

Background

- The City of Waukesha, Wisconsin was approved to divert and return water from Lake Michigan pursuant to the Great Lakes Compact for its new water supply (currently using groundwater).
- The Fox River in Waukesha, Wisconsin was monitored to determine its water quality baseline. The Waukesha Clean Water Plant (CWP) will cease discharge to the river, approximately 6 MGD, as of 2023.
- The water quality parameters measured were pH, temperature, alkalinity, dissolved oxygen, trace metals (Cr, Cd, Pb, Zn, Ni), base cations (Na, K, Ca, Mg), and common anions (Cl, SO₄²⁻, NO₃⁻, Br, PO₄³⁻).

Materials and Methods:

Sample Collection:

- Ten sample sites along a 36 mile stretch of the Fox River, one upstream and 8 downstream of the CWP, were sampled approximately once a month starting May 25th, 2019. The second sample site, 0.5 miles, was effluent directly from the CWP before entering the river.
- In situ measurements of temperature, pH, alkalinity and dissolved oxygen were made at each sample site.
- Water samples were collected in 250 mL polyethylene bottles for anion and cation analysis and glass amber bottles for analysis of PPCPs.

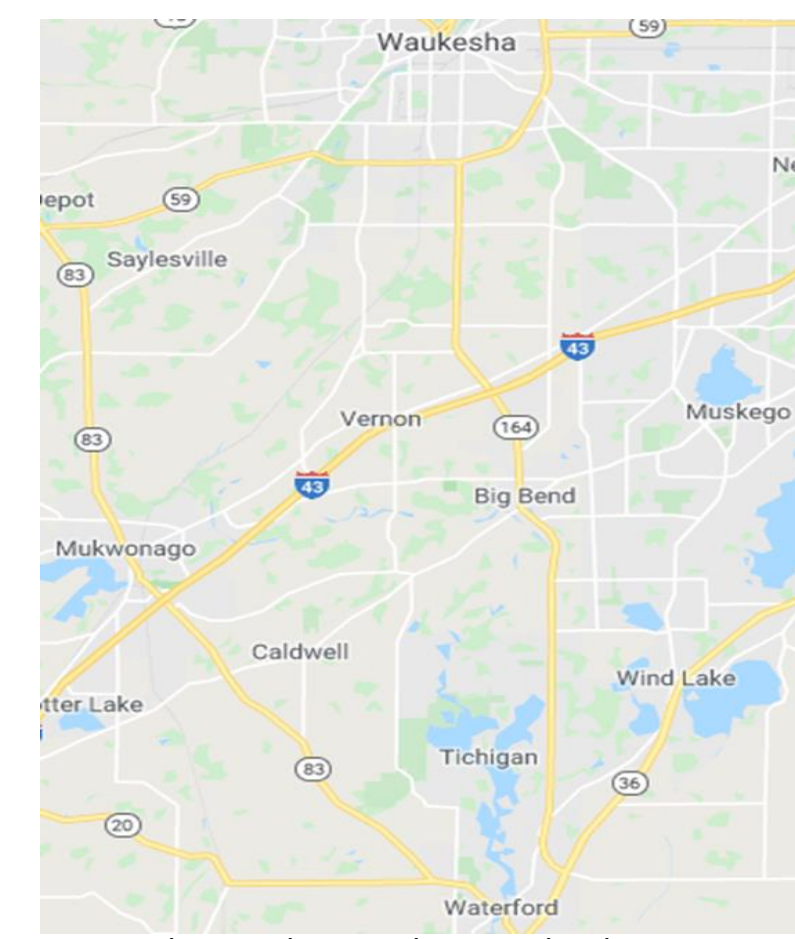


Figure 1a: Grab sample collection at the first sampling site, FR00, of the Fox River in Waukesha.

Figure 1b: Google map showing the distance between the first sampling site at Waukesha and the tenth site at Waterford.

Figure 1c: The last sampling site, FR09, at Waterford, 36 miles far from the first site.

Laboratory Analysis

- Water samples were filtered through a 0.2 micron membrane filter before analysis by ion chromatography or inductively coupled plasma mass spectrometry
- Ion Chromatography was used to analyze common anions in river system - Cl⁻, SO₄²⁻, NO₃⁻, Br⁻, PO₄³⁻ using external standard calibration



Figure 2a: IC set up used to analyze the anions from the water samples and the diluted standard series.



Figure 2b: Set of samples prepared in the conical flasks and 10 mL of it transferred in polyvials to analyze anions present in them.

- Inductively Coupled Plasma - Mass Spectrometry was used for analyzing trace metals and base cations. The isotopes of interest were ²³Na, ²⁴Mg, ³⁹K, ⁴⁴Ca, ⁵²Cr, ⁵⁸Ni, ⁶⁴Zn, ⁶⁵Cu, ¹¹¹Cd, and ²⁰⁸Pb.



Figure 3a: ICP-MS and the speciation column inside the system that ionizes the samples, produces flames and atomizes the sample for detection.



