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May 4, 2012

Dr. Neil Carriker
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Dr. Carriker,

Subject: Preliminary Evaluation of 2011 ORNL Results: *Fish Bioaccumulation*

We are pleased to submit to you our preliminary evaluation of 2011 *Fish Bioaccumulation* Task results.

The enclosed report covers the results for metal bioaccumulation in fish for the spring and fall fish collections.

We hope this preliminary update is useful to you. If you have any questions or require additional information, please call me at (865) 241-9405.

Sincerely,

Dr. Teresa Mathews
Principal Investigator, Fish Bioaccumulation
Environmental Sciences Division
Oak Ridge National Laboratory

c: M. J. Peterson
D. Jones
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Preliminary Evaluation of 2011 ORNL Results: *Fish Bioaccumulation*
May 4, 2012

Introduction

In December 2008, an ash dike at the Tennessee Valley Authority (TVA) Kingston Fossil Plant (KIF) ruptured, releasing over 1 billion gallons of coal fly ash into the Emory and Clinch Rivers. Coal fly ash may contain several contaminants of concern, but of these selenium (Se), arsenic (As), and mercury (Hg) have been highlighted because of their toxicity and tendency to bioaccumulate in aquatic food chains. To assess the potential impact of the spilled fly ash on humans and the environment, a comprehensive biological monitoring program was established, for which resident aquatic organisms are collected to determine contaminant exposure and evaluate the risk to humans and wildlife.

Results for fish bioaccumulation for the 2009-2010 sampling seasons have been previously reported (Adams et al. 2012), and these results were used to guide the Baseline Environmental Risk Assessment (BERA) for the TVA-KIF project (Young et al. 2012). Because Se and Hg, two of the primary fly ash contaminants of concern, are accumulated in fish predominantly through food chain rather than aqueous exposure (Pickhardt et al. 2006, Chapman et al. 2010), there may be a lag between the time these contaminants were released into the affected watersheds and the time body burdens in fish are affected. For this reason, although the BERA considers only 2009-2010 data, it was considered critical to evaluate the bioaccumulation data for the 2011 sampling seasons at the time of the BERA release. This letter report presents a preliminary spatial and temporal evaluation of Se and As concentrations in fish. Details of sampling locations, methods, and sampling strategy were presented in Adams et al. (2012). The current letter report also focuses on a spatial analysis of Hg results for samples collected in 2011. At the present time, results for mercury for samples collected prior to 2011 have not been validated due to low recoveries during analysis (Mathews et al. 2012). Temporal trends for Hg data, as well as a more detailed statistical analysis of data for Se, As, and other metals will be presented in a future report.

Preliminary Results

Selenium

Selenium concentrations in fillets of bluegill, channel catfish, largemouth bass, and redear sunfish show a strong spatial gradient, with the lowest concentrations observed at reference sites (Little Emory River Mile 2 (LERM 2), Emory River Mile 8 (ERM 8), and Clinch River Mile 8 (CRM 8)) and elevated concentrations at the sites affected by the ash spill in the Clinch and Emory Rivers (ERM 3, CRM 3.5, ERM 0.9, CRM 1.5). Selenium concentrations in fillets of all fish species were elevated in the vicinity of the spill site (ERM 3), and increased with increasing distance downstream such that Se concentrations in fish fillets from all species examined were generally highest at CRM 1.5 across all sampling seasons. Of all fish species, selenium concentrations were highest in fillets of redear sunfish across all seasons sampled. The elevated Se concentrations in redear with respect to other species are likely due to dietary preferences, which will be the focus of a future study (Otter et al. 2012). In general, Se concentrations in fish fillets from 2011 were similar to those in 2010, with decreases observed at some sites and increases at others (Table 1).

