CORRESPONDENCE/MEMORANDUM **State of Wisconsin**

DATE: February 3rd, 2023 FILE REF: WQ Sampling

TO: Jason Knutson, Environmental Engineer Supervisor

FROM: Craig Helker, Water Resources Management Specialist

SUBJECT: 2020-2022 WE Energies Tributary Sampling Summary

Overview

In 2020, the Department of Natural Resources undertook water quality monitoring efforts on intermittent and perennial streams draining to the Root River and Lake Michigan to investigate potential elevated metals concentrations in these waterways as reported by the local citizen monitoring group Southeast Wisconsin Clean Power Coalition. The purpose of the Department's 2020 water quality monitoring was to document low-level metals concentrations and perform Whole Effluent Toxicity Testing on local water-bodies. A previous document summarized these 2020 monitoring efforts. In 2021 and 2022, monitoring continued, seeking an ex-panded data set at a subset of previously monitored locations (Map 1.). These locations represented one of the streams draining the WE Energies closed fly-ash landfill and stormwater pond, one draining the active fly-ash disposal site on WE Energies property, and one stream serving as a control location.

The monitoring conducted in 2021 and 2022 consisted of low-level metals concentration monitoring , with the addition of sediment collections in 2022. This document summarizes the results of these collection events and includes the 2020 collection events for ref-erence.

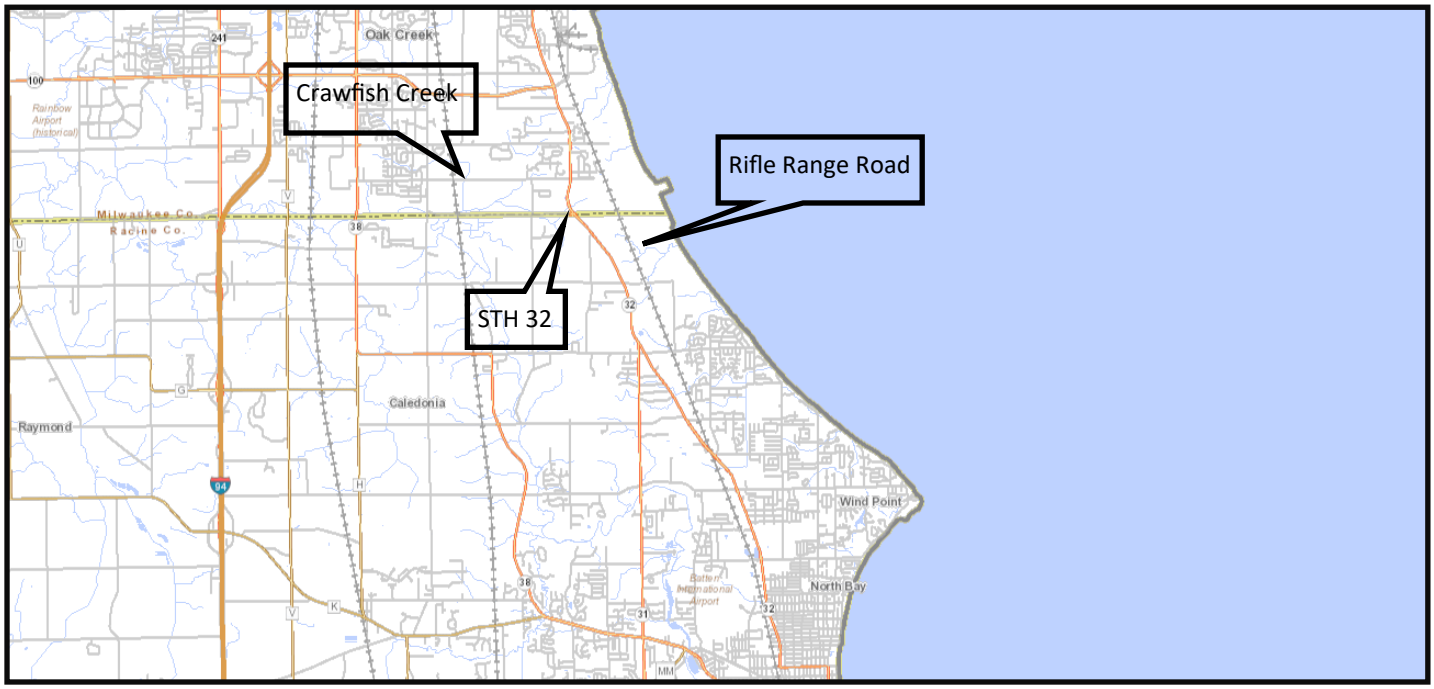
Water Quality Results and Discussion

Sampling Location

- Crawfish Creek, upstream of East Elm Road - (Control Location)
- Unnamed Tributary to Lake Michigan, downstream of Rifle Range Road
- Unnamed Tributary to Root River downstream of State Highway 32

The locations above were sampled August 27th, 2021; December 17th, 2021; June 9th, 2022; and June 29th, 2022. Water sampling followed standard DNR Water Quality Sampling protocols, with laboratory analysis conducted by the Wisconsin State Laboratory of Hygiene.

