Report of the 2005 & 2006 Chlorine Monitoring: Kootenai River at Bonners Ferry, Idaho

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Abstract

The Kootenai River near Bonners Ferry, Idaho is considered to be prime historic spawning habitat for many fish species, including the endangered Kootenai River white sturgeon. It has been suggested that physical (i.e. water depth) or chemical barriers may be inhibiting migration, spawning and successful reproduction of fish in and above this section of river. Chlorine is used by the City of Bonners Ferry for back-flushing of the city water intake and for municipal wastewater sterilization prior to releasing wastewater into the Kootenai River. Therefore, chlorine testing was undertaken to provide data to assess the potential effect on aquatic organisms in the Kootenai River. The results of this study showed in-river concentrations (0.02-0.09 mg/L daily average; 0.02-0.04 mg/L weekly average) that frequently exceeded method detection limits of 0.020 mg/L, and the method detection limit exceeded EPA freshwater Life Criteria (0.010 mg/L). The results of this study suggest that chlorine should be considered a potential limiting factor for aquatic productivity and a potential barrier to fish migration. Therefore, the recommendations provided at the end of this report should be implemented to further assess the potential of chlorine as a limiting factor to productivity and fish migration.

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Introduction

Chlorine is a powerful oxidizing agent with high solubility in water (Singleton 1989). In its free form, chlorine does not occur naturally except under unique circumstances; therefore, the occurrence of chlorine is generally the result of anthropogenic activities. Chlorine is primarily used as a sterilizing agent or disinfectant for sewage or drinking water. When chlorine is added to water, it hydrolyzes into compounds that are referred to as "Free Available Chlorine" or "FAC". The FAC may bind with other compounds in the water (such as ammonia in sewage effluent or receiving waters) to form chloramines, nitrogenous compounds or a mixture of these compounds. The compounds resulting from this binding action are referred to as the "combined available chlorine". The sum of FAC added to the "Combined Available Chlorine" (CAC) is referred to as "Total Residual Chlorine" or "TRC". Although both FAC and TRC are reported, TRC is the primary focus of this report because it is the form of chlorine for which available water quality criteria have been established.

Chlorine residuals in water generally decrease over time, but a significant amount may persist for up to 3 days (Esvelt et al. 1973). Proven physiological effects resulting from chlorine exposure include altered behaviour and response as well as cellular and genetic damage (Singleton 1989). In fact, aquatic organisms are particularly sensitive to residual chlorine (Singleton 1989).

The chemical mechanism by which residual chlorine incapacitates aquatic life is not completely understood. However, it has been suggested that the gills are the primary site of toxicity in fish (Bass and Heath 1977, Cairns et al. 1975) and that gill tissue damage as well as mucous accumulation result in acute death by asphyxiation. Chlorine toxicity has also been associated with chronic effects in aquatic organisms. For example, two studies assessing the effects of chlorine on fish cited changes in blood characteristics and decreased growth (Larson et al. 1977; Zeithoun et al. 1977). Rosenkranz (1973) found that chlorine exposure can result in behavior disruption through decreased activity. Additional studies assessing the effects of chlorine on invertebrates show that chlorine can negatively affect reproductive ability in water fleas (Done 1961), periphyton biomass can be decreased, and zooplankton mortality can increase (Carlson 1976; Grossnickel 1974).

The Kootenai River near Bonners Ferry is considered to be prime historic spawning habitat for many fish species, including the endangered Kootenai River white sturgeon (Paragamian et al. 2001). However, monitoring of white sturgeon spawning activities has shown limited spawning within this section of river (Paragamian et al. 2001). It has been suggested that physical (i.e. water depth) or chemical barriers are potentially blocking fish migration and preventing spawning in and above this section of river. Although DeGraeve and Ward (1977) have shown that fish residing within areas of sublethal chlorine exposure were capable of tolerating higher levels during consecutive exposures, non-resident fish that are merely migrating through an area of high chlorine concentration will not be acclimated to similar tolerance levels and are more likely to show physiological and behavioral response to exposure (i.e. avoidance).

