Powell River Project 2019-2020 Annual Research Report

Spatiotemporal Patterns of Major Ions and Trace Elements in the Powell River

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ABSTRACT

Freshwater mussel populations in the Powell River have been in decline over several decades, with no indication of recovery. Identification of the cause(s) of mussel decline and continued suppression is a critical step toward improving water quality and restoring mussel populations in the Powell River. Toxicity from major ions and/or trace elements released from coal-mine discharges is hypothesized as a candidate but experimentation is needed to test that hypothesis. This study generated critical data on concentrations of major ions and trace elements, along with their spatial and temporal variation, which will enable accurate characterization and thus replication of environmentally-relevant exposure conditions for such experiments. We sampled water-column (surface) and substrate interstitial (pore) water seven times over the course of one year at nine locations in Powell River spanning 157 river kilometers. We found major ions and trace elements exhibited considerable longitudinal and intra-annual seasonal variation, with highest concentrations observed for most measured constituents in late summer/fall concurrent with low river discharge, and in river segments nearest coal-mining and other land uses that can increase erosion potential (urbanization, agriculture, forestry). Concentrations of trace elements were generally low relative to water-quality criteria in filtered surface and pore water with the exception of selenium, which regularly exceeded 40% of its chronic criterion but rarely exceeded it. In contrast, substantial amounts of trace elements were associated with interstitial fine sediment particles, with all toxic elements except arsenic having potential to exceed their chronic criteria if they were to become bioavailable, especially copper and lead. Although most major ions were well-correlated between surface and pore water, trace elements were less so, rendering prediction of pore-water concentrations from surface-water concentrations less likely. These results demonstrate the potential unreliability of estimating potential toxic exposures to benthic organisms from surface-water concentrations alone, and underscore the need for further research of all environmental compartments that may serve as sources and routes by which aquatic life, especially freshwater mussels, may be exposed to trace elements. The data generated by this study will facilitate such research by enabling characterization of realistic exposures to trace elements, to include how their spatial and temporal variation influence such exposures.

INTRODUCTION

Freshwater mussel populations in the Powell River have been in decline over several decades, with no indication of recovery (Ahlstedt et al. 2016). Despite this decline, the Powell River remains one of the top biodiversity hotspots in the U.S.A. for rare and endangered fishes and mussels, and has high recreational value; thus its recovery is of paramount importance to natural resources managers. A critical management need is identification of the cause(s) of mussel decline such that stressor mitigation plans may be developed. Although the cause of mussel decline is unclear, toxicity from major ions and/or trace elements released from mine discharge is hypothesized as a candidate. Identifying the water quality constituent(s) that may be causing mussel decline is a critical step toward improving water quality and restoring mussel populations in the Powell River.

A comprehensive study to identify causal links between organism effects and in-stream contaminant exposure levels has not been conducted. We have observed mussel populations in the Powell River decline concurrently with an increase in mining land use and associated water quality alteration (Zipper et al. 2016). Recent experiments have added to the body of evidence that mussel growth may be inhibited directly by mining-influenced river water or its constituents. For example, we know that mussel growth declined with increasing mining-origin solute concentration in Powell River following an exposure in situ (Phipps 2019); and major ions (Zipper et al. 2016) as well as trace elements (Phipps 2019) are elevated in Powell River, with greatest concentrations nearest the river's mining influence; and a mixture of three trace metals found in Powell River inhibited mussel growth by over 50% at concentrations below their chronic water-quality criteria (Timpano et al. 2020). What remains unknown is whether an environmentally-relevant mixture of major ions and trace elements at the concentrations observed in Powell River can cause toxicity to mussels. In addition, it is not clear whether observed toxicity is the result of all solutes or is driven primarily by a subset of ions as suggested by Phipps (2019). Further ecotoxicological experimentation is necessary to answer the lingering question of what is causing mussel decline; but to replicate Powell River water quality we must first quantify it thoroughly.

Determining accurate environmentally-relevant exposure conditions requires several considerations. First, because water quality varies spatially in Powell River (Phipps 2019) and major ion concentrations of Appalachian coalfield streams in general vary seasonally (Timpano et al. 2018), measurement of spatial and temporal variation of water quality is critical to characterize accurately mining-origin contaminant exposures in Powell River. Second, because mussels are filter feeders, one must consider a trophic pathway of exposure in the form of "total", or particle-bound contaminants, in addition to "dissolved" concentrations. Finally, pore-water contaminant concentrations must also be considered in addition to water-column, as mussels spend much of their time buried in streambed sediment from which they filter interstitial water, which in the Powell River can be elevated in particulate-bound trace elements (Phipps 2019).

A thorough understanding of water quality patterns and mining-origin contaminant concentrations and exposures in the Powell River will enable experimentation necessary to identify causes of mussel decline and guide restoration efforts. This study generated data required to inform that critical research, which will ultimately inform experiments that will advance the environmental science mission of the Powell River Project to enhance management and restoration of environmental resources affected by mining in the Appalachian coalfield.

Objectives

Our overall goal was to generate foundational data necessary to inform design of environmentally-relevant experiments aimed at identifying causal links between major ions and/or trace elements and mussel population decline in Powell River. To accomplish this goal, our objectives were:

1) Quantify environmentally-relevant exposures to mussels of major ions and trace elements by measuring particulate (unfiltered) and dissolved (filtered) concentrations in water-column and pore-water samples.
2) Develop predictive or correlative associations where possible to relate pore-water to water-column concentrations.
3) Evaluate spatial patterns or trends of major ions and trace element concentrations in Powell River water.
4) Assess short-term temporal variability of Powell River water quality by collecting data at approximately 30-day intervals.

METHODS

Sampling-Site Selection

We sampled nine sites (Table 1, Figure 1) spanning 157.5 river kilometers (RKM) of the Powell River from Appalachia, Virginia (RKM 293.7) to near Tazewell, Tennessee (RKM 136.2). This project benefited from using seven study sites in Powell River established by Phipps (2019) and expanded on that foundational work. To those seven sites we added two additional sites to represent conditions in the mid-reach of Powell River (RKMs 186.8 and 233.5). All sites contained suitable mussel habitat (i.e., shoals), as that is where pore-water ion concentrations have most relevance for mussels.

Table 1. Powell River sampling site information.

Site Name	Site ID	River km	State	County	Latitude	Longitude
Appalachia	APP	293.7	VA	Wise	36.904303	-82.781520
Big Stone Gap	BSG	287.2	VA	Wise	36.863290	-82.785774
Dryden Boat Ramp	DRY	269.1	VA	Lee	36.782730	-82.924930
RT 70 Bridge	RT70	233.5	VA	Lee	36.662840	-83.094310
RT 833 Bridge	RT833	186.8	VA	Lee	36.620998	-83.284952
McDowell Shoals	MCD	171.9	TN	Hancock	36.574995	-83.362610
Upper Brooks Bridge	UBB	153.4	TN	Claiborne	36.535090	-83.441700
Oakley Property	OAK	144.2	TN	Claiborne	36.535754	-83.467856
Yellow Shoals	YEL	136.2	TN	Claiborne	36.527517	-83.507572

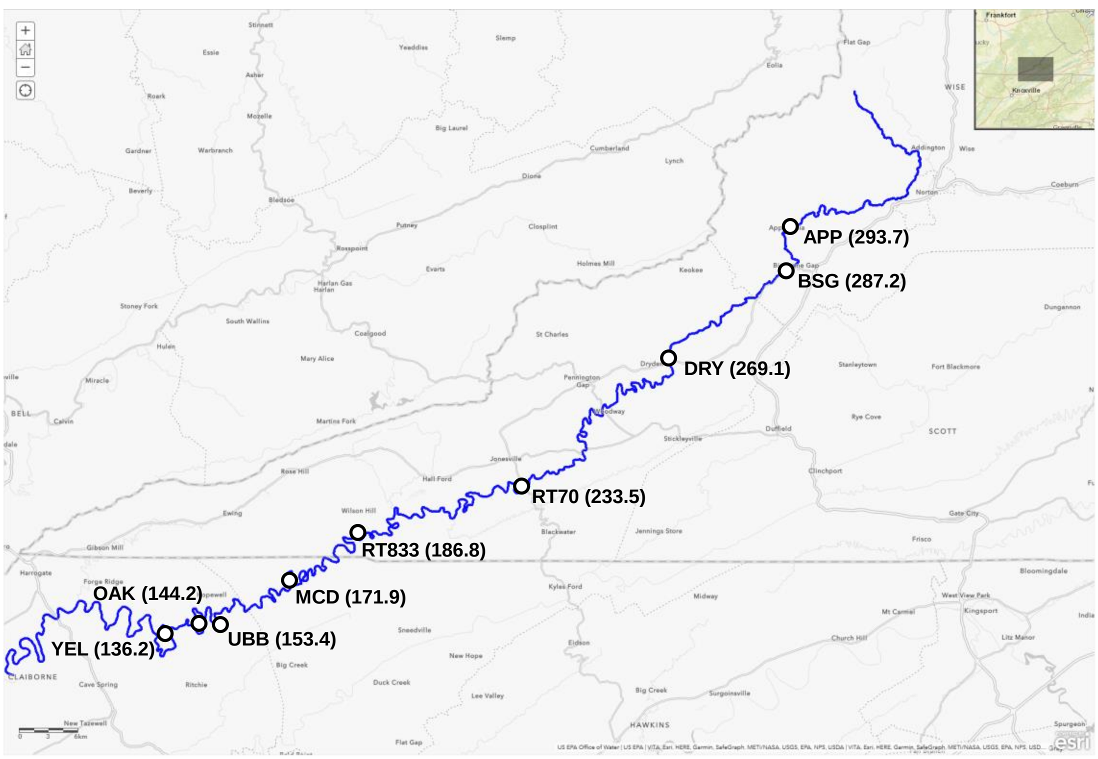

Figure 1. Map of Powell River sampling sites. Site identifiers are shown with river kilometer in parentheses.

Water Sampling

We collected water-quality samples during seven visits to Powell River: November 2019, January 2020, and monthly from June through October 2020. During each visit and at each of nine sites, flow-permitting (we were unable to sample RT70 in Jan 2020 because of unwadeable flow conditions), we collected pore-water samples from interstices of suitable mussel habitat (i.e., shoals) using a Drive-Point piezometer (6-inch Model 615, Solinst Canada Ltd., Georgetown, Ontario, Canada), driven to depth such that the mid-point of screened area (50-mesh) is approximately 10 cm (integrating water from 6 – 14 cm sample depth). Interstitial water and associated particles were collected under suction using a 60-mL polyethylene syringe-pump assembly connected to polyethylene and silicone tubing attached to the sampler barb. We discarded the first 120 mL of sample to flush the sampler of any residual water or sediment, as well as any surface water that was entrained into the sampler during installation. We then collected 100 mL of pore water in a polyethylene bottle. This procedure was conducted a total of 5 times at points randomly selected at each study site and subsamples combined to produce a composite 500-mL sample. A single grab sample of well-mixed surface water was collected in a polyethylene bottle from mid-depth. We measured temperature, pH, and electrical conductivity at the time of sample collection using a multi-parameter sonde (YSI 556, YSI Inc., Yellow Springs, Ohio USA).

Sample Processing and Analytical Chemistry

Water samples were processed in the field immediately after collection and partitioned into four sample types, which consisted of filtered and unfiltered surface water (abbreviated SF and SU, respectively), along with filtered and unfiltered pore-water (PF and PU, respectively). Filtration was accomplished with 0.45 um PVDF syringe filters (SF) or 0.45 um PES capsule filters and peristaltic pump (PF). Unfiltered samples (PU and SU) were poured directly into sample containers after shaking to homogenize the sample and suspend particles. Aliquots of filtered sample (PF and SF) were collected for analysis of alkalinity (potentiometric titration), chloride and sulfate (ion chromatography), non-purgeable organic carbon (representing dissolved organic carbon, or DOC), as well as major cations and trace elements (inductively-coupled plasma mass-spectrometry, or ICP-MS). Unfiltered samples (PU and SU) were collected for analysis of only major cations and trace elements, as the other analysis methods do not accommodate suspended solids in the respective instruments. Samples for major cation and trace elements were preserved with trace-metal grade nitric acid to $pH < 2$ (2% v/v), and samples for DOC were preserved with trace-metal grade hydrochloric acid (0.02% v/v). All samples were stored on ice for transport to the laboratory and thereafter refrigerated until analysis. Unfiltered samples (PU and SU) for major cations and trace elements were further processed by centrifugation to settle particles and the supernatant decanted and retained for analysis by ICP-MS. Bicarbonate and carbonate were calculated from pH and total alkalinity as measured by titration with standard acid.

Specific Conductance Datalogger

At the mid-reach study site near Jonesville, VA (RT70 Bridge, river km 233.5), we installed in November 2019 a freshwater conductivity datalogger (HOBO U24-001, Onset Computer Corp., Bourne, Massachusetts, USA) to record electrical conductivity and temperature every 30 minutes, from which we calculated SC (electrical conductivity standardized to 25 °C). The datalogger was downloaded, cleaned, and reinstalled at each visit. However, we were unable to visit the river because of elevated and unwadeable flow conditions for most of the spring, thus prohibiting access for datalogger maintenance. Therefore we were not able to record SC from approximately late March to mid-June.

Data Analysis

Water Chemistry Data Used

For analysis we used concentrations of eight major ions: calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), sodium (Na^{+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^{-}), chloride (Cl^{-}), and sulfate (SO_4^{2-}). In addition, we used two surrogate measures of salinity in analyses: the aggregate metric Sum of 8 Major Ions, which is the sum of the concentrations of the eight major ions measured and is used in lieu of total dissolved solids as the former better accounts for the high concentration of carbonates in alkaline waters; and SC, as a general indicator of salinization and influence from mining land use in the Powell River basin. We also used concentrations of 20 trace elements: aluminum (Al), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), strontium (Sr), tin (Sn), titanium (Ti), uranium (U), vanadium (V), and zinc (Zn). These 30 analytes will be referenced throughout as "ion(s)" for brevity.

We analyzed data to evaluate spatiotemporal patterns of ions, explore potential for ecological toxicity, and to determine the degree to which pore-water ion concentrations might be correlated with surface-water concentrations. Analyses used up to 30 ions across seven months, nine study sites, and four sample types, totaling over 800 relationships examined (see Appendices). All analyses were conducted in R statistical software (v. 4.0.2, R Core Team 2020) with test level of alpha = 0.05 unless specified otherwise. Boxplots in figures have the following convention: thick central line = median; box extents = interquartile range (IQR; 25th to 75th percentile); individual points = outliers, which are observations > (1.5)(IQR) from IQR extents; whisker ends = observations farthest from median that are not outliers.

Spatiotemporal Patterns

Differences in ion concentration among sites and months were assessed for each of 30 ions and four sample types using linear mixed models to account for temporal and spatial autocorrelation, as is produced from repeated sampling of the same sites. To assess whether water quality varied with sampling location in Powell River (spatial or site effect) we modeled ion concentration as a function of study site as a fixed effect and sample month as a random effect. We assessed whether time of year influenced water quality by modeling ion concentration as a function of sample month as a fixed effect and study site as a random effect. Mixed models were constructed using the *nlme* R package (v. 3.1-150; Pinheiro et al. 2020) and tested for significant predictor effects using Wald tests. We also assessed short-term seasonal (intra-annual) variation of major ions in Powell River by examining high-frequency SC data for conformance with the general seasonal sinusoidal pattern of SC exhibited by other salinized streams in the Appalachian coalfield region (Timpano et al. 2018).

Spatiotemporal trends were assessed through Mann-Kendall trend analysis of ion concentrations using R package *Kendall* (v. 2.2; McLeod 2011). Spatial trends were assessed moving downstream, to assess whether ion concentrations declined moving downstream from the influence of mining land use. Temporal trends were assessed using monthly sample data moving forward in time beginning in November 2019, but because the model computation requires no gaps in the dataset, we conducted the analysis on months treated ordinally rather than using actual sample dates, as we have no samples in December 2020 or from February through May 2020. In addition, because this trend analysis can accommodate only one observation per sample, we fit trends to site-wise or month-wise mean concentrations as appropriate.

Toxicity Potential of Trace Elements

To provide ecologically-relevant context to concentrations of trace elements that are considered pollutants, we compared concentrations of Al, Ag, As, Cd, Cu, Cr, Fe, Ni, Pb, Se, and Zn to their respective USEPA water quality criteria for freshwater aquatic. For elements with variable criteria, we calculated criteria using appropriate formulas and water quality parameters on a per-sample basis. For hardness-dependent criteria (Ag, Cd, Ni, Pb, Zn), we computed total hardness from Ca and Mg concentrations and used that value and the appropriate equations (USEPA 2020) to arrive at adjusted criteria. Because Cr concentrations represent un-speciated, or "total dissolved" Cr, we used the lower, fixed criteria for hexavalent Cr (VI), instead of hardness-dependent criteria for trivalent Cr (III). Thus Cr criteria used here serve as an indication of a "worst-case scenario" if all Cr present were of the more-toxic Cr (VI) speciation. For aluminum, we used the R code available on the USEPA website for aluminum criteria (USEPA 2018) to calculate adjusted criteria using total hardness, DOC, and pH for each sample. Finally, we used the Biotic Ligand Model (v. 2.2.3; HydroQual, Inc. 2007) to adjust copper criteria using temperature, pH, DOC, Ca, Mg, Na, K, SO_4, Cl, and total alkalinity.

We quantified the relative ecotoxicological risk of trace-element concentrations by calculating criterion ratios for each element, which is the concentration divided by the criterion, determined individually for each sample. Thus, toxic potential increases with criterion ratio, and notably a criterion ratio > 1 represents a criterion exceedance. This approach allowed standardization of toxicity potential among samples for elements whose criteria varied along with other water-quality attributes. It also allowed comparisons of ecotoxicological potential among elements of disparate toxicity.

For elements other than Cr with criteria that depend on hardness (Ag, Cd, Ni, Pb, Zn), criterion ratios are based on criteria calculated for each individual sample, regardless of sample type. For aluminum and copper, criterion ratios are based on criteria calculated for each individual sample but only for filtered samples (SF, PF). Criterion ratios for unfiltered samples (SU, PU) for those elements are based on unfiltered concentrations divided by criteria calculated for the respective filtered sample. This was done because the dissolved organic carbon data needed to calculate Al and Cu criteria were not available for SU or PU samples, as DOC can not be measured on unfiltered samples.

We summarized acute and chronic criterion ratios by constructing boxplots of criterion ratios by sample type for each element, using data pooled through space and time. We examined spatiotemporal differences in ecotoxicological potential by constructing linear mixed models in an identical manner as we did for ion concentrations, but using criterion ratios as the response variable in each model.

Relating Pore Water to Surface Water

To determine if pore-water and surface-water ion concentrations were related, we conducted Spearman rank correlation analysis of ion concentrations among sample-type pairs using function *corr.test()* in the R package *psych* (v. 2.0.9; Revelle 2020). In addition to pairwise correlations among sample-type pairs (SF, SU, PF, PU), we included SC as a correlate with each sample type in order to evaluate whether SC might be useful as a predictor of surface- or pore-water ion concentrations. To visualize sample-type associations using individual samples, we prepared pairwise scatterplot matrices using function *pairs()* in the R package *graphics* (R Core Team 2020). These analyses used data from all sites and months pooled by sample type (n = 62 for most ions).