Map 1. Sampling Locations



Water Quality Results and Discussion cont.

Table 1. shows metals concentrations in surface water collected during six sampling events from 2020 - 2022. Crawfish Creek is considered the control location, with the STH 32 and Rifle Range Road locations representing contribution locations from WE Energies property.

Sampling occurred under a range of flow conditions. Figure 1. shows sampling events in relation to previous rainfall in the local area. Note that no sample was taken at the Rifle Range Road location on 6/29/2022 due to the absence of water in the channel.

Noting obvious outliers in the sampling when compared amongst sites, the metals Boron, Sodium, and Manganese are noted as strong outliers at the Rifle Range Road and STH 32 sampling locations, as well as Lithium. Individually, elevated levels of Cadmium and Molybdenum are noted at STH 32. The Crawfish Creek control site location trends higher for the metals Aluminum, Copper, and Vanadium.

Ch. NR 105, Wis. Admin. Code establishes water quality criteria for toxic substances to protect public health and welfare, the present and prospective use of all surface waters for public and private water supplies, and the propagation of fish and aquatic life and wildlife. Utilizing ch. NR 105, Wis. Admin. Code as a basis of comparison, there were several exceedances of chronic toxicity criteria (CTC), human threshold criteria (HTC), and wildlife criteria (WC) for metals sampled in 2020, 2021, and 2022. Mercury results at all sampled locations during 2020, 2021, and 2022 (excepting Rifle Range Road on 12/17/2022) exceed the WC and the HTC. As a note, background Mercury concentrations of Wisconsin rivers and streams are typically above this threshold. See *https://dnr.wi.gov/Water/wsSWIMSDocument.ashx?documentSeqNo=73704740*.

Secondary values per ch. NR 105, Wis. Adm. Code are a temporary concentration of a substance that ensures adequate protection of the designated use until sufficient data is available to calculate a water quality criterion. Several metals from the sampling effort do not have criteria listed in ch. NR 105, Wis. Adm. Code, so the results are compared to available secondary values which are calculated according to ch. NR 105, Wis. Adm. Code. The instream results for Boron show exceedances for secondary CTC and HTC at Rifle Range Rd and STH 32. The secondary CTC for Manganese was exceeded at all sampling locations. The secondary CTC for Selenium was exceeded once at STH 32 (08/27/2021).

The results of sampling efforts in 2020, 2021, and 2022 show that there are elevated concentrations of certain metals in waters downstream of the active fly-ash storage site upstream of Rifle Range Road and the fly-ash landfill location upstream of STH 32. While none of the results show exceedances of acute and chronic surface water quality criteria, it is apparent that Lithium is present at the Rifle Range Road and STH 32 locations in significantly higher concentrations than the control site on Crawfish Creek. Cadmium and Molybdenum concentrations were notably higher at the STH 32 location.

Figure 1. Sampling events compared with rainfall at General Mitchell International Airport