A chemical barrier of concern is chlorine because the City of Bonners Ferry currently uses this chemical to sterilize primary sewage effluent and to back flush the city water intake. Under a U.S. EPA NPDES permit, the City of Bonners Ferry is allowed to discharge effluent containing TRC concentrations up to 0.500 mg/L (average monthly limit) or 0.750 mg/L (average weekly limit; U.S. EPA 2003) and is not required to monitor chlorine concentrations within the river, after mixing. In order to assess the potential impacts of chlorine on white sturgeon spawning, chlorine monitoring was initiated during the key sturgeon migration and spawning period.

Methods

Five chlorine monitoring transects were established in the Kootenai River between the Boundary County Fairgrounds and the Kootenai Tribal Hatchery (Figure 1). Surface water chlorine monitoring was conducted bi-weekly between the dates of April 9 and July 2, 2005, and for three, 3-4 day blocks of time over a one-month period during 2006. Surface water samples were collected from the right, middle and left channel section (facing upstream) of each transect. A DR/850 series Colorimeter (HACH Company, Loveland CO; AccuVac Ampule method) was used to measure FAC and TRC concentrations in surface water samples. Both FAC and TRC were monitored during 2005; however, due to high variability, poor accuracy, and high degree of atmospheric interference with Free Chlorine results, monitoring during 2006 included only TRC. Free Available Chlorine (2005 only) was measured using the USEPA Method 8021 for water, wastewater, and seawater. Total Residual Chlorine (2005 and 2006) was measured using USEPA method 8167 for water, wastewater, and seawater. Method detection limit for both FAC and TRC was 0.02 mg/L. All analyses were conducted in the field, immediately following sample collection.

Basic water quality parameters (dissolved oxygen, total dissolved solids, pH, and conductivity), and temperature (C) were measured with a Hach Sension 156 multi-parameter meter. Flow (m/s) was measured using a Marsh-McBirney Flowmate meter.

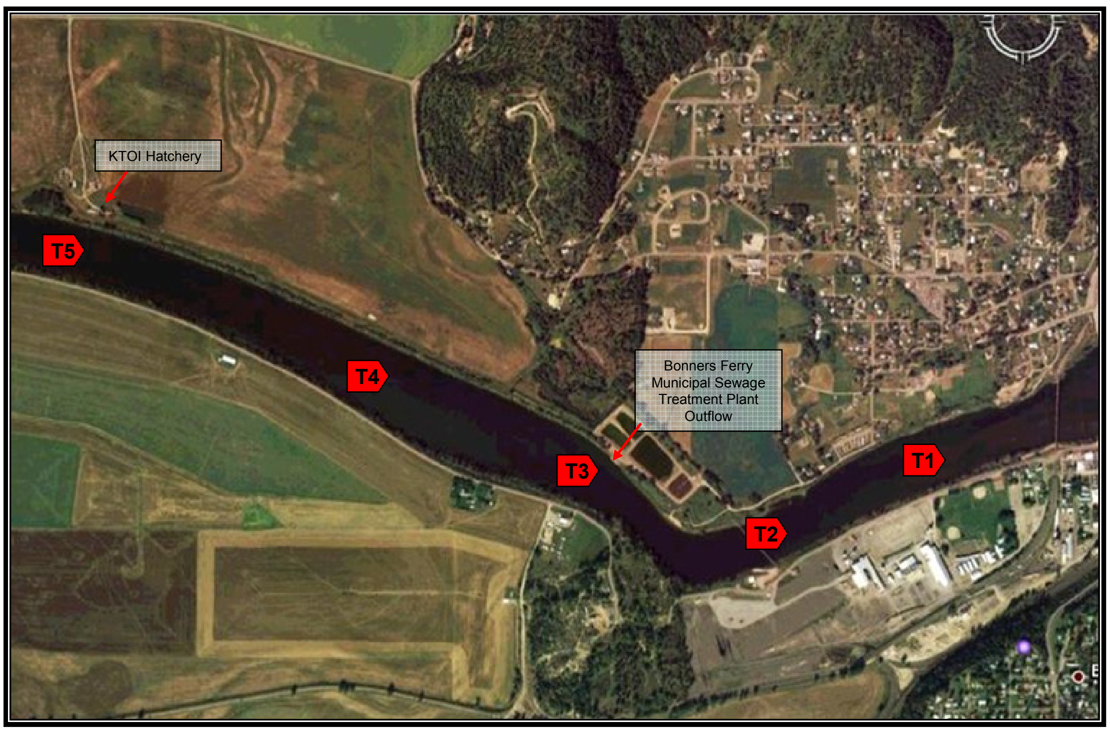

Figure 1. Location of chlorine monitoring sites in the Kootenai River at Bonners Ferry, Idaho.