RESULTS AND DISCUSSION

Major-Ion and Trace-Element Concentrations

Given the presence of substantial surface coal mining in the Powell River catchment, major ions concentrations were as expected. That is, samples were alkaline, with elevated Ca, Mg, HCO_3, and especially SO_4 (median 93.3 mg/L) in surface water samples (Table 2, Figure 2), relative to concentrations meeting USEPA reference criteria for the Central Appalachian and Ridge and Valley ecoregions (Griffith 2014) through which the Powell River flows. Sodium was elevated but median Cl was low (< 4 mg/L), which is comparable to findings from two recent studies of Powell River water quality (Zipper et al. 2016, Phipps 2019). Trace elements in filtered surface and pore water samples (SF, PF) were generally low (Table 2, Figure 3) and comparable to the same sample types collected by Phipps (2019) in the same section of Powell River. However, our unfiltered pore-water (PU) samples had very high concentrations for many trace elements (Table 2, Figure 3), which was not the case for Phipps (2019), likely because our PU sampling method included greater amounts of sediment particles.

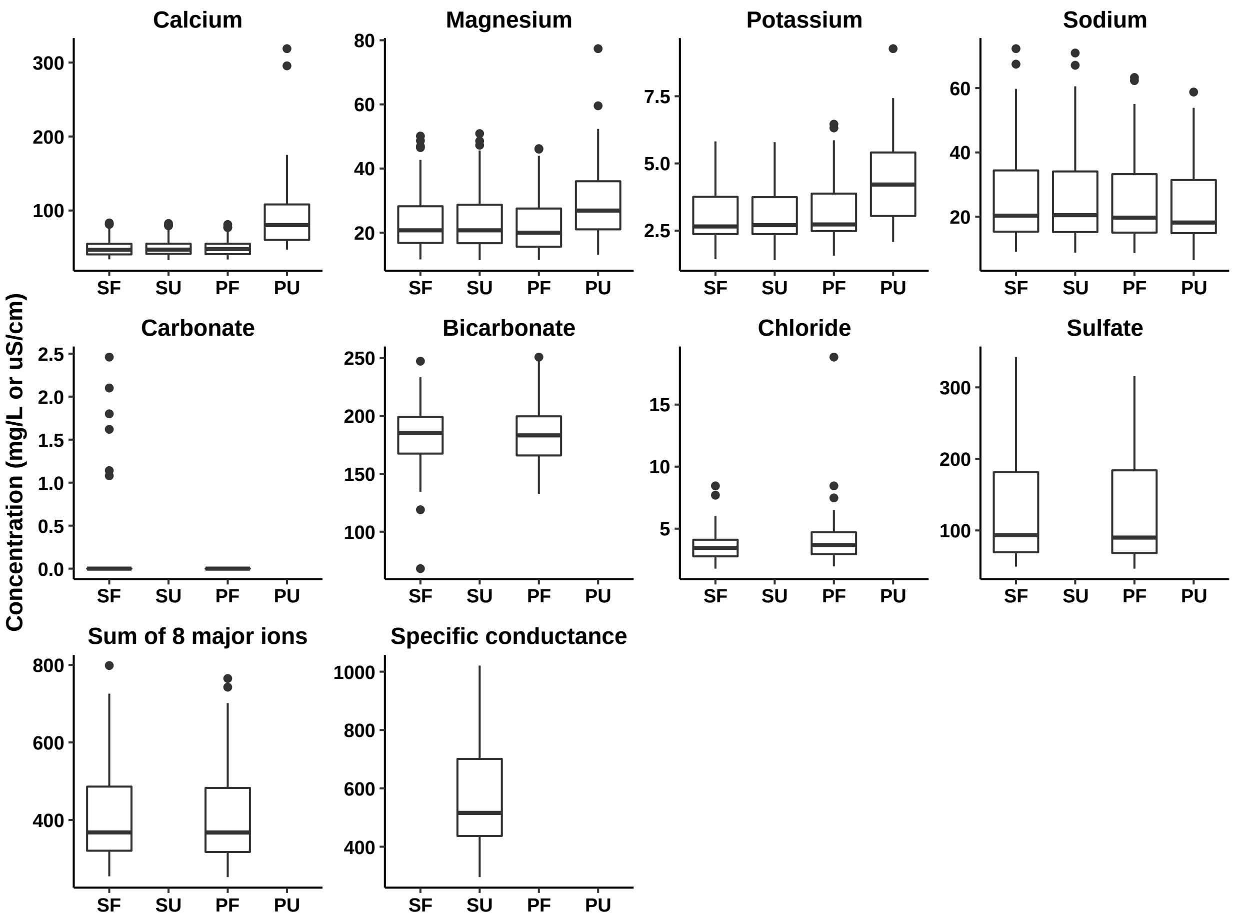

Figure 2. Boxplots of major ion concentrations by sample type. For each ion and sample type, data pooled across sites (≤ 9) and sample months (≤ 7); boxplot n ≤ 63. Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered.

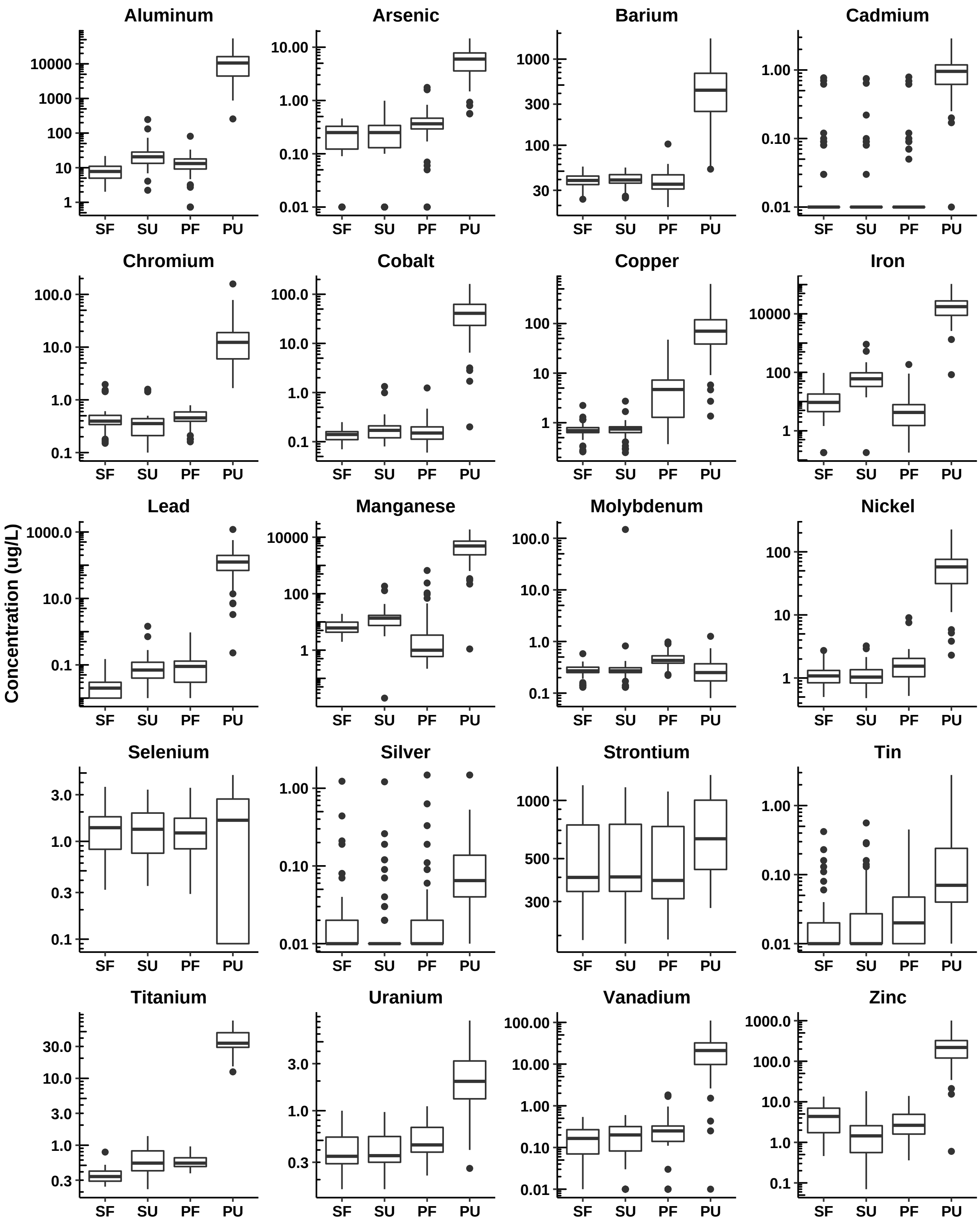

Figure 3. Boxplots of trace element concentrations by sample type. For each element and sample type, data pooled across sites (≤ 9) and sample months (≤ 7); boxplot n ≤ 63. Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered.

Table 2. Water sample median concentration (and range) for each ion and sample type.

Sample Types:	SF	SU	PF	PU
Specific conductance (uS/cm)				
SC	NA	516 (296 - 1020)	NA	NA
Major Ions (mg/L)				
Ca	46.9 (34.1 - 83.2)	47.2 (32.9 - 82.5)	47.9 (33.8 - 81.1)	80.4 (47.2 - 319)
K	2.66 (1.44 - 5.82)	2.71 (1.4 - 5.79)	2.73 (1.57 - 6.46)	4.22 (2.08 - 9.27)
Mg	20.7 (11.7 - 50.1)	20.7 (11.4 - 50.9)	20 (11.5 - 46.2)	26.9 (13.1 - 77.4)
Na	20.4 (9.1 - 72.3)	20.5 (8.86 - 70.9)	19.7 (8.75 - 63.3)	18.2 (6.51 - 58.8)
CO3	0 (0 - 2.46)	NA	0 (0)	NA
HCO3	185 (68.1 - 247)	NA	183 (133 - 251)	NA
Cl	3.45 (1.78 - 8.45)	NA	3.68 (1.96 - 18.8)	NA
SO4	93.3 (49.4 - 342)	NA	90 (46.6 - 316)	NA
Sum of 8 Major Ions				
	368 (255 - 798)	NA	368 (253 - 765)	NA
Trace Elements (ug/L)				
Ag	0.01 (0.01 - 1.23)	0.01 (0.01 - 1.21)	0.01 (0.01 - 1.48)	0.065 (0.01 - 1.48)
Al	7.78 (2.02 - 21.8)	20.6 (2.23 - 246)	13.2 (0.73 - 80.9)	10600 (256 - 54200)
As	0.25 (0.01 - 0.46)	0.25 (0.01 - 0.99)	0.365 (0.01 - 1.76)	5.98 (0.56 - 14.6)
Ba	39.1 (23.6 - 56.5)	39.5 (24.5 - 55.1)	35.3 (19.2 - 103)	436 (52.8 - 1740)
Cd	0.01 (0.01 - 0.77)	0.01 (0.01 - 0.75)	0.01 (0.01 - 0.79)	0.955 (0.01 - 2.89)
Co	0.14 (0.07 - 0.25)	0.17 (0.08 - 1.33)	0.15 (0.06 - 1.24)	40.9 (0.2 - 162)
Cr	0.395 (0.15 - 1.96)	0.355 (0.1 - 1.59)	0.455 (0.16 - 0.79)	12.3 (1.67 - 158)
Cu	0.695 (0.26 - 2.23)	0.745 (0.25 - 2.72)	4.68 (0.37 - 47.3)	70.2 (1.36 - 629)
Fe	9.37 (0.18 - 95.5)	60 (0.18 - 910)	4.25 (0.18 - 185)	17600 (83.2 - 105000)
Mn	6.1 (1.98 - 19.3)	13.6 (0.02 - 185)	0.995 (0.22 - 663)	4900 (1.1 - 18800)
Mo	0.27 (0.13 - 0.58)	0.27 (0.13 - 148)	0.43 (0.22 - 0.98)	0.25 (0.08 - 1.26)
Ni	1.08 (0.5 - 2.73)	1.04 (0.48 - 3.23)	1.54 (0.52 - 9.04)	57.7 (2.3 - 226)
Pb	0.02 (0.01 - 0.15)	0.07 (0.01 - 1.45)	0.09 (0.01 - 0.95)	125 (0.23 - 1190)
Se	1.38 (0.32 - 3.61)	1.33 (0.35 - 3.38)	1.22 (0.29 - 3.53)	1.65 (0.09 - 4.77)
Sn	0.01 (0.01 - 0.42)	0.01 (0.01 - 0.56)	0.02 (0.01 - 0.45)	0.07 (0.01 - 2.77)
Sr	400 (189 - 1200)	402 (182 - 1170)	386 (191 - 1110)	633 (278 - 1350)
Ti	0.34 (0.24 - 0.79)	0.54 (0.22 - 1.37)	0.54 (0.38 - 0.96)	33.5 (12.5 - 73.2)
U	0.345 (0.16 - 1)	0.35 (0.16 - 0.97)	0.45 (0.22 - 1.11)	1.98 (0.26 - 8.21)
V	0.165 (0.01 - 0.54)	0.2 (0.01 - 0.6)	0.25 (0.01 - 1.82)	21.2 (0.01 - 111)
Zn	4.36 (0.46 - 13.4)	1.44 (0.07 - 18.3)	2.64 (0.36 - 14)	219 (0.6 - 1010)

NA = not applicable (no analyte for that sample type). Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered.

Spatiotemporal Patterns of Major-Ion and Trace-Element Concentrations

Spatial Patterns

We observed strongly significant ($p < 0.0001$) differences among sites in nearly all spatial models of major ion concentration regardless of sample type (Table 3). We detected spatial differences in concentration for 13 trace elements in filtered surface water (SF), but trace element concentrations in filtered pore water (PF) samples exhibited more spatial consistency, with only 8 elements of that sample type differing by site (Table 3). Similarly to PF samples, trace elements in unfiltered surface water (SU) were spatially different for only 9 trace elements (Table 3). However, for unfiltered pore water (PU) samples, 17 of 20 trace elements differed by site (Table 3).

Differences among sites were predominantly characterized by negative Mann-Kendall spatial trends regardless of sample type, indicating decreasing ion concentration moving downstream (Table 4). This pattern was very evident in SF samples for several ions commonly elevated in waters draining Appalachian surface coal mines, such as the major ions Ca, Mg, Na, SO_4, HCO_3, and the trace elements Fe, Mn, Se, and Sr (Figure 4, Appendix A).

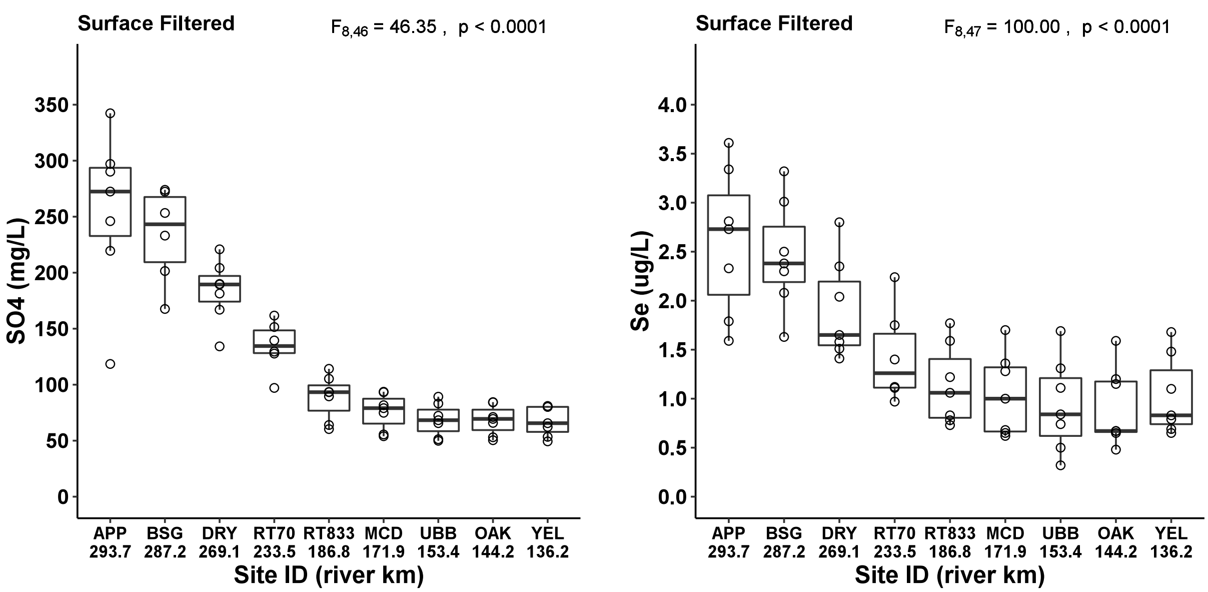

Figure 4. Boxplots of SO_4 and Se concentration by site for Surface Filtered samples. With Wald test F-statistic and p-value for differences among months. Both ions also exhibit significant negative downstream trends (Mann-Kendall trend $p < 0.05$).

The negative downstream trends that we observed for mining-indicator major ions and trace elements in surface water is consistent with the pattern of land use in Powell River, where surface coal mining dominates upstream of Appalachia, VA but mining influence on water chemistry declines moving downstream as the proportion of catchment mined decreases. Zipper et al. (2016) found a comparable spatial pattern, noting a significant decrease in Mn and Se surface-water concentrations moving downstream in Powell River. Our findings are also generally consistent with those of Phipps (2019), who found significant downstream trends in SC and surface-water and pore-water concentrations of a subset of our major ions and trace elements over the same river extent as we studied.

In contrast to SF concentrations, spatial differences were evident for more trace elements in unfiltered pore water (PU) samples (Table 3), but fewer trace elements exhibited significant downstream trends (Table 4). As with downstream trends observed for many ions in SF samples, spatial differences in PU trace elements often had relatively high concentrations at the most-upstream site (APP) where mining is a substantial proportion of catchment area, with lower concentrations in the next two sites downstream (BSG and DRY). However, the trend was often interrupted by large increases (relative to adjacent sites) in trace element concentrations at sites RT70 and MCD (Figure 5, Appendix A).

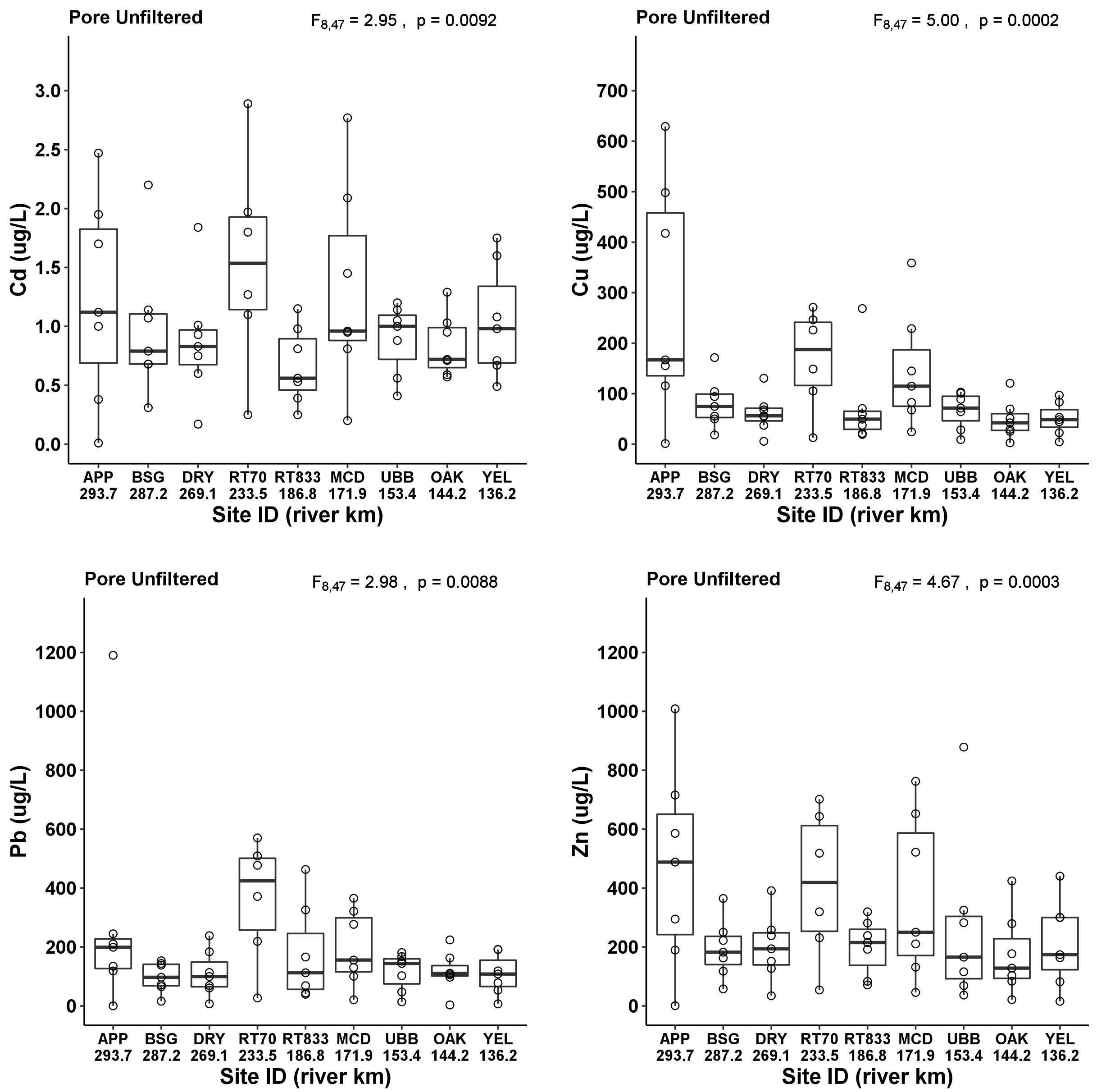

Figure 5. Boxplots of Cd, Cu, Pb, and Zn concentration by site for Pore Unfiltered samples. With Wald test F-statistic and p-value for differences among months. Note the increases in concentration at sites RT70 (downstream of North Fork Powell River, which is mining-influenced) and MCD (no known mining and no definitive non-mining source).