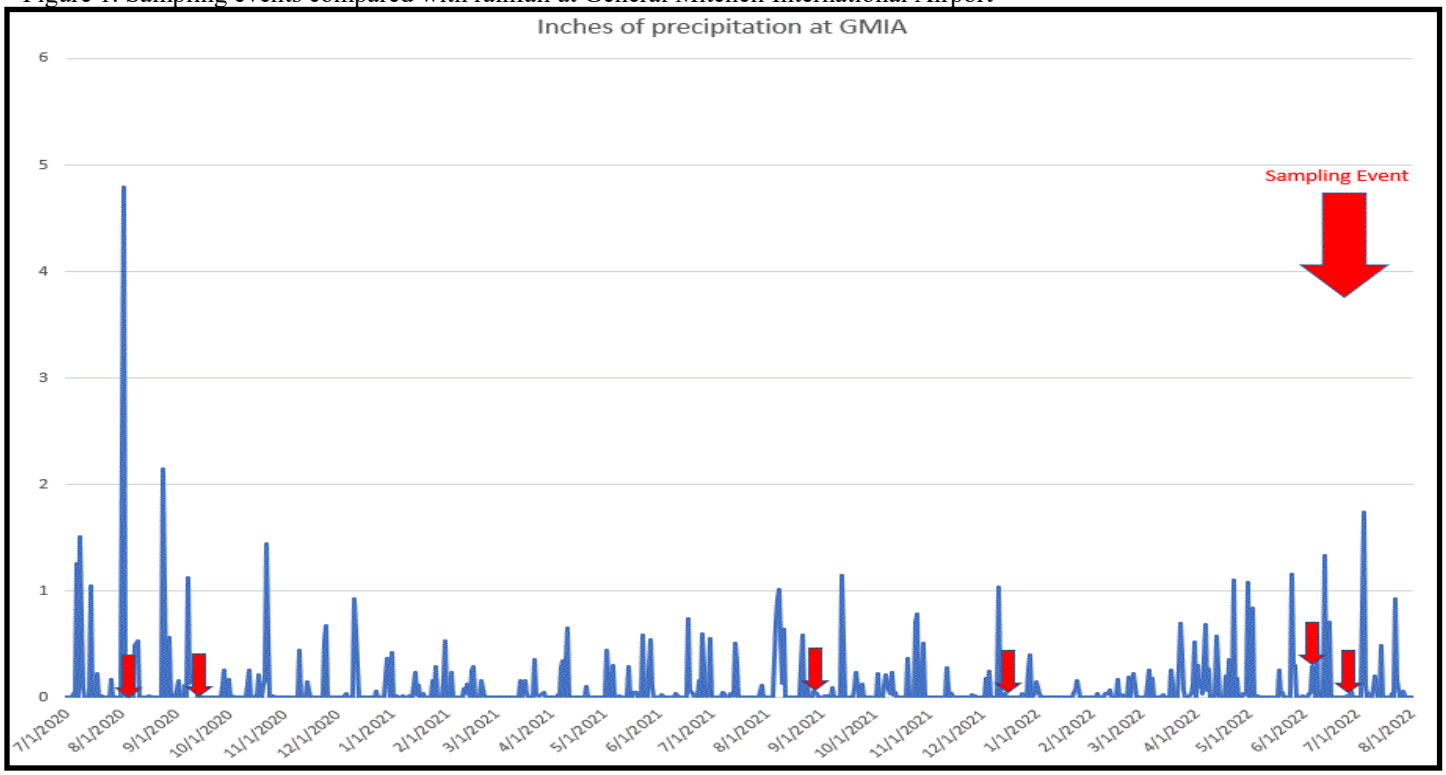


Table 1. Metals concentration

Report Units	µg/L	µg/L	µg/L		µg/L	µg/L	µg/L
Collection Date	8/4/2020	8/4/2020	8/4/2020		9/14/2020	9/14/2020	9/14/2020
Site Name	Crawfish Creek	Rifle Range Road	STH 32		Crawfish Creek	Rifle Range Road	STH 32
Aluminum	160	30.2	50.1		84	55.4	54.5
Arsenic	0.94	1.36	0.80		0.97	1.89	1.16
Boron	39.0	1737[1]	1128[1]		47.7	2204[1]	2384[1,2]
Cadmium	0.017	0.019	0.129		0.020	0.032	0.350
Chromium	0.322	0.155	0.175		0.308	0.170	0.199
Cobalt	0.159	0.126	0.159		0.260	0.300	0.271
Copper	1.81	0.51	1.30		1.12	0.34	0.50
Iron	368	180	220		529	738	288
Lead	0.234	0.045	0.075		0.130	0.133	0.128
Lithium	1.17	15.9	16.8		4.28	17.8	39.0
Manganese	29.9	129[3]	104		67.8	918[3]	266[3]
Mercury	0.004[4]	0.0068[4]	0.0042[4]		0.0026[4]	0.0027[4]	0.0042[4]
Molybdenum	1.54	4.05	31.4		2.79	5.19	73.6
Nickel	0.77	1.06	0.92		1.72	1.21	1.25
Selenium	0.402	1.58	1.34		1.010	1.55	2.41
Sodium	20491	107021	42310		68412	74746	109847
Vanadium	1.07	0.425	0.506		0.97	0.377	0.489
Zinc	2.68	1.69	1.77		1.06	3.02	1.18
[5]							

[1]Exceeds secondary CTC of 1000 µg/L per ch. NR 105, Wis. Adm. Code.

