Noxon Rapids Reservoir Fish Contaminant Study

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Introduction

The pulp and paper mill industry is one of the largest polluters of freshwater ecosystems (reviewed in McMaster et al 1991, Servos et al 1996). In particular, the compounds that are formed in the process of pulping and paper making are highly bio-accumulative and deleterious to human health and the environment including polychlorinated dibenzodioxins (dioxins), polychlorinated diibenzofurans (furans), and polychlorinated biphenyls (PCBs). In fact, 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) is considered the most toxic man-made substance ever created.

Upstream of Noxon Rapids Reservoir several industrial sites exist, in both the Clark Fork and Flathead River basins, including proposed and current EPA Superfund NPL (National Priority Lists) sites which have sources of dioxins, furans, and PCBs. These contaminants have been found in fish in the Clark Fork River, including sampling in 2013 where northern pike were found with levels that warranted an "AVOID" consumption advisory (Schmetterling and Selch 2013). Moreover, elevated concentrations of PCBs have also been previously found in the Flathead River basin.

The reservoirs on the Lower Clark Fork River are a natural "sink" for contaminants, and already contain some of the highest levels of mercury (Hg) in Montana (Montana Fish Consumption Advisories 2014). Elevated Hg levels are due to many factors, but the physico-chemical dynamics and the downstream catchment properties of the reservoirs play a major role in capturing, accumulating, and methylating Hg, making it bio-available to fish. These same factors result in other contaminants accumulating in reservoir sediments and ultimately bio-accumulating in resident fish, especially top-level predators such as northern pike, walleye, and smallmouth bass. These fish (along with lower trophic level fish like yellow perch) are highly sought by anglers for consumption which creates human health concern.

Owing to the suspected upstream source of contaminants from the pulp mill at Frenchtown and levels of dioxins, furans, and PCBs in northern pike, the objective of this study was to quantify the presence or absence of dioxins, furans, and PCBs in fish muscle tissue from Noxon Reservoir to determine risks for human consumption. Understanding the quantity of these toxins in fish fillets will help us to manage the fishery (through fishing regulations), inform anglers of risks through consumption advisories, if necessary, and help to gain an understanding of the potential ecological damage and impacts of the upstream industrial facilities. This information may also serve to guide the geographic scope and sampling needs for future risk assessments related to the proposed superfund site listing.

Methods

Fish were collected for analysis of contaminants in the spring and summer, 2014 and separated into 4-inch size groups. Target species/size groups included northern pike (22-26, 26-30, and 30+ inches), walleye (18-22, 22-26, and 26-30 inches), smallmouth bass (10-14, 14-18 inches), and yellow perch (6-10 and 10-14 inches). When available, 5-fish composite muscle samples (skin-off) were analyzed for PCB's, dioxins, and furans. Dioxin and furan congeners are individual substances that are closely related and have individual toxicity values and are compared to TCDD, the dioxin congener with the highest acute toxicity. The toxic equivalency factors (TEF) for each congener was used to calculate the toxic equivalent (TEQ) value for each composite sample to determine fish consumption limits for carcinogenic health endpoints. Individual congener PCB analysis were also conducted on the largest size group of northern

pike (30+ inches) and smallmouth bass (14-18 inches) to determine if dioxin-like (co-planar) PCB congeners were present. Co-planar PCBs are similar to dioxins and, if detected, were added to the overall TEQ value for a final meal guidance number. To reduce analytical costs, the smaller size groups were analyzed for PCB aroclors, which are mixtures of PCB compounds that are calculated separately from dioxins and furans for meal guidance advisories.

Sample analysis

Dioxins, furans, and PCB congeners were analyzed at ALS Environmental, Houston, Texas. Results from Dioxin, and Furans analyses were compared to EPA 823-B-00-007 *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories 3rd Edition, 2000* (Table 1). PCB aroclor analysis was conducted by ALS Environmental, Kelso, Washington. Results from PCB aroclor analyses were compared to human health meal guidance developed by the Montana Department of Health and Human Services (Table 2).