The increase in trace element concentration at the RT70 site is presumed to be attributable to elevated sediment and dissolved ion inputs from North Fork Powell River, which meets Powell River upstream from RT70 and drains mined, agricultural, and urbanized sub-catchments in Lee County, VA. The source of elevated ion concentrations at MCD is less clear. Three 2nd-3rd order tributaries enter Powell River between RT833 (where ion concentrations are lower) and MCD – Yellow Creek, Martin Creek, and Fourmile Creek. However, examination of aerial photos and mine permit data from Virginia Department of Mines Minerals and Energy for those streams, as well as USEPA STORET water quality data for the largest of them, Martin Creek, provided no definitive evidence of mining or other land uses to explain the increase in trace element concentrations at MCD. Because the increases in trace element concentration at MCD are observed only in particle-laden PU samples and not in SF samples, they are likely attributable to sediment sources rather than a consistent discharge of dissolved ions. This is supported by the fact that crustal materials such as Al and Fe are particularly elevated at MCD. Two sources of sediment may be forestry and/or agricultural operations. Aerial photos indicated areas of the Fourmile Creek catchment where land has been tilled for crops, as well as a substantial logging operation since 2013. Fine sediment in Powell River downstream from Fourmile creek could be a legacy of those activities or of ongoing ones not revealed in aerial photos. A final explanation could be that sediments at MCD contain a larger proportion of finer particles, more of which might pass through the 50-mesh (297 um) screen on our sampler, thus causing PU samples to contain more sediment particles, which could easily translate into higher concentrations after acid-extraction.

Temporal Patterns

Powell River appears to follow the general seasonal pattern of SC exhibited by many other salinized Appalachian rivers (Timpano et al. 2018). The pattern is characterized by highest annual SC occurring with lowest annual streamflow in summer/fall (Jul-Sep for Powell River; Figure 6), with lowest annual SC occurring with highest annual streamflow in winter/spring (Dec-Feb for Powell River; Figure 6). In addition, as in many other salinized Appalachian rivers and streams examined by Timpano et al. (2018), SC appears inversely proportional with and responsive to transient elevation of streamflow from precipitation runoff, as evidenced in the SC data (Figure 6) by many rapid decreases of SC followed by hysteresis and return to base flow (i.e., not runoff-influenced flow) SC levels before decreasing again, presumably from another runoff event. Because SC is an indicator of major ion concentrations, it is reasonable to expect that concentrations of both major ions and associated trace elements would exhibit similar seasonal patterns within Powell River.

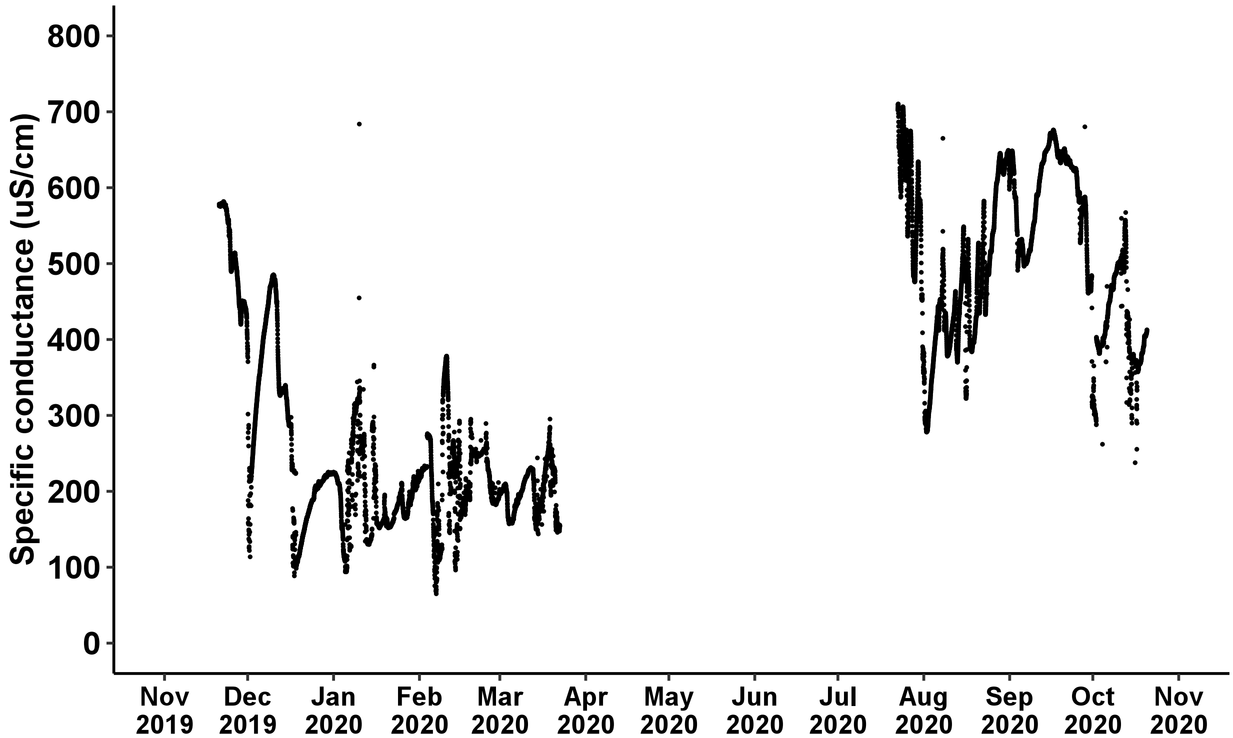

Figure 6. High-frequency specific conductance in Powell River at the Rt. 70 bridge near Jonesville, VA. Values from HOBO U24-001 conductivity datalogger recording with 30-minute interval. Data gap Apr-Jul due to flow conditions prohibiting wadeable access for datalogger maintenance.

Indeed, temporal mixed models revealed that concentrations of all major ions and nearly all trace elements differed by month, with most models indicating strongly-significant ($p < 0.0001$) temporal effects (Table 3). However, Mann-Kendall trend analysis revealed that for SF, SU, and PF sample types, no major ions and only two trace elements were trending (increasing or decreasing) through time (Table 4). This temporal pattern of ions aligns with expectations though, given that trend analysis spanned 12 months (November 2019 through October 2020) and the seasonal sinusoidal pattern of SC predicts a summer/fall peak salinity on both ends of that time frame, with a minimum in between during winter/spring (Figure 6). That pattern was especially the case for major ions, which tended to have highest concentrations in November 2019 and September 2020, with minima in January 2020 (Figure 7, Appendix B). A slightly different pattern dominated for most trace elements, however, with annual maximum concentrations occurring in the summer (June – August) and having declined by October 2020 (Figure 7, Appendix B).

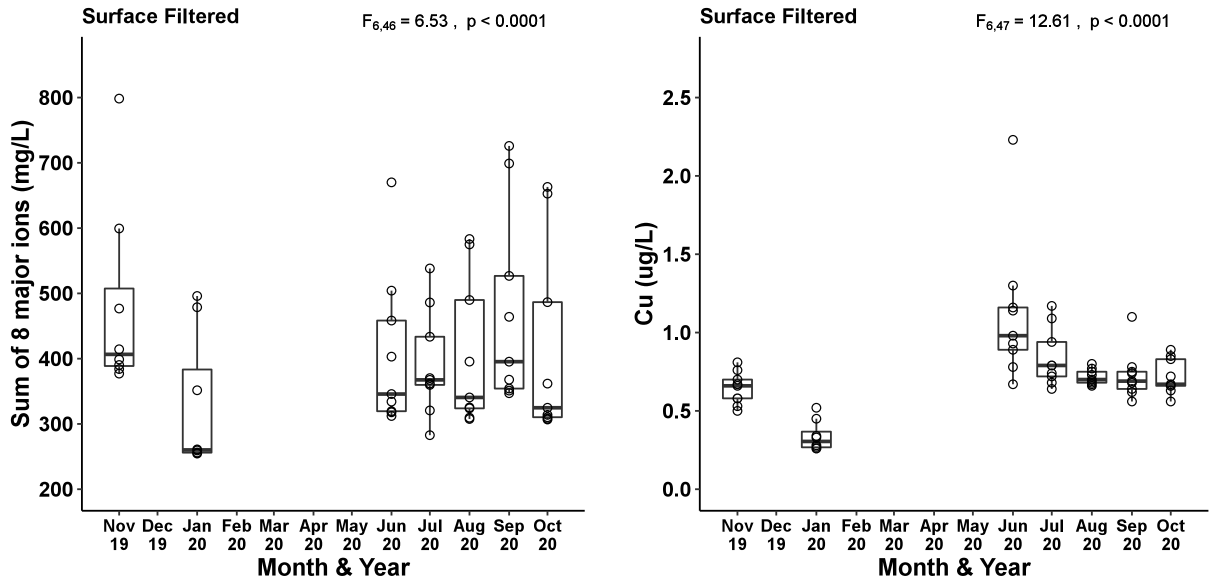

Figure 7. Boxplots of Sum of 8 Major Ions and Cu concentration by sampling month for Surface Filtered samples. With Wald test F-statistic and p-value for differences among months.

A notable contrast to the absence of temporal trends for SF, SU, and PF samples, PU samples exhibited increasing trends for three major cations and 12 trace elements (Table 4). Those trends appear to be driven by a steady increase in PU concentrations from June to October 2020 (Figure 8, Appendix B).

As PU samples contained substantial fine sediment, the increase in PU ion concentrations over the summer may be attributable to colmation, the process of accumulation of fine sediment in substrate interstices that occurs with seasonal decline of discharge in rivers with anthropogenic sediment sources (Wharton et al. 2017). Subsequent elevation of flows during winter, if high enough, can flush out entrained fine sediment (decolmation), which may act as a seasonal "reset", thus PU samples collected in winter/spring would contain less fine sediment and associated trace elements. Although our data from January 2020 do not represent an annual minimum concentration for most trace elements, it is possible that a high-flow "reset" event had not yet occurred by the time of our visit in late January when flows were still wadeable. Indeed, such an event may have occurred shortly after our visit, when a storm in early February raised river discharge at the RT70 Bridge site near Jonesville, VA from approximately 500 cubic feet per second (cfs) during our sampling visit on January 30, 2020, to approximately 18,000 cfs a week later (USGS 2021). If decolmation was facilitated by that and/or subsequent storms, it could explain why ion concentrations in PU samples were relatively low in June 2020. This hypothesis is further supported by anecdotal observations during mussel surveys by J. Jones, who notes that when dislodging mussels from the riverbed, more fine sediment tends to enter the water column during later summer/early fall months than during mussel surveys conducted earlier in the year.

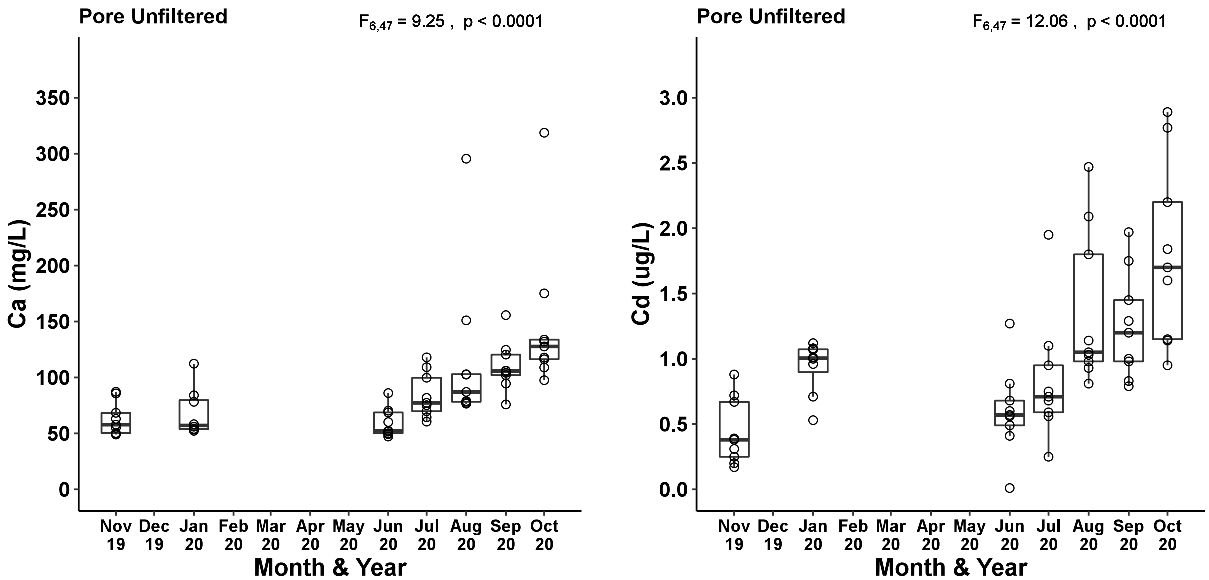

Figure 8. Boxplots of Ca and Cd concentration by sampling month for Pore Unfiltered samples. With Wald test F-statistic and p-value for differences among months. Both ions also exhibit significant positive trends through time (Mann-Kendall trend $p < 0.05$).

Table 3. Spatial and temporal mixed models for each ion and sample type.

	Spatial				Temporal			
Sample Type:	**SF**	**SU**	**PF**	**PU**	**SF**	**SU**	**PF**	**PU**
Specific conductance (uS/cm)	NA	****	NA	NA	NA	****	NA	NA
Major Ions (mg/L)								
Ca	****	****	****	***	****	****	****	****
K	****	****	****	****	****	****	****	****
Mg	****	****	****	****	****	****	****	****
Na	****	****	****	****	****	****	****	****
CO3	**	NA	NA	NA	ns	NA	NA	NA
HCO3	****	NA	**	NA	****	NA	****	NA
Cl	*	NA	****	NA	****	NA	*	NA
SO4	****	NA	****	NA	*	NA	****	NA
Sum of 8 Major Ions	****	NA	****	NA	****	NA	****	NA
Trace Elements (ug/L)								
Ag	ns	ns	ns	ns	ns	ns	ns	ns
Al	**	ns	ns	****	**	**	*	****
As	****	ns	ns	**	****	****	****	****
Ba	****	****	****	****	****	****	****	****
Cd	ns	ns	ns	**	****	****	****	****
Co	****	ns	ns	**	****	***	**	****
Cr	ns	ns	ns	*	***	***	****	**
Cu	*	*	ns	***	****	****	**	*
Fe	ns	*	ns	***	***	ns	**	****
Mn	****	ns	ns	*	****	**	ns	****
Mo	****	ns	****	ns	****	ns	****	ns
Ni	****	****	*	****	****	****	ns	****
Pb	ns	ns	ns	**	ns	**	*	***
Se	****	****	****	ns	****	****	****	****
Sn	ns	ns	ns	*	****	***	****	*
Sr	****	****	****	****	****	****	****	****
Ti	**	**	****	****	****	****	****	****
U	****	****	****	****	****	****	****	****
V	****	****	**	****	****	****	**	****
Zn	ns	ns	ns	***	****	ns	ns	****

p-value codes: **** $p < 0.0001$, *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$, ns = $p \geq 0.05$, NA = not applicable (no analyte for that sample type). Model p-values are results of Wald test for overall significance of differences in ion concentration among sites (spatial models) or months (temporal models) for each sample type. Determined for each ion/sample-type combination using a linear mixed model of ion concentration as a function of site as a fixed effect and sample month as a random effect (spatial models), or ion concentration as a function of sample month as a fixed effect and site as a random effect (temporal models). Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered.

Table 4. Spatial and temporal Mann-Kendall trends for each ion and sample type.

	Spatial (downstream)				Temporal (Nov 2019 to Oct 2020)			
Sample Type:	**SF**	**SU**	**PF**	**PU**	**SF**	**SU**	**PF**	**PU**
Specific conductance (uS/cm)	NA	-	NA	NA	NA	ns	NA	NA
Major Ions (mg/L)								
Ca	-	-	-	ns	ns	ns	ns	+
K	-	-	-	-	ns	ns	ns	+
Mg	-	-	-	ns	ns	ns	ns	+
Na	-	-	-	-	ns	ns	ns	ns
CO3	ns	NA	NA	NA	ns	NA	NA	NA
HCO3	ns	NA	ns	NA	ns	NA	ns	NA
Cl	ns	NA	ns	NA	ns	NA	ns	NA
SO4	-	NA	-	NA	ns	NA	ns	NA
Sum of 8 Major Ions	-	NA	-	NA	ns	NA	ns	NA
Trace Elements (ug/L)								
Ag	ns	ns	-	-	ns	ns	ns	ns
Al	-	-	ns	ns	ns	ns	ns	ns
As	+	ns	ns	-	ns	ns	ns	+
Ba	-	-	-	ns	ns	ns	ns	+
Cd	ns	+	ns	ns	ns	ns	ns	+
Co	-	-	ns	ns	ns	ns	ns	ns
Cr	ns	ns	ns	ns	ns	ns	ns	+
Cu	-	-	ns	-	ns	ns	ns	ns
Fe	ns	-	+	ns	ns	ns	ns	ns
Mn	-	-	-	ns	+	ns	ns	+
Mo	ns	ns	ns	ns	ns	ns	ns	ns
Ni	-	-	-	ns	ns	ns	ns	ns
Pb	ns	-	ns	ns	ns	ns	ns	+
Se	-	-	-	ns	ns	ns	ns	+
Sn	ns	ns	-	-	ns	ns	ns	+
Sr	-	-	-	-	ns	ns	ns	+
Ti	-	ns	ns	ns	ns	ns	ns	ns
U	-	-	-	ns	ns	ns	ns	+
V	+	+	+	ns	ns	ns	ns	+
Zn	ns	ns	ns	ns	ns	ns	ns	+

Trends determined using site-wise (spatial) or month-wise (temporal) means at test level $\alpha = 0.05$. Negative trends indicate concentrations are decreasing in the downstream direction or over time; positive trends indicate the opposite pattern. Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered. Trend codes: NA = not applicable (no analyte for that sample type); ns = trend was not statistically significant; **(-)** = trend was statistically significant and negative; **(+)** = trend was statistically significant and positive.