Summary of 2011 findings for Se:

- Selenium concentrations in redear fillets were higher in 2011 than in 2010 at all sites sampled, though these differences are not statistically significant ($p > 0.05$). (Fig. 1)

- At all fly ash-affected sites (ERM 3, CRM 3.5, ERM 0.9, CRM 1.5), Se concentrations in catfish fillets were higher in fall 2011 than all previous seasons sampled, but these differences were not statistically significant ($p > 0.05$). (Fig. 2)

- For largemouth bass, Se concentrations in fillets were significantly higher at fly-ash affected sites with respect to reference sites ($p < 0.05$). Concentrations in 2011 were generally lower than or similar to concentrations in previous years at most sites, with the exception of at CRM 1.5. A significant increase in Se concentrations was observed between the spring and fall of 2010 ($p < 0.05$), and concentrations remained elevated in 2011 at this site (Fig. 3).

- In bluegill, Se fillet concentrations at ash affected sites in 2011 were generally similar or slightly higher than in previous years, with the exception of CRM 1.5, where concentrations decreased in 2011 (Fig. 4). There are strong seasonal fluctuations observed in Se concentrations of these fish, but this is likely due to sex-related differences, as spring collections are predominantly comprised of females, and fall samples are either a mix of both sexes, or biased towards males. These trends will be examined in future studies.

- The draft ambient water quality criterion (AWQC) for Se currently proposed by the U.S. Environmental Protection Agency (EPA) is based on a fish tissue rather than an aqueous Se concentration (7.91 mg/kg whole body, dry wt.), as the tissue concentration integrates the route, duration, and magnitude of exposure and is therefore considered to be a more consistent indicator of exposure and risk (U.S. EPA 2004). All results presented in this report are for fish fillets, on a wet weight basis, while the criterion is for dry weight, whole body fish. A future study will focus on relating fish fillet to whole body concentrations (Mathews et al. 2012 (in prep)), but for a preliminary analysis, a 1:1 relationship can be assumed between fillet and whole body Se concentrations. Under these assumptions and using the % moisture to convert between wet and dry weight concentrations, the highest fillet concentrations, found in redear from CRM 1.5 in 2011 would translate to a whole body dry weight concentration of approximately 6 mg/kg—elevated, but below the draft criterion. Continued monitoring is needed to evaluate whether concentrations in these fish increase in the future.

Arsenic

Arsenic concentrations in fillets of bluegill, redear, and largemouth bass show a spatial gradient, but results are considerably more variable across seasons and species than for selenium (Table 2). Most results for channel catfish were below analytical detection limits, and are not

considered in this report as they are not drivers of ecological risk. Non-detect data will be considered in a future report. In order to more clearly visualize the spatial gradients in arsenic concentrations without the noise of temporal variation, arsenic concentrations in largemouth bass fillets from all sampling seasons were averaged together, and results are shown in Figure 5. Figure 5 shows that fillets in the vicinity of the ash spill (ERM 4.5, ERM 3, ERM 3.5) were elevated with respect to the reference sites (ERM 8, LERM 2), and decreased with distance from spill. Arsenic concentrations from fish in the Clinch River were higher upstream of the KIF spill, likely because of inputs from DOE facilities (Mathews et al. 2011). Arsenic concentrations in all fish species in 2011 were either similar to, or lower than concentrations in previous sampling seasons.

Spatial trends for Mercury results in 2011

Mercury concentrations in fillets of bluegill, channel catfish, and largemouth bass were lower than the U.S. EPA's National Recommended Water Quality Criterion (NRWQC) of 0.3 mg/kg (wet wt.) Hg in fish fillets, except at ERM 8 for largemouth bass and ERM 3 for channel catfish and largemouth bass (Table 3). Concentrations in bluegill fillets were low, and no spatial gradient was apparent. Elevated Hg concentrations have historically been found in fish in the Clinch River upstream of the KIF, due to Hg releases from the U.S. Department of Energy (DOE) facilities at Y-12 and ORNL, located approximately at CRM 12 (Brooks & Southworth 2011). The elevated Hg concentrations observed in catfish and largemouth bass fillets at CRM 8 are therefore likely due to inputs from DOE facilities. Elevated Hg concentrations in the Emory River were also observed in the Emory River, upstream of the KIF. Concentrations in the vicinity of the ash spill (ERM 3) were above the NRWQC in bass and catfish, but because of the elevated Hg concentrations throughout the Clinch and Emory River watersheds in the vicinity of the KIF, it is not possible to discern the role of the ash spill on Hg bioaccumulation in fish at this time.