Results

Fish captured from spring gill-netting and electrofishing efforts in Noxon Rapids Reservoir filled all the targeted species/size groups, except only three northern pike > 30 inches, no walleye > 26 inches, and no yellow perch > 10 inches were caught. Dioxins, furans, and co-planer PCBs were only detected in the muscle tissue of the largest size group of northern pike (30+ inches) and smallmouth bass (14-18 inches; Table 3). Co-planer PCBs were only analyzed in the largest northern pike (30+ inch) and smallmouth bass (14-18 inches), so it possible these were present in smaller size groups and other species. PCB aroclors (aroclor 1254) were analyzed in all smaller size groups, but were only detected in walleye (18-22 and 22-26 inch fish; Table 3).

Northern pike muscle tissues contained a total TEQ concentration of 2.128 ng/kg wet weight (ww.) when dioxin (0.244 ng/kg), furan (0.288), and co-planar PCBs (1.596) were included (Table 4). Total TEQ concentrations > 1.2 ng/kg ww. in muscle tissue are not recommended for consumption (Tables 1 and 4; EPA 2000). Moreover, non-co-planar PCBs found in 30+ inch northern pike contained concentrations that result in a recommendation of 4 meals/month. Smallmouth bass total TEQ concentration was 0.070 ng/kg ww. (Table 4) resulting in a recommended advisory of 8 meals/month. Non-co-planar PCBs and aroclors found in smallmouth bass and walleye were not at levels that warranted an advisory (Tables 1 and 4).

Comparing the results from 2014 sampling in Noxon Rapids Reservoir to 2013 sampling upstream on the Clark Fork River found that 13 of the 17 dioxins and furans found in northern pike and rainbow trout in the Clark Fork River were also found in Noxon Rapids Reservoir fish (Table 3). Northern pike >30 inches from Noxon Reservoir contained 0.5326 ng/kg ww. total TEQ dioxins and furans (not including co-planar PCBs since these were not sampled in 2013), while the same sized northern pike (>30 inches) in the Clark Fork River contained just 0.140 ng/kg total TEQ. A single northern pike composite (n=2, mean length=28.69 inches) analysis for dioxins and furans (co-planar PCBs were not analyzed) was analyzed

from fish collected from Thompson Falls Reservoir in fall 2014 (Note: this sample analytical cost was not paid for from AVISTA funds). Total TEQ concentration was 0.002 ng/kg ww. resulting in no consumption restriction (Table 4).

Discussion

The discovery of high concentrations of dioxins, furans, and co-planar PCBs in northern pike and smallmouth bass in Noxon Reservoir is concerning. The levels found in northern pike muscle tissues > 30 inches are the highest concentrations documented to date in Montana, however statewide data are limiting and these contaminates had not been analyzed by FWP prior to the 2013 Clark Fork River study. Co-planar PCBs were only analyzed in one > 30 inch northern pike composite sample, and one 14-18 inch smallmouth bass composite sample, yet in these samples the co-planar PCBs contributed 75 and 77 percent of the total TEQ concentrations. Moreover, 10 of the 12 co-planar PCBs were found in northern pike, and 9 of the 12 co-planar PCBs were found in the smallmouth bass. This finding is significant and suggests that all future fish muscle sampling surrounding the proposed NPL listing and assessment should include co-planar PCB analysis.