Toxicity Potential of Trace Elements

We detected no evidence of overtly toxic concentrations of trace elements in surface water or filtered pore water. Concentrations were generally low relative to their respective criteria, with acute and chronic criterion ratios for SF, SU, and PF samples typically between 0.01 and 0.1 (Figure 9 and Figure 10). In contrast, unfiltered pore water (PU) samples had much higher levels of trace elements, with median of chronic criterion ratios > 0.5 for all ions except As, and > 1 for Al, Cr, Cu, Fe, Pb, and Zn (Figure 9 and Figure 10). Extreme values of chronic criterion ratios were as high as 1-2 orders of magnitude greater than 1 for Al (54.2), Cr (14.3), Cu (45.8), Fe (105), Pb (111) (Figure 10). Further, trace elements that exceeded chronic criteria tended to do so frequently, with most ions exceeding criteria in ≥ 40% of PU samples (Table 5). Among other sample types, only Cu (PF) and Se (SF, SU, PF) exhibited non-trivial chronic criterion ratios (median > 0.1), but with infrequent criterion exceedances (≤ 5%) (Table 5).

Table 5. Criterion ratio median and criterion exceedance rate (%) by sample type.

	Acute				Chronic			
	SF	SU	PF	PU	SF	SU	PF	PU
Ag	< 0.01 --	< 0.01 --	< 0.01 --	< 0.01 --	NA	NA	NA	NA
Al	< 0.01 --	< 0.01 --	< 0.01 --	3.13 (92)	< 0.01 --	0.02 --	0.01 --	9.15 (97)
As	< 0.01 --	< 0.01 --	< 0.01 --	0.02 --	< 0.01 --	< 0.01 --	< 0.01 --	0.04 --
Cd	< 0.01 --	< 0.01 --	< 0.01 --	0.33 --	0.01 --	0.01 --	0.01 --	0.86 (40)
Cr	0.02 --	0.02 --	0.03 --	0.77 (32)	0.04 --	0.03 --	0.04 --	1.12 (53)
Cu	0.04 --	0.04 --	0.07 --	1.59 (74)	0.06 --	0.07 --	0.12 (2)	2.56 (81)
Fe	NA	NA	NA	NA	< 0.01 --	0.06 --	< 0.01 --	17.6 (98)
Ni	< 0.01 --	< 0.01 --	< 0.01 --	0.08 --	0.01 --	0.01 --	0.02 --	0.75 (27)
Pb	< 0.01 --	< 0.01 --	< 0.01 --	0.89 (44)	< 0.01 --	0.02 --	0.02 --	23.0 (95)
Se	NA	NA	NA	NA	0.45 (5)	0.43 (3)	0.39 (2)	0.53 (15)
Zn	0.03 --	< 0.01 --	0.01 --	1.33 (65)	0.03	< 0.01	0.01	1.33 (65)

NA = no criterion exists or not calculable from this dataset. Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered. Criterion ratio is an ion's concentration divided by its dissolved water-quality criterion. The criterion exceedance rate is the fraction of concentrations > criterion.

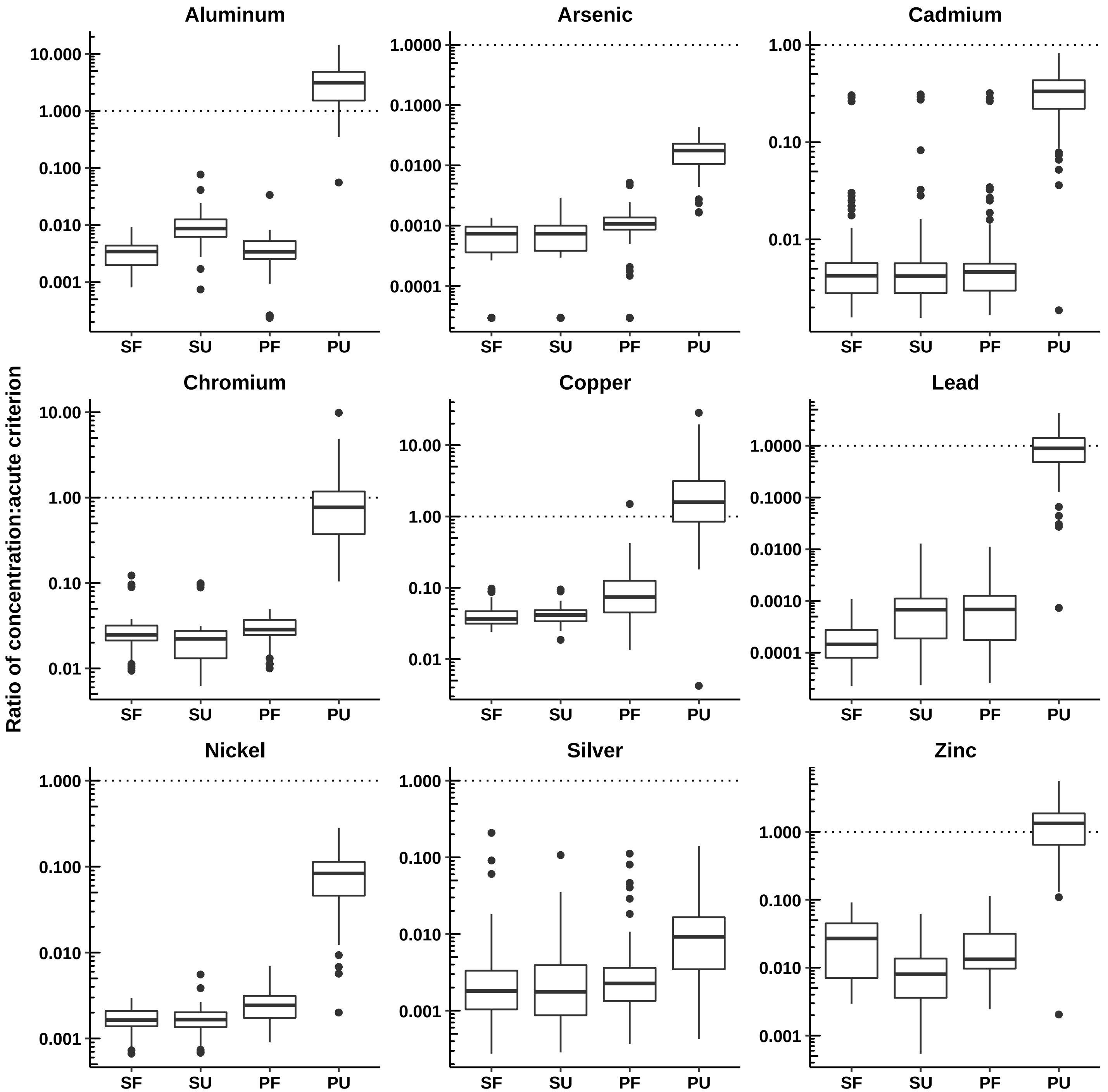

Figure 9. Boxplots of acute criterion ratios for each trace element by sample type. Based on USEPA recommended dissolved criteria for freshwater aquatic life, with sample-specific adjustments as appropriate using sample hardness, dissolved organic carbon, pH, and/or the Biotic Ligand Model (copper). Dotted line indicates ratio of concentration:criterion = 1. For each element and sample type, data pooled across sites (≤ 9) and sample months (≤ 7); boxplot n ≤ 63. Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered.

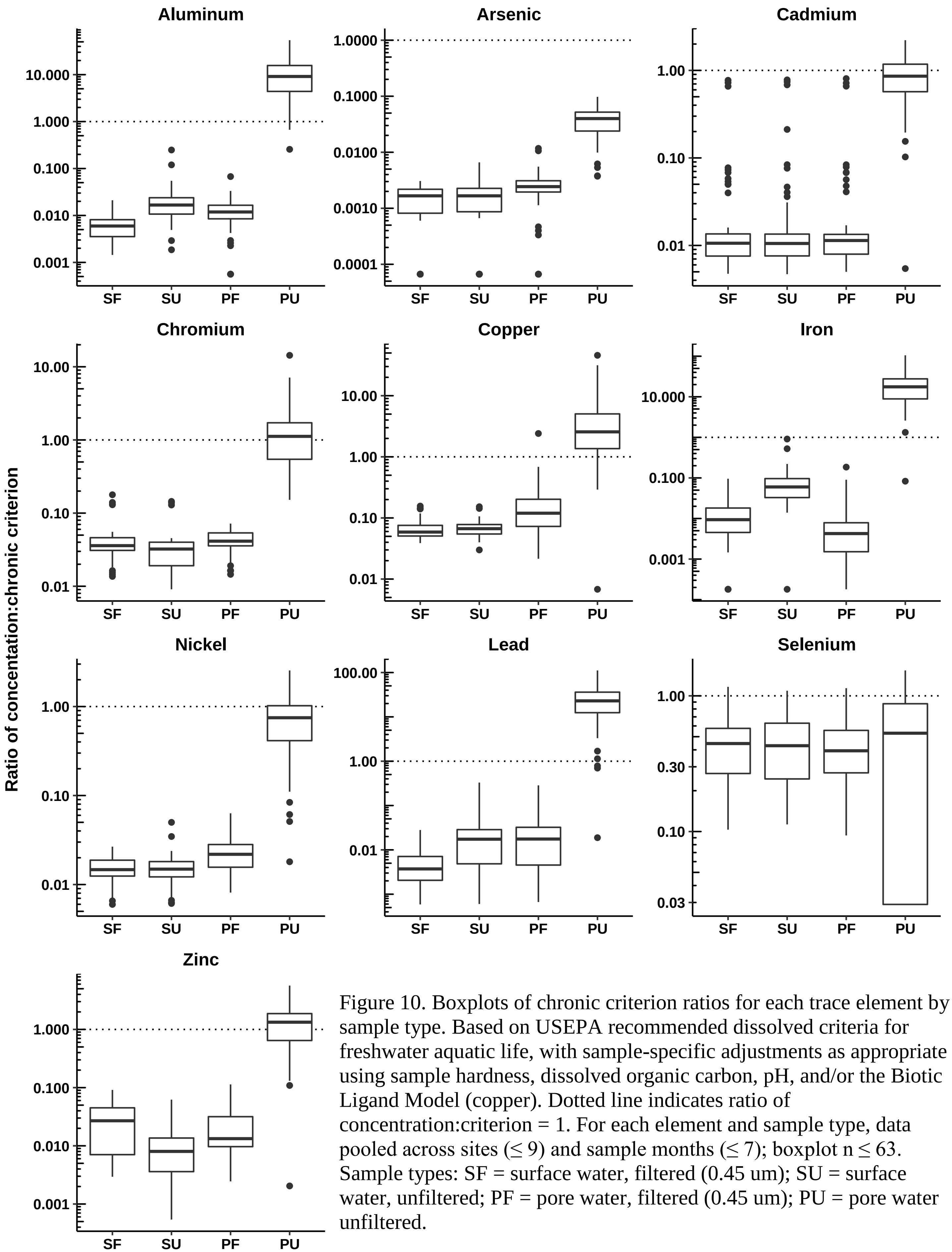

Figure 10. Boxplots of chronic criterion ratios for each trace element by sample type. Based on USEPA recommended dissolved criteria for freshwater aquatic life, with sample-specific adjustments as appropriate using sample hardness, dissolved organic carbon, pH, and/or the Biotic Ligand Model (copper). Dotted line indicates ratio of concentration:criterion = 1. For each element and sample type, data pooled across sites (≤ 9) and sample months (≤ 7); boxplot n ≤ 63. Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered.

It is important to note that criterion ratios for unfiltered pore water samples (PU) were derived using trace-element concentrations measured after acid-extraction of elements from samples containing much fine sediment. Therefore criterion ratios > 1 for unfiltered pore-water samples (PU) do not necessarily represent valid exceedances of "dissolved" water quality criteria *per se*. Instead, we interpret and present PU criterion ratios to illustrate the abundance of trace elements present in particulate form within substrate interstices, which have the potential to desorb and become bioavailable under the right conditions. One such condition could be ingestion and dissolution within the acidic environment of the gastrointestinal tract of freshwater mussels, but further research is needed to determine if interstitial sediment is a viable trophic route of exposure to trace elements for freshwater mussels.

Spatial mixed models of chronic criterion ratios generally mirrored patterns observed for ion concentrations, with spatial differences generally absent except for PU samples (Table 6, Appendix C), likely driven by the disparate sediment concentrations presumably resultant from spatial differences in mining influence and sediment sources as discussed previously for absolute concentrations. Temporal mixed models of chronic criterion ratios revealed that ratios for most ions and sample types varied with sample month, indicating that the toxicity potential of trace elements varies during the year (Table 6, Appendix D). Because criterion ratios are derived from concentration divided by criterion, most elements exhibited temporal patterns similar to those observed for concentration alone, which also varied by month. Slight variation in this pattern was evident for trace elements with toxicity dependent on other water quality parameters, but such instances were rare.

Comparison of spatiotemporal variations in ion concentrations and their criterion ratios suggests that solute concentrations in the ion matrix generally vary in unison, such that samples with higher absolute ion concentrations can be interpreted to represent relatively higher toxicity potential. However, determination of absolute toxicity potential requires comparison of concentrations to criteria on a sample-specific basis for those elements with variable criteria.

Table 6. Spatial and temporal mixed models of chronic criterion ratios for trace elements.

	Spatial				Temporal			
Sample Type:	**SF**	**SU**	**PF**	**PU**	**SF**	**SU**	**PF**	**PU**
Al	**	ns	ns	****	*	*	**	****
As	****	ns	ns	**	****	****	****	****
Cd	ns	ns	ns	***	***	****	***	****
Cr	ns	ns	ns	*	***	***	****	**
Cu	ns	ns	ns	***	****	****	***	ns
Fe	ns	*	ns	***	***	ns	**	****
Ni	ns	ns	ns	****	****	****	***	****
Pb	ns	ns	ns	***	***	*	ns	****
Se	****	****	****	ns	****	****	****	****
Zn	*	ns	ns	**	****	ns	*	****

p-value codes: **** $p < 0.0001$, *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$, ns = $p \geq 0.05$, NA = not applicable (no analyte for that sample type). Model p-values are results of Wald test for overall significance of differences in criterion ratios among sites (spatial models) or months (temporal models) for each sample type. Determined for each ion/sample-type combination using a linear mixed model of criterion ratios as a function of site as a fixed effect and sample month as a random effect (spatial models), or criterion ratios as a function of sample month as a fixed effect and site as a random effect (temporal models). Sample types: SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered.

Relating Pore Water to Surface Water

Spearman correlations among sample types SF, SU, PF, PU, and surface-water SC yielded 10 pairwise combinations (Appendix E), but we focus on the ones of primary interest ("primary pairs" hereafter), which are those relating pore-water ion concentrations to those in surface water: PF-SF, PU-SF; as well as the pairs that relate ion concentrations to the general indicator that is surface-water SC: PF-SC, PU-SC, and SF-SC.

Major cations were very strongly correlated among primary pairs without PU samples, with correlation coefficients ≥ 0.85 but lower for Ca, K, and Mg in pairs with PU samples (Table 7). This suggests dissolved major cation concentrations in pore water (PF) are driven by hydraulic connectivity with surface water containing those dissolved ions, while particulate forms (PU) are less strongly associated with surface water concentrations. For example, because PF ions are a subset of PU ions (from whence PF samples are filtered), concentrations of PU roughly equal to PF indicate little or no contribution from particulate forms in PU samples, as is the case for Na (Figure 2), for which PF and SF are strongly correlated (Table 7). Among major anions, HCO_3 was strongly correlated (Spearman rho ≥ 0.65) among primary pairs, but SO_4 was very strongly correlated (Spearman rho ≥ 0.90) among primary pairs (Table 7). Chloride was generally very low in both SF and PF samples (< 5 mg/L) relative to other major ions (Figure 2), and thus not correlated with SC, but was strongly correlated between PF and SF (Table 7). These results suggest that although SC may provide a suitable approximation of most, but not all, major ion concentrations in pore water, SF ion concentrations are likely to provide the best predictions of PF concentrations for major ions, as the two were very strongly correlated (Spearman rho ≥ 0.85) for all major ions (Table 7).

Trace elements in filtered pore water (PF) was most frequently correlated with filtered surface water (SF), with that pair having strong correlations (Spearman rho ≥ 0.5) for 13 of 19 ions, five of which had coefficients ≥ 0.88: Cd, Se, Sr, V, and U (Table 7). Specific conductance was strongly correlated with eight of 19 ions in filtered samples from both surface water and pore water, with only Ba, Sr, and U coefficients > 0.80 (Table 7). Unfiltered pore water (PU) ion concentrations had few strong correlations with surface-water measures, with SC strongly correlated with only one ion (Sr; Spearman rho = 0.72), and SF strongly correlated with only five ions, again with only one coefficient > 0.80 (Sr) (Table 7). Among the trace elements with water quality criteria for aquatic life analyzed here, filtered pore water (PF) concentrations were strongly correlated with those of filtered surface water (SF) for Se (rho = 0.92), Cd (0.88), Ni (0.75), As (0.72), Cr (0.63), and Cu (0.51). Trace-element PF concentrations for Ag, Al, Fe, Pb, and Zn were not significantly correlated with SF concentrations. Correlation analysis suggests that prediction of trace-element pore-water concentrations from surface-water concentrations is likely infeasible for most elements, and especially so for the majority of elements of toxic concern.

Table 7. Spearman rank correlation coefficients for each sample-type pairing by ion.

Sample-Type pair:	PF-SC	PF-SF	PF-SU	PF-PU	PU-SC	PU-SF	PU-SU	SF-SC	SF-SU	SU-SC
Major Ions (mg/L)										
Ca	0.86	0.97	0.97	0.26	0.20	0.28	0.28	0.85	1.00	0.85
K	0.90	0.97	0.97	0.72	0.56	0.73	0.73	0.94	1.00	0.94
Mg	0.92	0.97	0.97	0.65	0.67	0.68	0.68	0.96	1.00	0.96
Na	0.94	0.99	0.99	0.97	0.94	0.96	0.96	0.95	1.00	0.95
CO3	NA	NA	NA	NA	NA	NA	NA	0.29	NA	NA
HCO3	0.73	0.85	NA	NA	NA	NA	NA	0.65	NA	NA
Cl	0.24	0.88	NA	NA	NA	NA	NA	0.22	NA	NA
SO4	0.90	0.99	NA	NA	NA	NA	NA	0.91	NA	NA
Sum of 8 Major Ions	0.95	0.94	NA	NA	NA	NA	NA	0.91	NA	NA
Trace Elements (ug/L)										
Ag	-0.06	0.22	0.26	0.34	-0.05	0.18	0.06	-0.03	0.75	0.03
Al	0.43	0.14	0	-0.26	-0.27	0.31	0.51	0.37	0.55	0
As	-0.12	0.72	0.73	0.41	0.15	0.49	0.51	-0.05	0.98	-0.03
Ba	0.89	0.75	0.76	-0.16	-0.23	-0.12	-0.04	0.80	0.98	0.79
Cd	0.11	0.88	0.91	-0.49	-0.14	-0.44	-0.40	0.04	0.87	0.15
Co	0.51	0.66	0.54	-0.16	-0.20	-0.03	0.12	0.58	0.86	0.54
Cr	0.33	0.63	0.50	0.07	-0.24	0.14	0.42	0.41	0.77	0.12
Cu	0.20	0.51	0.36	0.25	0.08	0.11	0.12	0.50	0.64	0.67
Fe	-0.34	0.14	-0.18	-0.31	-0.03	-0.03	0.36	0.26	0.56	0.46
Mn	0.51	0.03	0.10	-0.32	-0.19	0.41	0.36	0.58	0.63	0.40
Mo	0.62	0.33	0.22	0.62	0.42	0.09	0.04	0.27	0.94	0.24
Ni	0.56	0.75	0.77	0.05	0	0.14	0.13	0.65	0.94	0.65
Pb	0.07	0.04	-0.06	0.32	-0.10	0.28	0.30	-0.14	0.34	-0.03
Se	0.59	0.92	0.88	0.43	0.19	0.50	0.54	0.64	0.95	0.59
Sn	-0.08	0.61	0.54	0.47	0.34	0.33	0.52	-0.21	0.42	-0.01
Sr	0.91	0.99	0.99	0.79	0.72	0.81	0.81	0.93	1.00	0.93
Ti	0.28	0.94	0.92	0.73	0.20	0.73	0.73	0.34	0.94	0.34
U	0.84	0.88	0.90	0.24	-0.04	0	0.05	0.93	0.99	0.93
V	-0.28	0.89	0.85	0.50	-0.37	0.55	0.55	-0.36	0.95	-0.29
Zn	-0.27	-0.06	-0.13	-0.01	-0.04	0.50	0.07	0.06	0.45	0.30

Sample types: SC = specific conductance (uS/cm) of surface water, unfiltered; SF = surface water, filtered (0.45 um); SU = surface water, unfiltered; PF = pore water, filtered (0.45 um); PU = pore water unfiltered. NA = not applicable (no analyte for that sample type). Data pooled among all sites and months; for each sample type, $n \leq 63$.