Figure 3b: 10 mL of standard, diluted water samples from the sites and diluted water samples in 15 mL falcon tubes ready for analysis in ICP-MS.

Results and Discussions

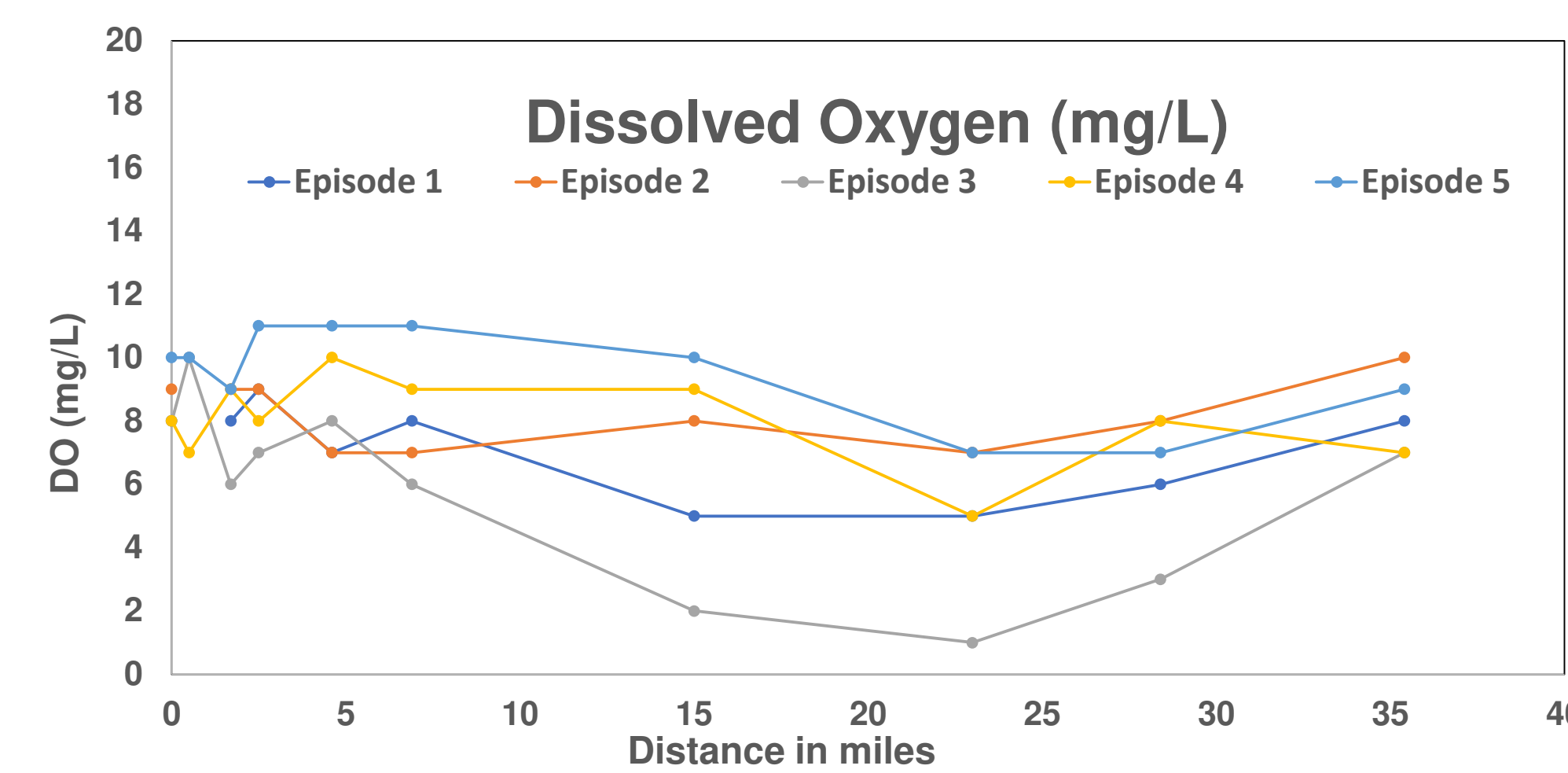


Figure 4: DO (mg/L) as a function of distance from the Waukesha Clean Water Plant for each sampling episode. In general, DO values ranged from 6-12 mg/L, therefore the system remained aerobic.

