ENHANCED MONITORING RESULTS

SLAVE RIVER AT FORT SMITH

AMÉLIORÉ DES RÉSULTATS DE SURVEILLANCE

RIVIÈRE DES ESCLAVES, À LA HAUTEUR DE FORT SMITH

Precautionary enhanced monitoring in response to industrial wastewater seepage and an uncontrolled release to the receiving environment from the Kearl Lake Oil Sands Mine Site in Alberta

Réponse aux infiltrations d'eaux usées industrielles et à un rejet non contrôlé dans l'environnement récepteur par la mine de sables bitumineux du lac Kearl en Alberta

Government of Northwest Territories
Gouvernement des Territoires du Nord-Ouest

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May 2024

Executive Summary

In response to industrial wastewater seepage and an uncontrolled release to the receiving environment at the Kearl Lake Oil Sands Mine Site in Alberta, a precautionary enhanced water quality sampling program was initiated in March 2023 for the Slave River at Fort Smith. The program continued until May 2023, when routine monitoring resumed. This sampling program was carried out by the Government of Northwest Territories (GNWT) Environment and Climate Change (ECC) in collaboration with the Fort Smith Métis Council, Town of Fort Smith, and Smith's Landing First Nation.

The monitoring focussed on chemical components known to be associated with oil sands processing and development, including major ions, metals, polycyclic aromatic hydrocarbons, and naphthenic acids. In short, the monitoring results did not reveal any evidence of contamination to the Slave River near Fort Smith. Results were within historical values and guidelines, where guidelines exist.

Sommaire

En mars 2023, un programme d'échantillonnage accru de la qualité de l'eau a été lancé par précaution pour surveiller les eaux de la rivière des Esclaves à la hauteur de Fort Smith en réponse aux infiltrations d'eaux usées industrielles et à un rejet non contrôlé dans l'environnement récepteur par la mine de sables bitumineux du lac Kearl en Alberta. Ce programme, s'étant poursuivi jusqu'à la reprise de la surveillance de routine en mai 2023, a été réalisé par le ministère de l'Environnement et du Changement Climatique (MECC) du gouvernement des Territoires du Nord-Ouest (GTNO) en collaboration avec le Conseil des Métis de Fort Smith, la Ville de Forth Smith et la Première Nation de Smith's Landing.

Le programme d'échantillonnage était axé sur les composants chimiques connus qui sont associés au traitement et à l'exploitation des sables bitumineux, notamment les ions majeurs, les métaux, les hydrocarbures aromatiques polycycliques et les acides naphténiques. En somme, les résultats obtenus n'ont révélé aucun signe de contamination de la rivière des Esclaves à la hauteur de Fort Smith. Les résultats se sont avérés être dans les limites des valeurs historiques et conformes aux lignes directrices, le cas échéant.

1.0 Introduction

The Kearl Oil Sands Project is an oil sands mine in the Athabasca Oil Sands region near Kearl Lake, about 70 kilometres north of Fort McMurray, Alberta and approximately 330 kilometres south of the Alberta/NWT Border (Figure 1). Kearl is owned by Imperial Oil Resources Limited (Imperial) and is controlled by Imperial's parent company, ExxonMobil.

On May 19, 2022, Imperial reported to the Alberta Energy Regulator (AER) that discoloured surface water was found north and northeast of the boundary of Kearl Oil Sands Mine Processing Plant. The impacted area includes muskeg and forested public lands in proximity to tributaries that feed into the Firebag and Muskeg rivers, which both flow into the Athabasca River. On February 4, 2023, Imperial reported to AER another spill of industrial wastewater which overflowed from a storage pond that collects and stores seepage and runoff water from site. AER's inspection estimated the spill amount to be 5,300 m^3 (5.3 million litres) of industrial wastewater. The overflow was later determined to have started on January 31, 2023.

The Government of the Northwest Territories (GNWT) learned of both incidents on March 1, 2023. In response, GNWT-ECC in collaboration with the Fort Smith Métis Council, Town of Fort Smith, and Smith's Landing First Nation initiated a precautionary enhanced water quality sampling program for the Slave River at Fort Smith on March 2, 2023.

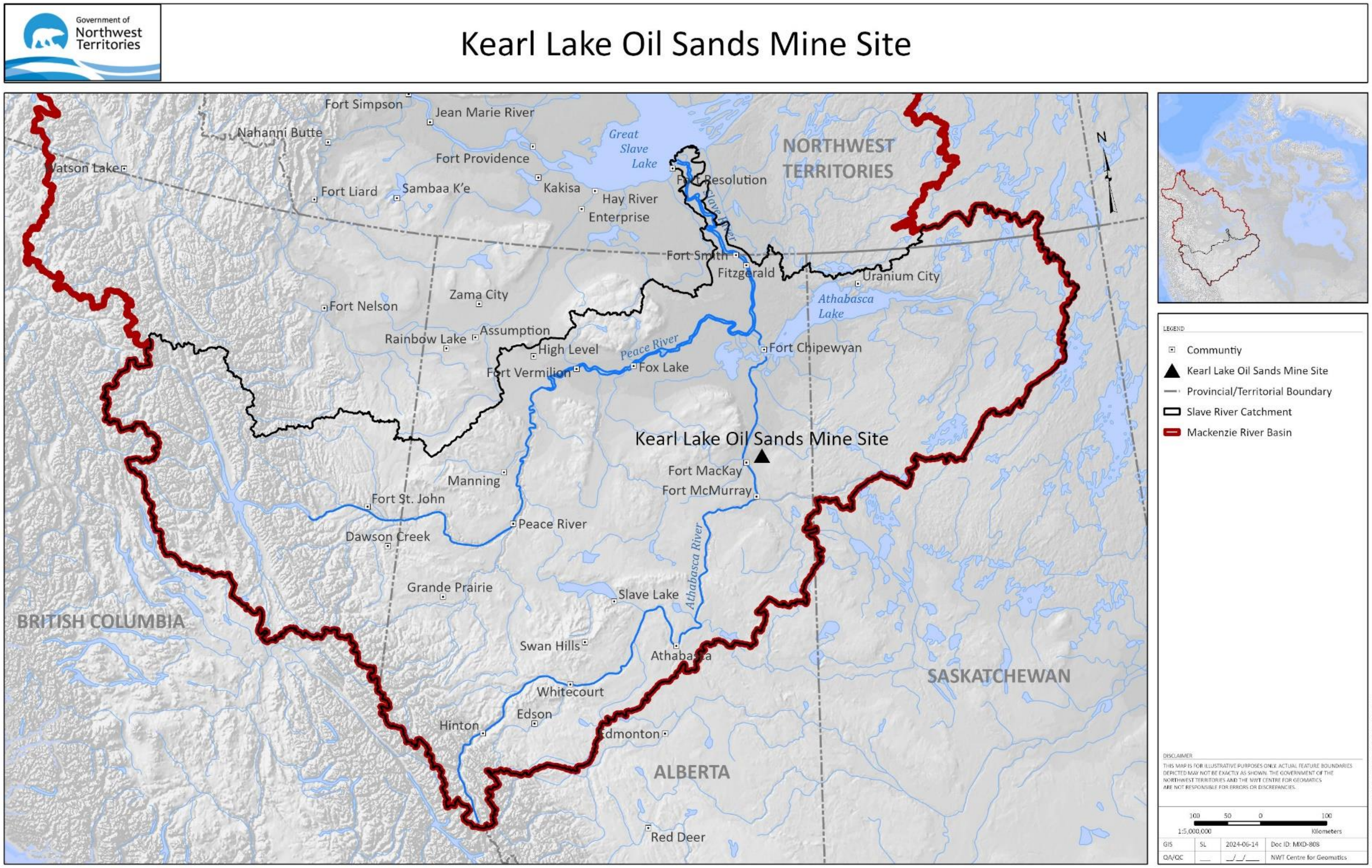

Figure 1. Map of the Slave River Catchment showing location of the Kearl Lake Oil Sands Mine relative to the NWT/Alberta Border and Fort Smith.

This report focusses on the water quality results collected as part of the Slave River Enhanced Monitoring Program with a focus on chemical components known to be associated with oil sands processing and development activities, including:

- Major ions: chloride, sulphate, calcium, magnesium, sodium, and potassium;
- Metals: molybdenum, nickel, rhenium[1], and vanadium;
- Polycyclic aromatic hydrocarbons (PAHs): organic substances that are naturally occurring but also related to oil and gas-related activities and are associated with oil sands process water; and
- Naphthenic acids (NAs): natural constituents of bitumen and regional groundwater but are often enriched in oil sands process water.

2.0 Sampling Methods

The results included in this report represent data compiled from three different sampling locations: Slave River at Fort Smith (mid-river), Slave River at Fort Smith (shore/boat launch) and Slave River at Fort Smith (from within the water treatment plant). For this report, these sampling locations are collectively named, “Slave River at Fort Smith”.

This monitoring program included:

- Water quality sampling at the Town of Fort Smith water treatment plant intake building and directly from the river near the town boat launch. Samples were analyzed for general water quality, total and dissolved metals, PAHs, and NAs.

- Polyethylene membrane devices (PMDs) were deployed in the Town of Fort Smith water intake building. PMDs were analyzed for PAHs.

- Routine sampling, as part of the existing long-term water quality monitoring programs, began May 24th and included both grab samples and the deployment of PMDs at the mid-river location.

The sample collection schedule is presented in Table 1.

[1] Rhenium was not assessed as it is not routinely analyzed.

Table 1. Slave River Enhanced Monitoring Sampling Schedule

Description	Date	Sample Type
Slave at water treatment plant	2023-03-02	Grab sample
Slave at water intake building	2023-03-03	PMD
Slave at Smith (through ice)	2023-03-05	Grab sample
Slave at water treatment plant	2023-03-09	Grab sample
Slave at Smith (through ice)	2023-03-09	Grab sample
Slave at water intake building	2023-03-13	PMD
Slave at water treatment plant	2023-03-20	Grab sample
Slave at Smith (through ice)	2023-03-20	Grab sample
Slave at water treatment plant	2023-03-27	Grab sample
Slave at Smith (through ice)	2023-03-27	Grab sample
Slave at water treatment plant	2023-04-03	Grab sample
Slave at Smith shore	2023-04-03	Grab sample
Slave at water treatment plant	2023-04-11	Grab sample
Slave at water treatment plant	2023-04-20	Grab sample
Slave at water treatment plant	2023-04-20	Grab sample
Slave at water treatment plant	2023-05-04	Grab sample
Slave at Smith shore	2023-05-09	Grab sample
Slave at Smith below rapids	2023-05-15	Grab sample and PMD
Slave at Smith below rapids	2023-05-24	Grab sample and PMD
Slave at Smith below rapids	2023-06-30	Grab sample and PMD

The following section describes the methods taken to assess the Slave River water quality following the Kearl wastewater releases.

3.0 Approaches to Water Quality Assessment

According to the AER, the Kearl long-term leak started approximately nine months before it was reported on May 19, 2022. Given this, the data used to assess the Kearl wastewater release on the Slave River was collected between September 2022 and October 2023 (Post-Kearl). Pre-Kearl data refers to information collected prior to September 2022.

<u>Major Ions and Metals</u>

To assess differences between pre- and post-Kearl data, data were divided according to hydrologic season[2] based on month as recommended by Glozier et al. (2009):

- Under-ice = January, February, March, April, November, December

[2] Given that the 2023 break-up occurred early, for 2023 high water was defined as April 21st to May 30th, and regular open water was defined as June 1st to October 30th.

- High water = May, June, July
- Regular open water = August, September, October

Box and whisker plots were used to examine the data. Box plots are highly effective and relatively easy to read, as they can summarize data from multiple points in time (e.g., pre- and post-Kearl) or hydrologic seasons (e.g., under-ice, high water, regular open water), allowing for comparisons between different data categories for more effective decision-making. They highlight the variability (spread) of the data, including expected (normal) values, as well as minimum and maximum values, based on the season. Additionally, in the context of screening the data related to the incidents at Kearl, box and whisker plots can highlight outliers (unexpected data), which may suggest an influence from Kearl.

From a chemical perspective, water is a mixture of many elements and compounds, which the laboratory reports as individual concentrations for multiple elements and compounds. Mixtures of elements and compounds are considered compositions, as defined by Aitchison (1986), where each individual element and/or compound is part of a whole. The post-Kearl data were also considered as compositions. Here, additive log ratio (ALR) transformations[3] were applied to the compositional data, and box and whisker plots were used in the same way as the concentration data. The ALR transformations improve the ability to detect patterns and understand the processes that might be driving data patterns.

To reduce overall variability, flow was taken into account. Flow is a primary driver of variability in river water quality. Since increases in flow typically correspond with decreases in major ions and increases in metals, accounting for flow would increase our ability to detect changes in water quality.

Regressions were used to account for flow for major ions and metals using the ALR transformed data against flow with generalized additive models (GAMS)[4] using pre-2022 data. A GAM was produced for each water quality parameter to predict what the post-Kearl data should have been given the flow rate at the time of sample collection (what are normal or expected data, and what are unusual or unexpected data). Using this methodology, the following statements can be made with 95% confidence:

- Samples less than the lower limit of the confidence interval are normal (expected).
- Samples between the lower and upper limits of the confidence interval are normal but close to being different (unexpected).
- Samples above the upper limit of the confidence interval are different (unexpected).

The type of signals that would suggest an impact from the Kearl incidents would be one or more successive observations being higher than the upper limit of the confidence interval for multiple parameters known to be associated with tailings effluent. An observation

[3] The method to transform the data using the Additive Log Ratio (ALR) technique is fully described in Appendix A.
[4] The method to produce the Generalized Additive Models (GAMS) is fully described in Appendix A.

above the upper limit of the confidence interval for only one or two parameters is more likely a field and/or laboratory error and unlikely a result of Kearl.

Polycyclic Aromatic Hydrocarbons (PAHs) and Naphthenic Acids (NAs)

PAHs and NAs were not assessed using the same approaches as detailed for major ions and metals. Instead, the distributions of these data before September 2022 (pre-Kearl) and after September 2022 (post-Kearl) were compared. The type of signal that could suggest a Kearl impact would be PAH or NA post-Kearl data being higher than the pre-Kearl data.

During the post-Kearl period, eleven water samples were collected and analyzed for PAHs and NAs, whereas eight PMDs were deployed (including those deployed as part of the routine monitoring). PMDs have excellent detection sensitivity, integrate chemicals over time and are easier to analyze than the biological organisms (e.g. fish) that they are trying to mimic. PMDs are deployed for about one month at a time and give a good indication of bioavailability of PAHs that are in the water (see Stalwick et al 2024 for more information).

4.0 Results

4.1 Major Ions

The major ions assessed as part of this report are known to be associated with oil sands processing and development activities including calcium, potassium, sodium, chloride and sulphate. Figures for major ions are included in Appendix B.

Concentrations of calcium (Figure B1) and magnesium (Figure B2) appear to have one under-ice 2023 value above the normal range. Otherwise, all other data were normal. Potassium (Figure B3), sodium (Figure B4), sulphate (Figure B5), and chloride (Figure B6) values were all normal but sulphate levels during the high-water season seemed somewhat elevated. ALR-transformed results showed greater seasonal differences and generally had the effect of reducing the spread (i.e., variability) of data within a season. ALR-transformed plots did not indicate any abnormal values. Examination of the distribution of 2022 and 2023 major ions samples shows no difference compared to the distribution of historical data.

When flow is accounted for, all 2022 and 2023 values of calcium (Figure B7), magnesium (Figure B8), potassium (Figure B9), sodium (Figure B10), sulphate (Figure B11), and chloride (Figure B12) were normal. The April 3, 2023, value for magnesium was borderline in the “close to being different” zone (Figure B8) but still below the upper limit of confidence. All major ions were linearly related to flow when ALR-transformed.

Examination of the distribution of post-Kearl major ions data relative to flow shows no difference compared to the distribution of historical data.

4.2 Metals

The metals assessed as part of this report are known to be associated with oil sands processing and development activities, including molybdenum, nickel, and vanadium. Figures for metals are included in Appendix C.

2022 and 2023 total vanadium (Figure C1) and dissolved vanadium (Figure C2) samples were normal and as expected for each respective season. Total nickel (Figure C3) and dissolved nickel (Figure C4) samples were mostly normal, with few values close to being unexpected. Total molybdenum (Figure C5) values were also mostly normal, but the distribution of dissolved molybdenum (Figure C6) was more scattered, with values being close to unexpected. Concentrations of these metals appear to be higher in 2022 than 2023, which is expected because flow was higher in 2022. ALR-transformed results showed greater seasonal differences in concentrations and generally had the effect of reducing the spread (i.e., variability) of data within a season. ALR-transformed plots did not indicate any abnormal values. Examination of the distribution of 2022 and 2023 metal data show no differences when compared to the distribution of historical data.

When flow is accounted for, all 2022 and 2023 vanadium (Figures C7 & C8) nickel (Figures C9 & C10), and molybdenum (Figures C11 & C12) were normal. The March 5, 2023, sample for total nickel was close to being abnormal but still below the upper threshold boundary (Figure C10). Examination of the post-Kearl vanadium, nickel, and molybdenum data, while accounting for flow, shows no differences compared to the distribution of historical data.

Results for molybdenum, and nickel, and vanadium were below the Canadian Council of Ministers of the Environment (CCME) Canadian Environmental Quality Guidelines for the Protection of Aquatic Life (2024).

4.3 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are released into the Canadian environment from both natural and human sources. Forest fires are the single most important natural source of PAHs in Canada. Human sources are numerous and result in the release of PAHs throughout the ecosystem. The greatest anthropogenic sources of PAHs released to the atmosphere are residential wood heating and aluminum smelters (ECCC, 2022). Major sources of PAHs to the aquatic and soil environments include creosote-treated products, spills of petroleum products, metallurgical, coking and oilsands plants, as well as the deposition of atmospheric PAHs into water bodies (ECCC, 2022).

