Preliminary Investigations into the Toxicity of Game Fish in the Clark Fork River downstream from the Smurfit Stone Container Mill

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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 especially deleterious to human health and the environment including polychlorinated dibenzodioxins (dioxins), and polychlorinated diibenzofurans (furans) (reviewed in Sreekrishnan 2001)

The recent discovery of contamination of the Smurfit Stone Container site and shallow groundwater with dioxins, furans and polychlorinated biphenyls (PCB's) (Missoula County, unpublished data) have prompted us to evaluate fish in the adjacent Clark Fork River for contamination related to the historic mill operations. Indeed, the process of milling paper and specifically the effects of chlorine bleaching are long lasting in the environment and well studied (e.g., see Servos et al. 1996). The toxins (specifically PCB's dioxins and furans) reported at the site are not found nearby and their presence in the river or aquatic biota downstream would indicate the mill as a source for contamination and degradation of the aquatic ecosystem.

Our goal is to understand the effects of the toxins on both human health and the environment. Understanding the two will take a significant investment of time, sampling and expenses. The effect of many of the toxins in the environment is complex and encompasses many trophic orders and species. For the first phase our investigations, we wanted to understand what threats these toxins, specifically polychlorinated biphenyls (PCBs), dioxins, and furans pose to human heath and whether we need to issue consumption advisories for this area. In the future we hope to expand this work to understand the geographic and ecological scope of the contamination from the Smurfit Stone Container Site.

The objective of this study was to quantify the presence of dioxins, furans, PCB's, Se, and Hg in fish muscle tissues from the area generally immediately downstream of the Smurfit Stone Container Site to determine risks for human consumption. Understanding the quantity of these toxins in fish fillets would help us to manage the fishery (through fishing regulations influenced by fish consumption advisories), and help to gain an understanding of the potential ecological damage and impacts of the pulping operations at the Smurfit Stone Container Site. These data will help us determine the next steps in monitoring and evaluating the ecological heath of the Clark Fork River.

Methods

In order to determine risks to human heath, we collected fillets from northern pike (*Esox lucius*) and rainbow trout (*Oncorhynchus mykiss*), two highly sought after game fish, from a 10 km reach of river downstream of the Smurfit Stone Container Site (Figure 1). We selected rainbow trout under 375 mm TL (Total Length), which are legal fish for harvest in this section of river (2013 Montana Fishing Regulations, page 29). We selected fish lengths, a priori, that represented a narrow range of sizes- those that anglers would likely harvest (between 300- 375 mm TL). We also collected northern pike that represented different ages, and thus would reflect a different potential for bioaccumulation.

On May 17, 20, and 21, 2013, we captured northern pike by electrofishing backwaters and sloughs (areas known to contain northern pike and areas frequented by anglers). We captured rainbow trout by electrofishing the margins of the main channel of the Clark Fork River (Figure 1).

The three person crew conducted electrofishing with a 6.0 meter aluminum jet boat with 2 bow mounted boom anodes. The power from a 6600 watt generator was routed through a Smith Root VVP 15-B rectifying unit, that delivered 375 volts to create an electrical field around 3-6 amperes. Once electrofished, netters removed all trout species and northern pike from the electrical field and placed them in a live well.

We sorted fish by species and length, to acquire three samples consisting of five fish, for each species. We measured fish for TL in mm and weight in g, and randomly selected individuals for use in our analyses. Rainbow trout not selected were immediately released to the river.

In order to analyze contaminates (see below) we collected a skinless fillet from each fish in the field. To avoid cross contamination of the specimens, we used a new scalpel blade for each fish, and we cleaned the work area with water between handling each fish. We wrapped each fillet in aluminum foil, then bagged each in its own freezer bag and stored all the prepared samples in a cooler containing ice in the field. Once we returned from the field, we placed the fillets in a freezer for preservation prior to further sample preparation and analysis.