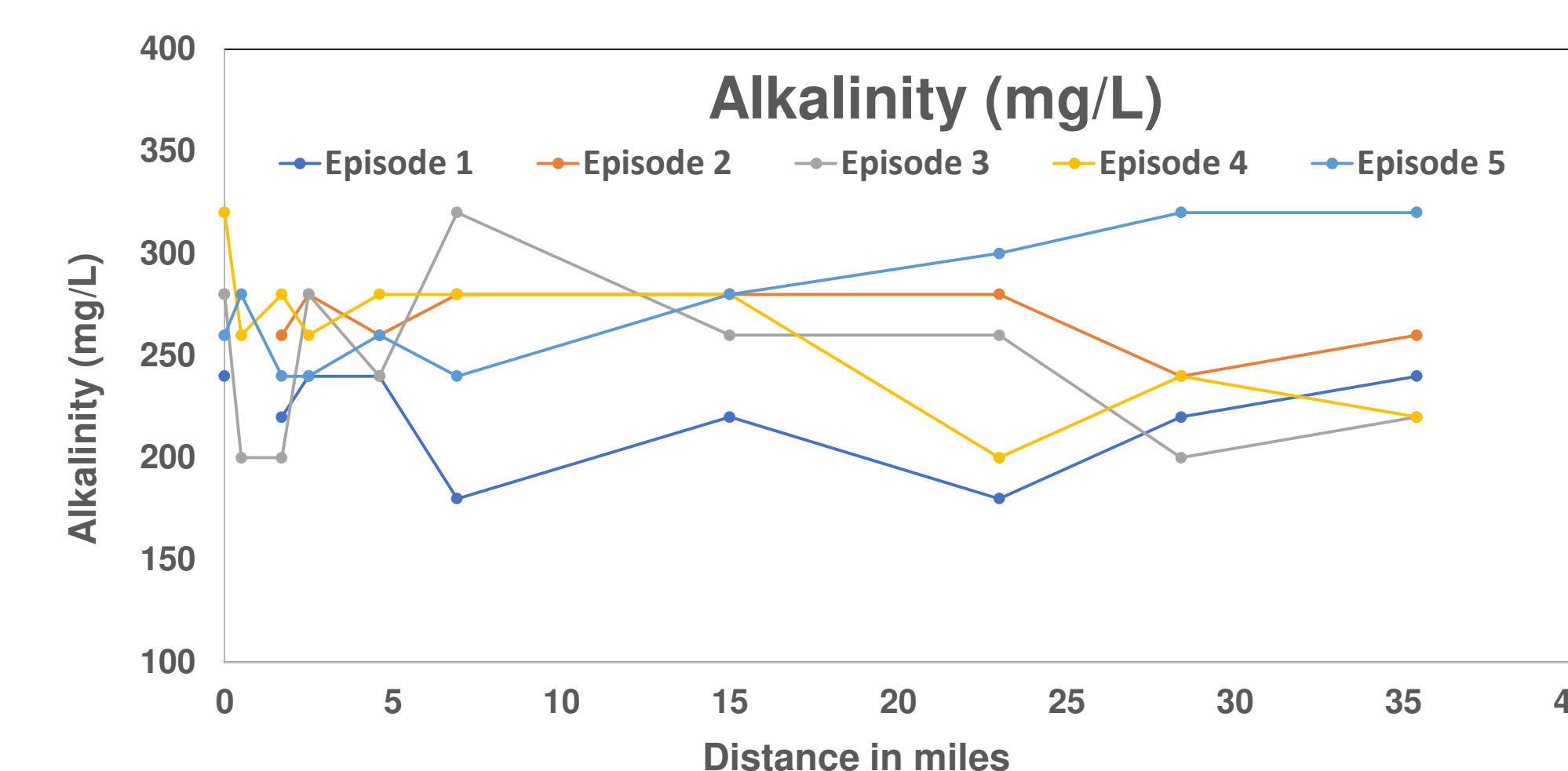


Figure 5: Alkalinity (mg/L) as a function of distance from the CWP for each sampling episode. The range of alkalinity was between 200 -300 mg/L, indicating a well buffered system.