The detection of dioxins and furans in only the largest size group of northern pike and smallmouth bass was surprising. Whereas the largest, oldest fish typically contain the highest concentrations of contaminants, the fact that there were not any detectable concentrations in the smaller size groups was unexpected. The objective of this study was to evaluate the presence or absence of dioxins, furans, and PCB's in fish muscle tissue and did not include replicate samples, so this phenomenon may simply be explained by low sample size or by the presence of a highly contaminated individual fish in one of the composites. It is possible a fish analyzed may have lived in a different habitat within the reservoir or may have moved downstream from a source of contamination (like near Frenchtown). It could also be that an individual northern pike or smallmouth bass was simply older and thus accumulated more contamination through time. One of the three northern pike in the composite sample of fish > 30 inches was 37 inches, and one of the five smallmouth bass in the composite sample of fish 14-18 inches was nearly 18 inches, suggesting they were likely old fish. Still, the high concentrations detected in the large northern pike composite suggest this is not an incidental result and regardless of the sources or sample size, the results are unequivocal and warrant a consumption advisory. Moreover, detection of low levels of dioxins and furans in a smaller size group (26-30 inch) of northern pike from Thompson Falls reservoir upstream further supports the wide-spread presence of these toxins.

Noxon Rapids Reservoir contains fish with some of the highest concentrations of Hg in the State (Montana Fish Consumption Advisories 2014). Because of this, the results from dioxins, furans, and PCB analyses did not warrant changes to most of the current fish consumption advisories. For example, even though results from dioxin, furan, and co-planar PCB analysis recommends 8 meals/month for 14-18 inch smallmouth bass, the current advisory based on Hg already recommends 3 meals/month for men, and 1 meal/month for women and children, so the recommendation in place is already more restrictive. This is not the case for northern pike > 30 inches. The previous fish advisory based on Hg for men is 2 meals/month, and 1 meal/month for women and children. Based on the results from our dioxin, furan, and PCB testing on northern pike > 30 inches, the new advisory for all consumers is to "AVOID" eating

these fish. This change has already been incorporated into our online fish advisory chart, and signs have been placed at boat ramps to notify anglers of the advisory.

The EPA has proposed placing the former Smurfit-Stone Container Corp. mill site near Frenchtown, MT on the National Priorities List (NPL) and final NPL designation is expected to occur in 2015. If listed, extensive efforts to characterize ecological and human health risks associated with the mill-site will likely begin. Based on the results of this study, it appears that the geographic extent of contamination extends at least through Noxon Reservoir, likely into Cabinet Gorge Reservoir, and may extend below all three Lower Clark Fork Reservoirs. Future studies surrounding the proposed NPL listing should characterize the downstream extent of contamination, evaluate replicate samples from all size groups of fish species, and be sure to analyze all muscle tissues for dioxins, furans, and co-planer PCBs.

Table 1. EPA fish muscle tissue consumption guidance for dioxins/furans. Table reconstructed from *EPA 823-B-00-007 Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories 3rd Edition, 2000.*

Dioxins/Furans All Consumers		
TEQ range (ng/kg ww.)		meals/month
>1.2		AVOID
>0.600	1.200	0.5
>0.300	0.600	1
>0.200	0.300	2
>0.150	0.200	3
>0.075	0.150	4
>0.050	0.075	8
>0.038	0.050	12
>0.019	0.038	16
<0.019		Unrestricted

Table 2. State of Montana muscle tissue consumption guidance for polychlorinated biphenyls (PCBs).

Polychlorinated biphenyls (PCBs) All Consumers		
PCB range (mg/kg ww.)		meals/month
>0.47		AVOID
>0.11	0.47	1
>0.025	0.11	4
<0.025		Unrestricted

Table 3. Results from dioxin, Furan, and PCB analysis on fish collected from Noxon Reservoir in 2014. Analyte Toxic Equivalence Factors (TEF) were used to assess the toxicity of dioxin and "dioxin-like" compounds relative to the TCDD dioxin. Individual congeners shown with an asterisk (*) next to them represent contaminants that were also detected in the Clark Fork River Sampling conducted in 2013. Species include northern pike (NP), smallmouth bass (SMB), walleye (WE), and yellow perch (YP). Numbers listed below species abbreviations represent the size group (inches) of the fish composited for analysis. Boxes marked with an "X" signify the congeners found in analysis for a given species/size group. Boxes that are blank represent congeners that were analyzed but not found above detection limits. Boxes shaded in grey signify that analyses were not conducted for those contaminants, species/size group.

