Extra quality assurance and quality control measures were taken to ensure data comparability and laboratory accuracy and precision. In the current study, the concentrations of 43 PCB congeners were summed for the assessment of total PCB concentrations and potential impacts on human health through consumption of food products^{2,3}. With co-elutions, total PCB concentrations were based on the sum of 61 congeners (see Table 1). For congeners below the detection limit, ¹/₂ the detection limit was used in the total PCB calculation. Utilizing data from Frame et al. (1996), cosine theta analysis was conducted on the fish tissue PCB congeners to determine which Aroclor mixture they most closely resembled⁷.

In its <u>Guidance For Assessing Chemical Contamination Data For Use In Fish Advisories</u> (2000)⁴, the US EPA provides agencies with the necessary methodology for developing detailed, specific fish consumption advisories that maximize the protection of human health while simultaneously minimizing unnecessary impacts on economic and nutritional interests associated with affected water bodies. Four volumes of

guidance are available with recommendations on fish sampling and analysis (Vol. I), risk assessment and fish consumption limits (Vol. II), risk management (Vol. III), and risk communication (Vol. IV). In the current study, US EPA guidance from Volumes I and II were followed and explored to identify areas where multiple interpretations of the guidance might alter the development and impact of a fish advisory. Issues related to risk management and communication are not addressed in this study.

The US EPA's monthly fish consumption limits for carcinogenic and non-carcinogenic health endpoints provide agencies a variety of options for developing health-protective fish consumption limitations. Based on measured PCB levels in fish, agencies can advise consumption limitations that include no consumption, 0.5 to 16 meals per month, or unrestricted consumption of >16 meals per month. Fish tissue concentrations associated with consumption limits are protective of non-cancer health effects based on the US EPA reference dose (RfD) for Aroclor 1254 (0.00002 mg/kg/d) and cancer health effects based on a 1 X 10⁻⁶ excess cancer risk (cancer slope factor of 2.0 per mg/kg/d). In order to simplify the comparisons and examples in this study, we have focused on the non-cancer health endpoint guidance. In addition, US EPA provides specific guidance on preparation-related reduction of the dose of PCBs consumed per fish meal assuming that information about fish filleting, trimming, and cooking methods are available for the affected population. Several authors have demonstrated the effect of cooking fish on reduction of persistent organic pollutants including PCBs⁴⁻⁶. Based on these studies, a 25% reduction of PCBs through cooking was applied in this study to demonstrate reduction of dose of PCBs consumed from fish. Removing skin has been demonstrated to reduce PCBs in fish fillets during the cooking process, but this reduction was not added in the current study because skin was removed from the fillets before analysis.

Results and Discussion

The core of fish consumption advisories is dependent on a successful and well planned field sampling program as well as a solid analytical data foundation. The field program requires that a statistically representative sampling is achieved for all species to be considered in the assessment. Consideration of dietary consumption is also necessary along with relationships of contaminant load and the age, length, or weight of the fish species. If conducted appropriately, fish species and size could be incorporated into the fish consumption advisory. Unfortunately, the fish samples for the assessment were sampled without consideration for these potential issues, therefore, the assessment was completed without factoring for these potential confounders since most species were sampled in inadequate quantities to confidently establish these relationships. In addition, there has been a recent push for agencies to utilize congener-specific methods for analysis of PCBs in fish and other media in order to increase accuracy and precision of PCB quantification.