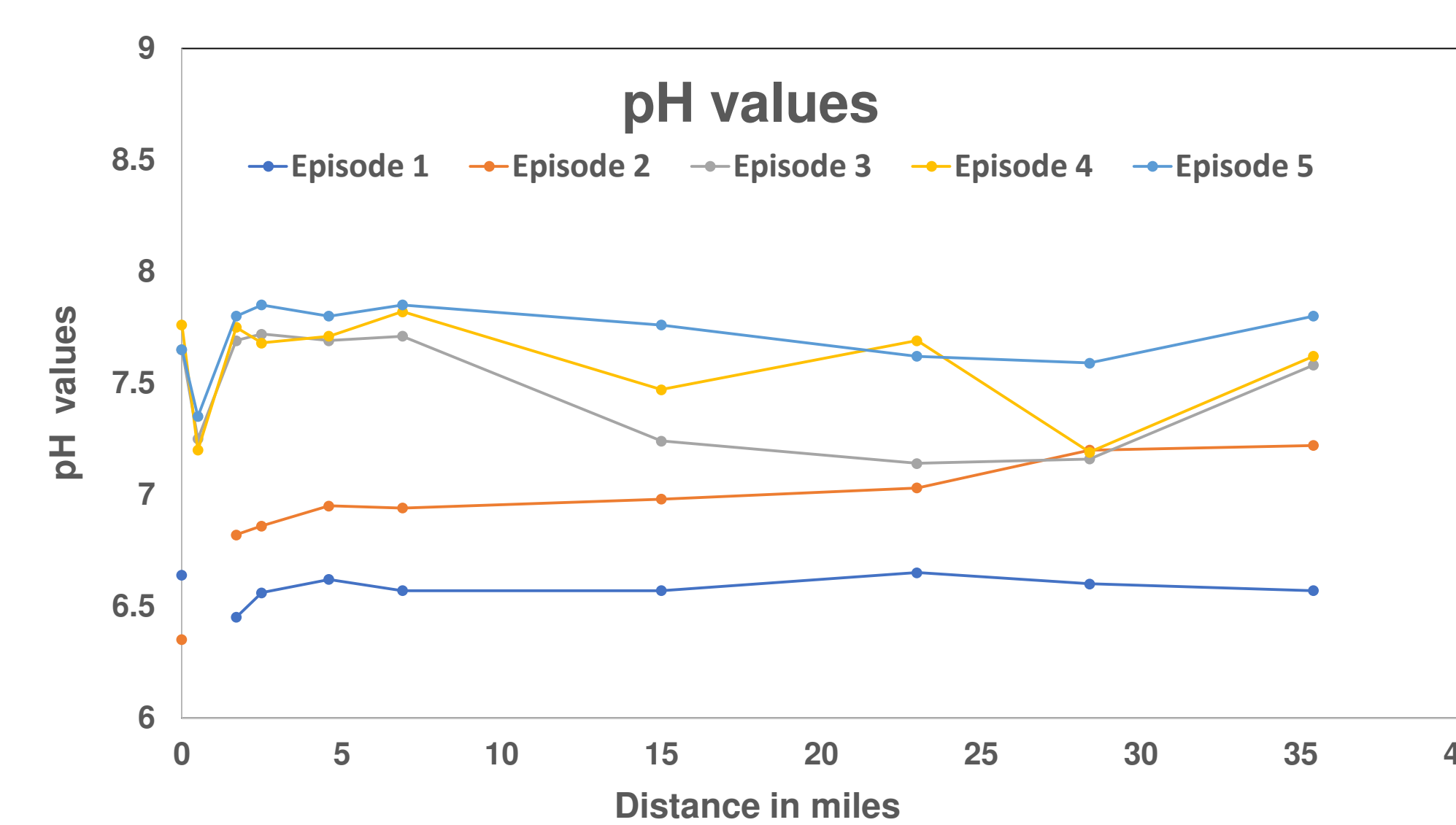


Figure 6: pH as the function of distance from the Waukesha Clean Water Plant for each sampling episode. The pH range is constant and fell in the range of 6-8 for all the sampling episodes.