Two basic types of PAHs exist: parent and alkylated. Most studies, including the long-term Slave River Monitoring Program, has focused specifically on 16 parent PAHs as they were deemed priority by US Environmental Protection Agency (Andersson and Achten, 2015). However, in more recent years, the alkylated PAHs have gained more attention. Alkylated PAHs are considered more abundant, persistent, and toxic than parent PAH compounds.

They also tend to bioaccumulate to a greater degree. Parent and alkylated PAHs are important for target analyses when assessing impacts to the environment from oil spills and tailings leaks (Culp et al., 2021). The long-term Slave River Monitoring Program includes the analyses of both parent and alkylated PAHs.

One sample collected for the analysis of PAHs generates results for 75 different individual hydrocarbon compounds. Of these, 49 compounds are known to occur naturally within the Athabasca oil sands deposit. However, oil sands development and mining operations can contribute PAHs to receiving water bodies above those naturally occurring (Yang et al., 2011, Culp et al., 2021, Mundy et al., 2019, Kelly et al., 2009).

Here, we focus on these 49 compounds, broken down into 19 individual parent PAHs and 30 individual alkyl-substituted PAHs (as per Yang et al., 2011). Table 2 includes the 49 compounds that were used to calculate total PAHs in surface water (shaded cells include the compounds used to calculate total PAHs in PMDs).

Post-Kearl results were compared to pre-Kearl water quality results in surface water and PMDs. Figures for PAHs are included in Appendix D.

Table 2. List of parent and alkyl-substituted individual PAH compounds used to assess Total PAHs in the surface water samples collected from the Slave River. ***Shaded cells represent the individual PAHs used to calculate Total PAHs in the PMDs deployed in the Slave River.***

Parent PAHs	Alkyl-Substituted PAHs	
Acenaphthene	Biphenyl	C3-Dibenzothiophenes
Acenaphthylene	C1-Acenaphthenes	C3-Fluoranthenes/Pyrenes
Anthracene	C1-Benz(a)anthracenes/Chrysenes	C3-Fluorenes
Benz(a)anthracene	C1-Benzofluoranthenes/Benzopyrenes	C3-Naphthalenes
Benzo(a)pyrene	C1-Biphenyls	C3-Phenanthrenes/Anthracenes
Benzo(b)fluoranthene	C1-Dibenzothiophenes	C4-Benz(a)anthracenes/Chrysenes
Benzo(e)pyrene	C1-Fluoranthenes/Pyrenes	C4-Dibenzothiophenes
Benzo(g,h,i)perylene	C1-Fluorenes	C4-Fluoranthenes/Pyrenes
Benzo(j,k)fluoranthene*	C1-Naphthalenes	C4-Naphthalenes
Chrysene	C1-Phenanthrenes/Anthracenes	C4-Phenanthrenes/Anthracenes
Dibenz(a,h)anthracene	C2-Benz(a)anthracenes/Chrysenes	Dibenzothiophene
Fluoranthene	C2-Benzofluoranthenes/Benzopyrenes	
Fluorene	C2-Biphenyls	
Indeno(1,2,3-c,d)pyrene	C2-Dibenzothiophenes	
Naphthalene	C2-Fluoranthenes/Pyrenes	
Perylene	C2-Fluorenes	
Phenanthrene	C2-Naphthalenes	
Pyrene	C2-Phenanthrenes/Anthracenes	
Retene	C3-Benz(a)anthracenes/Chrysenes	

*Benzo(j)fluoranthene is reported in PMDs, not benzo(k)fluoranthene or benzo(j,k)fluoranthene

Figure D1 (surface water) and Figure D2 (PMD) show that for total PAHs, post-Kearl data fell within the historical range of the pre-Kearl data, indicating that a signal from Kearl was not evident. Figure D1 does, however highlight a few interesting patterns:

- PAH levels are generally higher in spring and summer than in the fall;
- PAH levels are lowest during the winter;
- PAH levels in July 2020 were higher than any other monitoring event;
- PAH levels in May and June of 2023 are higher than the preceding months (March and April of 2023); and

- There do not appear to be any trends in PAH concentrations, meaning that levels are neither increasing nor decreasing.

PAHs have low water solubility, which means the individual compounds tend to attach to the sediment particles in the river (McGrath, 2019). This helps explain why levels are higher during the summer compared to the fall and winter. In the summer, the Slave River carries an enormous amount of sediment, mainly composed of clay and silt, which are soils rich in organic carbon. The organic carbon provides a large surface area to which the PAHs can attach and be carried downstream. Conversely, in the winter, the river carries much less sediment of which is primarily made up of sand. Sand contains much less organic carbon for PAHs to bind to.

In July, the typical flow average for the Slave River is 4,730 m^3/s. However, in July 2020, the flow measured 7,449 m^3/s. That year, the snowmelt and heavy rain in northern Alberta resulted in record-high water levels in Great Slave Lake and increased sediment in the Slave River, which was reflected in the concentrations of hydrocarbons. As can be seen in Figure D1, levels of PAHs were higher in mid-July 2020 than any other sampling event.

PAH concentrations were higher in May and June compared to March and April of the same year (2023). To understand these data, it is best to compare them to previous data. This will help identify what is normal and what is not. Unfortunately, sampling the Slave River in May is not conducted regularly due to breakup and potentially unsafe ice conditions; therefore, the data from the previous June were used as a surrogate (Figure D3). Figure D3 shows that June 2023 PAH concentrations (962 ng/L) were within the range of past June values (158 – 1,112 ng/L).

Lastly, there appears to be no long-term trend in the levels of total PAHs in the Slave River, suggesting that levels of PAHs are neither increasing nor decreasing.

The guidelines for the protection of aquatic life (CCME 2024) were used to assess PAH levels in the surface water of the Slave River. Of the many PAHs analyzed in the water samples collected from the Slave River, guidelines only exist for 9 compounds (Table 3).

Between 2017-2023, the guidelines were exceeded on one occasion for four compounds including benz(a)anthracene, benzo(a)pyrene, fluoranthene and pyrene (Figure D4). These exceedances occurred in July 2020 associated with a period of high water and sediment load (and prior to the Kearl wastewater release). Otherwise, PAH levels have been within the guidelines to protect aquatic life.

Table 3. PAHs results for nine compounds measured in the Slave River at Fort Smith.

PAH (ng/L)	**2017-2023 (n=10)**	**Guideline (ng/L)**
Acenaphthylene	0.043-0.277	5,800
Anthracene	0.07-2.49	12

PAH (ng/L)	2017-2023 (n=10)	Guideline (ng/L)
Benz(a)anthracene	0.1-21.8	18
Benzo(a)pyrene	0.12-27.9	15
Fluoranthene	0.39-36.5	40
Fluorene	0.06-29	3,000
Naphthalene	1.4-81	1,100
Phenanthrene	1.2-189	400
Pyrene	0.65-58	25

4.4 Naphthenic Acids

Naphthenic acids have been identified as chemicals of concern associated with oil sands process water (OSPW). Since naphthenic acids are also natural components of bitumen and regional groundwaters, it can be challenging to determine their source when these compounds are detected and/or concentrations are higher than expected (Bauer et al., 2022).

Given that these compounds are associated with upstream development, the GNWT began monitoring naphthenic acids in the Slave River in 2014. Post-Kearl NA data were consistent with pre-Kearl data (Appendix D, Figure D5).

Currently, guidelines do not exist for naphthenic acids.

5.0 Conclusion

Following the collaborative enhanced water quality monitoring done, no evidence of contamination to the Slave River near Fort Smith could be attributed to the wastewater released from the Kearl Oil Sands Mine Processing Plant. Water quality results were within historical values and, for oil sands parameters where guidelines exist, were below the recommended thresholds.

6.0 Acknowledgements

We are grateful for support from the Town of Fort Smith, Fort Smith Métis Council, and Smith's Landing First Nation to conduct this work. Many individuals were involved in planning, sampling, data analysis, and reporting. Sampling was made possible with the help of Sadele Paulette, Kelly Mandeville, Anthony Vermillion, Colton Heron, Zayn Pischinger, Dayan Bourque, Josh Gauthier, Wendy Bidwell, Jessie Foote, Joel Mercredi, and Emily Collucci in the field or in planning. Technical reviews were provided by Jon McDonald and Ryan Pischinger of the Environment Division, Fort Smith Métis Council and Pete Cott and Robin Staples of ECC, GNWT.

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Appendix A – Assessment Methodology (Major Ions and Metals)

Section 2.0 (Approaches to Water Quality Assessment) was shortened to accommodate the reader. A more thorough description of the approaches used to assess the post-Kearl major ion and metal water quality data is included below.

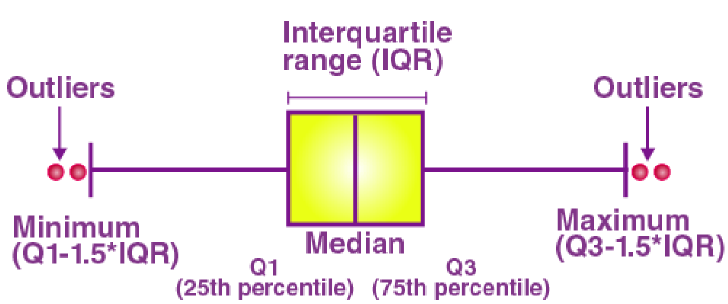
Major Ions and Metals

To assess differences between pre- and post-Kearl data while accounting for flow, data were divided according to hydrologic season[5] based on month as recommended by Glozier et al. (2009):

- Under-ice = January, February, March, April, November, December
- High water = May, June, July
- Regular open water = August, September, October

Box and whisker plots (example below) were constructed using pre-Kearl data, grouped by season, and the post-Kearl data were plotted on top to compare distributions. For this report, the top of a box is the 75th percentile of historic data, the bottom is the 25th percentile of historic data, the median (i.e., 50th percentile) is indicated by a bolded line between the top and bottom of the box, and the whiskers extend to the farthest historic points that are 1.5x the interquartile range (difference between the 75th and 25th percentiles).

Points exceeding the whiskers are often considered outliers. In the context of screening water quality data for a signal related to the Kearl incidents, points above the upper whisker would indicate higher than expected results based on hydrologic season, which may suggest an influence from Kearl.



In addition to box and whisker plots, data were also considered as compositions. From a chemistry perspective, water is a mixture of many elements and compounds that are reported by the laboratory as individual concentrations for multiple elements and

[5] Given that the 2023 break-up occurred early, for 2023 high water was defined as April 21st to May 30th, and regular open water was defined as June 1st to October 30th.

compounds. Mixtures of elements and compounds are considered compositions as defined by Aithchison (1986) where each individual element and/or compound are parts of a whole. Numerous statistical techniques are recommended for the analysis of such compositions to improve the ability to detect patterns and understand the processes that might be driving the patterns.

To explore these patterns, an Additive Log Ratio (ALR) transformation was applied to composition data, which involved dividing each constituent of a sample by one part of the sample and taking the logarithm of the quotient. In the case of the Slave River at Fort Smith data, each parameter was divided by the reported concentration of chloride[6] in each sample and then log transformed. An ALR-transformed data point that is above 0 indicates that the parameter is present in greater amounts than chloride, and points below 0 indicate that the parameter is present in lower amounts than chloride. Box and whisker plots were then used to assess the ALR-transformed data in the same way as the concentration data as reported by the lab.

To reduce overall data variability, flow was taken directly into account in addition to season because flow is a primary driver of variability in river water quality. Since increases in flow usually correspond with decreases in major ions and increases in metals, taking flow into account would also increase our ability to detect changes in water quality.

Regressions were used to account for flow for metals and major ions using ALR transformed against flow with generalized additive models (GAMs) using pre-2022 data. GAMs were used because they can account for nonlinear relationships, do not require transformations, and can accommodate results below detection limits. Flow data were obtained from the Fitzgerald, AB, hydrometric station (07NB001). GAMs were constructed using historical water chemistry and flow data, and these models were used to predict expected values for 2022 and 2023 data. To assess 2022 and 2023 data, nonparametric 95% confidence intervals (i.e., $\alpha = 0.05$) were calculated for the 95th percentile for regression residuals, and back transformed the 95th percentile and upper and lower limits to the original scale, following well established scientific principles to describe the "normal" range. The 95th percentile was selected because it is analogous to having 95% of observations within 2 standard deviations of the mean, which is often described as the "normal range." This threshold is used so that only observations above it are of interest, while those below 2 standard deviations are not considered relevant in this assessment. The purpose of constructing a confidence interval was to incorporate the uncertainty of the calculation of the 95th percentile (Millard 2013).

The interpretation of the data is that the following statements can be made with 95% confidence:

[6] Chloride was selected because it is the most consistent parameter, and its primary source is groundwater thus tends to dilute at high flows in the Slave River, which indicates that the surficial landscape in the watershed is not a source of chloride. To assess chloride, sodium was used in the denominator for ALR transformation.

- Samples less than the lower limit of the confidence interval were within the normal range, as we expected.
- Samples between the lower and upper limit of the confidence interval were with still within the normal range, but in some cases higher than we expected.
- Samples above the upper limit of the confidence interval were higher than normal and above what we expected.

The type of signals that would suggest a Kearl wastewater release would be one or more successive observations being higher than the upper limit of the confidence interval for multiple parameters known to be associated with tailings effluent. An observation above the upper limit of the confidence interval for only one or two parameters is more likely a quality assurance/quality control (QA/QC) issue of the sample(s) in question rather than a true signal relating to the Kearl wastewater release.

Confidence limits for a percentile are the same as tolerance intervals and equivalence tests (Kilgour et al. 2016), whereas the 95^{th} percentile (or any other percentile) is a nonparametric prediction interval (Helsel et al. 2020). A prediction interval, in this case upper prediction limit, is best suited to circumstances where one sample is compared to a reference sample population. If more than one sample is being compared, then the upper limit must be corrected for multiple comparisons, which results in a higher limit. The need for correction is to control for false positives (i.e., the result looks higher but in fact, it is not). However, if there are many comparisons the upper limit moves up and this increases the false negative rate (i.e., the result is in fact higher but was not detected when it was assessed). Since all 2022 and 2023 samples were assessed simultaneously, a tolerance interval is more appropriate in this case. No corrections of confidence intervals were made for inflated false positive rates to remain conservative and not risk increasing the false negative rate (i.e., not detecting a signal when there is a signal).