Analytical data quality, the foundation of a fish advisory, should: 1) show precision and accuracy in the measurements; 2) demonstrate reproducibility; and 3) have low enough detection limits compared to the relevant health criteria. For PCB impacts on fish advisories, the last component is of the utmost importance as the US EPA guidelines are in the sub-ppm range of concentrations. Total PCB concentrations as the sum of 43 congeners in the fish measured in this study ranged from 0.016 to 2.3 ppm, and detection limits for most congeners ranged from 0.000001 to 0.00001 ppm allowing for highsensitivity quantification. By utilizing HRMS, non-detected congeners accounted for less than 0.05% of the total PCB concentrations in the analyzed fish samples. With such sensitive detection limits, the total PCB concentration is not significantly affected by non-detected congeners. Furthermore, even if some or all of the 43 PCB congeners are not detected, the contribution of ¹/₂ detection limits on the calculated PCB total is insignificant, or at the least does not add up to a level that nears the risk-based tissue PCB concentrations for consumption advisory considerations. However, many laboratories continue to quantitate PCBs using gas chromatography and low-resolution mass spectrometry. Low-resolution mass spectrometry achieves detection limits for individual congeners that are near 0.001 ppm, or 100-1000 times less sensitive than high-resolution methods. Assuming that non-detected PCB congeners are generally assigned a value of 1/2 the detection limit, there can be stark differences between high- and lowresolution methods in the relative contribution of the non-detected congeners to the total PCB calculation. For instance, if all 43 congeners are not detected at a detection limit of 0.001 ppm, summing ¹/₂ detection limits will give a PCB total of 0.0215 ppm (43 X 0.0005 ppm). If used in a risk assessment, this level would fall within the range of PCB concentrations that warrant consideration of some consumption limits on the fish even though no PCBs were actually detected in the tissue. Cosine theta analysis indicated that the PCBs in ECR fish most closely resemble the congener pattern of Aroclor 1260. This pattern is different from that of Aroclor 1254, the mixture whose toxicity is the basis of the US EPA risk assessment for PCBs used in fish advisories. A discussion of the applicability of the Aroclor 1254 RfD to the results in this study and other studies where the PCB congener patterns do not match Aroclor 1254 is beyond the scope of this paper.

The mean PCB concentrations of the six fish species collected from ECR are summarized in Table 2. Mean concentrations of PCBs in WC of 0.033 ppm indicate an allowable consumption level of 4-7 meals per month (>0.023 - 0.047). Additional considerations for PCB reduction due to cooking gives a probable mean consumption dose of 0.025 ppm for WC. This value is still within the allowable risk range for 4-7 meals per month. For the single FHCF that was sampled, the tissue PCB level was 0.041 ppm, a level that indicates an allowable consumption level of 4-7 meals per month. Cooking considerations lowered the estimated PCB concentration to 0.031 ppm, still within the same range of allowable meals per month. The LMB had an average PCB level of 0.106 ppm which falls in the range of allowable consumption of 1-2 meals per month (>0.094-0.190 ppm). When reductions for cooking are considered, the estimated PCB dose for LMB falls to 0.080 ppm, a level that allows consumption of 2-3 LMB meals per month. CARP and CC had average PCB concentrations of 0.212 ppm and 0.241 ppm, respectively, levels that fall within the range of allowable consumption of 0.5-1 meal per month (0.190-0.380 ppm). When making reductions for cooking, estimated PCB dose for CARP and CC fall to 0.159 ppm and 0.181 ppm, respectively, levels that allow consumption of 1-2 meals per month. Finally, the top-predator HSB had an average PCB concentration of 0.925 ppm, a level that falls in the range (>0.38 ppm) that exceeds the lowest allowable level of consumption. Reduction of the PCB concentration in HSB due to cooking did not result in any change in the number of meals allowed per month.