[2]Exceeds secondary HTC of 2490 µg/L per ch. NR 105, Wis. Adm. Code.

[3]Exceeds secondary CTC of 93.48 µg/L per ch. NR 105, Wis. Adm. Code.

[4]*Exceeds* Wisconsin ch. NR 105 Wildlife Criteria and Human Threshold Criteria of 0.0013 mg/L and 0.0015 mg/L.

[5]Additional metals were analyzed, but not shown here for brevity sake. See attachment for full list.

Table 1. (cont)

Report Units	µg/L	µg/L	µg/L		µg/L	µg/L	µg/L
Collection Date	8/27/2021	8/27/2021	8/27/2021		12/17/2021	12/17/2021	12/17/2021
Site Name	Crawfish Creek	Rifle Range Road	STH 32		Crawfish Creek	Rifle Range Road	STH 32
Aluminum	143	1.39	82.8		104	14.00	14.5
Arsenic	2.90	0.51	2.34		0.50	1.55	0.56
Boron	88.3	5370[1,2]	5670[1,2]		110.0	7880[1,2]	4090[1,2]
Cadmium	0.065	0.10	2.040		0.069	0.23	2.630
Chromium	0.251	0.10	0.487		0.207	0.10	0.289
Cobalt	0.226	0.04	0.446		0.166	1.04	0.128
Copper	0.84	0.34	0.50		1.57	1.03	1.12
Iron	631	11.10	628		227	809	108
Lead	0.252	0.01	0.141		0.110	0.08	0.024
Lithium	8.14	16.20	84.0		3.89	42.50	59.0
Manganese	130.0[3]	10.80	2640[3]		24.3	1890[3]	80
Mercury	0.0230[4]	0.0029[4]	0.0366[4]		0.0036[4]	0.0009	0.0036[4]
Molybdenum	6.18	12.00	235.0		6.79	22.70	297.0
Nickel	1.07	1.34	1.75		0.90	3.75	1.01
Selenium	1.770	2.12	7.81[5]		0.818	3.29	3.38
Sodium	30200	258000	82300		214000	370000	535000
Vanadium	2.39	0.13	1.470		0.65	0.41	0.263
Zinc	1.09	0.05	1.21		1.84	0.12	1.46
[6]							

[1]Exceeds secondary CTC of 1000 µg/L per ch. NR 105, Wis. Adm. Code.

[2]Exceeds secondary HTC of 2490 µg/L per ch. NR 105, Wis. Adm. Code.

[3]Exceeds secondary CTC of 93.48 µg/L per ch. NR 105, Wis. Adm. Code.

[4]*Exceeds* Wisconsin ch. NR 105 Wildlife Criteria and Human Threshold Criteria of 0.0013 mg/L and 0.0015 mg/L.

[5]Exceeds secondary CTC of 5 µg/L per ch. NR 105, Wis. Adm. Code.

[6]Additional metals were analyzed, but not shown here for brevity sake. See attachment for full list.

Table 1. (cont)

Report Units	µg/L	µg/L	µg/L		µg/L	µg/L	µg/L
Collection Date	6/9/2022	6/9/2022	6/9/2022		6/29/2022	6/29/2022	6/29/2022
Site Name	Crawfish Creek	Rifle Range Road	STH 32		Crawfish Creek	Rifle Range Road	STH 32
Aluminum	217	11.10	10.4		74		3.5
Arsenic	1.27	0.79	0.85		1.78		1.68
Boron	54.2	2180[1]	2260[1]		55.3		1080[1]
Cadmium	0.037	0.11	0.821		0.026		0.269
Chromium	0.413	0.11	0.156		0.239		0.255
Cobalt	0.240	0.13	0.456		0.367		1.310
Copper	1.98	0.43	0.60		0.58		0.37
Iron	600	74	314		1160	Not taken	1280
Lead	0.188	0.03	0.020		0.130	Dry	0.014
Lithium	2.50	10.80	2.5		2.66		12.4
Manganese	71.2	128[3]	468[3]		365.0[3]		2800[3]
Mercury	0.0080[4]	0.004[4]	0.0100[4]		0.0130[4]		0.0070[4]
Molybdenum	3.23	12.00	96.7		2.26		33.7
Nickel	1.10	1.10	1.36		0.97		2.27
Selenium	1.320	2.42	3.58		1.530		3.93
Sodium	96200	86200	144000		79800		145000
Vanadium	1.18	0.20	0.253		1.17		0.442
Zinc	1.68	1.16	1.72		0.73		1.06
[5]							

[1]Exceeds secondary Chronic Toxicity Criteria of 1000 µg/L per ch. NR 105, Wis. Adm. Code.