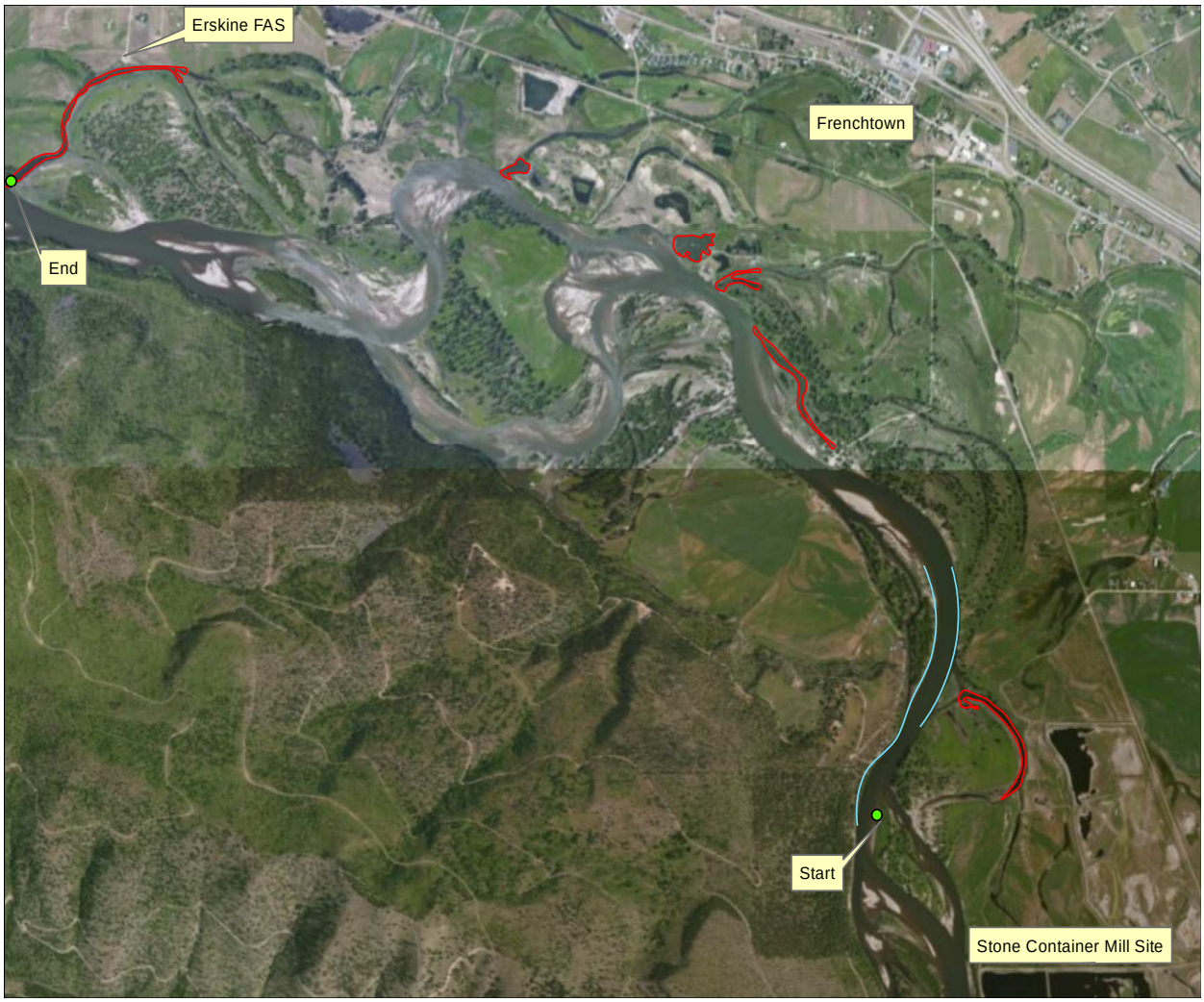

Figure 1. Study area of the Clark Fork River downstream of the Smurfit Stone Container Mill site near Frenchtown, Montana. The red lines depict sampling locations of northern pike and blue lines show where rainbow trout were captured.

Sample preparation and analysis

Northern pike and rainbow trout were separated into 100 mm length groups for compositing. Three, 5-fish samples were analyzed for mercury, selenium, PCBs, dioxins, and furans. Northern pike samples included 5-fish composites 560-660, 660-760, and >760mm TL. One blind duplicate analysis was also submitted from the >760 mm northern pike sample to each lab. Rainbow trout samples include 2, 5-fish composites 285- 350 mm and 350-377 mm TL. Mercury, selenium, and PCBs were analyzed at Energy Laboratories, Billings, Montana.

Dioxins and furans were analyzed at ALS Environmental, Houston, Texas. Dioxins and Furans congeners were analyzed individually and toxic equivalency factors (TEF) for each congener were used to calculate the toxic equivalent (TEQ) value for each composite sample to determine fish consumption limits for carcinogenic health endpoints. Results from Hg and PCB analyses were compared to human health meal guidance developed by the Montana Department of Health and Human Services (Table 3). Results from Se, 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 3).