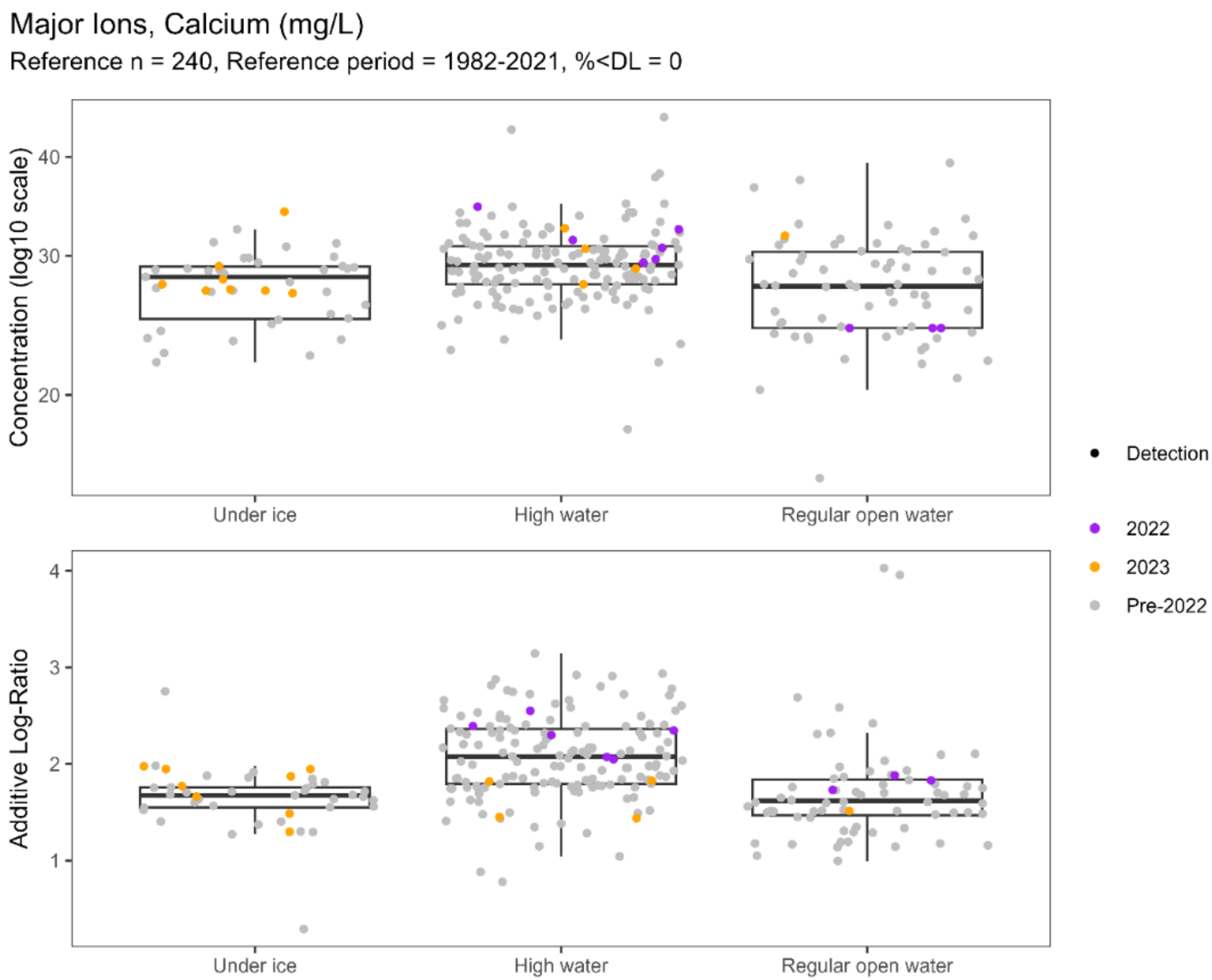


Figure B1. Calcium in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

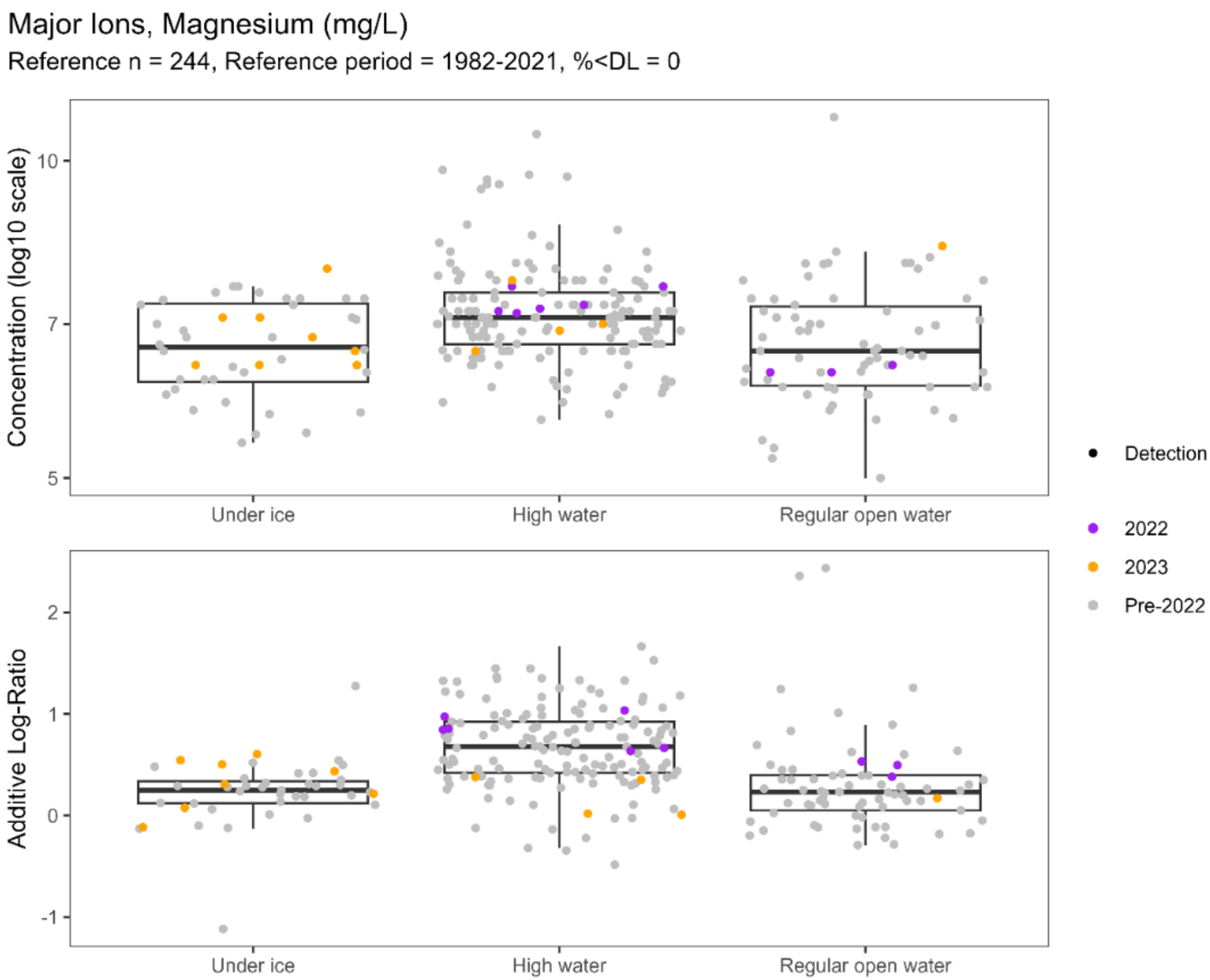


Figure B2. Magnesium in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

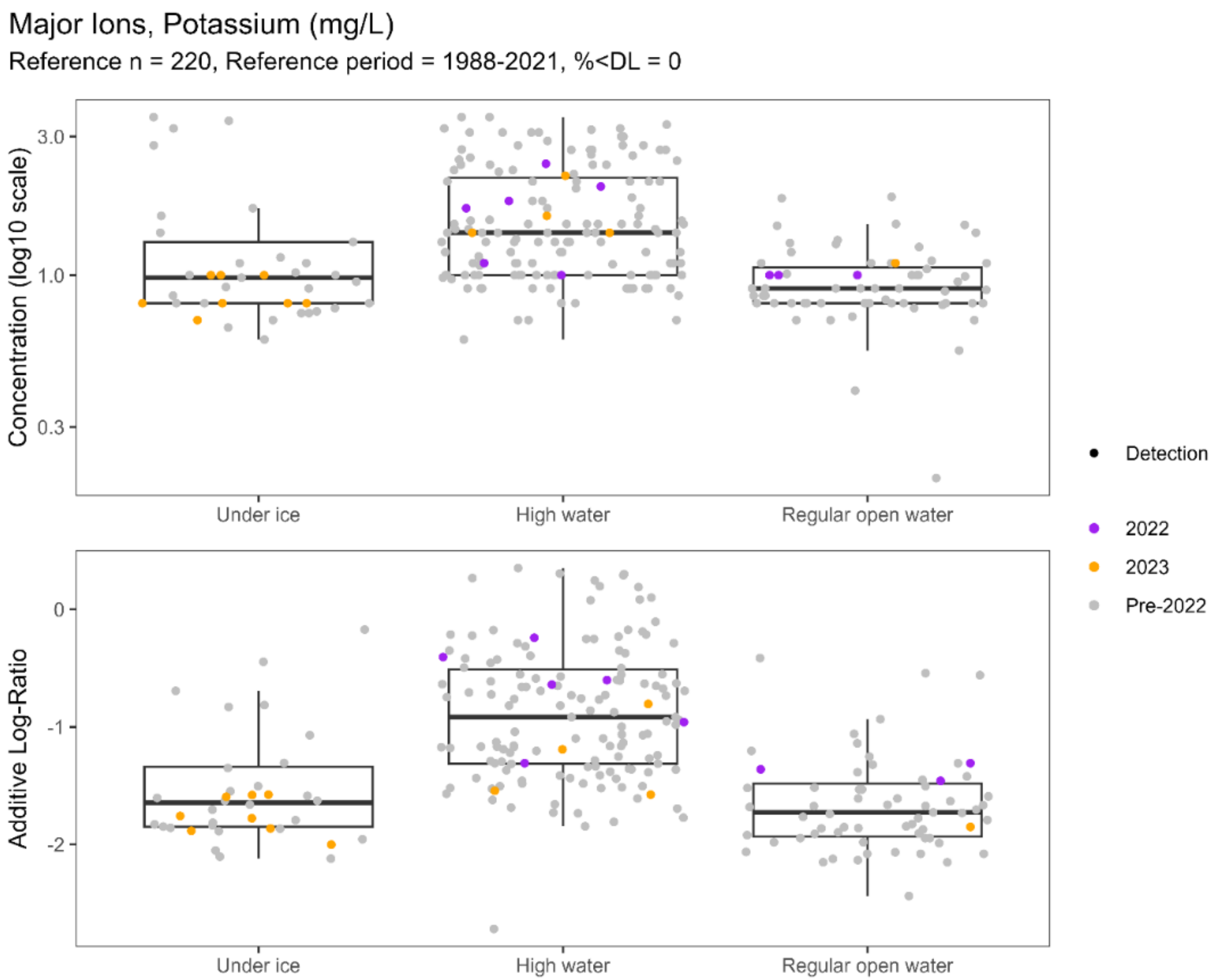


Figure B3. Potassium in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

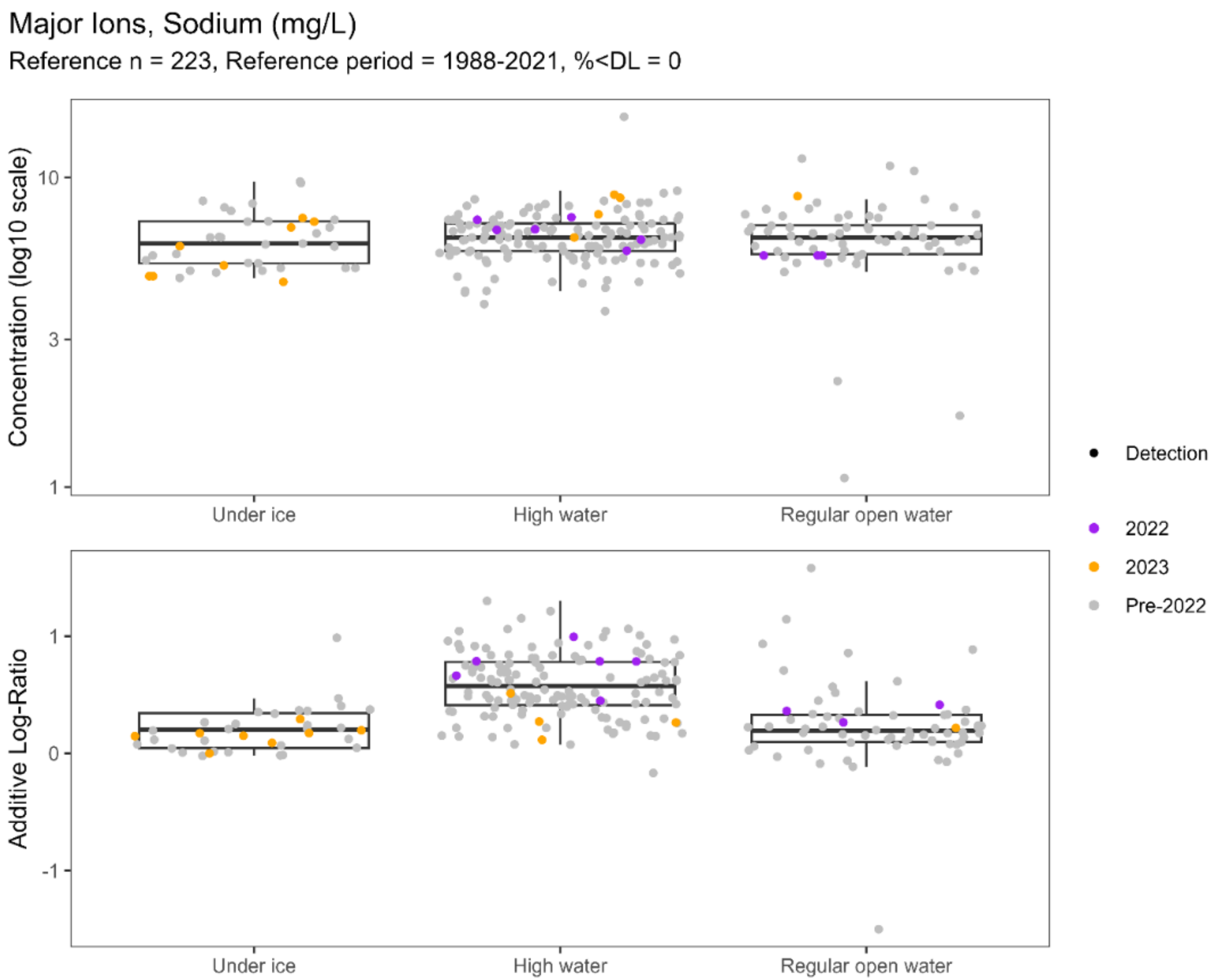


Figure B4. Sodium in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

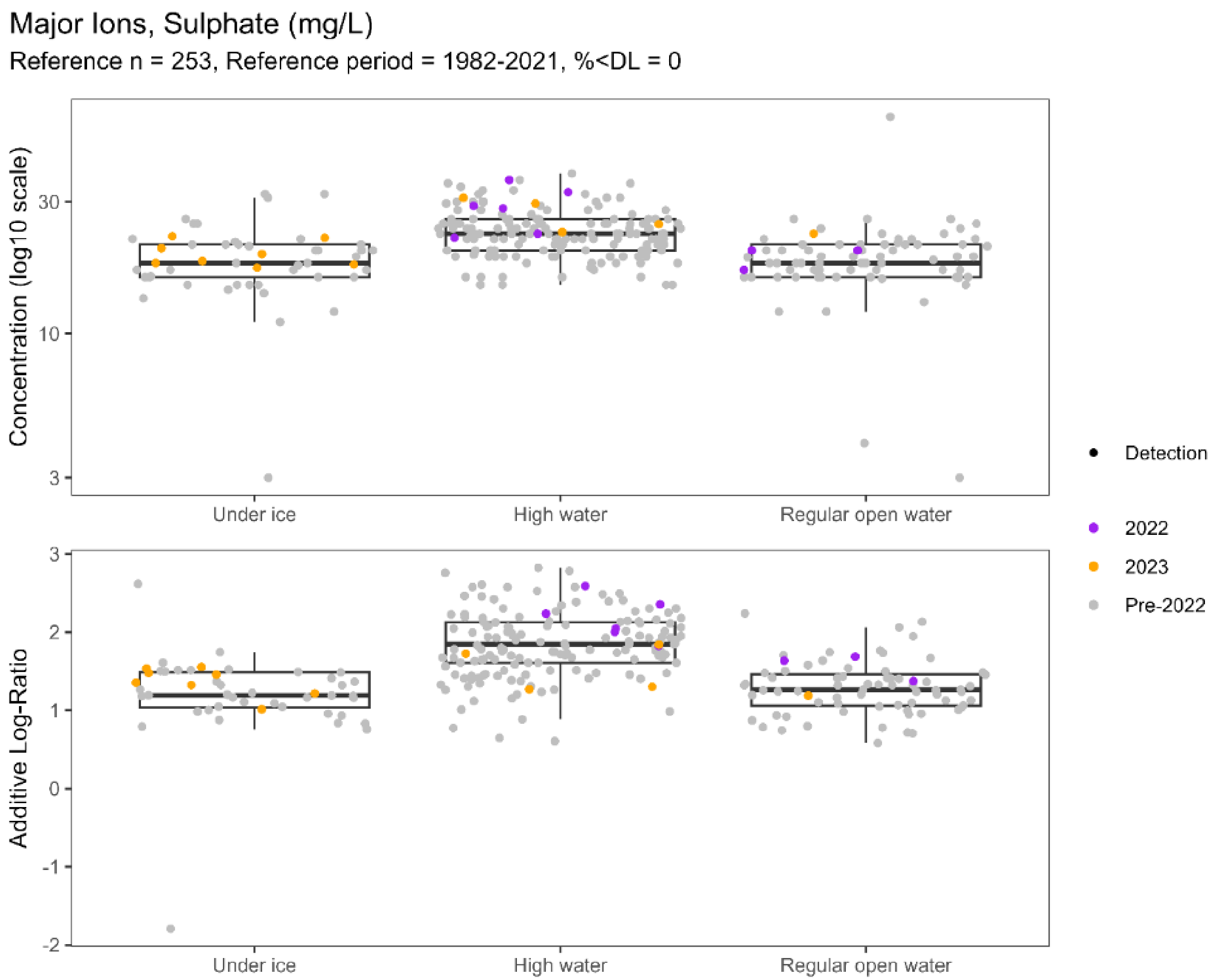


Figure B5. Sulphate in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

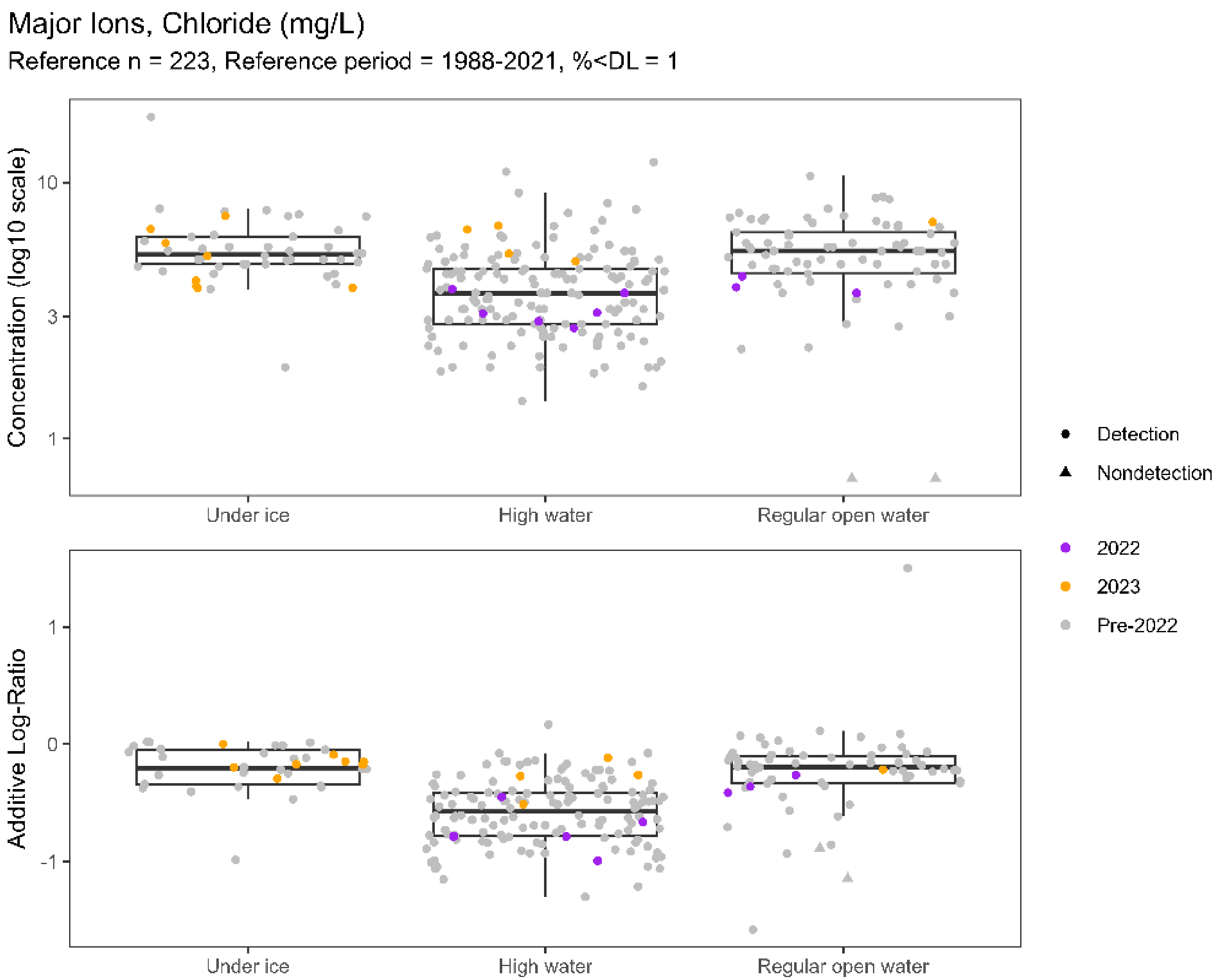