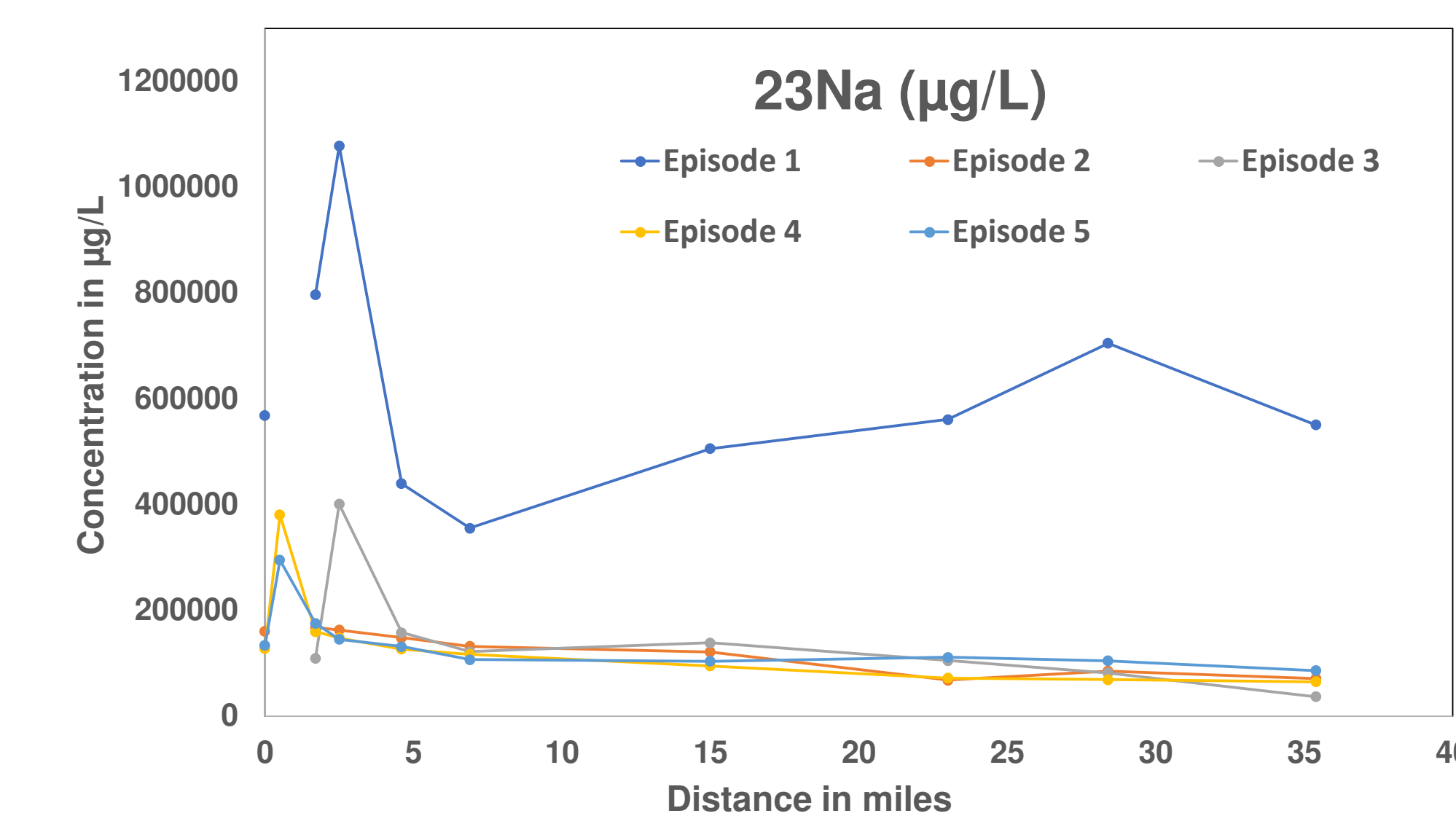


Figure 7: Sodium concentration (µg/L) as a function of distance from the CWP for each sampling episode. There is a decrease in concentration of Na in the river on increasing the distance. Episode 1, sampled on 05/25/2019, has a higher concentration which might be due to spring melt flow.