Results

Mercury, selenium, PCBs, dioxins, and furans were all detected in fish collected from the Clark Fork River immediately below the Smurfit Stone Container facility (Table 1). Mercury was detected in all fish composites, including levels in northern pike that warranted consumption advisories for women and children (all size groups) and adults (>760 mm; Tables 2 and 3). Concentrations of selenium detected in fish tissues were found at normal concentrations (<0.5 mg/kg) and did not warrant consumption advisories for either species. PCB Aroclor 1254 was detected in the two size groups of northern pike (both 560-660 and >760 mm). In the > 760 mm northern pike group, mean PCB concentrations of 0.0655 mg/kg ww result in a consumption advisory of 4 meals/month (Tables 2 and 3). Dioxin and furans were detected in all fish composite samples (Tables 1 and 2). Toxic equivalent (TEQ) values were highest in the 2 larger size groups of northern pike (Table 2), however all fish composites warranted fish consumption advisories based on the TEQ concentrations detected (Tables 2 and 3).

Discussion

Mercury and selenium were analyzed due to their bioaccumulative potential and human health concerns. Whereas Selenium and Mercury have been found in varying concentrations in the region, PCBs and dioxins/furans were previously detected on the Smurfit Stone Container Mill site and the concentrations of these contaminants detected in the fish tissues likely originated from this source.

This phase of sampling and analysis represents a preliminary and screening level study, since fish were not collected upstream or further downstream of the Smurfit Stone Container site, nor were other species collected. Collecting additional samples from a variety of locations in the future would help to

explain the extent of the exposure area. Moreover, an extensive aquatic health study would better characterize the risk of these contaminants to biota and humans consuming fish from this area of the Clark Fork River. Despite the small sample sizes and limited scope of this study, these data unequivocally demonstrate the presence of deleterious toxins, specifically PCB's, dioxins and furans in the environment that likely originated from the Stone Container Mill site. It will be important in the future to determine the spatial scale of the toxins in the environment, the ecological effects and effects on other organisms and further characterize risks to human health. Furthermore, monitoring clean up of the site will be imperative to understand the efficacy of such remedial activities.

In the meantime, these data suggest that it is advisable that consumption of northern pike consumption should be reduced to 1 meal/ month. Since many species of fish in the Clark Fork river are vagile organisms , their presence in the reach immediately downstream of Smurfit Stone Container constitutes a small portion of their life history or habitat use, it is possible they are a vector for the spread these toxins over a large geographic scale. Investigating a sedentary species might be a better indicator of pervasiveness in the aquatic environment, for example longnose dace (*Rhinichthys cataractae*), common in this reach of river, whereas sculpin species (*Cottus spp*) have been used as very effective animal for monitoring and detecting anthropogenic pollution in rivers including pulp mill effluent monitoring (e.g., Galloway et al 2003). However, since the 1980's sculpin have not been detected in this part of the Clark Fork River. Moreover, benthic macro-invertebrates are often collected and analyzed as bio-indicators for local sources of pollution and are easily collected.

Whereas because of biomagnification and accumulation we do not expect lower trophic position and shorter lived fish (like rainbow trout) to display very high levels of dioxins, furans or PCB's, however, longer lived and animals that are in a higher trophic position, i.e., and feed on rainbow trout (or any fish), e.g., American mink (*Mustela vison*), Osprey (*Pandion haliaetus*), and Great Blue Heron (*Ardea herodias*) can be at risk.

The toxicology results from these samples may represent a very conservative assessment of the toxicity of fish to ecological health. Since the intent of this study was to characterize risks to human heath via consumption of fish, we only tested fillets. However, since most toxins are accumulated and stored in fat and organs it is likely that the levels of these toxins (PCB's, dioxins, furans, Se and Hg) probably occur in fish organs and fats in a higher quantity and, thus, are a hazard to animals that consume them. However, the toxicology results from these samples represent the toxicity of fish to human health; risks to ecological receptors were not specifically evaluated.

Table 1. Results of contaminant detections for 3 northern pike (NP) and 2 rainbow trout (RB) size groups (mm TL) collected from the Clark Fork River immediately below the Smurfit Stone Container facility.