Results and Discussion

Raw individual detected TRC values for sub-samples (3 per transect, per sample date) ranged from non-detect to 0.090 mg/L in 2005, and non-detect to 0.070 mg/L in 2006. Mean concentrations of TRC (by sample date) fell within the range of non-detect (<0.02 mg/L) and 0.070 mg/L (Figures 2 and 3).

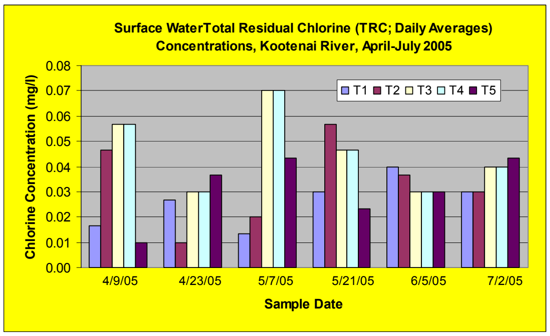

Figure 2. Mean TRC concentrations (by date, all transects) detected in Kootenai River water at Bonners Ferry, Idaho, April-July 2005.

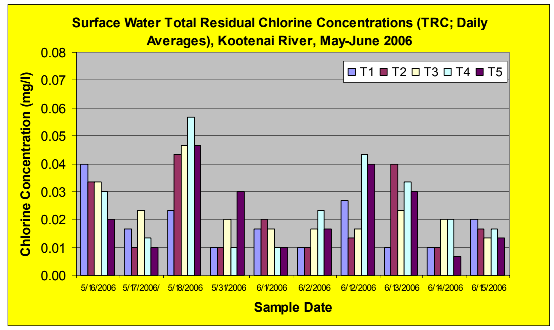

Figure 3. Mean TRC concentrations (by date, all transects) detected in Kootenai River water at Bonners Ferry, Idaho, May-June 2006.

Mean TRC concentrations (by transect) ranged between 0.026 mg/L (T1) and 0.046 mg/L (T3) in 2005 (Figure 4), and non-detect (T1) to 0.026 mg/L (T4) in 2006 (Figure 5). During 2005, mean concentrations of FAC only exceeded method detection limits at T2 (0.021 mg/L). Since sewage effluent is a common source of chlorine in waterways, it was expected that concentrations at sites within the mixing zone (T3-T5) would be higher than those above the mixing zone (T1 & T2).

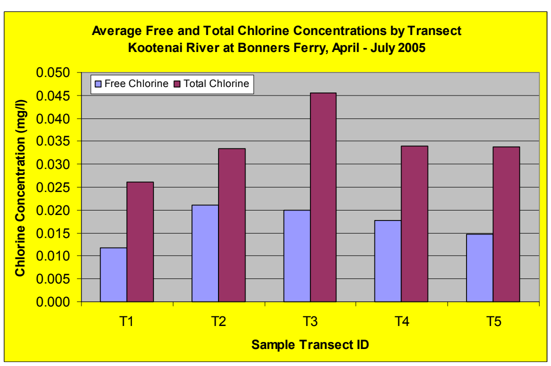

Figure 4. Average FAC and TRC concentrations (by sample transect, all dates) detected in the Kootenai River at Bonners Ferry, Idaho, April – July 2005.