Table 1. Selenium concentrations in fish fillets(mg/kg wet weight) for the TVA KIF project (2009-2011). Values presented represent mean concentrations, ± one standard deviation.

		2009				2010				2011			
		Spring		Fall		Spring		Fall		Spring		Fall	
	Site	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
Bluegill	LERM 2			0.49	0.04	0.50	0.06	0.53	0.10	0.55	0.06	0.56	0.26
	CRM 24			0.51	0.13	0.56	0.16						
	CRM 8	0.59	0.07	0.60	0.09	0.55	0.06	0.63	0.10	0.54	0.07	0.47	0.07
	ERM 8	0.43	0.07	0.55	0.22	0.56	0.28	0.43	0.04	0.46	0.03	0.32	0.04
	ERM 4.5					0.58	0.10	0.53	0.08				
	ERM 3	0.80	0.10	0.83	0.11	0.85	0.16	0.69	0.11	0.92	0.10	0.77	0.11
	CRM 3.5					0.78	0.11	1.09	0.30				
	ERM 0.9	0.77	0.07	0.97	0.16	0.75	0.13	0.88	0.13	0.95	0.07	0.79	0.13
	CRM 1.5	0.70	0.16	0.99	0.13	0.82	0.15	1.30	0.17	1.08	0.14	0.84	0.12
Largemouth bass	LERM 2			0.50	0.05	0.46	0.06	0.52	0.05	0.47	0.08	0.49	0.08
	CRM 8	0.60	0.18	0.48	0.04	0.50	0.06	0.55	0.15	0.62	0.14	0.51	0.11
	ERM 8	0.53	0.13	0.44	0.06	0.45	0.05	0.45	0.13	0.40	0.04	0.43	0.06
	ERM 4.5					0.53	0.12	0.62	0.13				
	ERM 3	0.59	0.11	0.60	0.09	0.66	0.14	0.76	0.05	0.70	0.18	0.58	0.15
	CRM 3.5					0.56	0.08	0.73	0.11				
	ERM 0.9	0.61	0.09	0.68	0.12	0.62	0.07	0.75	0.05	0.65	0.25	0.66	0.11
	CRM 1.5	0.47	0.08	0.42	0.08	0.44	0.05	0.77	0.19	0.77	0.12	0.65	0.20
Redear	LERM 2					0.62	0.04			0.74	0.12		
	CRM 8					0.79	0.09			0.82	0.17		
	ERM 8					0.56	0.06			0.57	0.12		
	ERM 3					0.89	0.18			1.13	0.11		
	ERM 0.9					1.05	0.16			1.17	0.08		
	CRM 1.5					1.02	0.29			1.23	0.27		
Channel catfish	LERM 2							0.29	0.02			0.29	0.08
	CRM 8			0.22	0.05	0.25	0.07	0.27	0.09			0.23	0.05
	ERM 8	0.25	0.09	0.21	0.05	0.24	0.08	0.21	0.02			0.18	0.07
	ERM 3			0.34	0.02			0.37	0.07			0.39	0.11
	CRM 3.5					0.32	0.04	0.25	0.09				
	ERM 0.9			0.35	0.08			0.38	0.08			0.46	0.12
	CRM 1.5	0.37	0.14	0.34	0.11	0.38	0.08	0.38	0.06			0.45	0.10

Table 2. Arsenic concentrations in fish fillets (mg/kg wet weight) for the TVA KIF project (2009-2011). Values presented represent mean concentrations, ± one standard deviation. The majority of arsenic results for channel catfish were below analytical detection limits, and are not presented here.