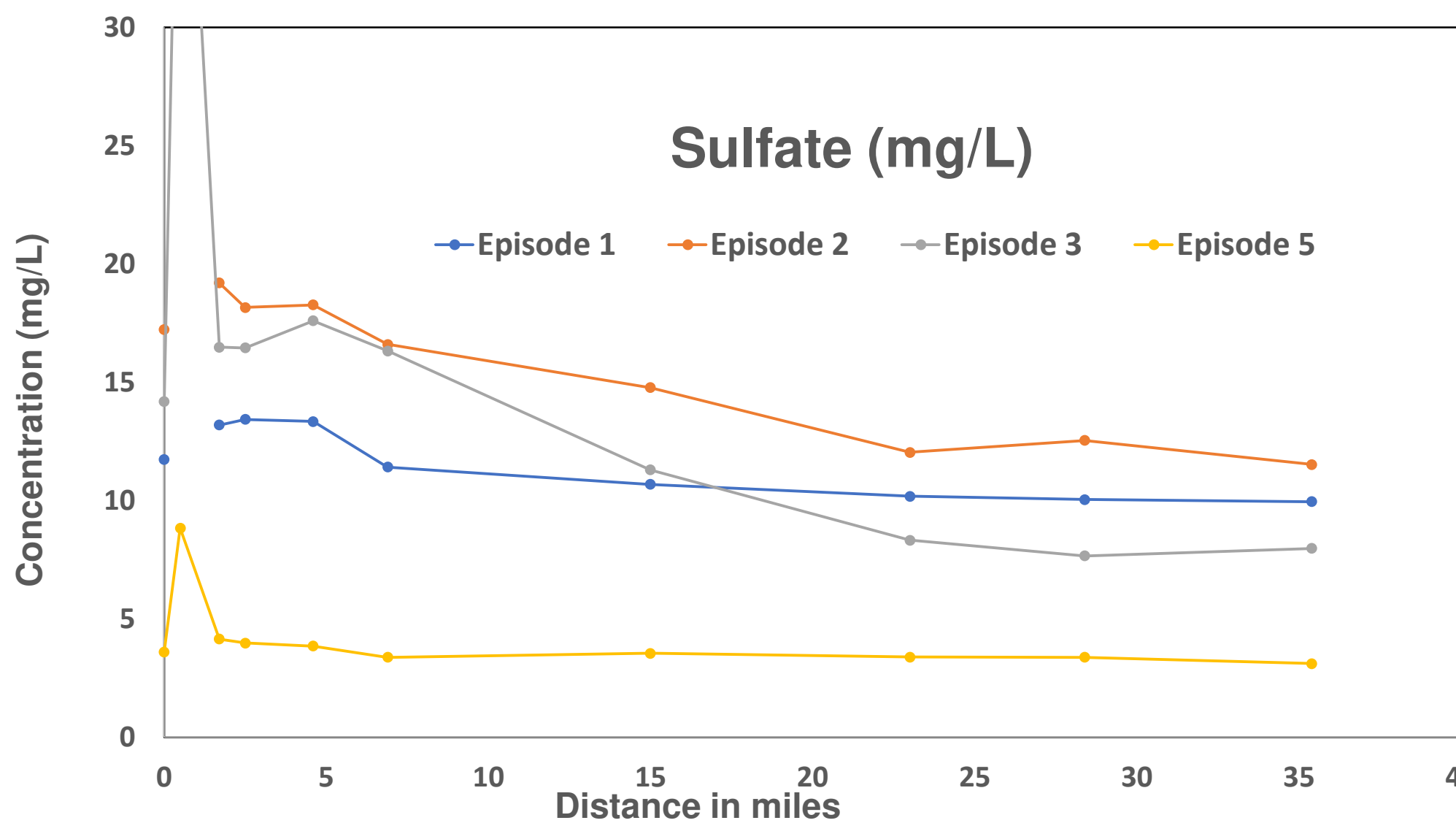


Figure 8: Sulfate concentration (mg/L) as a function of distance from the CWP for each sampling episode. The sulfate concentration slowly decreased over the stretch of Fox river but stayed constant for all the sampling episodes for each site. There is a spike at FR01 (46 mg/L; off scale), the CWP site, where the sample was collected directly at the discharge point before it hits the Fox River.

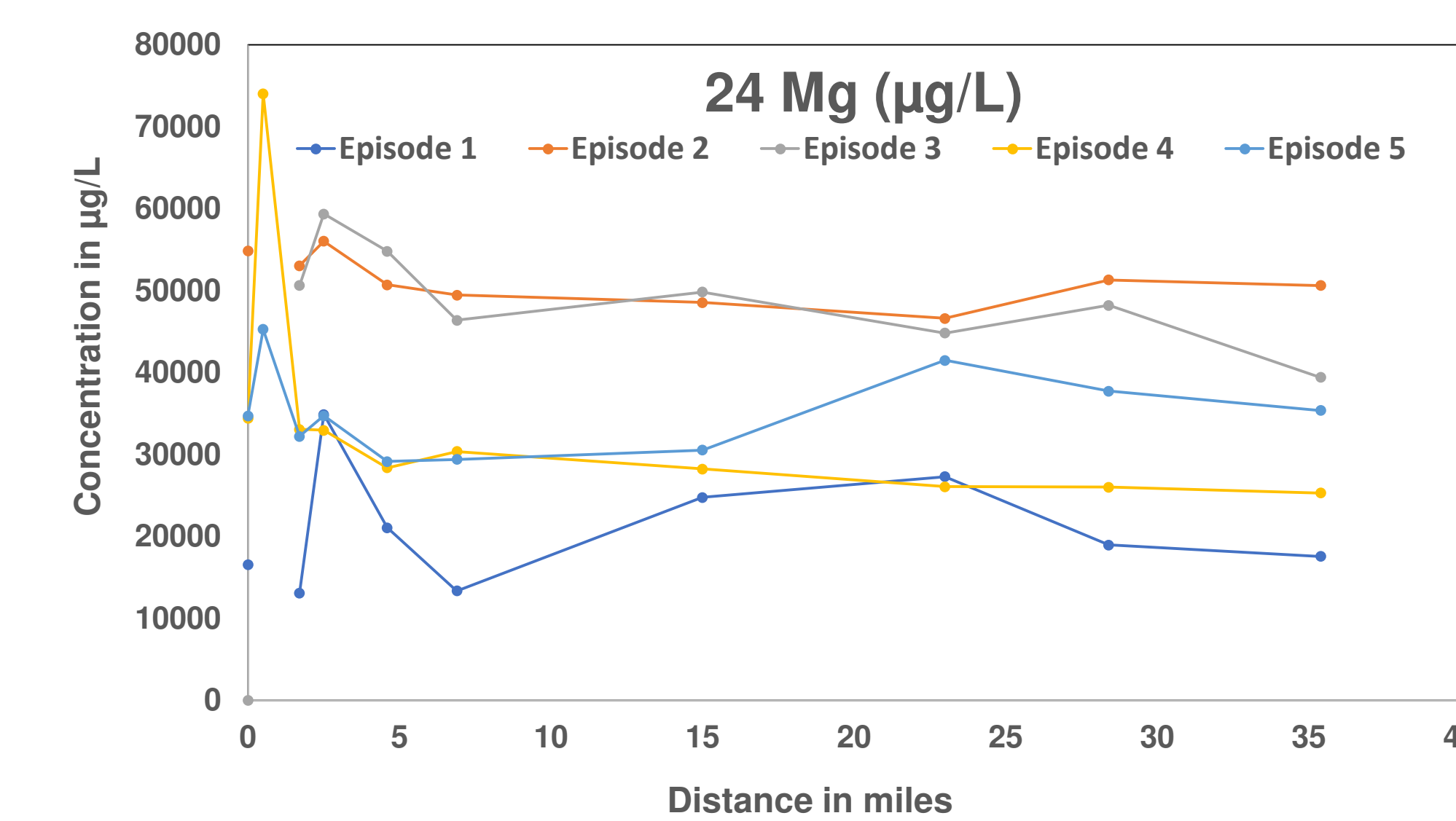


Figure 9: Magnesium concentration (µg/L) as a function of distance from the CWP for each sampling episode. The concentration of Mg is constant at each sampling site with a spike at FR01.