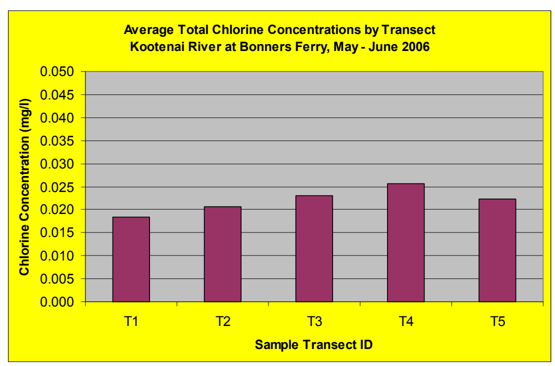

Figure 5. Average TRC concentrations (by sample transect, all dates) detected in the Kootenai River at Bonners Ferry, Idaho, May–June 2006.

Basic water quality parameters, FAC, and TRC concentrations are displayed by sample week in Table 1. Concentrations of TRC peaked during May of both sample years (Figure 6). Although Figure 6 indicates that chlorine concentrations exceeded recommended Water Quality Criteria, these exceedances are suspect because they are based on non-detects equal to ½ MDL, and the method detection limits were higher than established water quality criteria.

Table 1. Mean chlorine concentrations (free and total residual; mg/L) and water quality parameters measured in the Kootenai River at Bonners Ferry, Idaho, April – July 2005 and 2006. Dashed lines indicate dates for which samples were not collected.

Parameter	Sample Week													
	Week 1 - April		**Week 3 - April**		**Week 1 - May**		**Week 3 - May**		**Week 5 – May/Week 1- June**		**Week 3 - June**		**Week 1 - July**	
	2005	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**	**2005**	**2006**
FRC (mg/l)	0.02	---	0.01	---	0.02	---	0.02	---	0.01	---	---	---	0.01	---
TRC (mg/l)	0.03	---	0.03	---	0.04	---	0.04	0.03	0.03	0.02	---	0.02	0.04	---
Conductivity (us/cm)	172.7	---	163.7	---	---	---	191.7	152.3	219.5	210.9	---	209.3	225.6	---
DO (mg/l)	11.0	---	12.2	---	10.2	---	10.7	10.3	9.6	11.0	---	10.5	12.0	---
DO (% saturation)	98.0	---	117.5	---	97.4	---	99.2	102.5	99.4	121.0	---	105.7	125.2	---
Velocity (m/s)	1.7	---	0.32	---	0.42	---	0.45	0.71	0.40	0.55	---	175.0	0.38	---
pH	8.31	---	8.29	---	8.16	---	7.86	7.94	8.40	8.35	---	---	8.35	---
Total Dissolved Solids (mg/l)	82.6	---	78.1	---	---	---	91.7	71.0	105.2	100.9	---	100.0	108.1	---
Temperature (C)	5.7	---	8.7	---	9.4	---	7.8	9.2	11.5	9.9	---	12.1	13.2	---

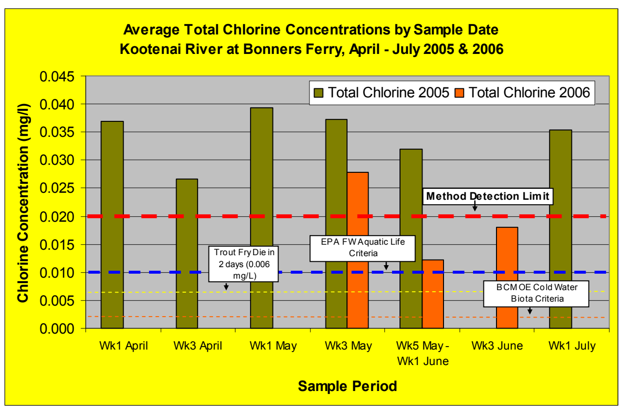

Figure 6. Weekly average TRC concentrations in relation to established Water Quality Criteria, Kootenai River at Bonners Ferry, Idaho, April-July 2005 & 2006.