		2009				2010				2011			
		Spring		Fall		Spring		Fall		Spring		Fall	
	Site	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
Bluegill	LERM 2			0.02	0.02	0.04	0.02	0.02	0.01	0.01	0.00	0.03	0.02
	CRM 24			0.06	0.06	0.08	0.09						
	CRM 8	0.06	0.01	0.05	0.02	0.06	0.02	0.08	0.03	0.04	0.01	0.06	0.03
	ERM 8	0.02	0.01	0.01	0.01	0.08	0.07	0.02	0.01	0.01	0.00	0.02	0.01
	ERM 4.5					0.08	0.02	0.03	0.01				
	ERM 3	0.04	0.01	0.03	0.02	0.07	0.01	0.09	0.04	0.05	0.02	0.06	0.03
	CRM 3.5					0.16	0.04	0.14	0.08				
	ERM 0.9	0.07	0.02	0.05	0.03	0.08	0.04	0.12	0.07	0.06	0.02	0.04	0.02
	CRM 1.5	0.06	0.02	0.03	0.03	0.16	0.10	0.07	0.04	0.06	0.03	0.05	0.02
Largemouth bass	LERM 2			0.11	0.06	0.10	0.04	0.12	0.04	0.15	0.05	0.11	0.06
	CRM 24			0.26	0.13	0.34	0.11						
	CRM 8	0.27	0.05	0.20	0.02	0.24	0.07	0.27	0.07	0.29	0.06	0.20	0.06
	ERM 8	0.18	0.07	0.12	0.06	0.15	0.03	0.15	0.06	0.15	0.04	0.16	0.05
	ERM 4.5					0.17	0.04	0.30	0.07				
	ERM 3	0.15	0.05	0.17	0.02	0.17	0.02	0.21	0.06	0.29	0.04	0.16	0.04
	CRM 3.5					0.25	0.05	0.27	0.07				
	ERM 0.9	0.22	0.06	0.16	0.07	0.27	0.11	0.30	0.09	0.30	0.09	0.19	0.06
	CRM 1.5	0.23	0.05	0.18	0.09	0.21	0.10	0.19	0.07	0.27	0.08	0.21	0.05
Redear	LERM 2					0.06	0.03			0.08	0.04		
	CRM 24					0.24	0.03						
	CRM 8					0.21	0.07			0.25	0.14		
	ERM 8					0.06	0.03			0.03	0.04		
	ERM 4.5												
	ERM 3					0.11	0.03			0.15	0.06		
	CRM 3.5												
	ERM 0.9					0.23	0.04			0.23	0.09		
	CRM 1.5					0.23	0.06			0.19	0.05		

Table 3. Mercury concentrations in fish fillets(mg/kg wet weight) for the TVA KIF project (2011). Values presented represent mean concentrations, ± one standard deviation. Red font indicates concentrations above the U.S. Environmental Protection Agency's National Recommended Water Quality Criterion (0.3 mg/kg wet wt).

	Bluegill		Catfish		Bass	
Site	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
LERM 2	0.07	0.02			0.19	0.03
CRM 24	0.05	0.00				
CRM 8	0.09	0.02	0.24	0.19	0.23	0.10
ERM 8	0.11	0.04	0.26	0.15	0.36	0.16
ERM 4.5						
ERM 3	0.08	0.03	0.37	0.60	0.33	0.23
CRM 3.5						
ERM 0.9	0.09	0.02	0.10	0.03	0.21	0.09
CRM 1.5	0.08	0.02	0.15	0.07	0.19	0.06

Fig. 1. Mean (± 1 standard deviation) selenium concentrations in redear sunfish fillets (mg/kg wet wt.) 2010-2011.