Figure B6. Chloride in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

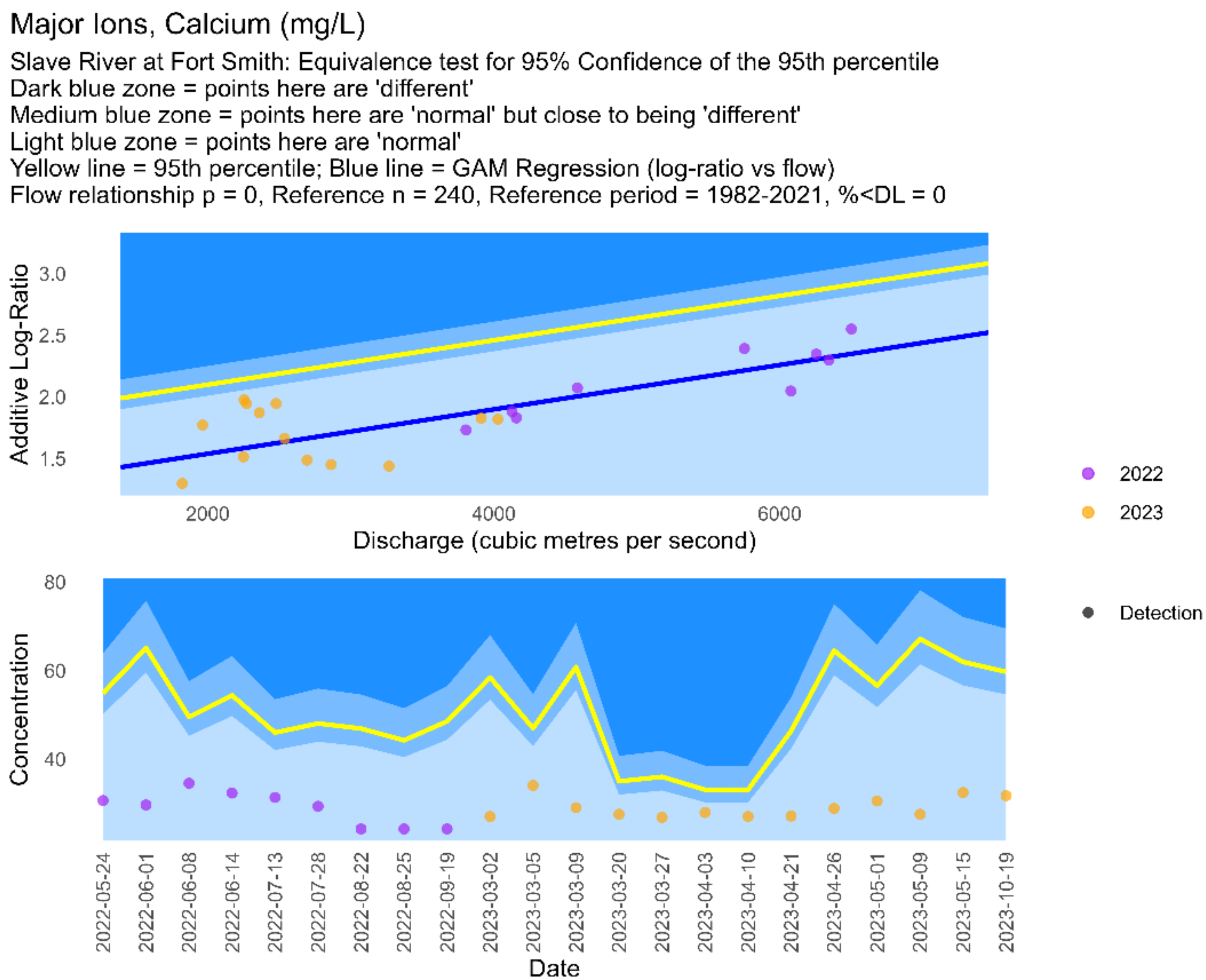


Figure B7. Evaluation of calcium relative to flow. <DL%: percentage of data below detection limit.

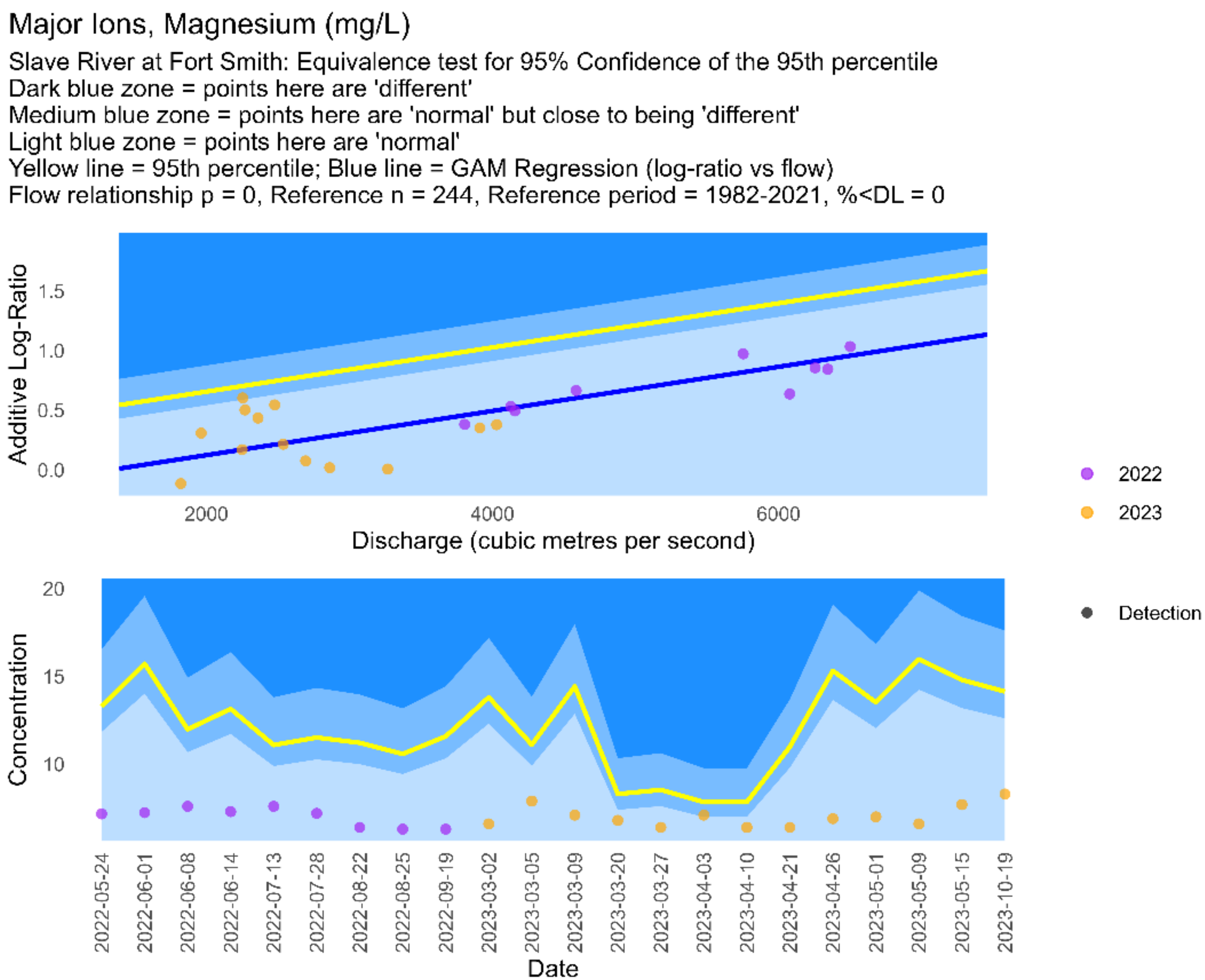


Figure B8. Evaluation of magnesium relative to flow. <DL%: percentage of data below detection limit.

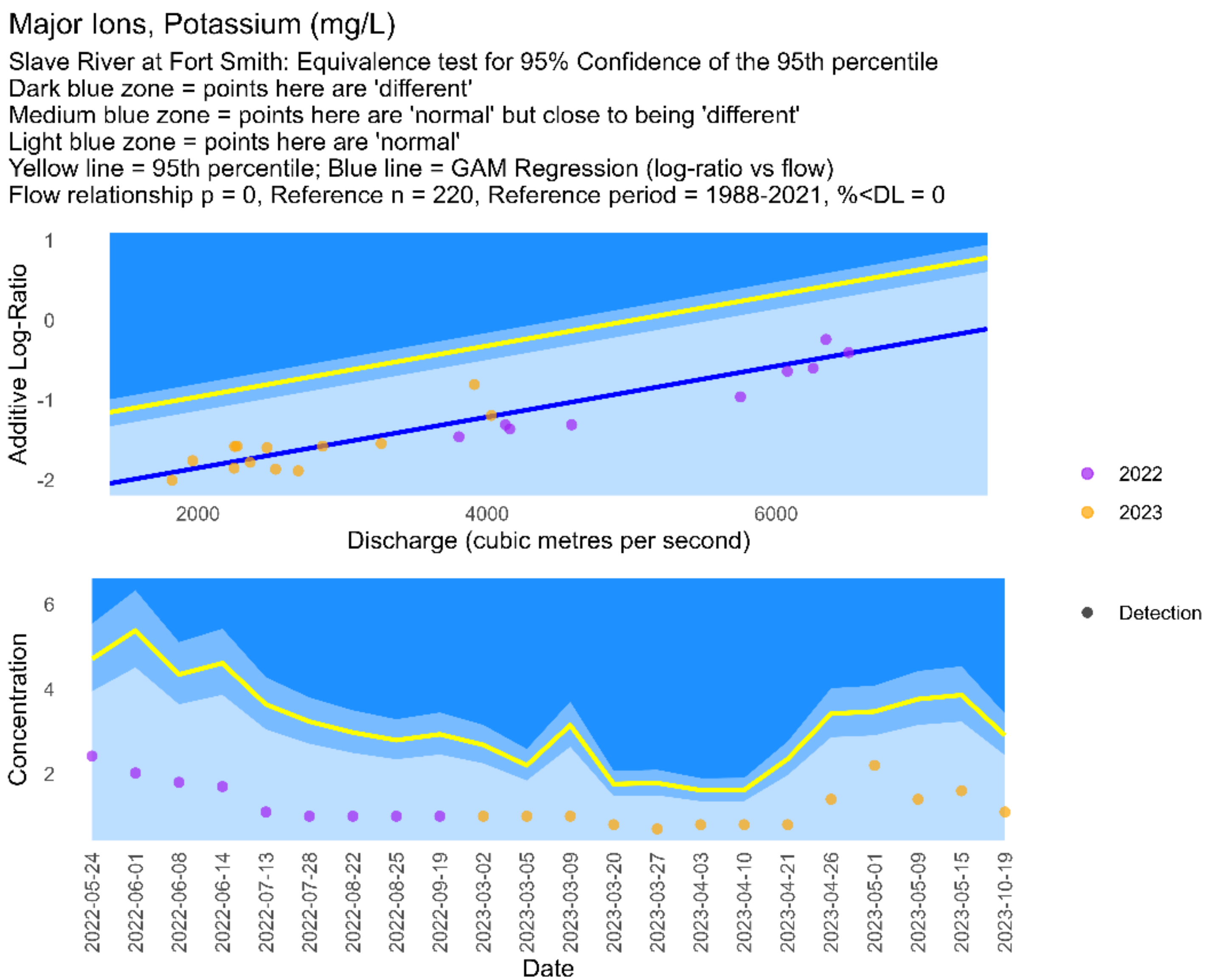


Figure B9. Evaluation of potassium relative to flow. <DL%: percentage of data below detection limit.

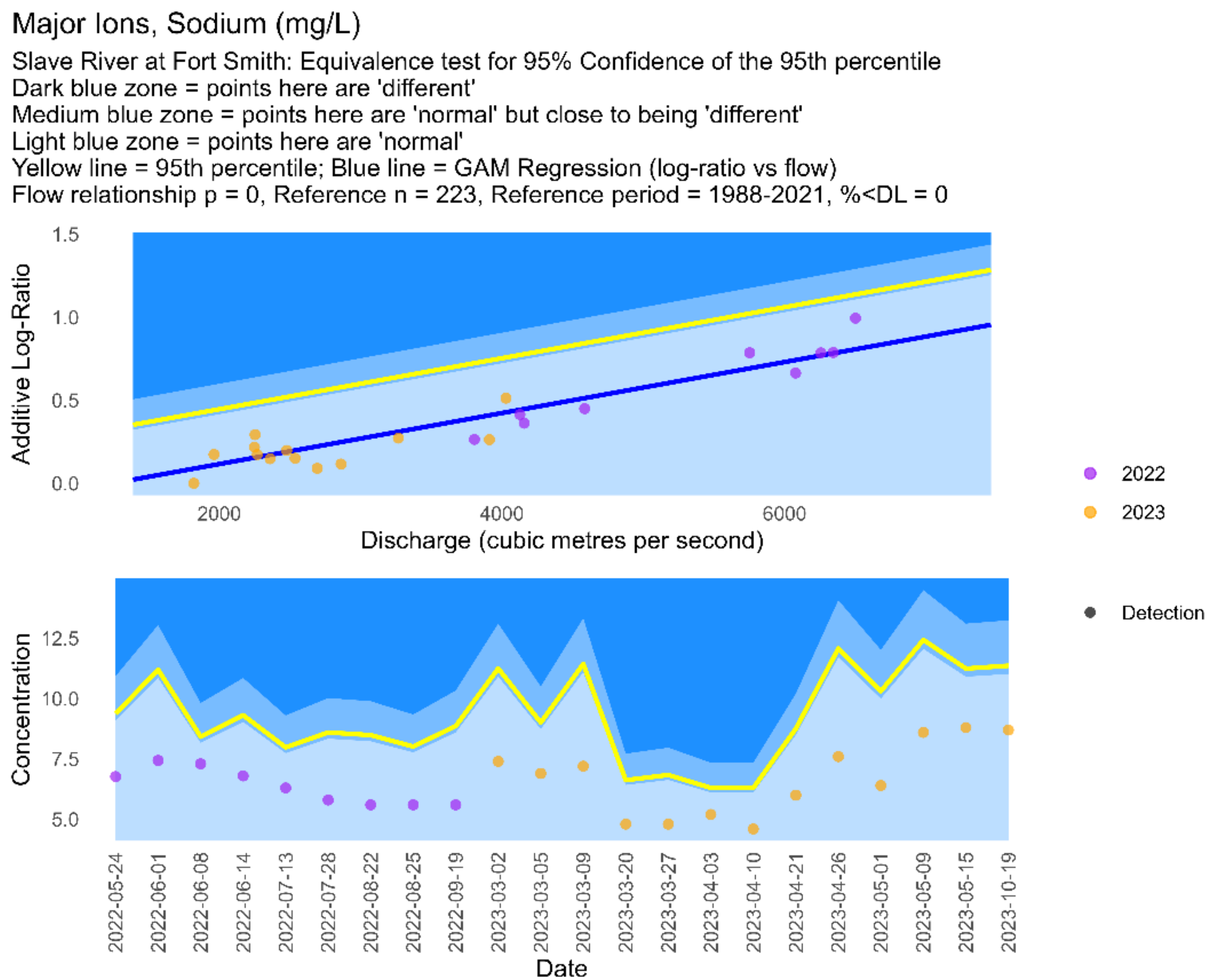


Figure B10. Evaluation of sodium relative to flow. <DL%: percentage of data below detection limit.