The U.S. EPA freshwater aquatic life criteria (U.S. EPA 1985, Idaho Department of Environmental Quality 2005) for TRC is established at 0.011 mg/L (4-day average concentration; not exceeded more than once every 3 years) and 0.019 mg/L (1-hour average concentration; not exceeded more than once every 3 years). Presently Idaho water quality criteria are identical to EPA criteria; however, in the 1985 Idaho Water Quality Standards and Wastewater Treatment Requirements, the recommended criterion for chlorine was established at 0.002 mg/l (Idaho Department of Health and Welfare 1980). This later value is identical to cold water biota criteria established for British Columbia, Canada (Canadian Council of Resource and Environmental Ministers 1987). The Canadian criteria appear to be based on a conservative approach that protects a wider range of organisms (than USEPA criteria) and addresses the type of exposure (i.e. continuous or intermittent). Recommended CCME criteria for intermittent exposures of up to 120 minutes duration are listed in Table 2. If detected concentrations represent true concentrations throughout the full course of a given day, our results suggest that the 90-120-minute intermittent exposure criteria may have been exceeded. It also appears that the 45 and 60-minute criteria may have been exceeded over the course of several days and at several of the sample transects.

Table 2. CCME criteria for intermittent chlorine exposure (Canadian Council of Resource and Environmental Ministers 1987)

Duration of Exposure (minutes)	TRC Concentration (mg/L)
Less than 25	0.100
30	0.087
45	0.064
60	0.052
90	0.038
120	0.031
>120	Use continuous exposure criterion

Based on the results of this study, and assuming that concentrations remained constant within the detected range over the entire two and one-half month period, it is clear that during 2005, TRC concentrations in Kootenai River water at Bonners Ferry exceeded the U.S. EPA and Idaho criteria by two or more times the allowable concentration and they clearly exceed CCME standards by an even larger gap (Idaho Department of Environmental Quality 2005, USEPA 1985, British Columbia Ministry of Health 1982, Canadian Council of Resource and Environmental Ministers 1987). Water Quality Criteria exceedances during 2006 are suspect due to low method detection limit; however, it appears that criteria were exceeded during the third week of May.

Although studies investigating chronic and acute toxicities of TRC on freshwater organisms show a wide range, some basic guidelines are provided by these studies. Table 3 shows a summary of results from several of these published studies in relation to effects of residual chlorine on aquatic organisms.

Table 3. Summary of aquatic organism effects of total residual chlorine (TRC), at concentrations within the range of those detected in the Kootenai River near Bonners Ferry, Idaho, 2005 and 2006.

Organism	Concentration (mg/l)	Duration of Exposure	Effect	Reference
Periphyton	0.001 & 0.004	15-wk	Decrease in biomass	Carlson 1976
Phytoplankton	$\leq$0.028	24-hr	50% Reduction in Nitrogen Uptake	Toetz et al. 1977
Rotifer	0.032	1-hr	LC50	Grossnickle 1974
	0.027	4-hr	LC50	Grossnickle 1974
	0.013	24-hr	LC50	Grossnickle 1974
	0.019	4-hr	LC50	Beeton et al 1976
Copepods	0.041	48-hr	LC50	Ward and DeGraeve 1980
	0.063	48-hr	LC50	Ward and DeGraeve 1980
Water flea (*D. magna*)	0.002	1 wk	LC50	Arthur et al. 1975
	0.002	2 wk	Decreased reproduction	Arthur et al. 1975
	0.070	10.5-hr	100% Mortality	Ward et al. 1976
	0.011	48-hr	30% mortality	Ward et al. 1976
	0.002-0.007	7-day	LC50	Arthur et al. 1975
Amphipod	0.035	15-wk	80% Mortality	Arthur and Eaton 1971
	0.003-0.016	15-wk	Reduced reproductive success	Arthur and Eaton 1971
	0.019	20-wk	Decreased reproduction	Arthur et al. 1975