Analyte	Congener	NP (560-660 mm)	NP (660-760 mm)	NP (>760 mm)	RB (250-350 mm)	RB (>350 mm)
Hg		x	x	x	x	x
Se			x	x	x	x
PCBs	Aroclor 1254	x		x		
Dioxins	2,3,7,8-TCDD					
	1,2,3,7,8-PeCDD	x		x		
	1,2,3,4,7,8-HxCDD					
	1,2,3,6,7,8-HxCDD		x	x	x	
	1,2,3,7,8,9-HpCDD			x	x	
	1,2,3,4,6,7,8-HpCDD	x	x	x	x	x
	OCDD	x	x	x	x	x
Furans	2,3,7,8-TCDF	x	x	x	x	x
	1,2,3,7,8-PeCDF			x		
	2,3,4,7,8-PeCDF	x		x		
	1,2,3,4,7,8-HxCDF	x		x		
	1,2,3,6,7,8-HxCDF	x				
	2,3,4,6,7,8-HpCDF					
	1,2,3,7,8,9-HxCDF				x	x
	1,2,3,4,6,7,8-HpCDF	x	x	x	x	x
	1,2,3,4,7,8,9-HpCDF					
	OCDF	x	x	x	x	x

Table 2. Contaminant results from 5-fish composite muscle tissue analyses of northern pike (NP) and rainbow trout (RB) collected from the Clark Fork River immediately below the Smurfit Stone container facility (see Figure 1). W&C represents women and children; Adults represents men > 18 years old and women not of childbearing age. m/m represent the number of meals/month (8-ounce serving) that can be safely consumed base on the level of the contaminant found in the fish muscle tissue. Results shown with "U" represent unrestricted consumption. Results shown with "ND" represent a sample that resulted in a non-detect of the analyte. All results are reported in wet weight.

Species	Length Group (mm)	Hg (mg/kg)	Hg (W&C) m/m	Hg (Adults) m/m	Se (mg/kg)	Se m/m	PCBs (mg/kg)	PCBs m/m	Dioxins-Furans (TEQ, ng/kg)	Dioxins-Furans m/m
NP	560- 660	0.150	7	U	ND	U	0.023	U	0.236	2
NP	660- 760	0.188	6	U	0.099	U	ND	U	0.143	4
NP	> 760	0.253	4	11	0.138	U	0.064	4	0.233	2
NP	> 760 dup.	0.240	4	11	0.120	U	0.067	4	0.338	1
RB	250- 350	0.046	U	U	0.132	U	ND	U	0.131	4
RB	250- 350	0.031	U	U	0.132	U	ND	U	0.126	4
RB	> 350	0.034	U	U	0.126	U	ND	U	0.120	4
RB	>350	0.046	U	U	0.132	U	ND	U	0.130	4

Table 3. Fish consumption meal guidance for mercury (Hg), selenium (Se), PCBs, and Dioxins/Furans. All concentrations are evaluated as wet weight (ww).

Mercury (Hg) Women & children		
Hg range (ug/g ww)		meals/month
>1.18		None
0.59	1.18	1
0.39	0.59	2
0.29	0.39	3
0.23	0.29	4
0.20	0.23	5
0.17	0.20	6
0.15	0.17	7
0.13	0.15	8
0.12	0.13	9
0.11	0.12	10
0.10	0.11	11
0.09	0.10	12
<0.09		Unrestricted

Mercury (Hg) Other Adults		
Hg range (ug/g ww)		meals/month
>2.85		None
1.42	2.85	1
0.95	1.42	2
0.71	0.95	3
0.57	0.71	4
0.47	0.57	5
0.41	0.47	6
0.36	0.41	7
0.32	0.36	8
0.29	0.32	9
0.26	0.29	10
0.24	0.26	11
0.22	0.24	12
<0.22		Unrestricted

Selenium (Se) All Consumers		
Se range (ug/g ww)		meals/month
>94		None
>47	94	0.5
>23	47	1
>16	23	2
>12	16	3
>5.9	12	4
>3.9	5.9	8
>2.9	3.9	12
>1.5	2.9	16
<1.5		Unrestricted

Dioxins/Furans All Consumers		
TEQ range (ng/kg ww)		meals/month
>1.2		None
>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

PCBs All Consumers		> 0.47	0.11-0.47	0.025-0.10	< 0.025
(ug/g ww)	meals/month	None	1	4	Unrestricted

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