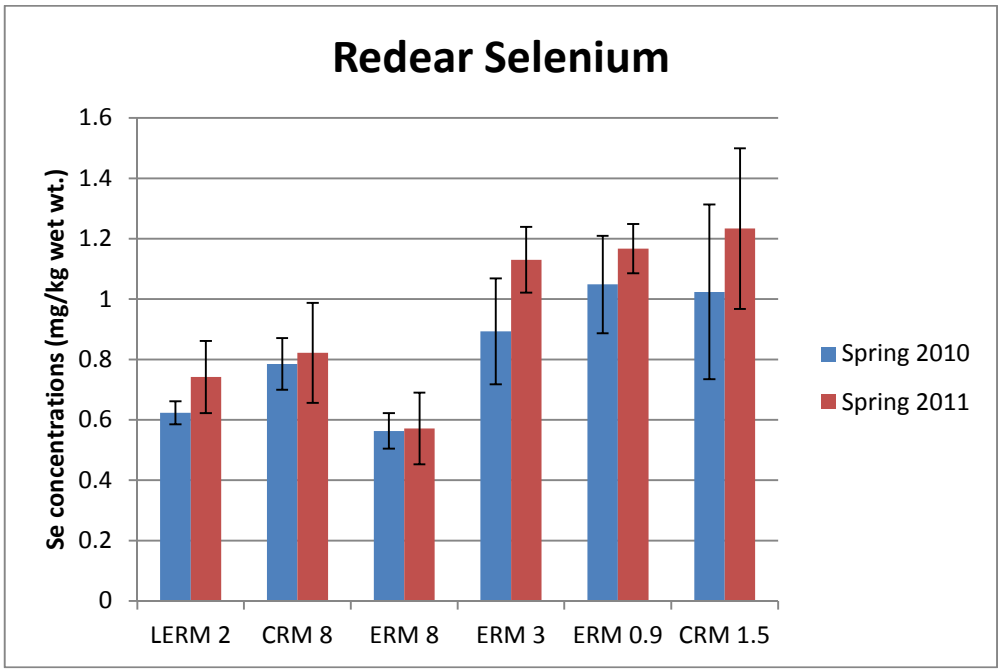


Fig. 2. Mean selenium concentrations in channel catfish fillets (mg/kg wet wt.) 2009-2011.

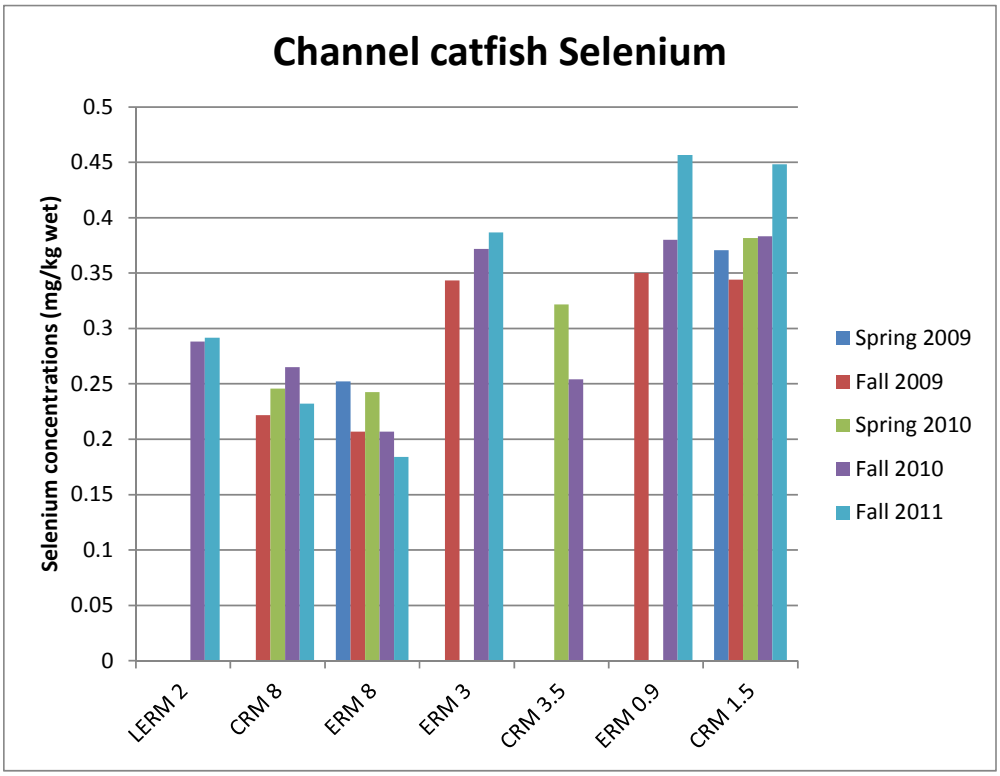


Fig. 3. Mean selenium concentrations in largemouth bass fillets (mg/kg wet wt.) 2009-2011.