Analyte (TEF)	**Congener**	**NP (22-26)**	**NP (26-30)**	**NP (30+)**	**SMB (10-14)**	**SMB (14-18)**	**WE (18-22)**	**WE (22-26)**	**YP (6-10)**
Dioxins (1)	2,3,7,8-TCDD								
(1)	1,2,3,7,8-PeCDD*			X					
(0.1)	1,2,3,4,7,8-HxCDD								
(0.1)	1,2,3,6,7,8-HxCDD*			X		X			
(0.1)	1,2,3,7,8,9-HpCDD*								
(0.01)	1,2,3,4,6,7,8-HpCDD*			X		X			
(0.001)	OCDD*			X		X			
Furans (0.1)	2,3,7,8-TCDF*			X					
(0.03)	1,2,3,7,8-PeCDF*								
(0.3)	2,3,4,7,8-PeCDF*			X					
(0.1)	1,2,3,4,7,8-HxCDF*								
(0.1)	1,2,3,6,7,8-HxCDF*								
(0.1)	2,3,4,6,7,8-HpCDF								
(0.1)	1,2,3,7,8,9-HxCDF*								
(0.01)	1,2,3,4,6,7,8-HpCDF*								
(0.01)	1,2,3,4,7,8,9-HpCDF*								
(0.003)	OCDF*								
Co-Planar PCBs (0.0001)	3,3'4,4'-TCB (77)			X		X			
(0.0003)	3,4,4',5-TCB (81)								
(0.1)	3,3',4,4',5-PeCB (126)			X					
(0.00003)	2,3,3',4,4'-PeCB (105)			X		X			
(0.00003)	2,3,4,4',5-PeCB (114)			X		X			
(0.00003)	2,3',4,4',5-PeCB (118)			X		X			
(0.00003)	2',3,4,4',5-PeCB (123)			X		X			
(0.00003)	2,3,3',4,4',5-HxCB (156)			X		X			
(0.00003)	2,3,3',4,4',5'-HxCB (157)			X		X			
(0.00003)	2,3',4,4',5,5'-HxCB (167)			X		X			
(0.03)	3,3',4,4',5,5'-HxCB (169)								
(0.00003)	2,3,3',4,4',5,5'-HpCB (189)			X		X			
PCB Congeners	Non co-planer PCB congeners (Full list)			X		X			
PCB Aroclors	1016								
	1221								
	1232								
	1242								
	1248								
	1254						X	X	
	1260								

Table 4. Summary results from dioxin, furan, and PCB analysis on fish collected from Noxon Reservoir in 2014. Species include northern pike (NP), smallmouth bass (SMB), walleye (WE), and yellow perch (YP). N represents the number of fish used in composite analysis. m/m represents the number of meals per month recommended for consumption based on levels of contaminants found.

Species	**N**	**Length Group (mm)**	**Length group (in)**	**PCBs Aroclors/ Congeners (mg/kg)**	**PCB Aroclors/ Congeners m/m**	**Total TEQ Dioxins/Furans Co-Planer PCBs (ng/kg)**	**Dioxins/FuransCo-Planer PCBs m/m**
NP	5	559- 660	22-26	ND	U	ND	U
NP	5	660- 762	26-30	ND	U	ND	U
NP	3	> 762	30+	**0.0806**	**4**	**2.128**	**Avoid**
SMB	5	254-355	10-14	ND	U	ND	U
SMB	5	355-457	14-18	0.0134	U	**0.070**	**8**
WE	5	457-559	18-22	0.0069	U	ND	U
WE	5	559-660	22-26	0.0095	U	ND	U
YP	5	152-254	6-10	ND	U	ND	U

References:

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