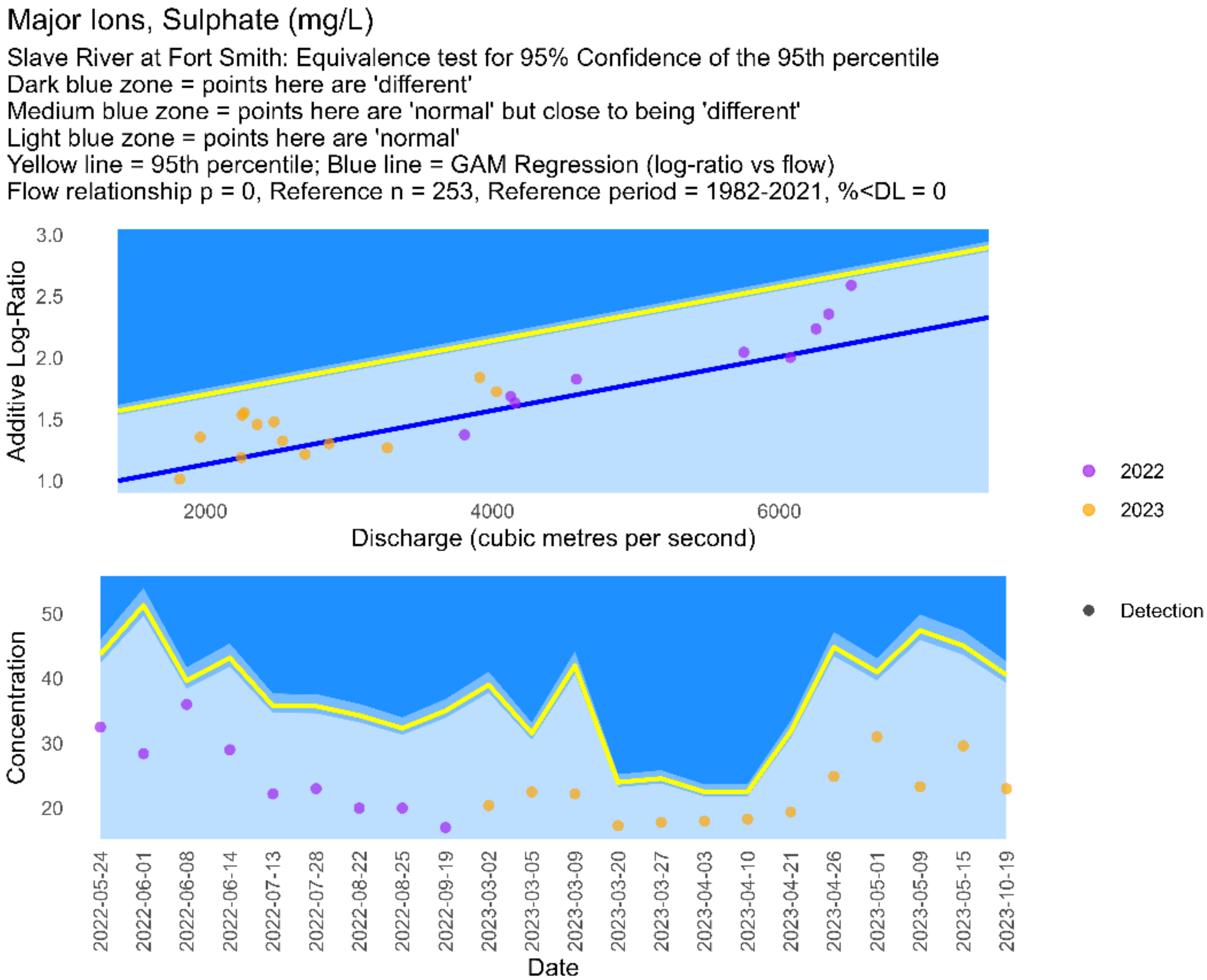


Figure B11. Evaluation of sulphate relative to flow. <DL%: percentage of data below detection limit.

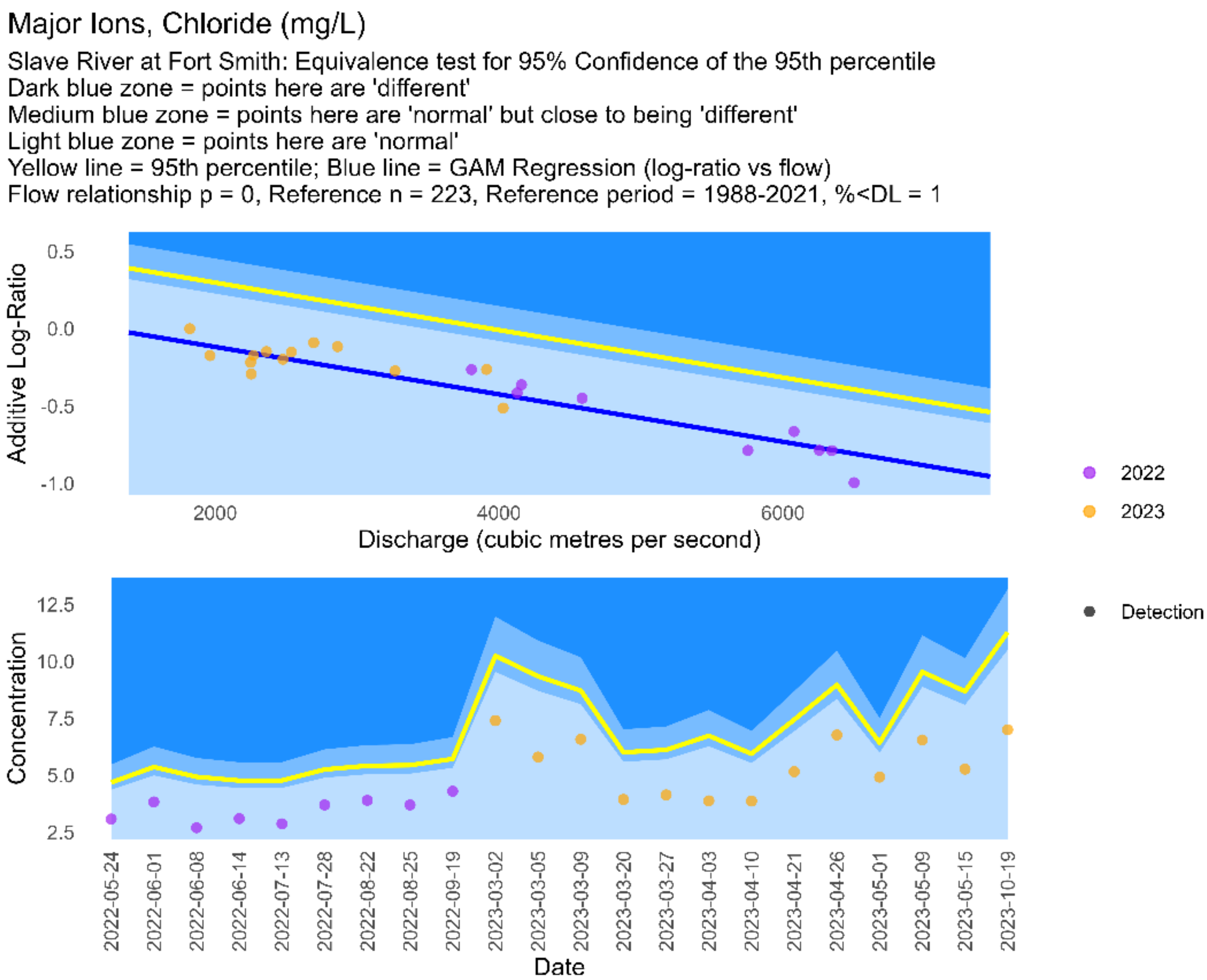


Figure B12. Evaluation of chloride relative to flow. <DL%: percentage of data below detection limit.

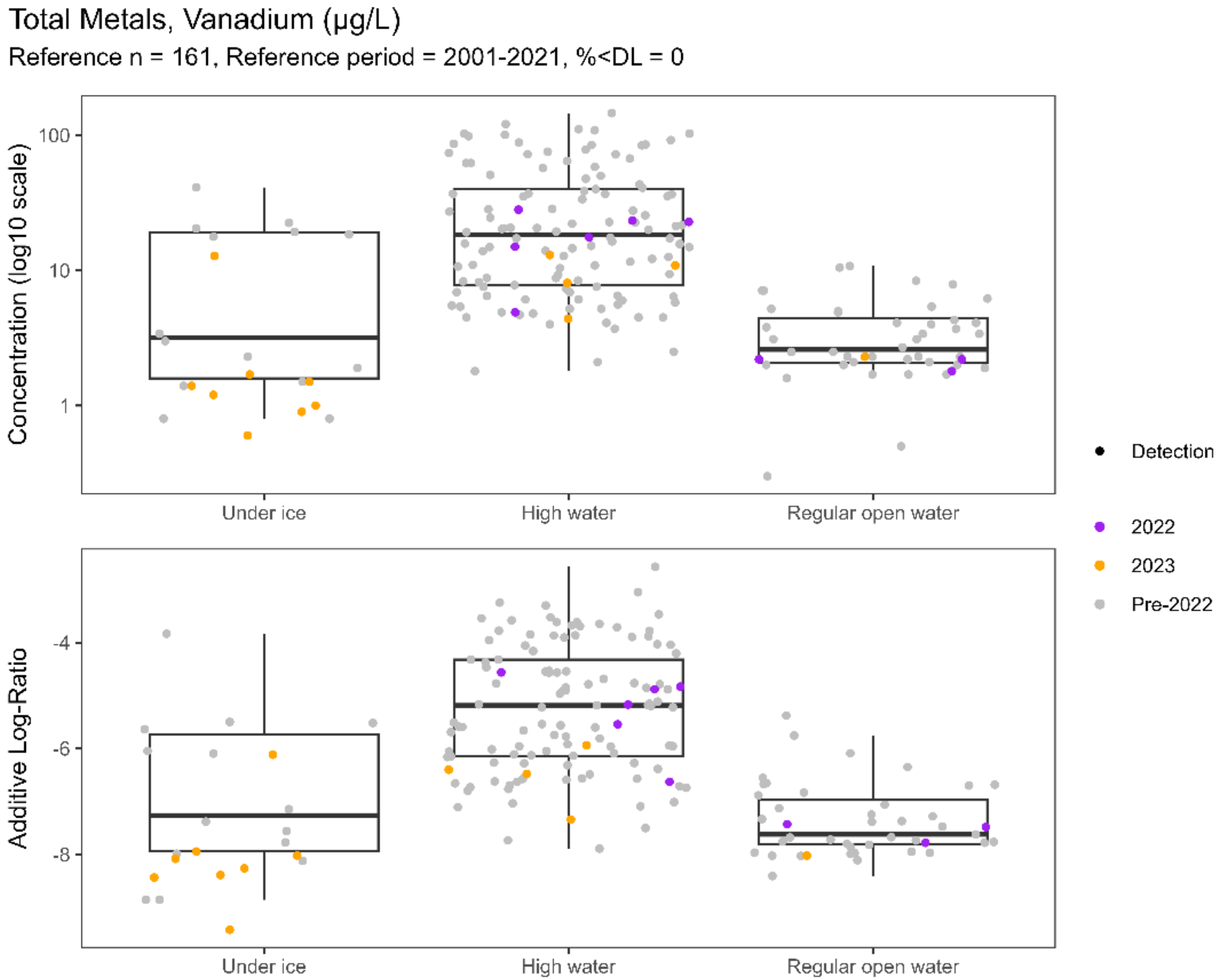


Figure C1. Total vanadium in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

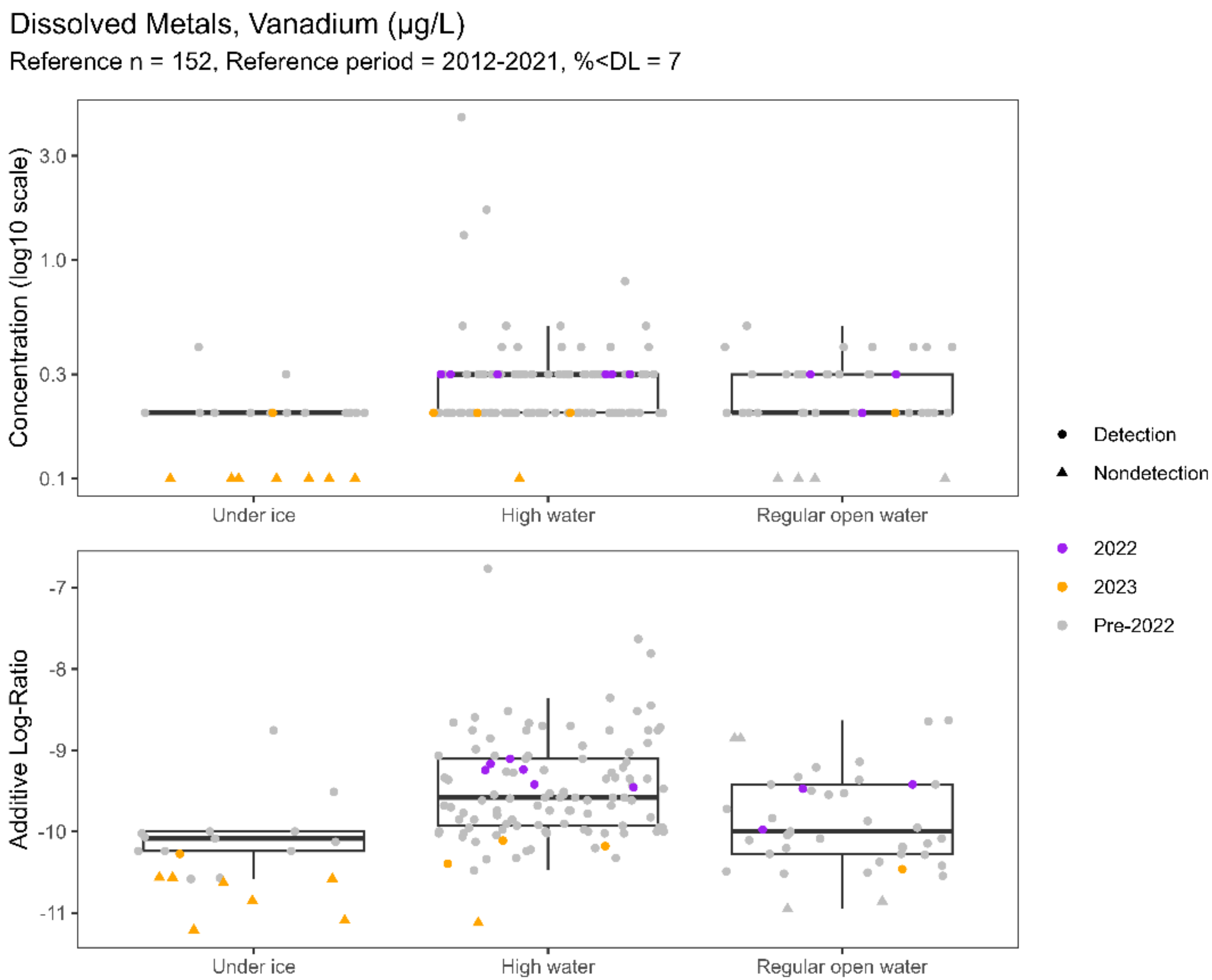


Figure C2. Dissolved vanadium in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