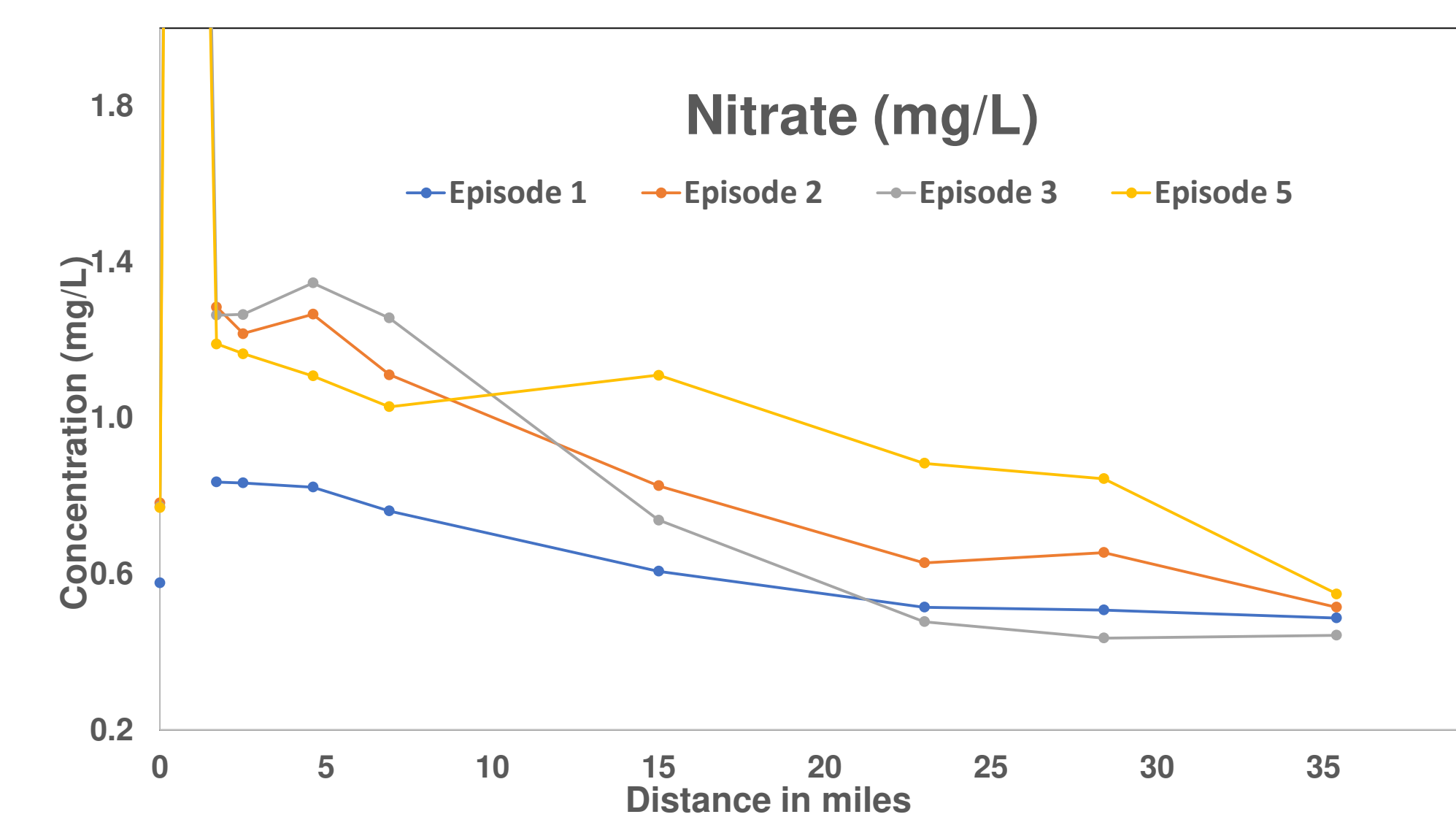


Figure 10: Nitrate concentration (mg/L) as a function of distance from the CWP for each sampling episode. The nitrate concentration decreased with the stretch of Fox river but stayed constant for all the sampling episodes for each site. There is a spike at FR01, the CWP site, where the sample was collected directly at the discharge point before it hits the Fox River (Ep3 7.2, Ep5 6.5 mg/L).