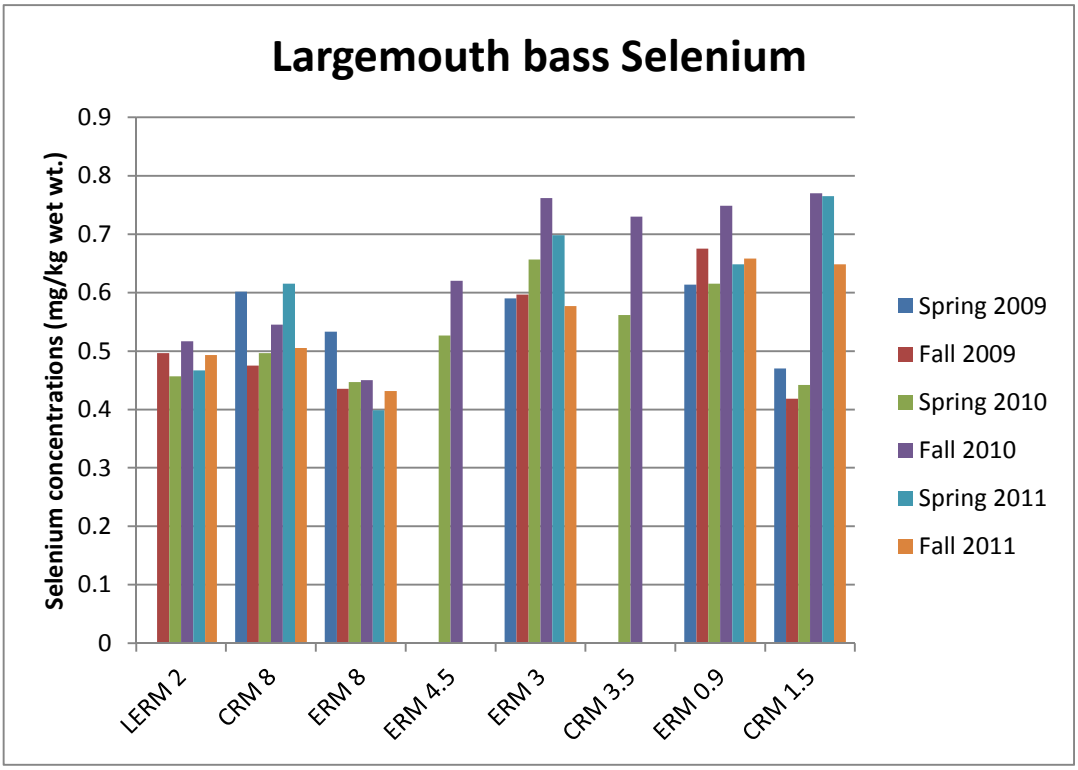


Fig. 4. Mean selenium concentrations in bluegill fillets (mg/kg wet wt.) 2009-2011.