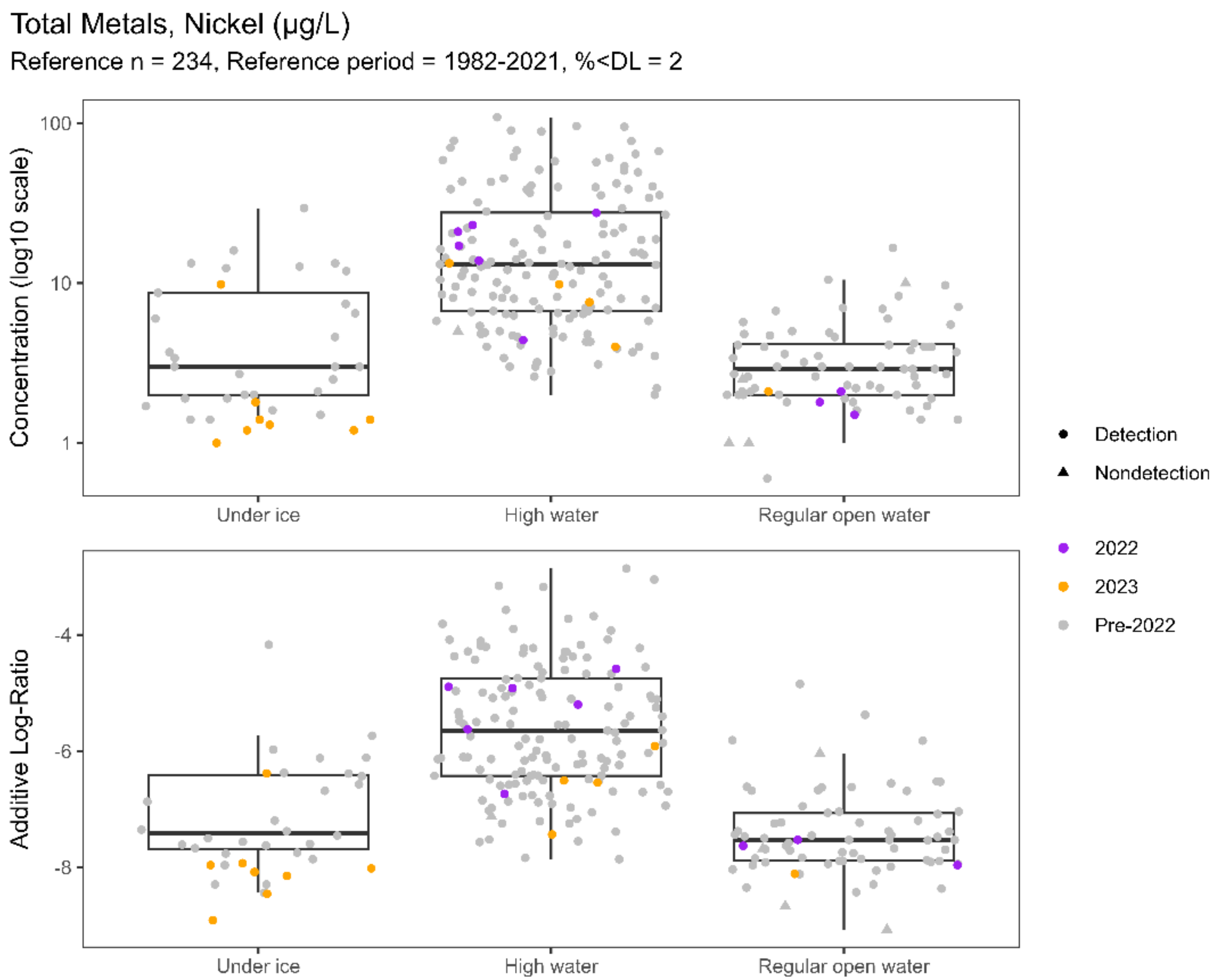


Figure C3 Total nickel in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

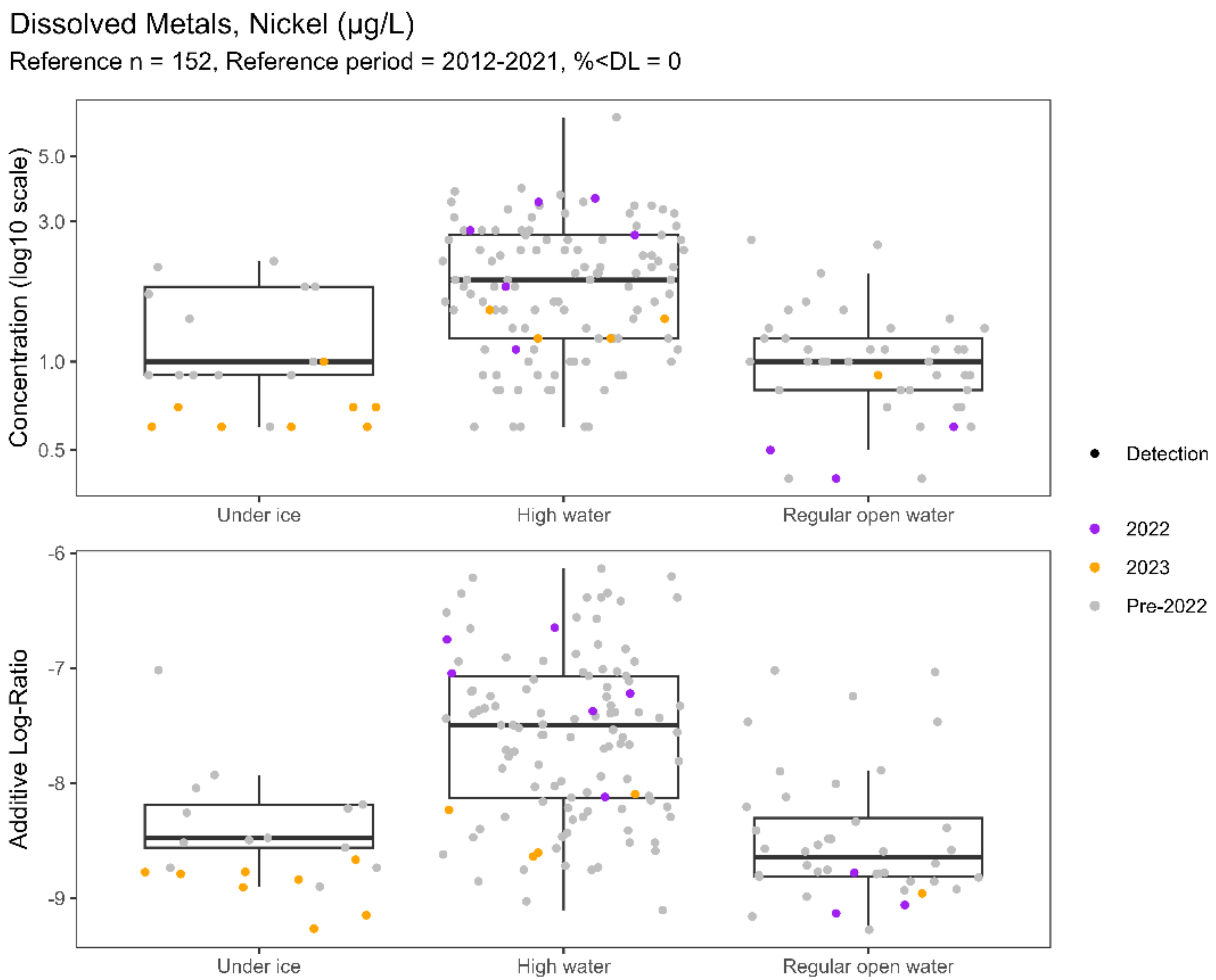


Figure C4. Dissolved nickel in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

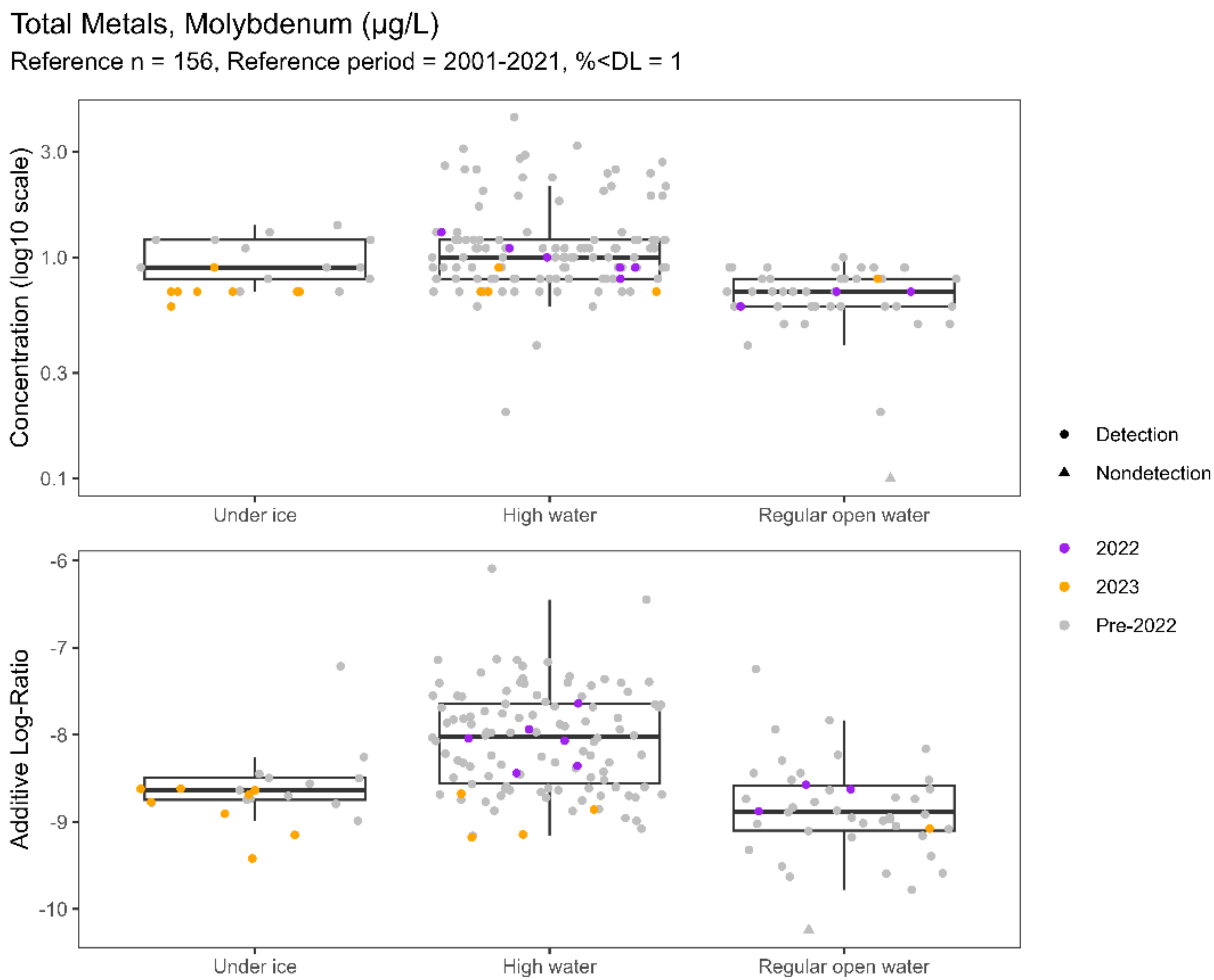


Figure C5. Total molybdenum in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

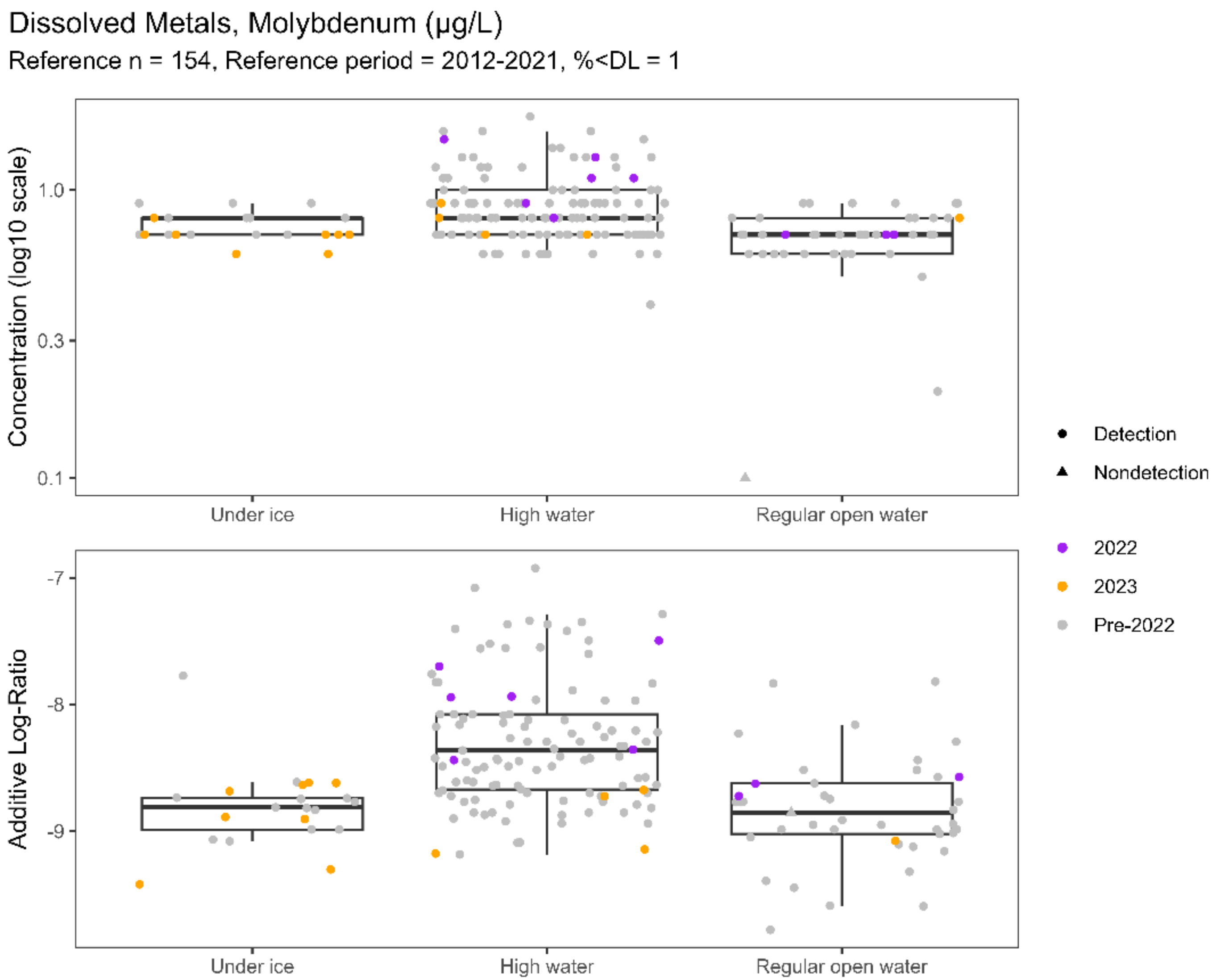


Figure C6. Dissolved molybdenum in the Slave River at Fort Smith. <DL%: percentage of data below detection limit.

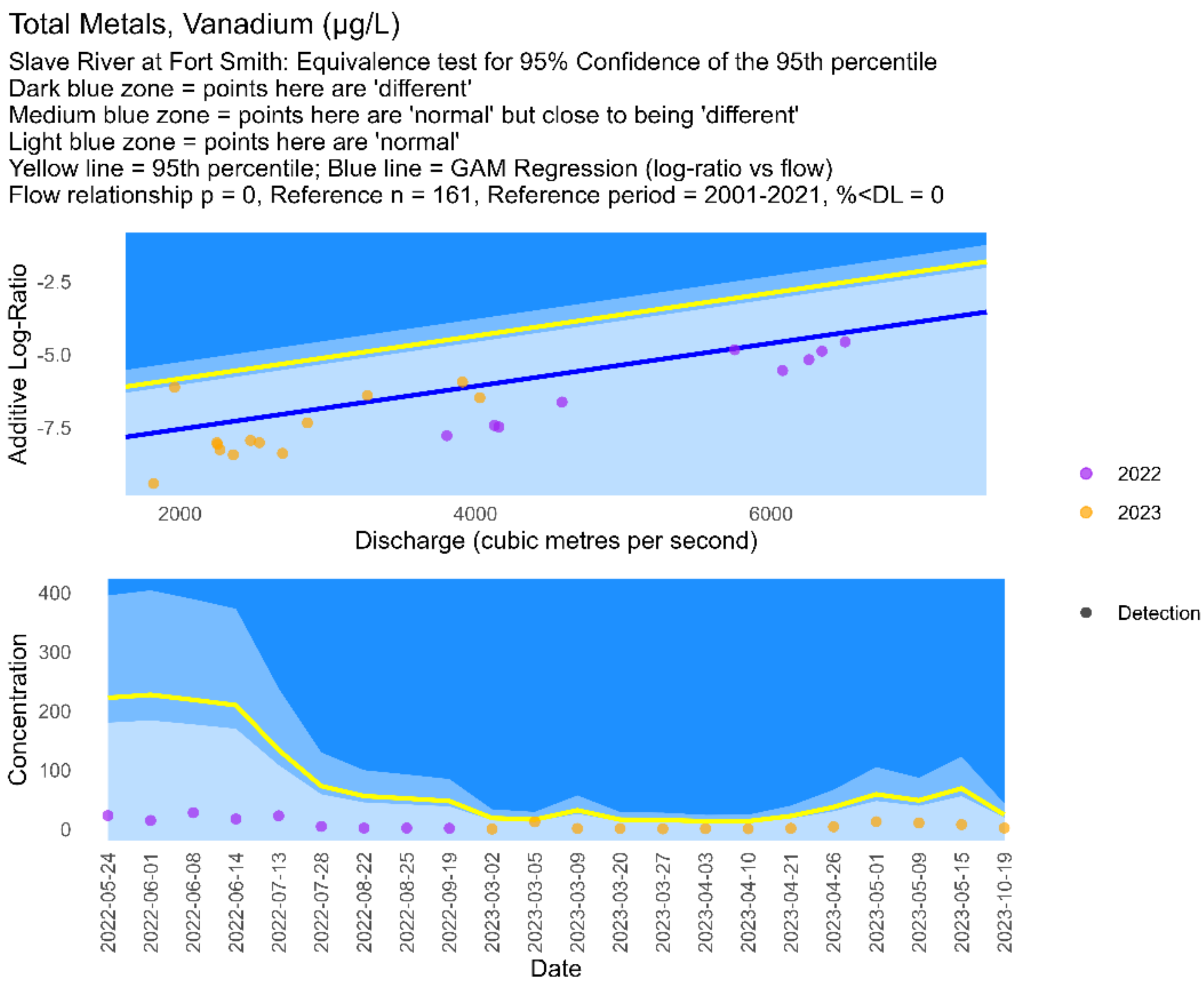


Figure C7. Evaluation of total vanadium relative to flow. <DL%: percentage of data below detection limit.

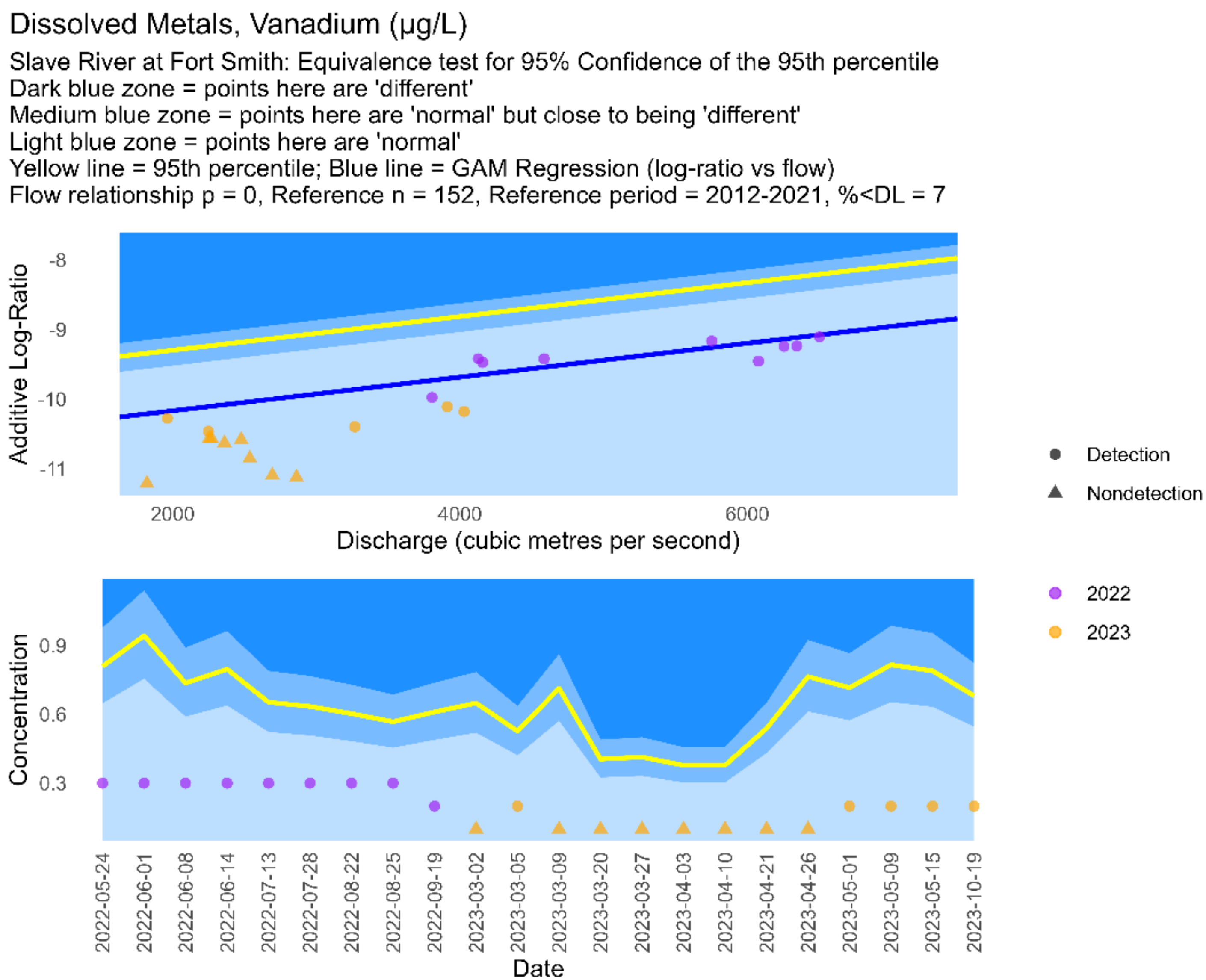


Figure C8. Evaluation of dissolved vanadium relative to flow. <DL%: percentage of data below detection limit.