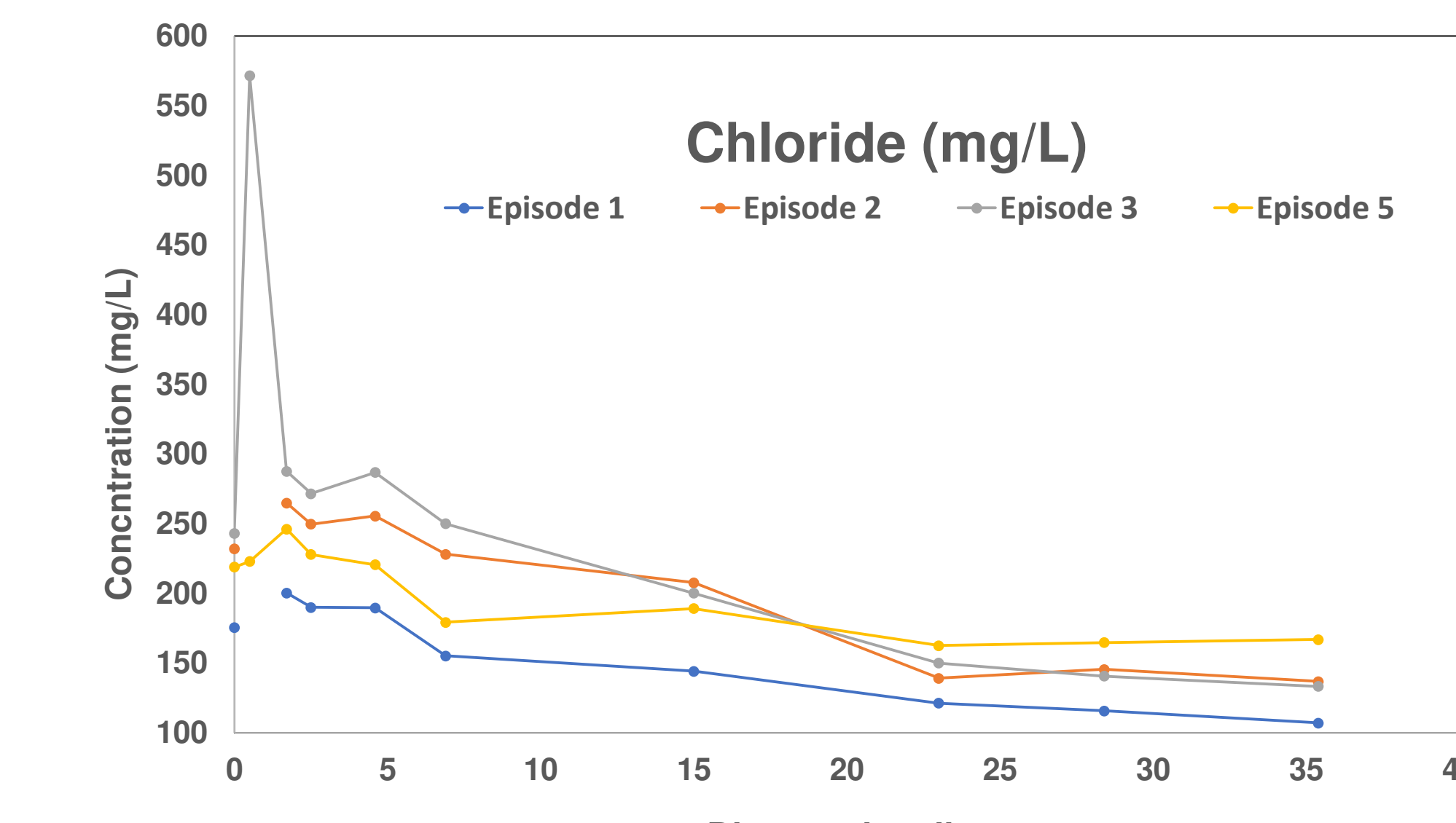


Figure 11: Chloride concentration (mg/L) as a function of distance from the CWP for each sampling episode. The chloride concentration of the river was gradually decreased with the distance. FR01, the CWP sampling site has the spike.

Summary

- The pH, Alkalinity, DO measured from the Fox River were quite stable over river distance and from site to site.
- The river was well-buffered and aerobic throughout the study.
- Chloride concentration in the range of 200-600 mg/L, with spikes at the CWP (likely due to water softening)
- For anions, levels of nitrate (< 1ppm) and sulfate (10-15 ppm) were measurable above LOD. Their range of values remained within "healthy" limits. Phosphate levels were mostly BDL.
- Sodium (> 150 ppm) concentrations were consistently high to match the chloride profile (likely due to water softening).
- Magnesium (30-50 ppm) concentrations were expected to be higher because of limestone/dolomitic subsurface geology. Ca was quantified 1x higher than the Mg. Quantification of K was problematic and the samples requires to be re-run.
- Trace metals except Nickel, Zinc and Chromium below limit of detection.
- LOD and LOQ and actual concentration of the cations and anions was determined.

Table1: The LOD and LOQ values (ug/L) of the cations calculated from the external working curves for episode 2 are represented in the table.

Episode 2	Slope	LoQ	LoD
23Na	63684.4	851	255
24Mg	40192.0	211	63.3
39K	77516.3	1573	472
44Ca	2817.7	759	228
52Cr	79855.0	196	58.8
58Ni	49320.0	232	69.5
64Zn	43225.0	217	65.0
65Cu	25597.0	229	68.7
111Cd	33179.0	108	32.5
208Pb	209901.0	129	38.7

Future works

- Sampling is continuing monthly to get a year-round data set to identify any seasonal fluctuations.
- The PPCPs data (UWM-School of Public Health) will be integrated into this data set.
- The ICP-MS samples will be re-run in KED mode to determine if this performs better than STD mode.

Acknowledgements

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