	0.054	16-wk	Decreased survival	Arthur et al. 1975
Mayfly	0.053	11-hr	LT50	Gregg 1975
	0.010-0.011	24-hr	LC50	Williams et al. 2003
	0.005-0.007	48-hr	LC50	Williams et al. 2003
	0.004-0.005	96-hr	LC50	Williams et al. 2003
Coho Salmon	0.016	24-hr	Mortality threshold	Rosenberger 1972
	0.004	96-hr	Mortality threshold	Rosenberger 1972
	0.023	3-wk	Decrease in growth	Larson et al. 1977
	0.003-0.05	12-wk	Hemolytic anemia	Buckley 1976
Rainbow Trout	0.010	96-hr	Minimum LC50	Cairns and Conn 1979
	0.040	96-hr	Average LC50	Cairns and Conn 1979
	0.014	96-hr	Minimum LC50	Basch et al. 1971
	0.020	96-hr	Average LC50	Basch et al. 1971
	0.069	96-hr	LC50	Ward and DeGraeve 1978
Brown Trout	0.020	11-hr	50% Mortality	Pike 1971
	0.050	6-hr	50% Mortality	Pike 1971
Brook Trout	0.005	7-day	Locomotory activity depressed	Dandy 1972
	0.010	7-day	Lethal Threshold	Dandy 1972

Summary and Recommendations for Future Monitoring and Management

The presence of chlorine in surface waters is the result of anthropogenic sources; therefore, TRC detected in this study is likely a component of sewage and water treatment operations conducted for the City of Bonners Ferry at both the sewage treatment plant and the water intake upstream of the city center. Although the results of this study suggest that chlorine concentrations in the Kootenai River may be a potential limiting factor for productivity, two limitations prevent definitive interpretation:

1) **The number of samples taken was limited to one per day:** One sample per day is likely insufficient because in order to determine if continuous or intermittent exposure criteria apply, and to assure that the 2-hour per day exposure duration established by USEPA has not been exceeded, interval sampling should be conducted over full 24-hour periods. This 2-hour per day exposure duration is assumed to allow enough time between exposures for complete recovery of aquatic organisms and thus prevent toxic carry-over.

2) **Method detection limits for the DR/850 series Colorimeter are higher than established water quality criteria:** Equipment method detection limits are not adequate for indicating the degree that water quality criteria are exceeded in cases where concentrations were below the method detection limit and are substituted with ½ MDL. Because water quality criteria fall below the method detection limit, substitution of any value other than zero for <MDL values indicate (possibly erroneously) that results represent an excursion above water quality criteria. Therefore, the closer the method detection limit is to zero, the more accurate the interpretation.

Considering the limitations of this study, it is suggested that future chlorine monitoring efforts be modified to include the following:

1) Current Idaho and EPA continuous exposure water quality criteria for TRC are established at 0.011 (4-day average) and 0.019 mg/l (1-hour average; Idaho Department of Environmental Quality 2005, USEPA 1985), however, it is nearly impossible to reach these method detection limits with currently available field sampling equipment (ENKON and Norelco, Dames and Moore 1997). **Consideration should be given to use of more accurate automated sampling equipment at the outflow** (i.e. a 9184sc Amperometric Free Chlorine Sensor - available through HACH

Corporation). This piece of equipment is able to measure chlorine concentrations down to 0.005 mg/l or 5 ppb and will, therefore, decrease method detection limits and improve accuracy of results.

2) **In-river monitoring of the mixing zone should be conducted during the spring of 2010**, following implementation of the reissued NPDES permit for the City of Bonners Ferry.

3) **Monitoring dates and times (in-situ monitoring) should be coordinated with treatment and release schedules at the sewage treatment plant and city water intake.** Monitoring should be conducted prior to, during and after release of chlorinated by-products from the sewage treatment plant and/or the city water intake. Monitoring should be conducted frequently during the release period and until the concentration at the edge of the initial dilution zone drops below the continuous exposure criterion of 0.002 mg/L (Singleton 1989). Mean concentrations of TRC during any release period should be based on numerical values listed in Table 3 and criteria should not be exceeded beyond any 2-hour block in a 24-hour time period.

4) **Sample volume (in-situ monitoring) should be held to a minimum of 5 samples per day over a 4-day period**; however, more samples may be collected for a period as long as 30 days (Singleton 1989).

5) **Consideration should be given to dechlorination of effluent and use of alternative methods of cleaning the intake system** in order to eliminate the issues with chlorine release altogether.

The Chlorine Monitoring and Dechlorination Techniques Handbook (ENKON and Norelco, Dames and Moore 1997) is an excellent resource for information about chlorine monitoring and dechlorination resources. This handbook is available on-line at: http://www.gvrd.bc.ca/water/chlorin/handbk2.pdf.

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