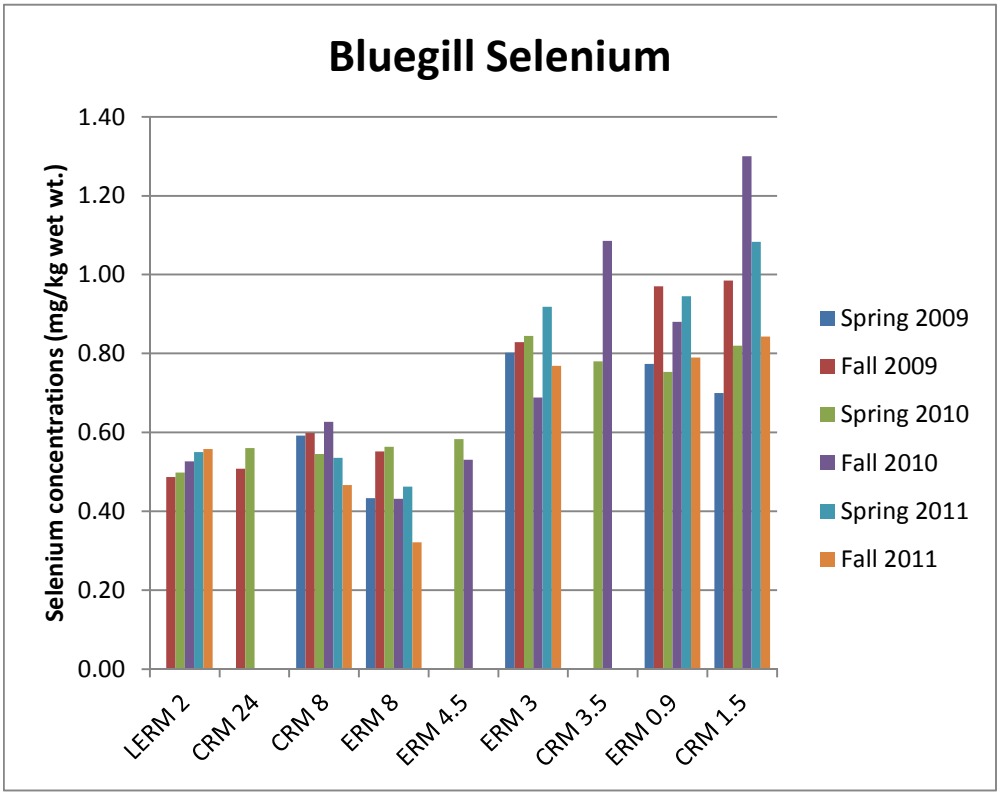
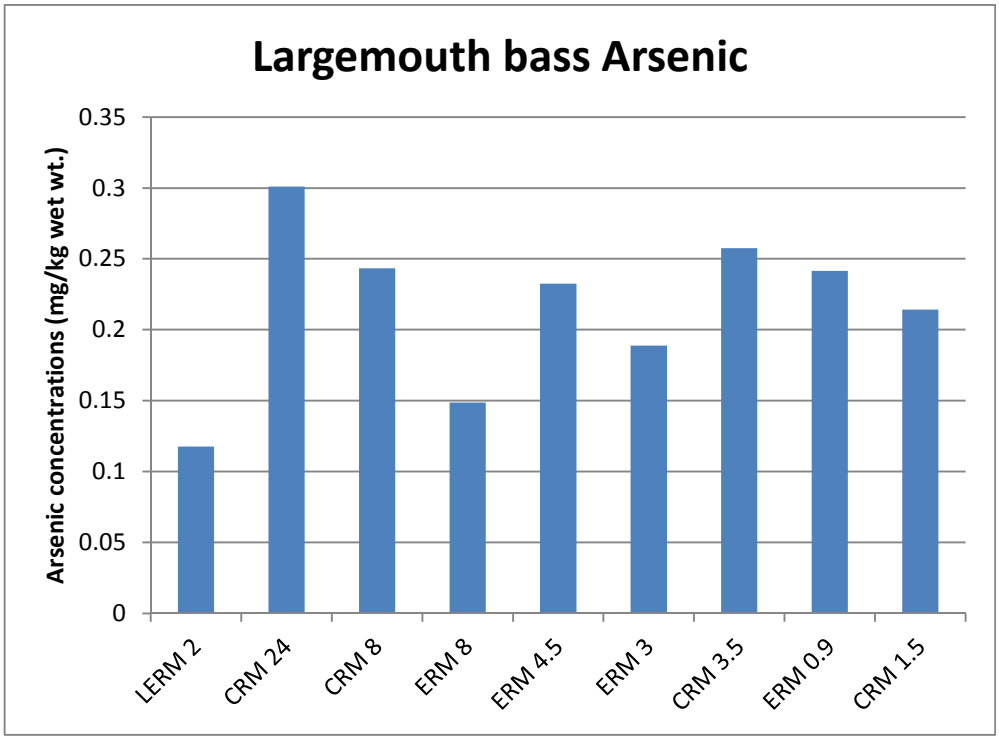


Fig. 5. Mean arsenic concentrations in largemouth bass fillets (mg/kg). Data shown in this figure represent the mean concentrations of all available data, 2009-2011. (See Table 2 for data from each season).



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