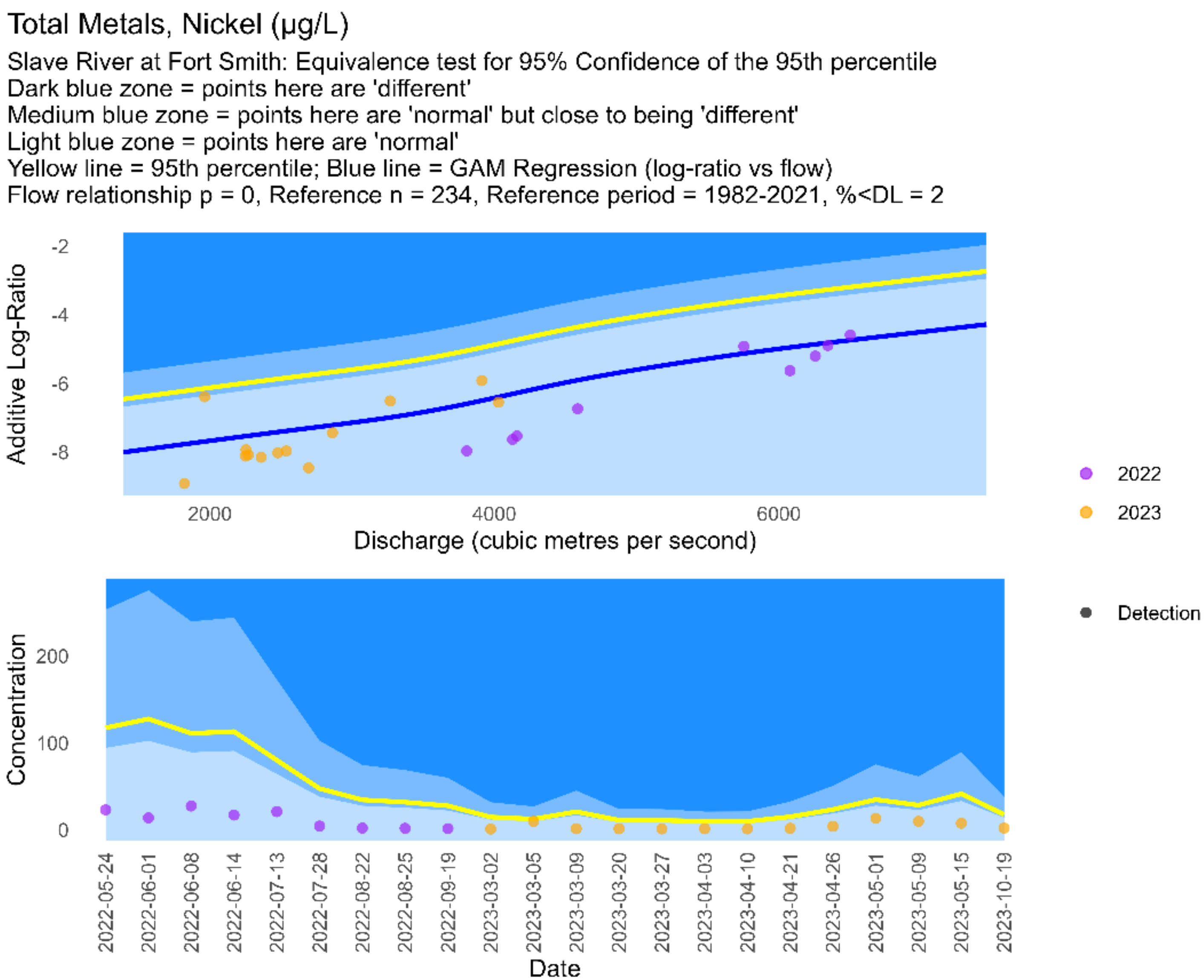


Figure C9. Evaluation of total nickel relative to flow. <DL%: percentage of data below detection limit.

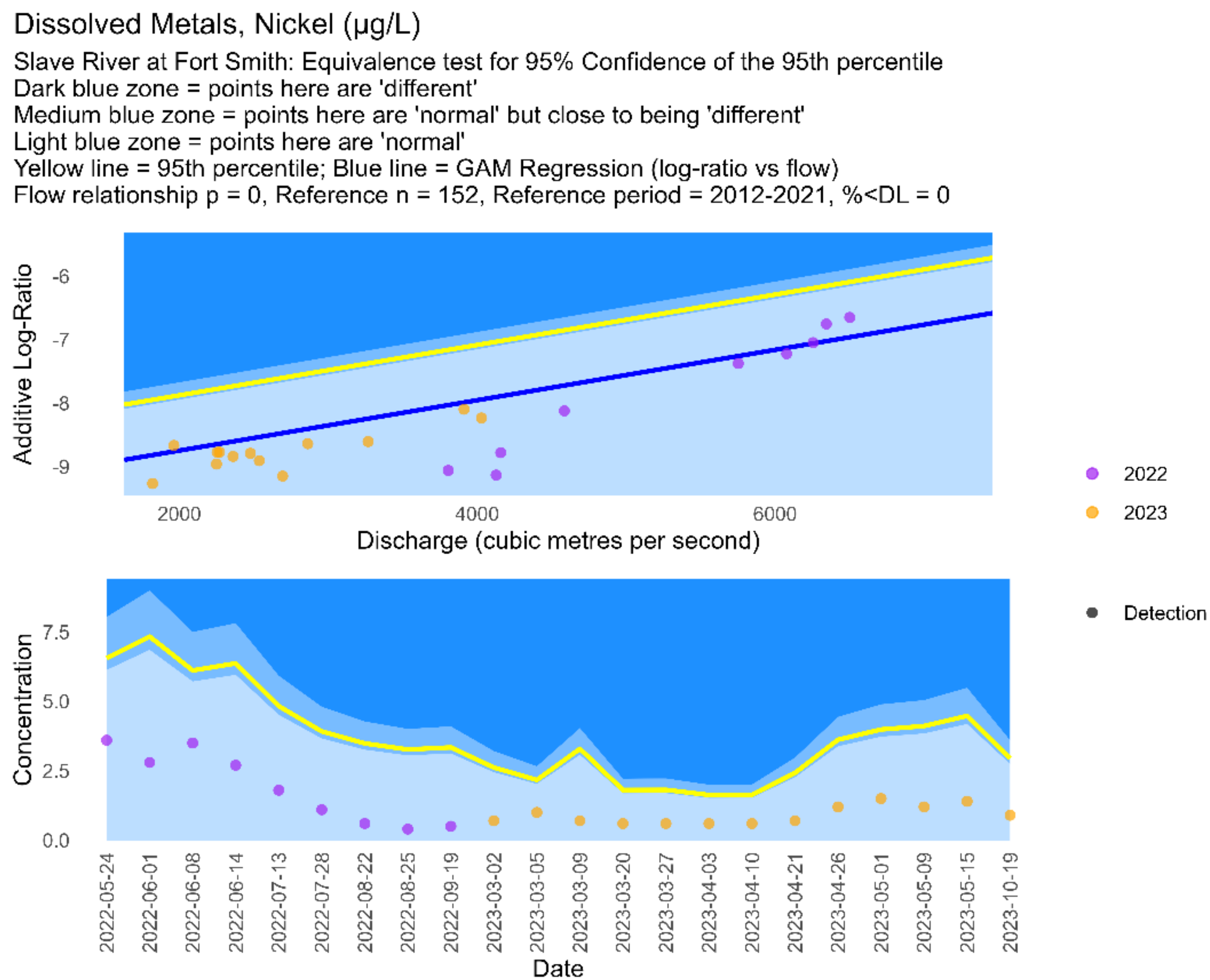


Figure C10. Evaluation of dissolved nickel relative to flow. <DL%: percentage of data below detection limit.

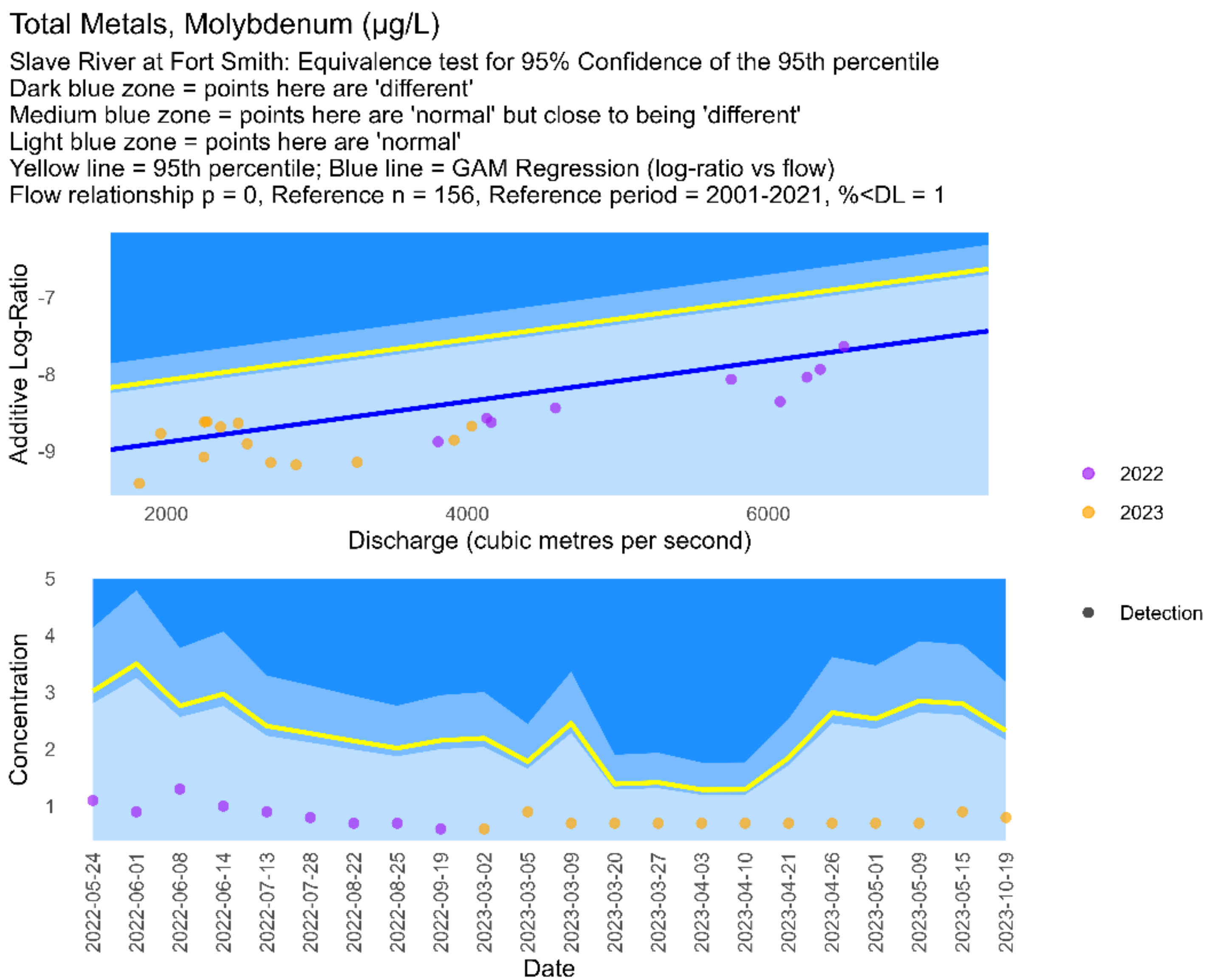


Figure C11. Evaluation of total molybdenum relative to flow. <DL%: percentage of data below detection limit.

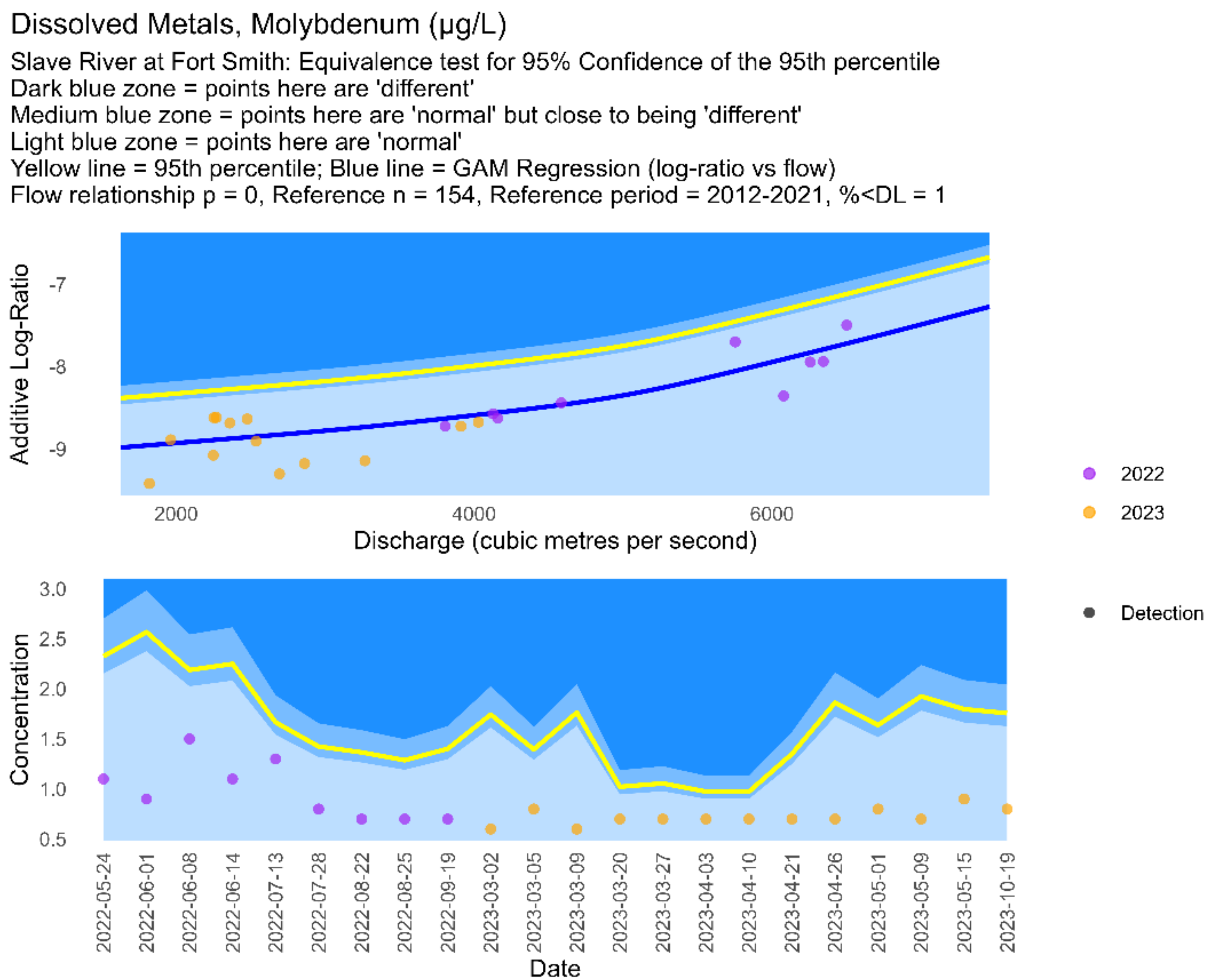


Figure C12. Evaluation of dissolved molybdenum relative to flow. <DL%: percentage of data below detection limit.