CONCLUSIONS

Concentrations of major ions and trace elements in Powell River exhibited considerable longitudinal and intra-annual seasonal variation, with highest concentrations observed for most measured constituents in late summer/fall concurrent with low river discharge, and in river segments nearest coal-mining and other land uses that can increase erosion potential (urbanization, agriculture, forestry). Among the trace elements with aquatic-life water-quality criteria analyzed here, concentrations were generally low in filtered surface and pore water, typically found at less than 10% of chronic criterion values. The exceptions were Cu and Se; Cu surpassed 12% of its chronic criterion in half of the filtered pore water samples and Se surpassed 39% of its chronic criterion in half of the samples for all sample types. However, criterion exceedances were rare for both elements (≤ 5% of samples). In contrast, unfiltered pore water indicated substantial amounts of trace elements associated with interstitial fine sediment particles, with all toxic elements except As having potential to exceed their chronic criteria if they were to become bioavailable, especially Cr, Cu, and Pb. All major ions in filtered surface water were well-correlated with their filtered pore-water concentrations, suggesting it is feasible to predict the latter from the former. However, unfiltered samples indicated particle-bound trace elements were less frequently and strongly correlated with – and thus likely less predictable from – surface-water filtered concentrations. This limits the feasibility of predicting realistic contaminant exposures for freshwater mussels and other benthic organisms when the vast majority of trace elements in the river are present in particulate form within substrate interstices. These results demonstrate the potential unreliability of predicting toxic exposures from surface-water concentrations alone, and underscore the need for further research of all environmental compartments that may serve as sources and routes by which aquatic life, especially freshwater mussels, may be exposed to trace elements at potentially toxic concentrations, to include how their spatial and temporal variation may influence such exposures.

Our findings will inform decisions regarding management of Powell River aquatic resources that consider spatial and temporal variation of major-ion and trace-element concentrations and their potential influences on aquatic life. In addition, this study has provided critical information needed to inform design and conduct of ecotoxicological experiments to test hypotheses surrounding freshwater mussel exposure to dissolved and particulate trace elements.

The results of this study will inform a proposal for submission to a freshwater mussel stakeholder such as US Fish and Wildlife Service or The Nature Conservancy to conduct ecotoxicological experimentation to test the hypothesis that toxicity from trace elements is a cause of decline and/or ongoing suppression of freshwater mussel populations within Powell River. This study has provided critical information necessary to design exposures simulating conditions in situ, including spatial variation and annual timing of trace-element concentrations. Further, we now know that interstitial particulate forms of trace elements have high toxicity potential if they were to become bioavailable through, for example, trophic exposures. These data together enable us to simulate environmentally-realistic ion concentrations and routes of exposure as they occur when and where mussels are most susceptible. Such experimentation will contribute to our ultimate goal of determining the cause(s) of mussel decline and ongoing suppression in Powell River.

ACKNOWLEDGEMENTS

We thank the Powell River Project for their support of this critical research and our broader efforts to conserve and restore aquatic life in Powell River. We are grateful to the following individuals for their contributions to this project: Zach Taylor for assistance with field work; Madeleine Schreiber for use of sampling equipment; Guillaume Pilot for use of laboratory equipment; Stephen Schoenholtz for use of sampling equipment and laboratory instruments; Kelly Peeler and Jeff Parks for analytical chemistry; Andrew Phipps for assistance with site selection; and Carl Zipper for many helpful suggestions on study design, data analysis, and reporting.

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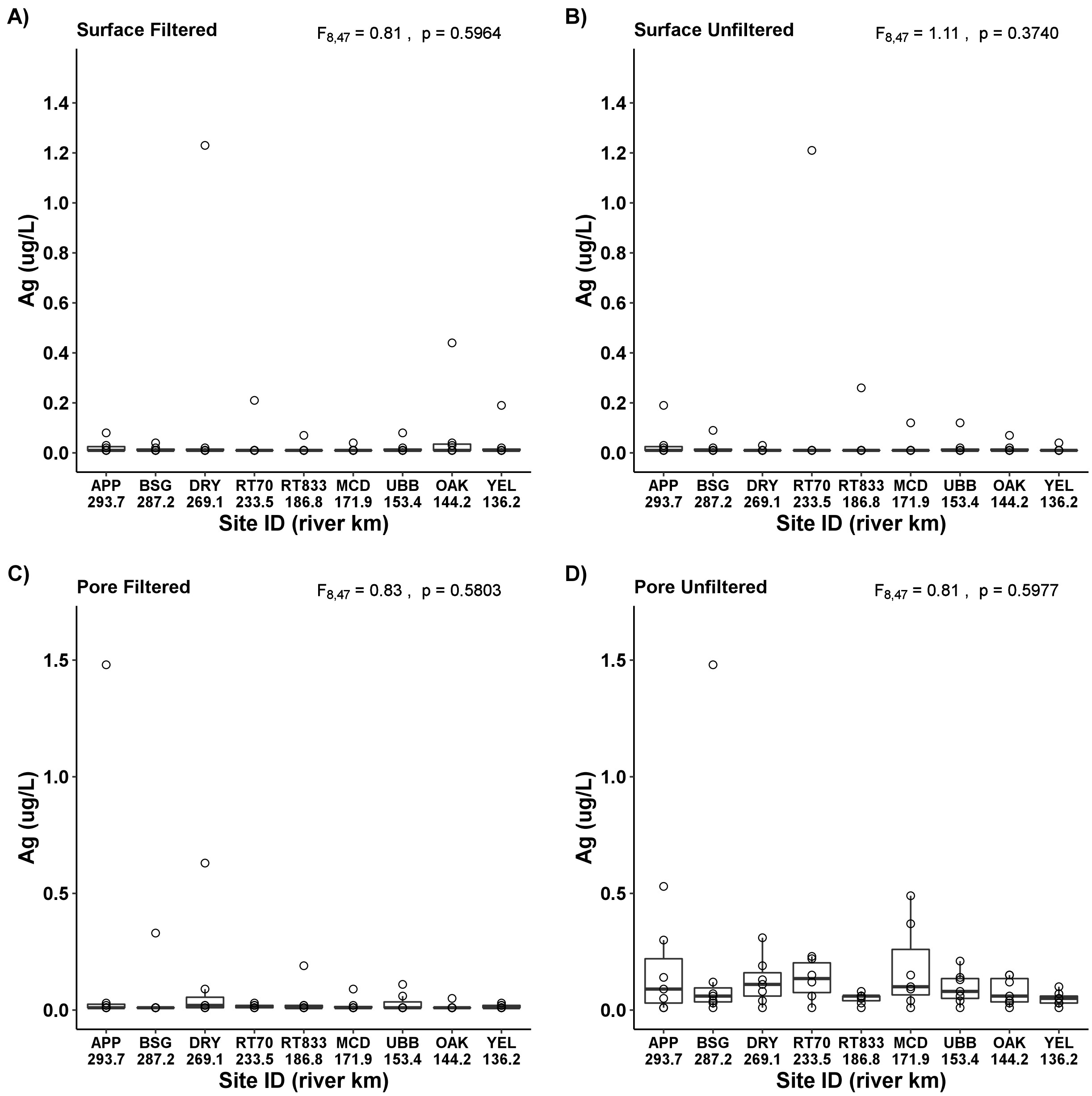
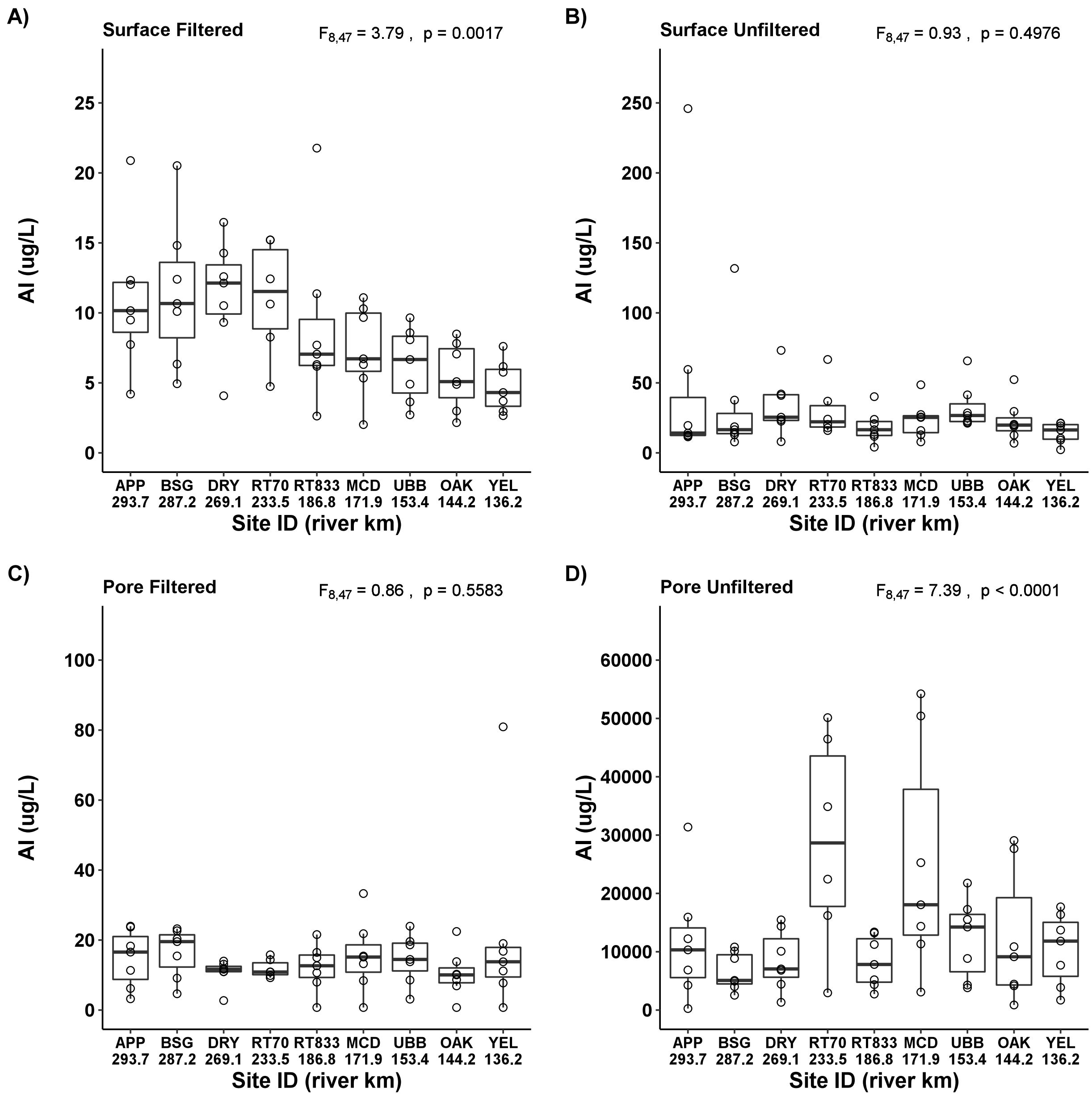
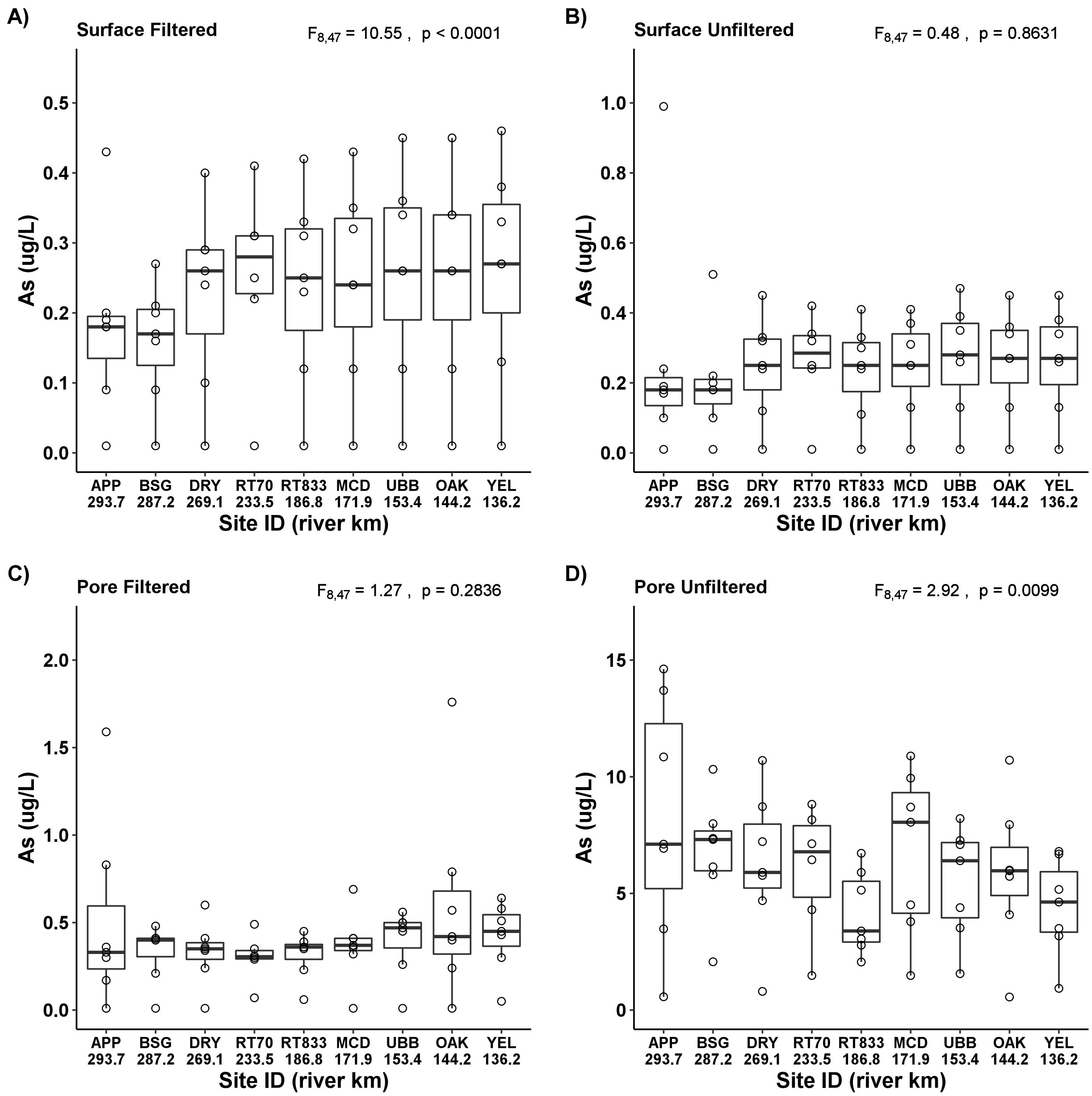
APPENDIX A – SPATIAL MIXED MODEL BOXPLOTS: ION CONCENTRATION BY SAMPLE TYPE

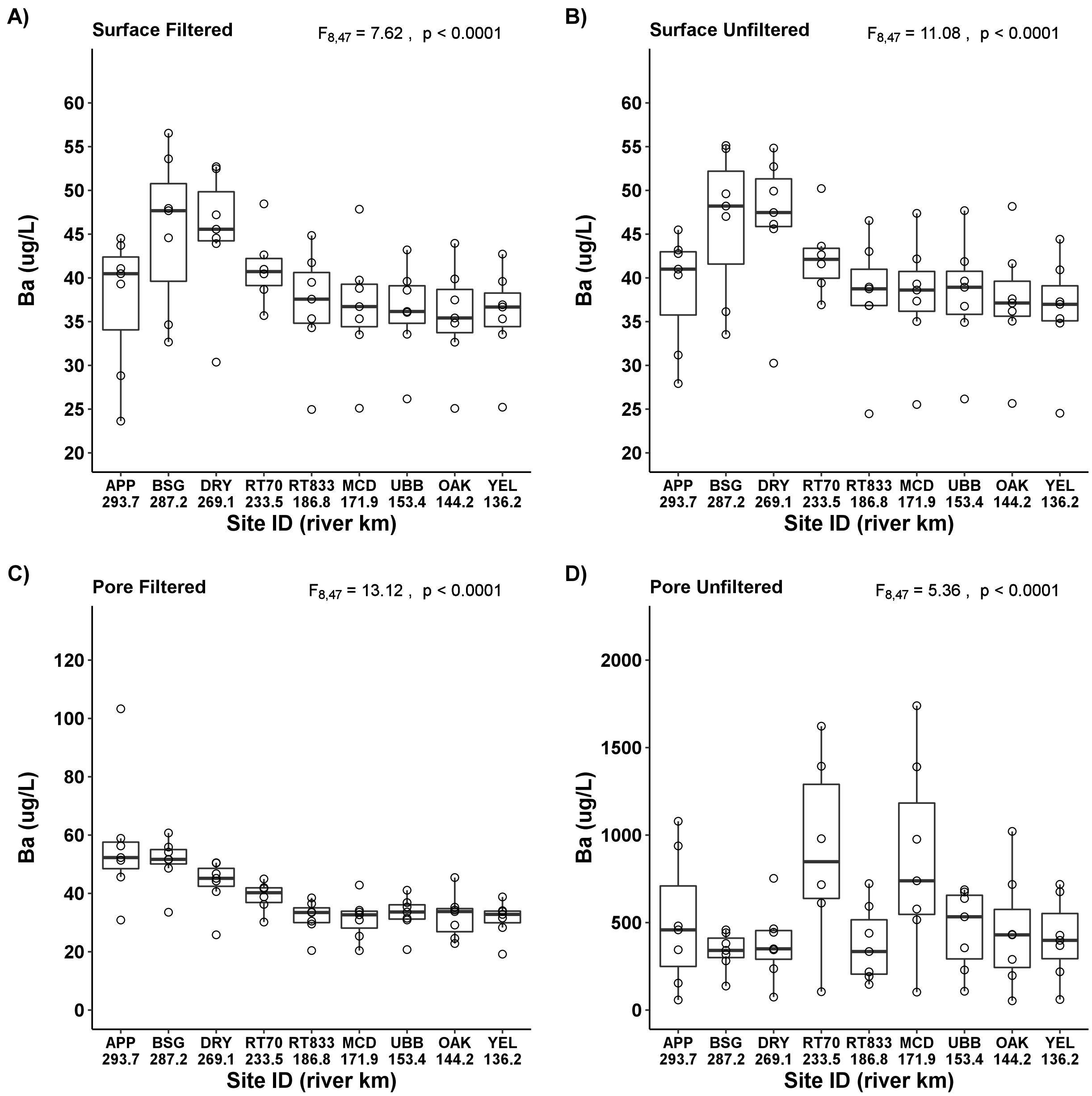
These models evaluate differences in ion concentrations among sampling sites, with sampling date as a random effect to account for multiple samples being collected from each site during the 12-month study period.