[2]Exceeds secondary Human Threshold Criteria of 2490 µg/L per ch. NR 105, Wis. Adm. Code.

[3]Exceeds secondary Chronic Toxicity Criteria of 93.48 µg/L per ch. NR 105, Wis. Adm. Code.

[4]*Exceeds* Wisconsin ch. NR 105 , Wis. Adm. Code Wildlife Criteria and Human Threshold Criteria of 0.0013 mg/L and 0.0015 mg/L.

[5]Additional metals were analyzed, but not shown here for brevity sake. See attachment for full list.

Sediment Sampling Results and Discussion

Sampling Location

- Unnamed Tributary to Lake Michigan, upstream of Rifle Range Road
- Unnamed Tributary to Crawfish Creek, downstream of State Highway 32

Reference Location - Historically sampled

- Crawfish Creek, downstream of East Elm Road (Sampled in 2003 by C. Helker, WDNR)

The locations (Map 2.) above were sampled June 9th, 2022, following standard DNR equipment cleaning and sediment sampling methods, and analyzed at the State Lab of Hygiene.

Results (Table 2.) from the June 9th, 2020 sampling events were compared with the WDNR Consensus Based Sediment Quality Guidelines (CBSQG): *https://dnr.wi.gov/DocLink/RR/RR088.pdf.* The CBSQG are utilized as a predictor of toxicity to aquatic benthic organisms from contaminants. Thresholds of contamination are described in the document, where substances, "...have a lower (Threshold Effect Concentration - TEC) and upper (Probable Effect Concentration - PEC) effect level at which toxicity to benthic-dwelling organisms are predicted to be unlikely (below TEC) and probable (above PEC) respectively." MEC is utilized simply to denote the Midpoint Effect Concentration, or 1/2 of TEC+PEC. Table 2. also contains sediment data collected in 2003 at Crawfish Creek by the author as reference. Note that some metals sampled in 2022 are not shown for 2003. This is due to different lab analysis methods and analytes for the 2003 sampling event.

The results show exceedances of the TEC for Copper, Iron, and Nickel at Rifle Range Road and STH 32, and Manganese at STH 32. The PEC is exceeded for Manganese and Silver at Rifle Range Road, and for Silver at STH 32. The 2003 data, representing the control location, show a possible TEC exceedance for Antimony, but the result is approximate due to laboratory control methods.

Map 2. Sediment Sampling Locations

Table 2. Sediment sampling results

Report Units	Mg/Kg	Mg/Kg		Mg/Kg		Mg/Kg	Mg/Kg	Mg/Kg
Collection Date	6/9/2022	6/9/2022		2003		TEC[1]	MEC[1]	PEC[1]
Site Name	Rifle Range Road	STH 32		Crawfish Creek				
Aluminum	15100	11200		14700*				
Antimony	No detect	No detect		<5*		2	13.5	25
Arsenic	2.69	5.05		9		9.8	21.4	33
Barium	209	78.7		109				
Beryllium	1.13	0.194		0.73				
Boron	49.6	18.5		31				
Cadmium	0.87	No detect		No detect		0.99	3	5
Calcium	47900	31300						
Chromium	31.4	23.4		20.5		43	76.5	110
Cobalt	11.8	12.0						
Copper	33.8	34.3		23.6		32	91	150
Iron	27800	25800				20000	30000	40000
Lead	28	23.0		31		36	83	130
Magnesium	28100	17500						
Manganese	4990	958		370		460	780	1100
Molybdenum Total	ND	42.9						
Nickel	30.7	23.1		19		23	36	49
Potassium	2560	1880						
Selenium	No detect	No detect		No detect				
Silver	7.29	7.07				1.6	1.9	2.2
Sodium	501	1300						
Strontium, Total in solid sample	54.7	29.2						
Thallium	2.6	1.64		68				
Titanium	346	212						
Vanadium	42.6	30.5						
Zinc	161	103		103*		120	290	460

[1], From *https://dnr.wi.gov/DocLink/RR/RR088.pdf*. Note: Not all sampled metals are covered by the CBSQG document

Colors in yellow show TEC exceedances

Colors in orange show MEC exceedance

Colors in red show PEC exceedances

* Matrix spike exceeded