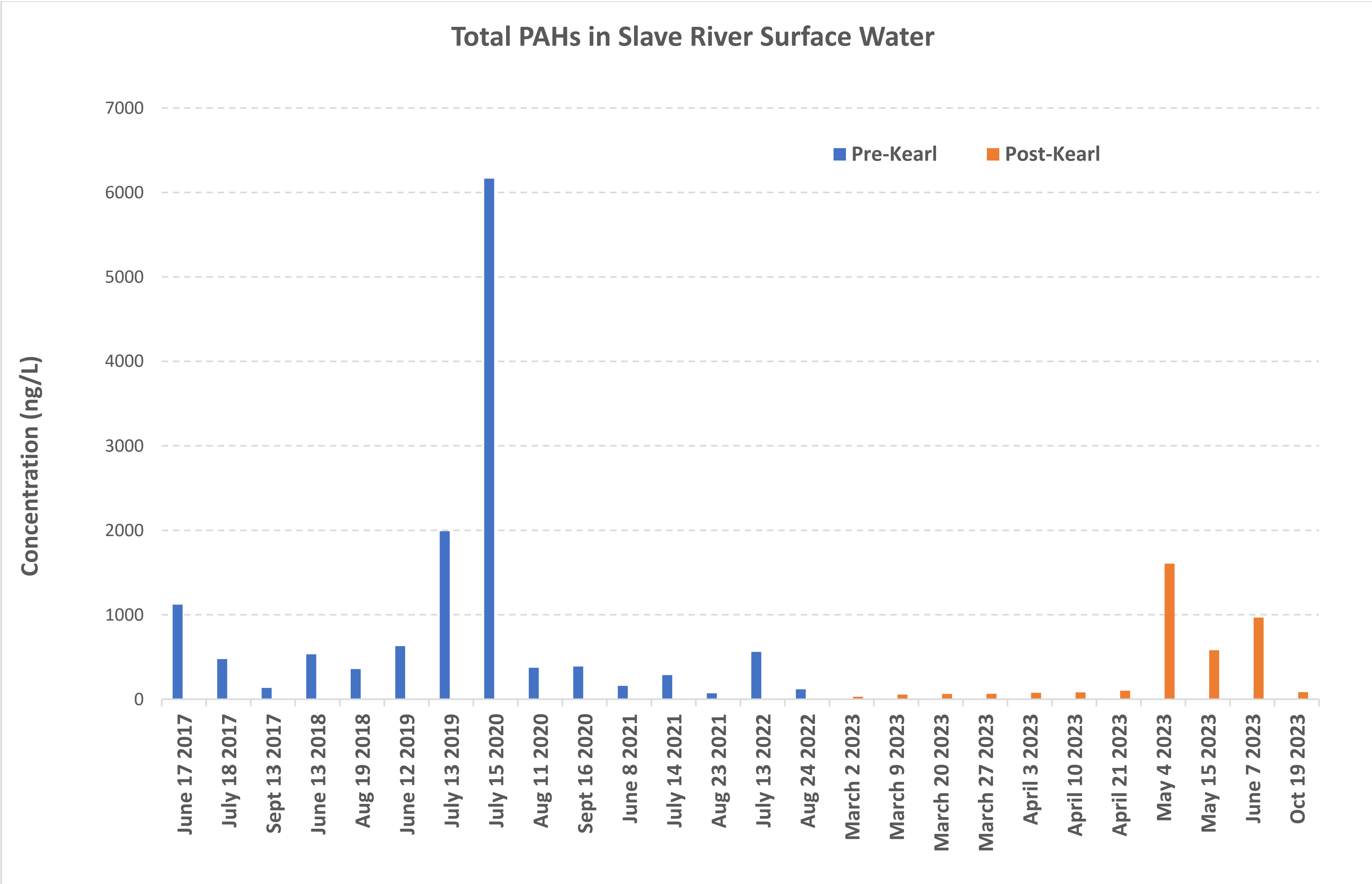


Figure D1. Total PAHs (Σ19 parent PAHs and Σ30 alkyl-substituted PAHs) measured in the Slave River (at Fort Smith) between 2017 and 2023.

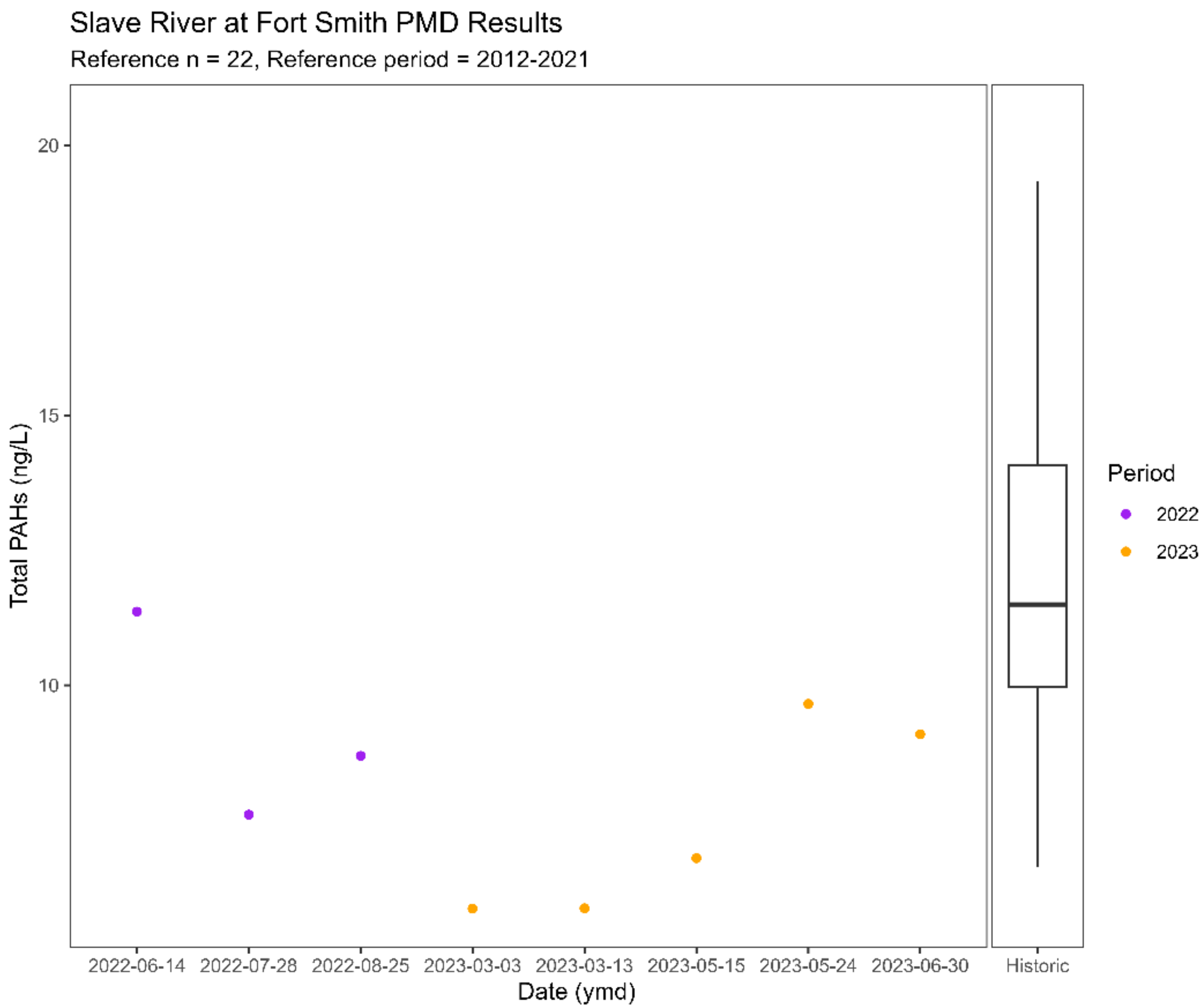


Figure D2. Total PAHs measured in PMDs deployed in the Slave River. The inset box-and-whisker plot was constructed using data from before 2022 (Pre-Kearl).

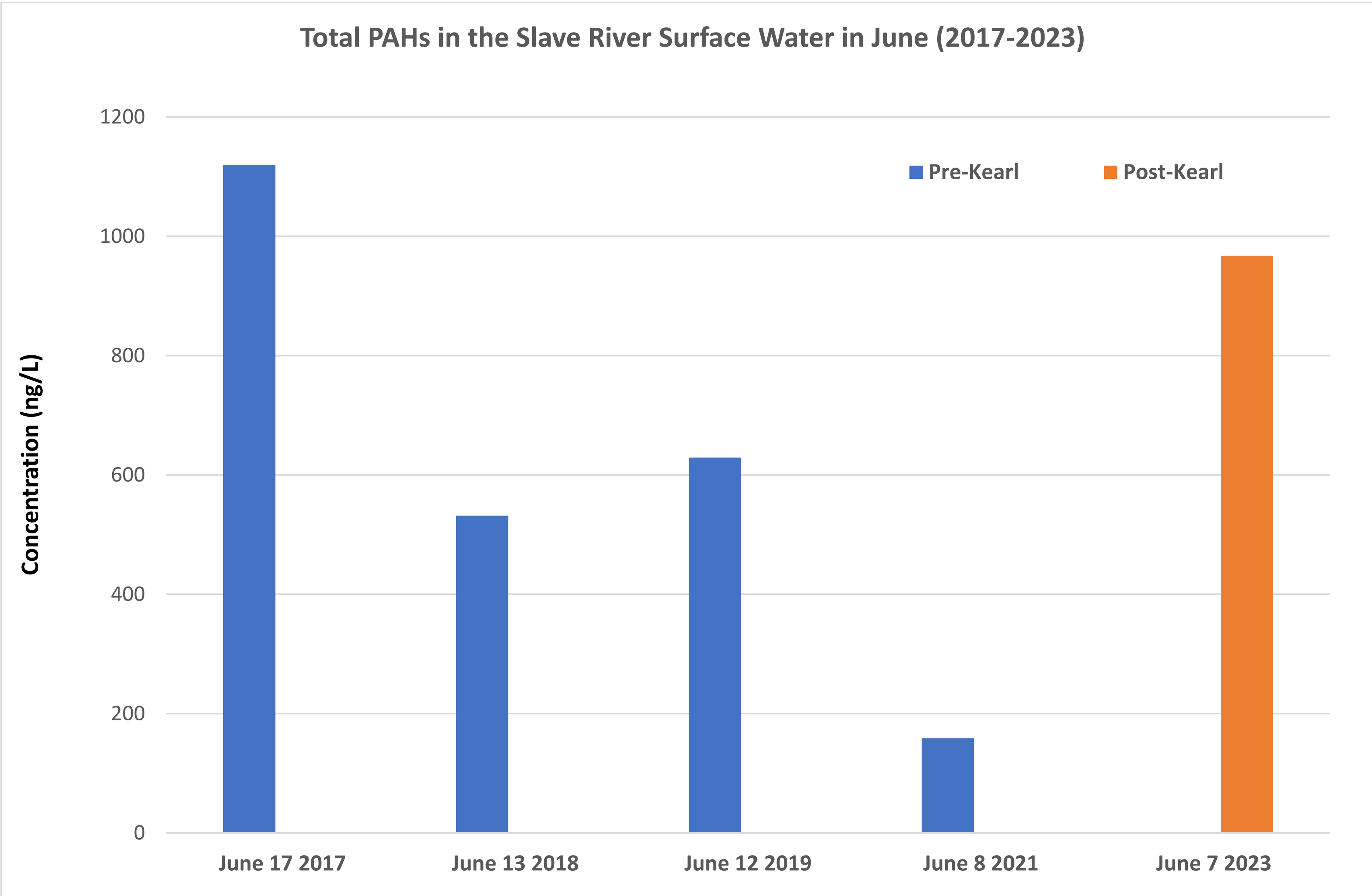


Figure D3. Total PAHs (Σ19 parent PAHs and Σ30 alkyl-substituted PAHs) measured in water samples collected in June from the Slave River (at Fort Smith) between 2017 and 2023.

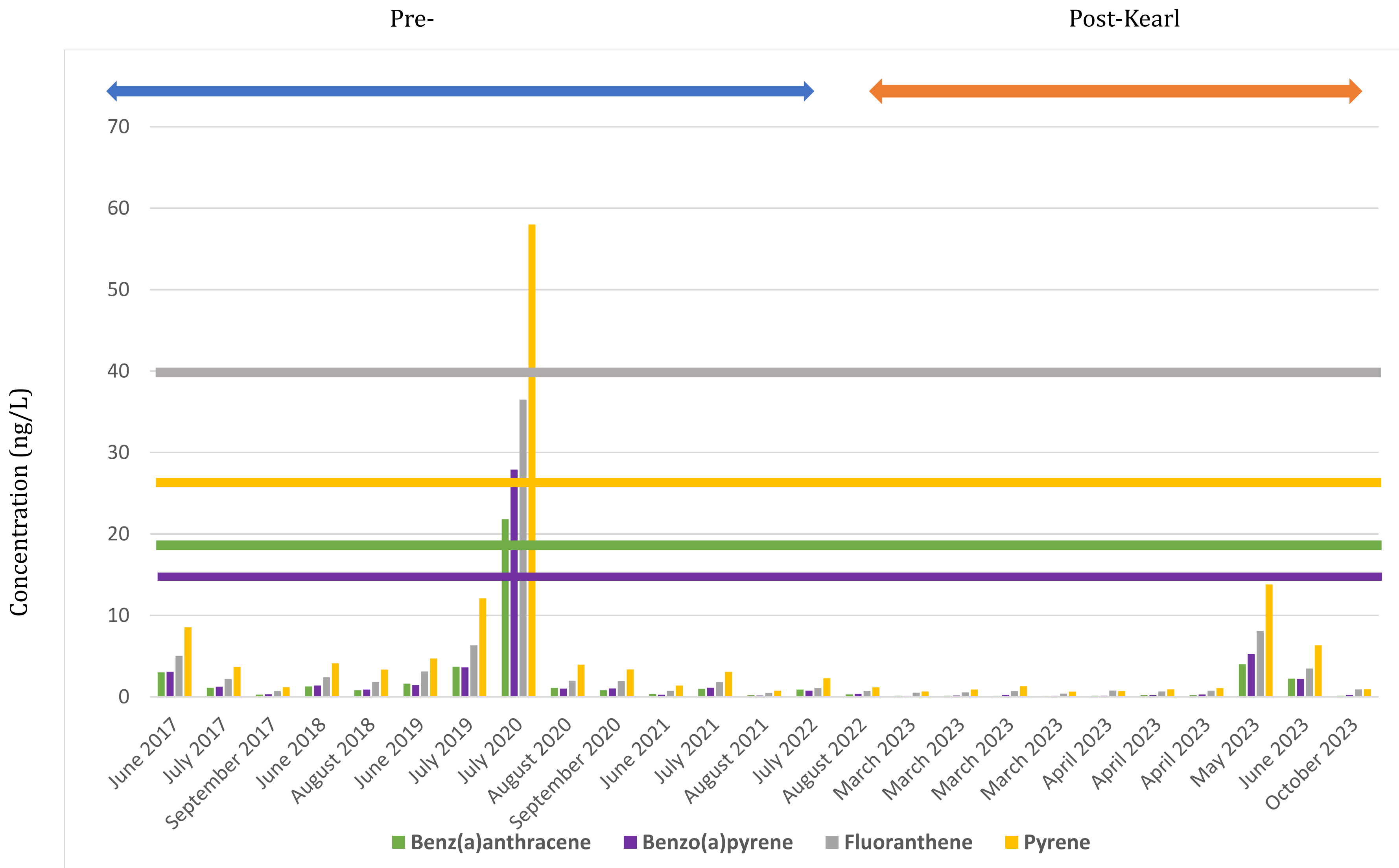


Figure D4. Comparing concentrations of benz(a)anthracene, benzo(a)pyrene, fluoranthene and pyrene (ng/L) in the Slave River at Fort Smith between 2017-2023 between pre- and post-Kearl time periods. Freshwater aquatic life guidelines are represented by the colored straight lines.

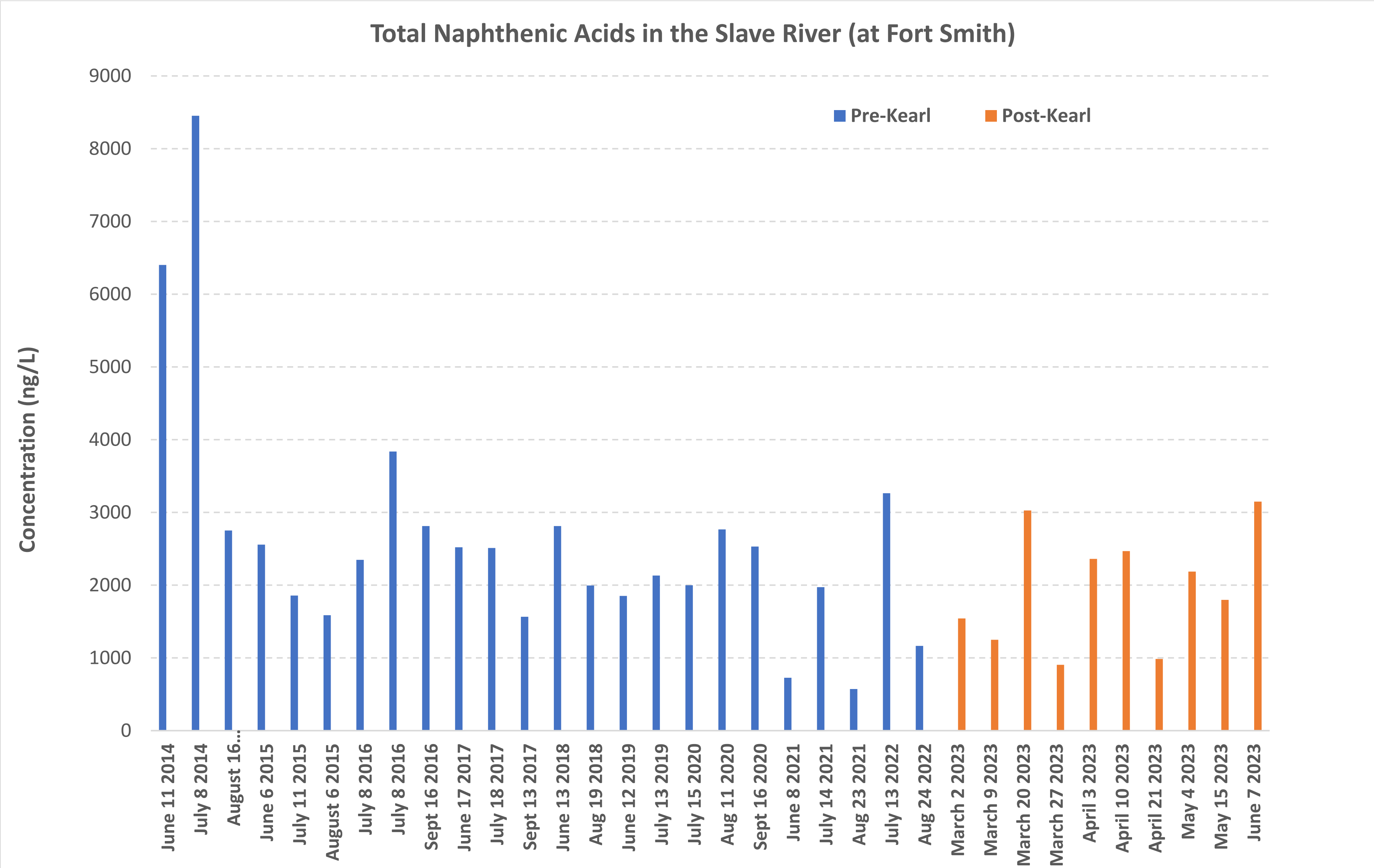


Figure D5. Total Naphthenic Acids (Σ60 individual NA compounds) measured in the Slave River (at Fort Smith) between 2014 and 2023.