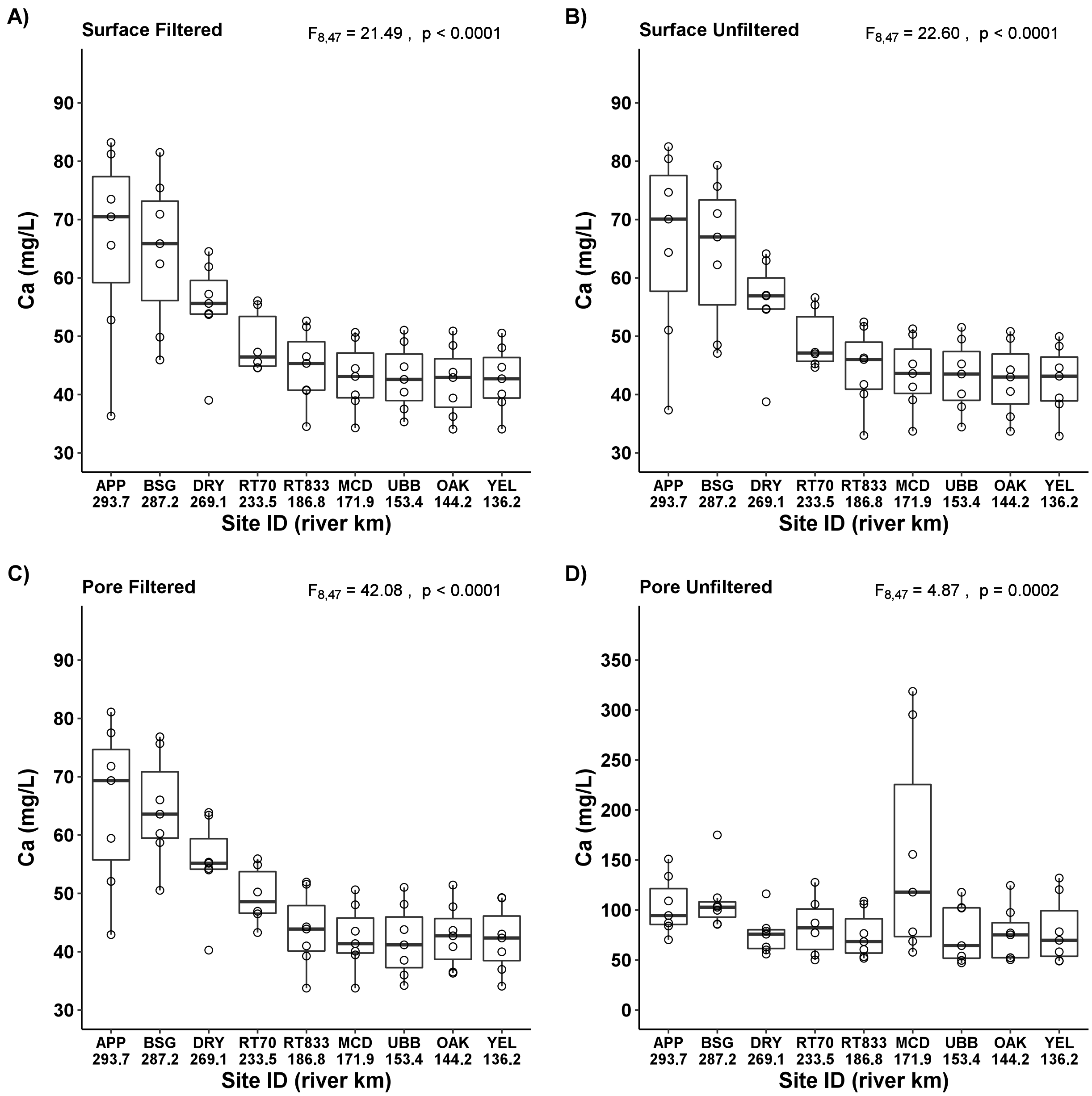
Each page addresses a single ion, with up to four boxplots representing the up to four types of samples collected: Filtered and Unfiltered Surface Water, as well as Filtered and Unfiltered Pore Water. Open circles are individual observations, with up to seven observations per site measured roughly monthly from November 2019 through October 2020. The vertical axis indicates the ion and units of concentration; note that axis range is independent among panels. The horizontal axis indicates the abbreviated identifier and river kilometer of the nine sample locations, arranged moving downriver from left to right from Appalachia, Virginia to near Tazewell, Tennessee. On the upper-right border of each plot are Wald test F-statistics and p-values for overall site-wise effects.

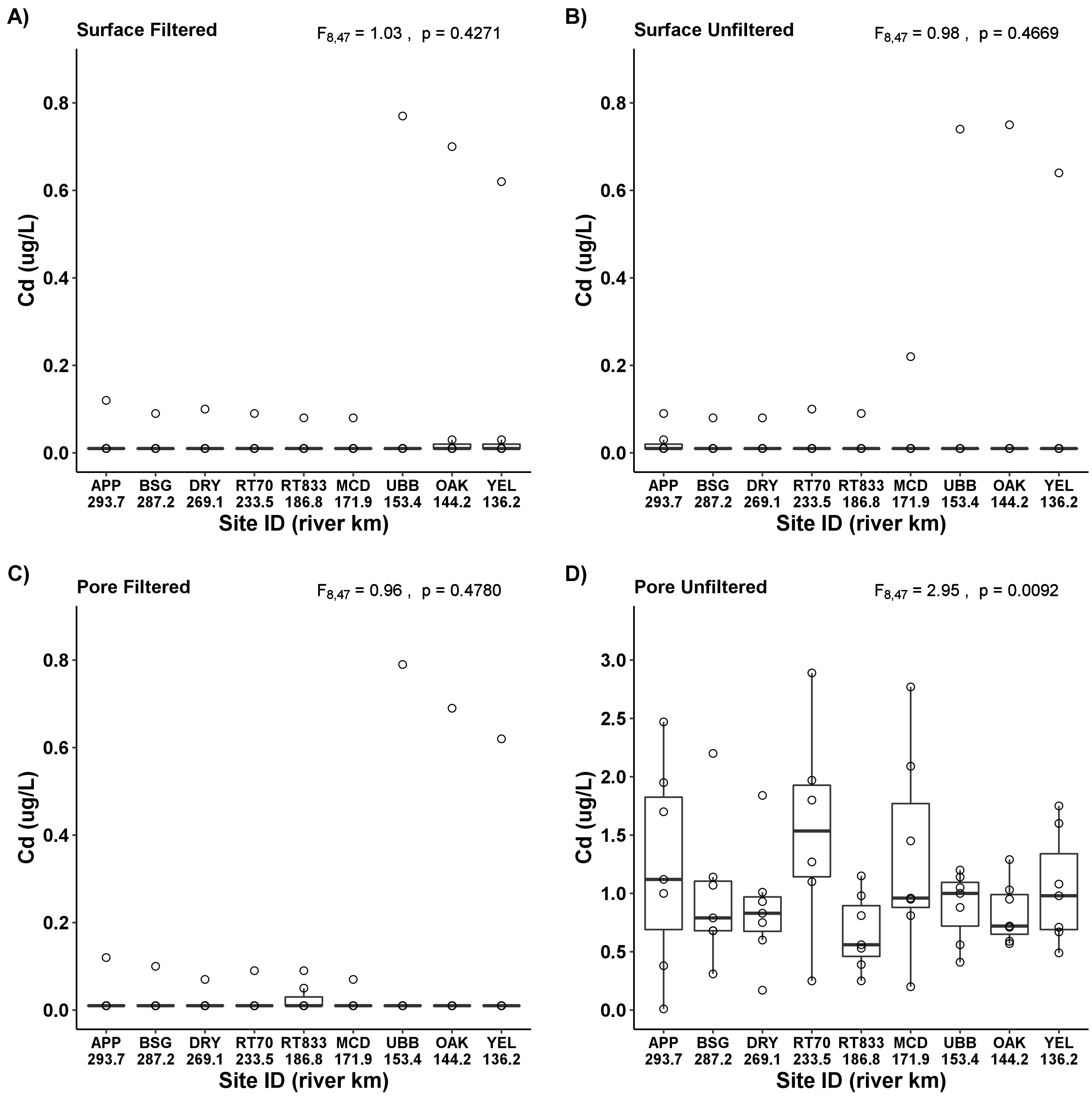

A)
Surface Filtered
$F_{8,47}$ = 0.81 , p = 0.5964
B)
Surface Unfiltered
$F_{8,47}$ = 1.11 , p = 0.3740
C)
Pore Filtered
$F_{8,47}$ = 0.83 , p = 0.5803
D)
Pore Unfiltered
$F_{8,47}$ = 0.81 , p = 0.5977
Ag (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

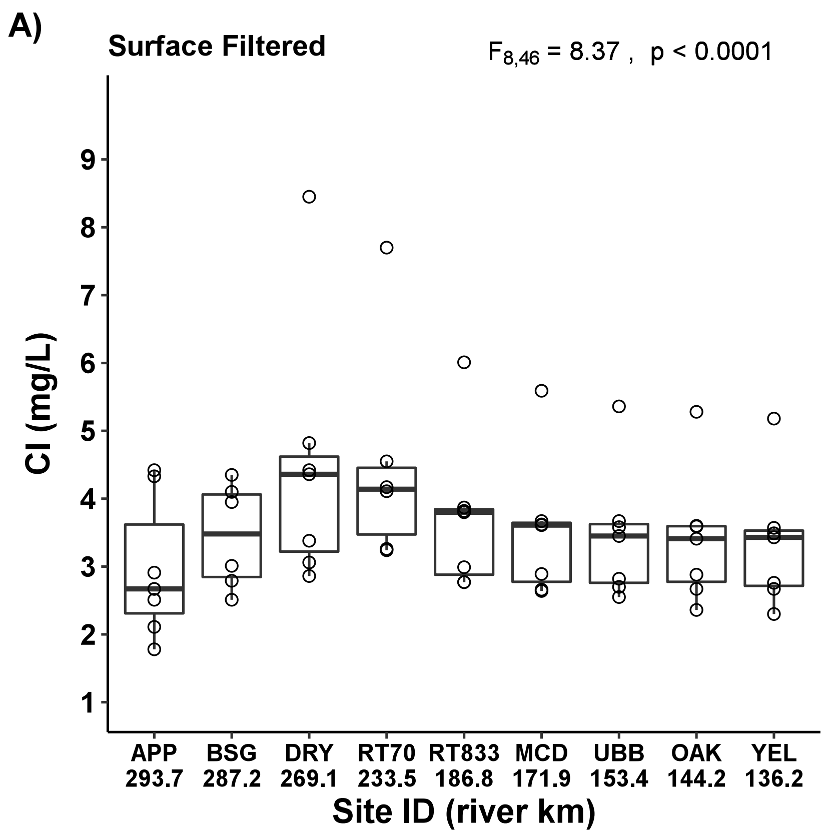

A)
Surface Filtered
F8,47 = 3.79 , p = 0.0017
B)
Surface Unfiltered
F8,47 = 0.93 , p = 0.4976
C)
Pore Filtered
F8,47 = 0.86 , p = 0.5583
D)
Pore Unfiltered
F8,47 = 7.39 , p < 0.0001
Al (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

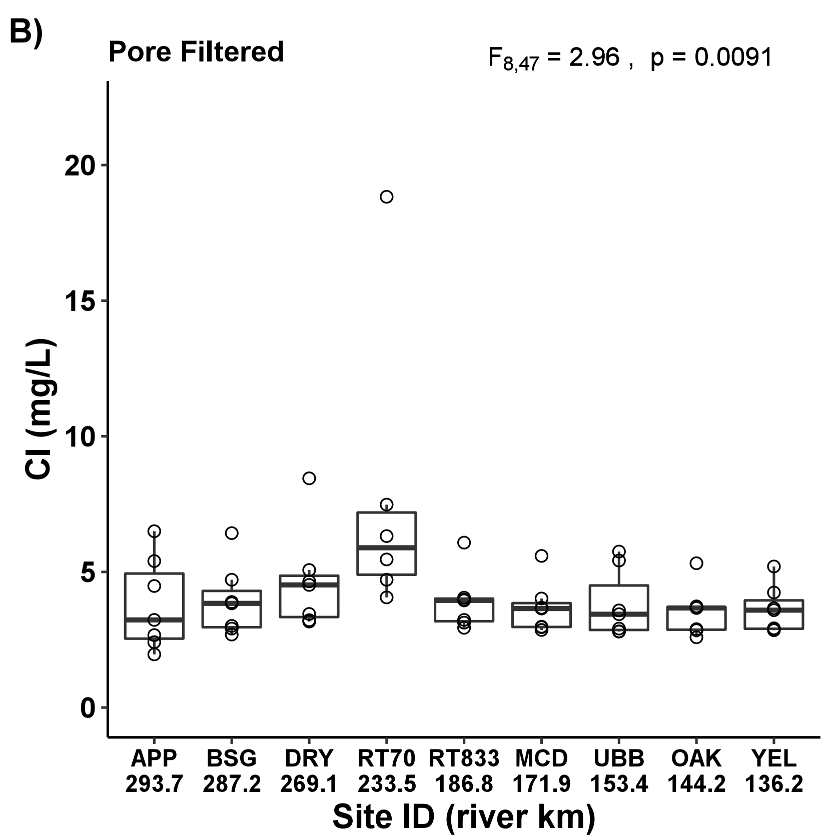

A)
Surface Filtered
$F_{8,47}$ = 10.55 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 0.48 , p = 0.8631
C)
Pore Filtered
$F_{8,47}$ = 1.27 , p = 0.2836
D)
Pore Unfiltered
$F_{8,47}$ = 2.92 , p = 0.0099
As (ug/L)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

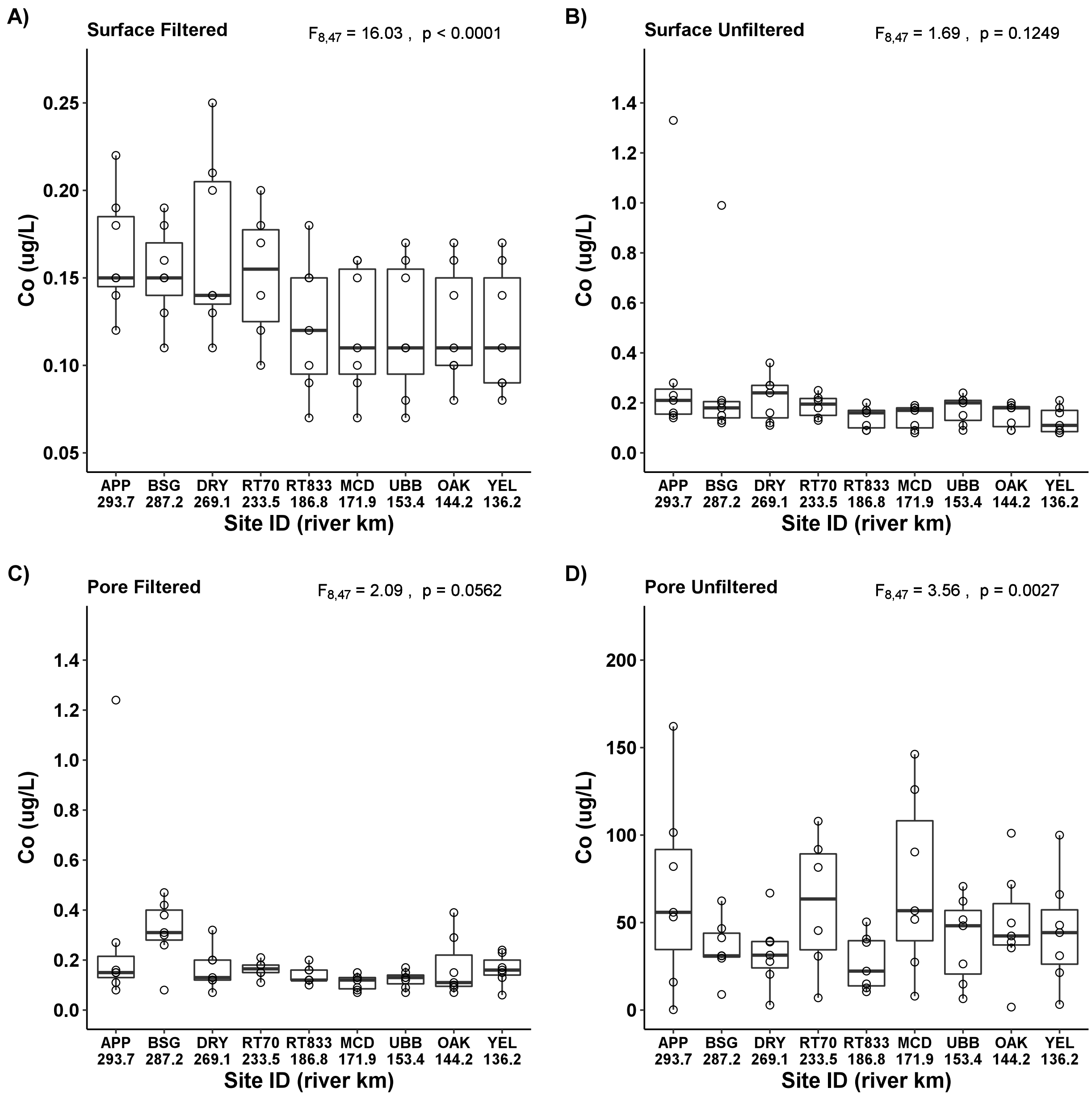

A)
Surface Filtered
$F_{8,47}$ = 7.62 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 11.08 , p < 0.0001
C)
Pore Filtered
$F_{8,47}$ = 13.12 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 5.36 , p < 0.0001
Ba (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

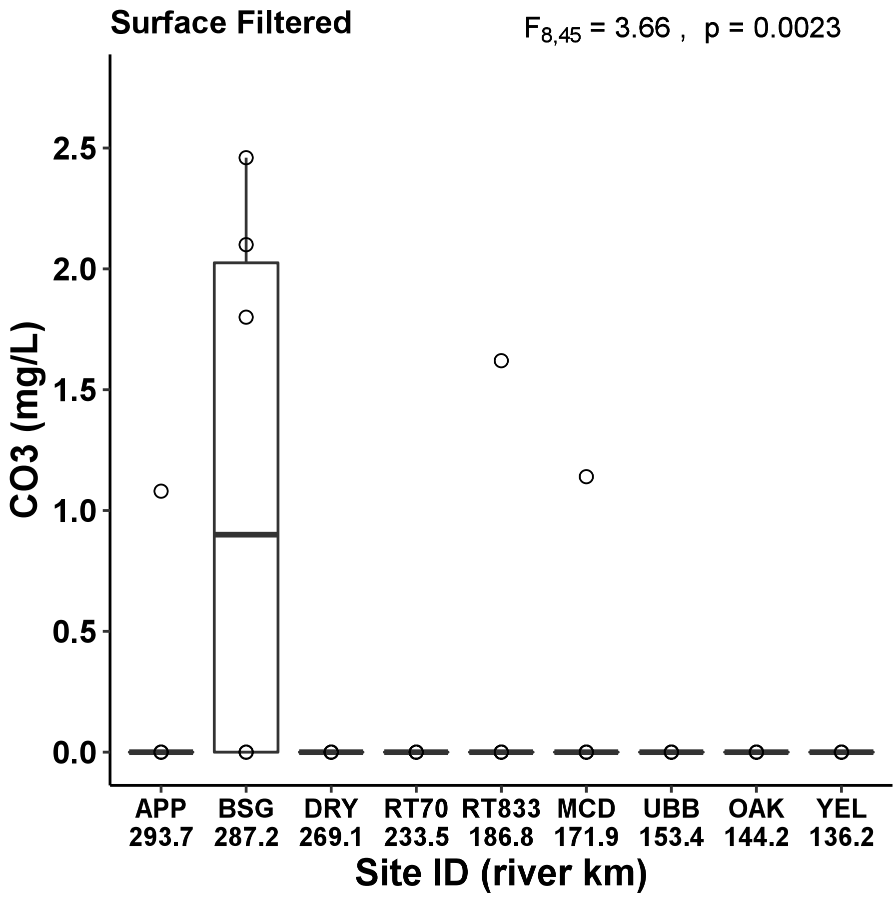

A)
Surface Filtered
$F_{8,47}$ = 21.49 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 22.60 , p < 0.0001
C)
Pore Filtered
$F_{8,47}$ = 42.08 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 4.87 , p = 0.0002
Ca (mg/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
$F_{8,47}$ = 1.03 , p = 0.4271
B)
Surface Unfiltered
$F_{8,47}$ = 0.98 , p = 0.4669
C)
Pore Filtered
$F_{8,47}$ = 0.96 , p = 0.4780
D)
Pore Unfiltered
$F_{8,47}$ = 2.95 , p = 0.0092
Cd (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