Risk Based Consumption Limit	Non-Cancer Health Endpoints	Reservoir Fish Data			
Fish Meals/Month	Fish Tissue Concentrations (<i>ppm</i> , <i>wet weight</i>)	Species (n)	Mean (<i>ppm</i> , <i>wet weight</i>)	Species	"After Cooking" Mean (ppm, wet weight)
Unrestricted	0 - 0.0059				
16	>0.0059 - 0.012				
12	>0.012 - 0.016				
8	>0.016 - 0.023				
4	>0.023 - 0.047	WC (2) FHCF (1)	0.033 0.041	WC FHCF	0.025 0.031
3	>0.047 - 0.063				
2	>0.063 - 0.094			LMB	0.080
1	>0.094 - 0.19	LMB (9)	0.106	CARP	0.159
				CC	0.181
0.5	>0.19- 0.38	CARP (5)	0.212		
		CC (10)	0.241		
None (<0.5)	>0.38	HSB (7)	0.925	HSB	0.694

Table 1 - Monthly fish consumption recommendations for ECR fish based on US EPA guidelines for fish consumption advisories³: Averages for raw fish and after considerations for cooking.

Total PCBs consisted of the sum of the following congeners (with co-elutions): 8, 18 (30), 28 (20), 37, 52, 44 (47, 65), 49 (69), 66, 70/74 (76, 61), 77, 81, 87/119 (108, 86, 97, 125), 99, 101 (90, 113), 105, 118, 123, 110, 114, 126, 128 (166), 153 (168), 138 (129, 163), 158, 151 (135), 156/157, 167, 169, 170, 177, 180 (193), 187, 183, 189, 194, 195, 201, 206, 209.

US EPA guidelines support the following fish consumption advisory for fish taken from ECR: Consumers should limit consumption of WC and FHCF to less than 8 meals per month, LMB to less than 3 meals per month, and CARP and CC to less than 2 meals per month. HSB from this reservoir should not be eaten.

This example of advisory development demonstrates the versatility of the US EPA's advisory guidance and the amount of detail that agencies can incorporate into their advisories. The importance of using the guidance to create detailed, species-specific advisories may be best demonstrated by an example of how the guidance may be misused. Assume for this example that an agency's policy is to base fish advisories on a single, static fish consumption limit of two meals per month. Therefore, any fish species with mean PCB levels exceeding the non-cancer health endpoint level for two meals per month (0.094 ppm) would be issued a "no consumption" advisory. Likewise, consumption of fish species with mean PCB levels less than 0.094 ppm would be unrestricted. The agency then samples fish and finds that the WC, CC, and LMB have mean PCB levels of 0.050, 0.100, and 0.200 ppm, respectively. According to their assumption that PCB levels less than 0.094 ppm warrant no consumption limits, the agency deems the WC safe for unlimited consumption whereas the CC and LMB are deemed unsafe for consumption at any level. Several problems arise with this type of application. First, a "no consumption" advisory has been placed on the CC and LMB. For CC, whose mean PCB levels fall in a range of >0.094 - 0.19 ppm, US EPA guidance indicates that people could eat 1-2 meals per month without any appreciable risk of adverse health effects. So the "no consumption" label unnecessarily advises consumers to eliminate CC from their diets. The same goes for the LMB (>0.19- 0.38 ppm) that could be eaten 0.5-1 meals per month. Conversely, the WC have mean PCB levels that would actually warrant an advisory to limit consumption to 3-4 meals per month. However, in this example, the agency places no restrictions on WC consumption while WC consumers of 4 or more meals per month would exceed limits of PCB intake based on US EPA estimates of the non-cancer hazard (as derived from the toxicity of Aroclor 1254) of PCBs. Tailoring the application of the guidance to fit the data that are available is crucial to the issuance of a fair, effective, and health protective fish consumption advisory.

In summary, development of fish advisories for PCBs requires sound analytical methodology and interpretation of PCB data in fish. Close adherence to US EPA methodology and guidance can aid in the development of advisories that are adequately protective of human health yet not unduly burdensome to the economic and nutritional interests of local populations. Inadequate sampling, insufficient analytical methodologies, poor statistical interpretations, and static fish consumption thresholds can lead to erroneous advisories that produce undue stress on local populations and business without necessarily increasing the benefit to human health. To avoid these problems, regulatory agencies must be careful to fully explore the results and issues for each water body under investigation and base their advisories on sound science and policy.

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