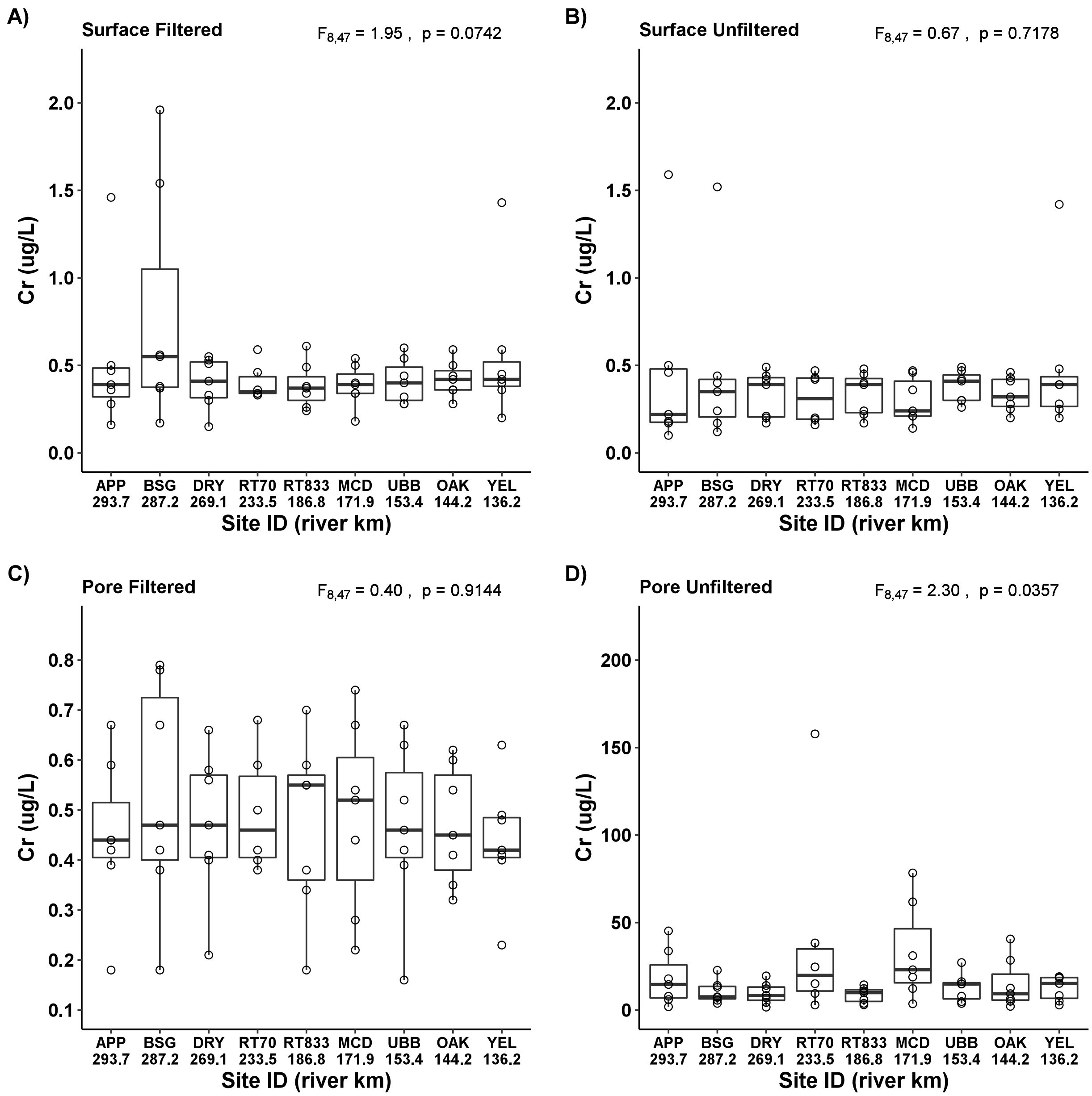

A)
Surface Filtered
$F_{8,46}$ = 8.37 , p < 0.0001
Cl (mg/L)
1
2
3
4
5
6
7
8
9
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

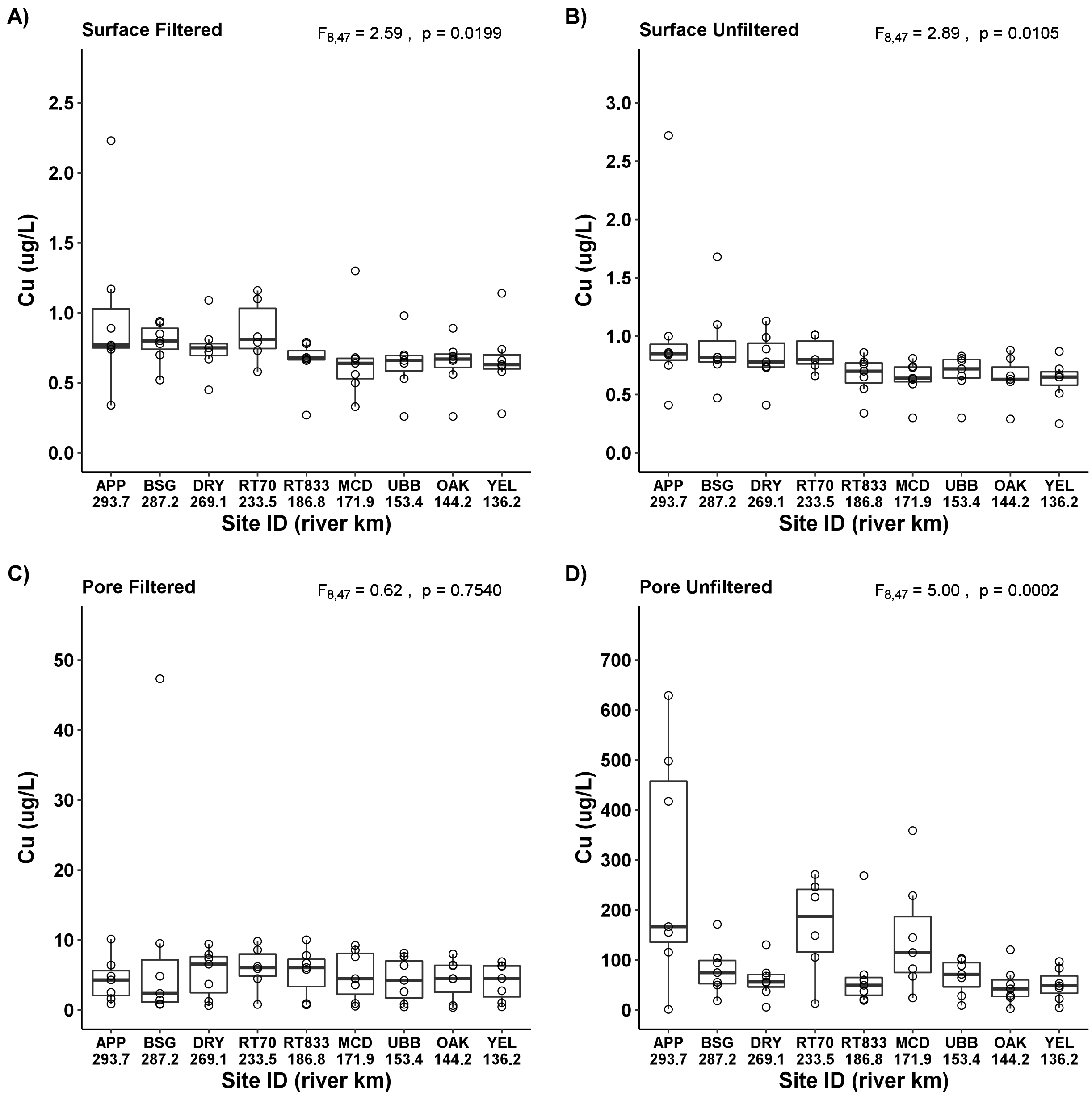

B)
Pore Filtered
$F_{8,47}$ = 2.96 , p = 0.0091
Cl (mg/L)
0
5
10
15
20
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

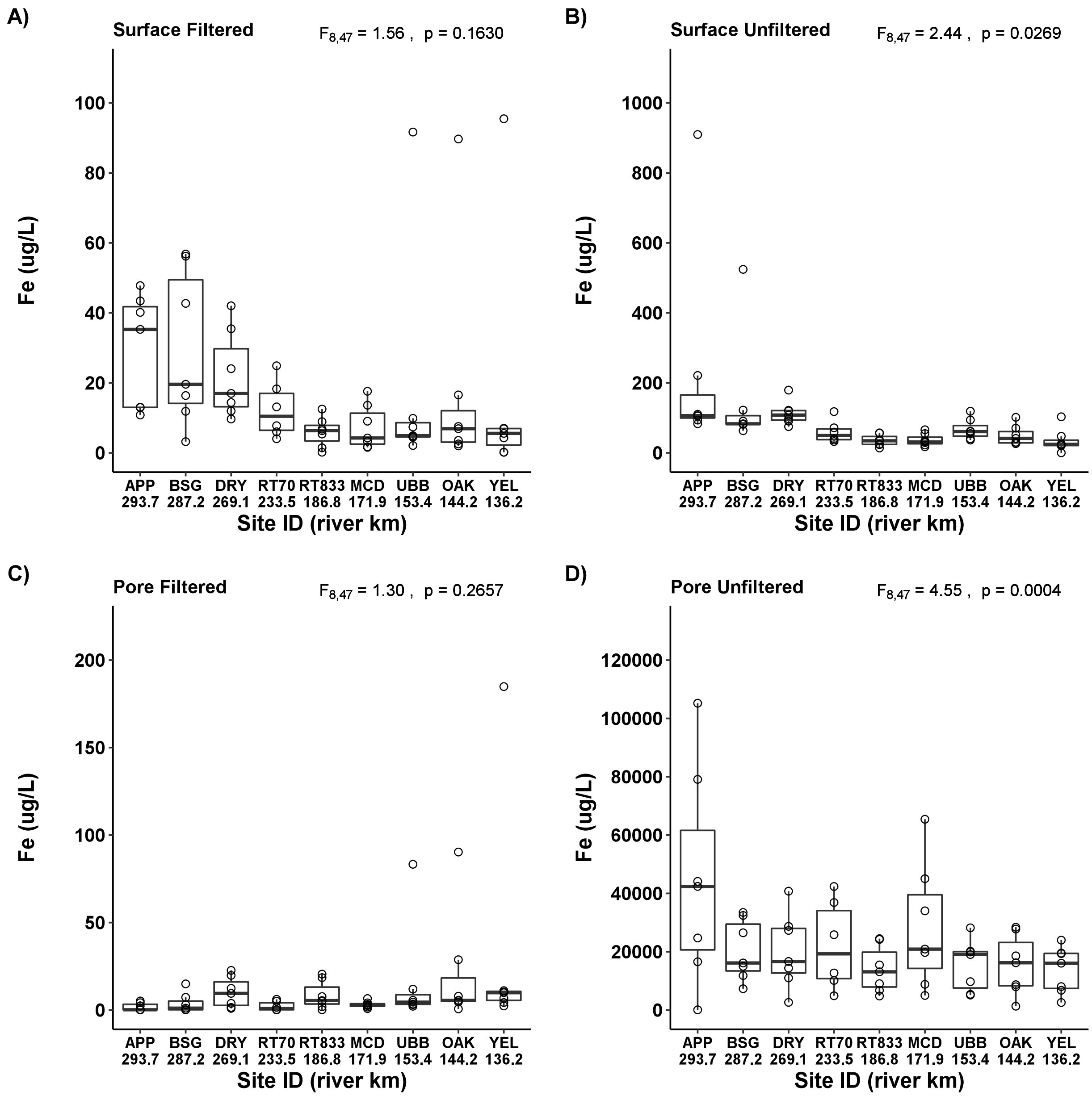

A)
Surface Filtered
$F_{8,47}$ = 16.03 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 1.69 , p = 0.1249
C)
Pore Filtered
$F_{8,47}$ = 2.09 , p = 0.0562
D)
Pore Unfiltered
$F_{8,47}$ = 3.56 , p = 0.0027
Co (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2



Surface Filtered
F8,45 = 3.66 , p = 0.0023
CO3 (mg/L)
2.5
2.0
1.5
1.0
0.5
0.0
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

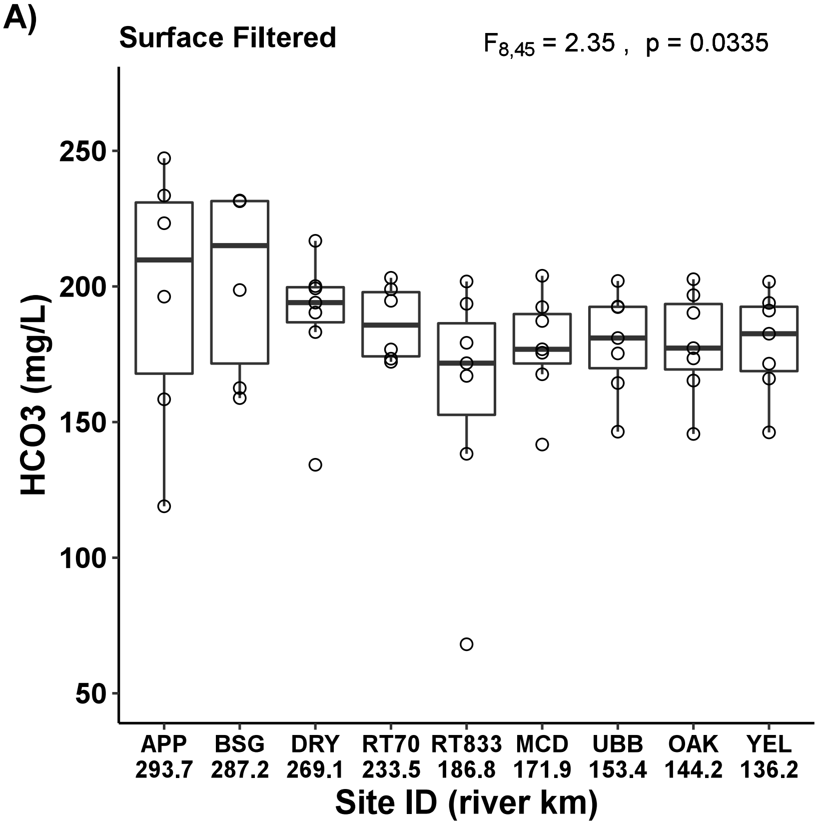

A)
Surface Filtered
$F_{8,47}$ = 1.95 , p = 0.0742
B)
Surface Unfiltered
$F_{8,47}$ = 0.67 , p = 0.7178
C)
Pore Filtered
$F_{8,47}$ = 0.40 , p = 0.9144
D)
Pore Unfiltered
$F_{8,47}$ = 2.30 , p = 0.0357
Cr (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
$F_{8,47}$ = 2.59 , p = 0.0199
Cu (ug/L)
Site ID (river km)
B)
Surface Unfiltered
$F_{8,47}$ = 2.89 , p = 0.0105
C)
Pore Filtered
$F_{8,47}$ = 0.62 , p = 0.7540
D)
Pore Unfiltered
$F_{8,47}$ = 5.00 , p = 0.0002
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2



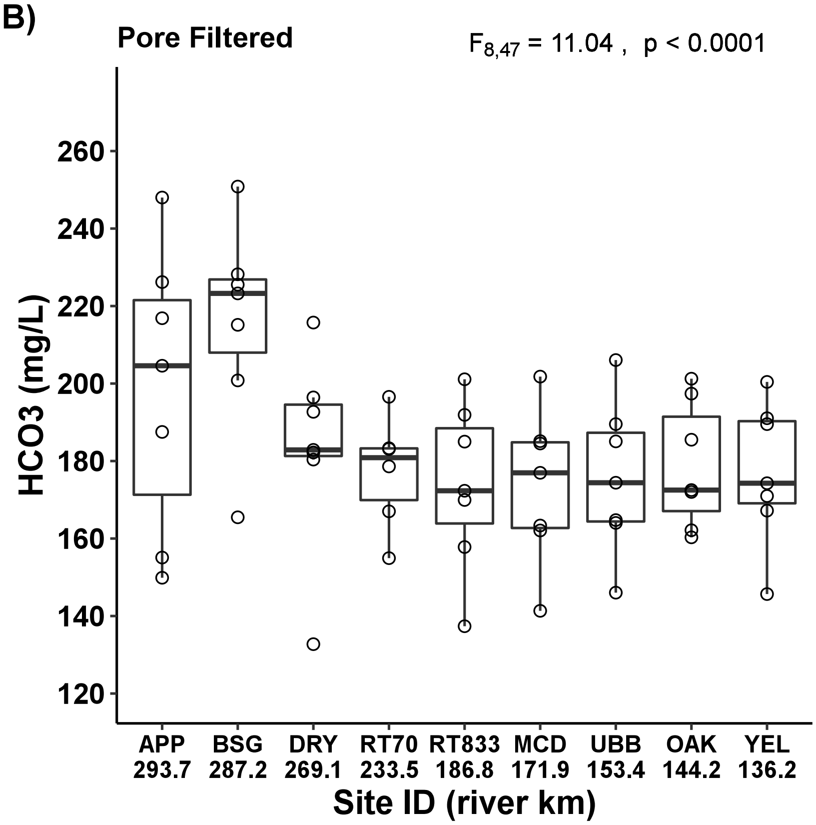
A)
Surface Filtered
$F_{8,47}$ = 1.56 , p = 0.1630
B)
Surface Unfiltered
$F_{8,47}$ = 2.44 , p = 0.0269
C)
Pore Filtered
$F_{8,47}$ = 1.30 , p = 0.2657
D)
Pore Unfiltered
$F_{8,47}$ = 4.55 , p = 0.0004
Fe (ug/L)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

A)

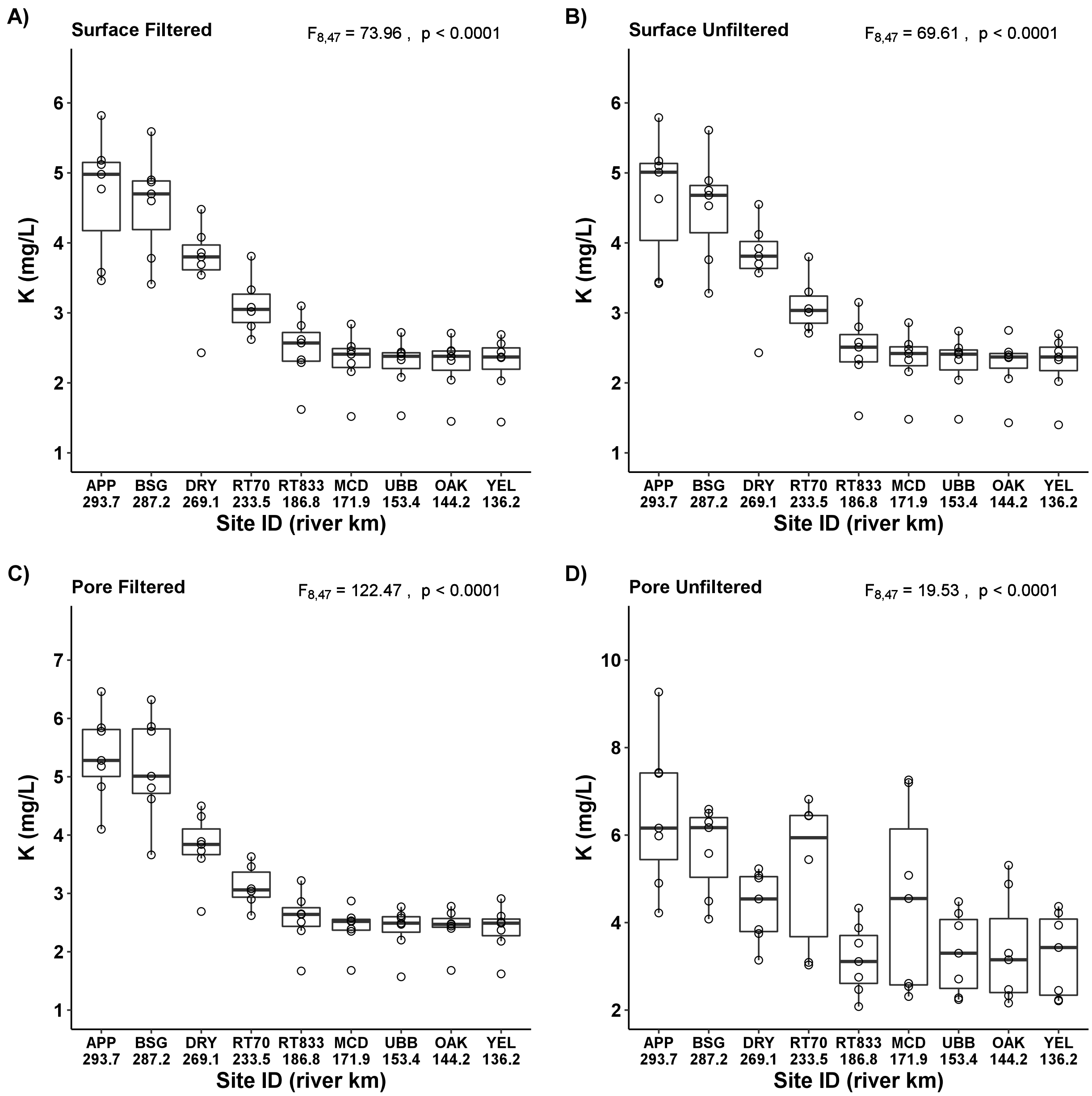


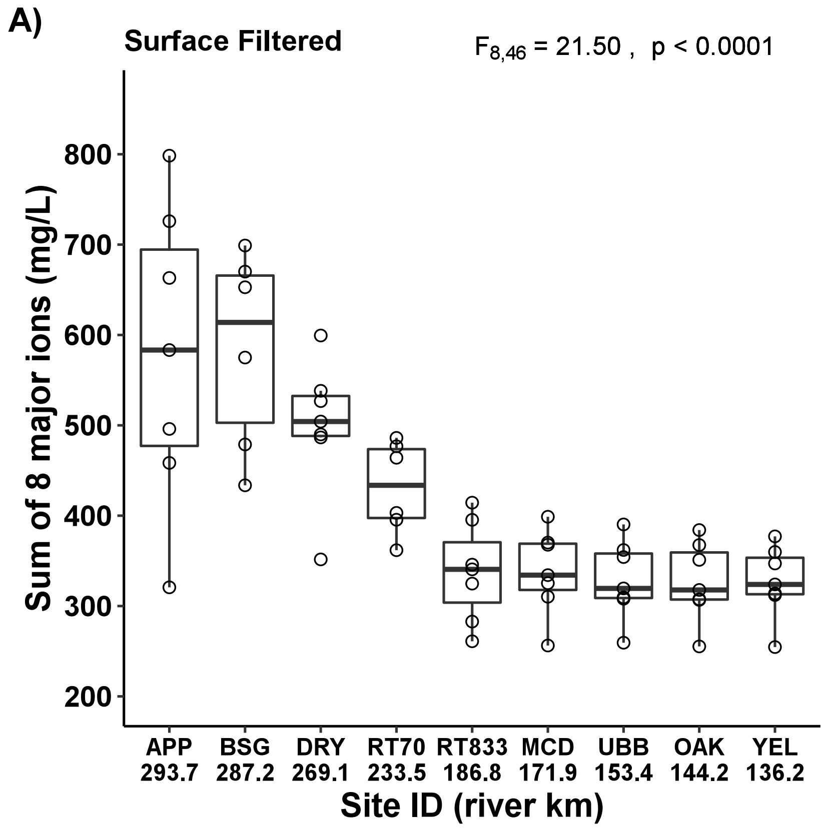
Surface Filtered
$F_{8,45}$ = 2.35 , p = 0.0335
HCO3 (mg/L)
250
200
150
100
50
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

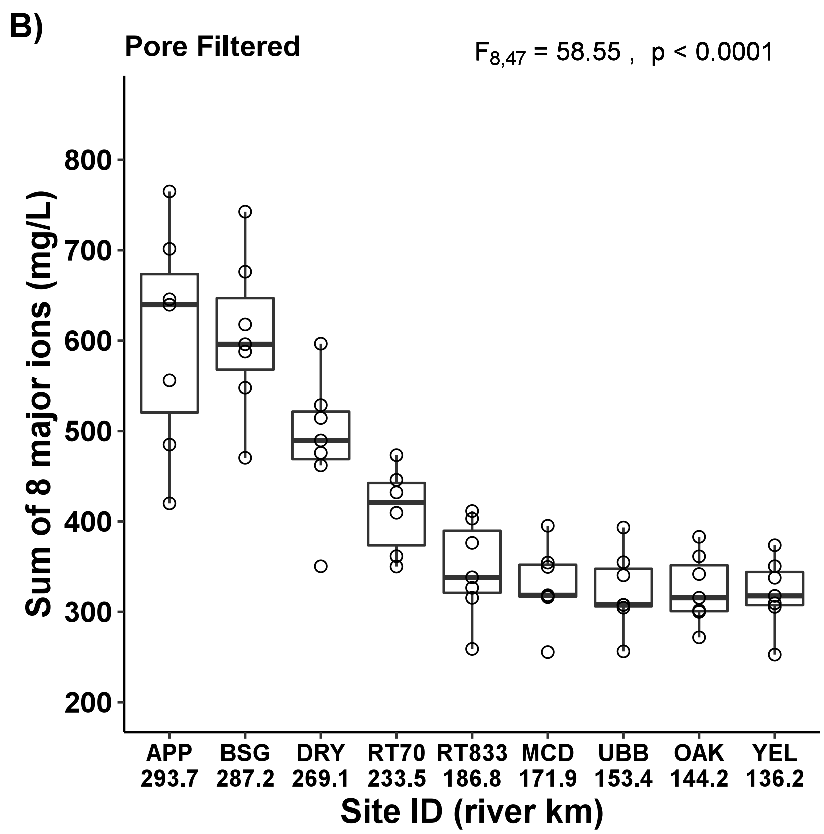
B)

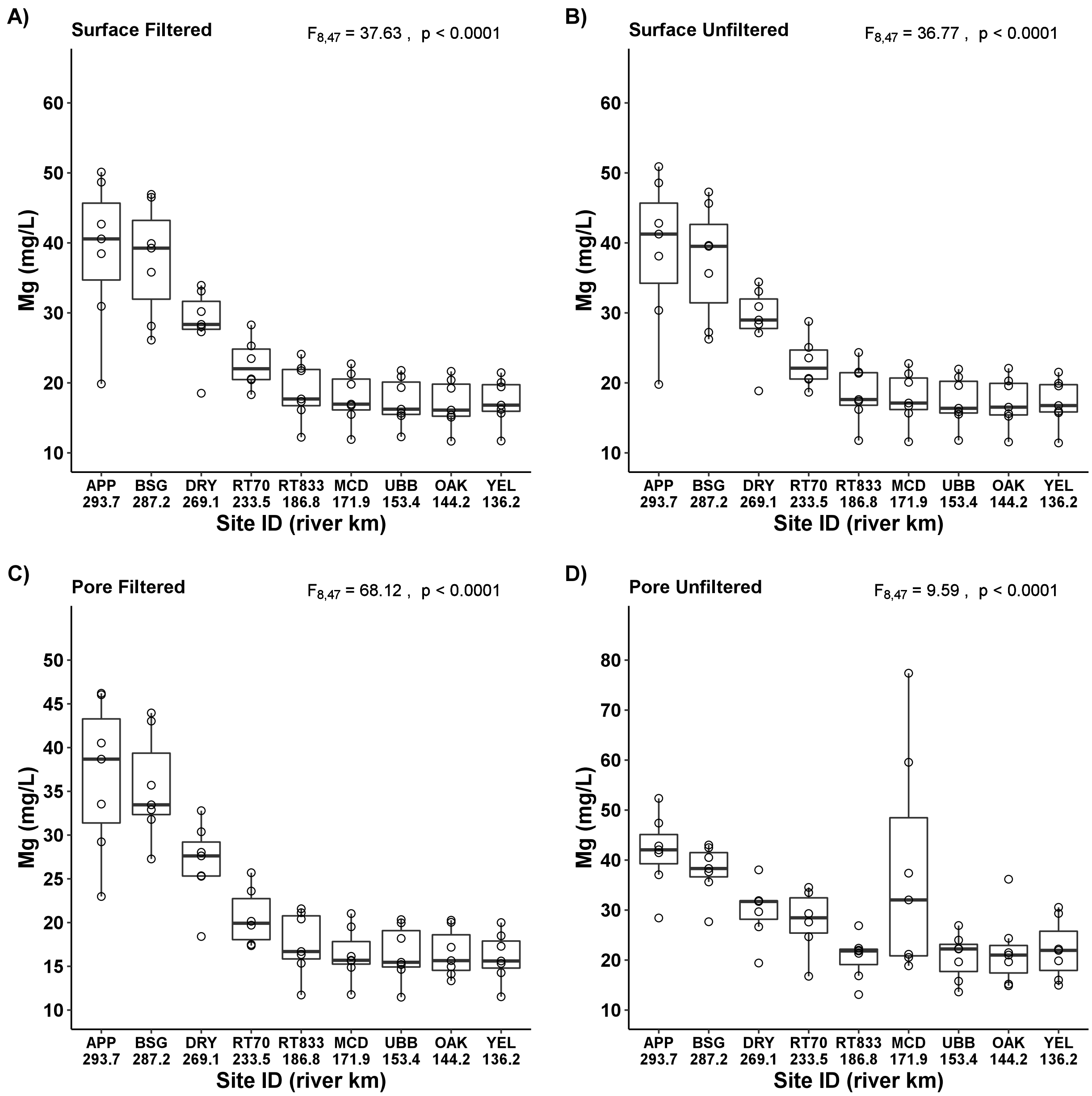


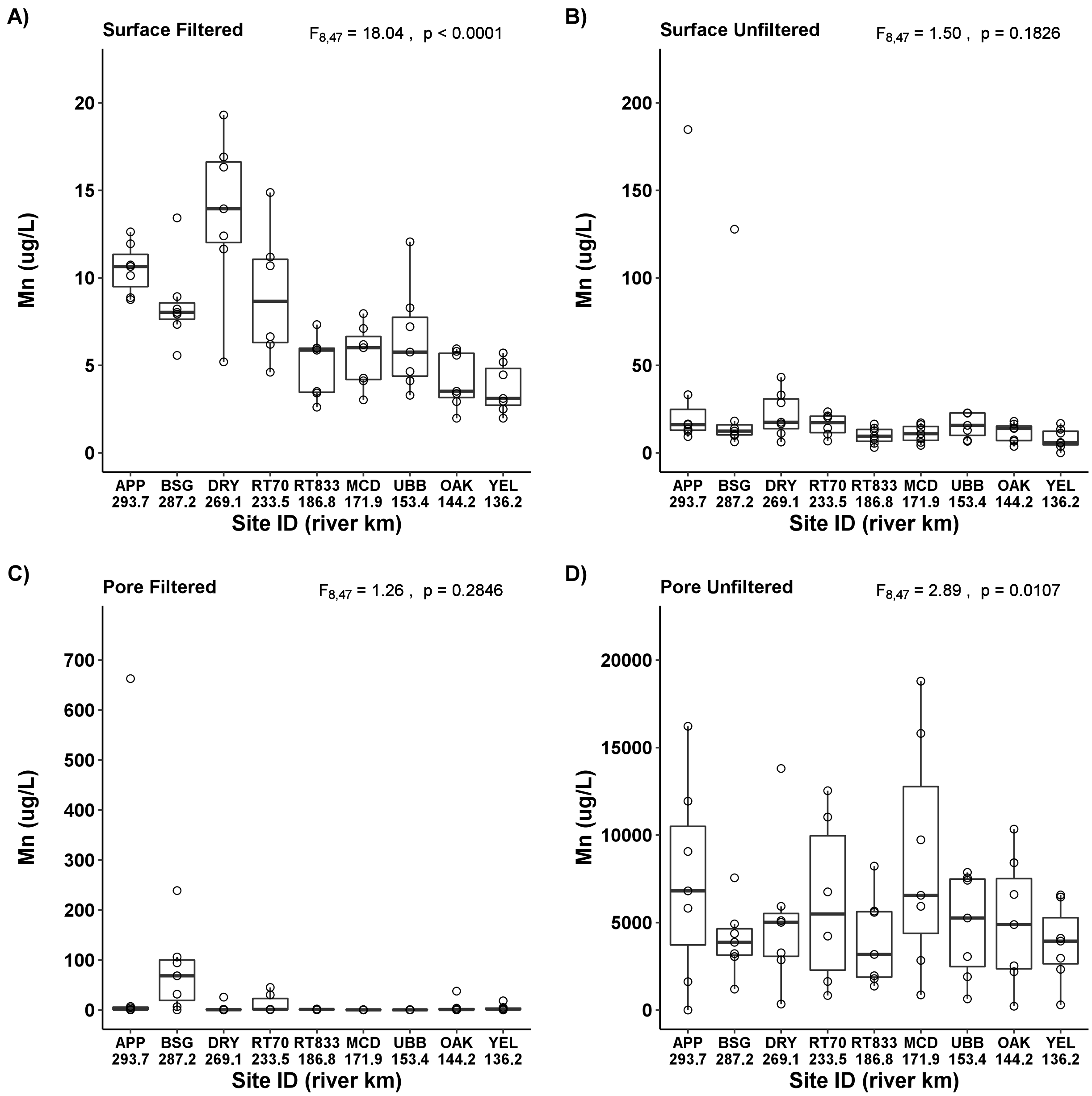
Pore Filtered
$F_{8,47}$ = 11.04 , p < 0.0001
HCO3 (mg/L)
260
240
220
200
180
160
140
120
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

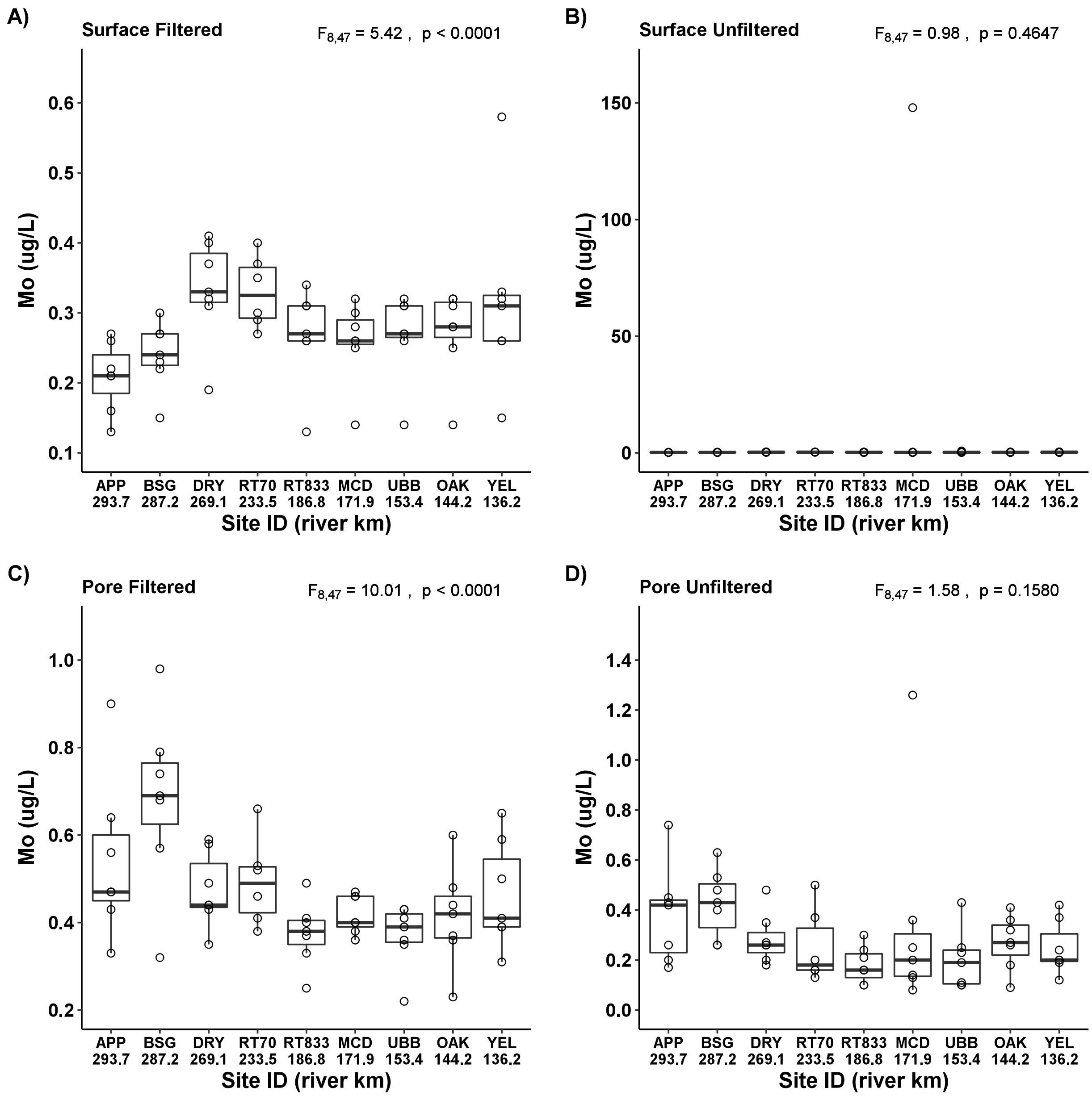

A)
Surface Filtered
$F_{8,47}$ = 73.96 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 69.61 , p < 0.0001
C)
Pore Filtered
$F_{8,47}$ = 122.47 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 19.53 , p < 0.0001
K (mg/L)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)


A)
Surface Filtered
F8,46 = 21.50 , p < 0.0001
Sum of 8 major ions (mg/L)
800
700
600
500
400
300
200
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

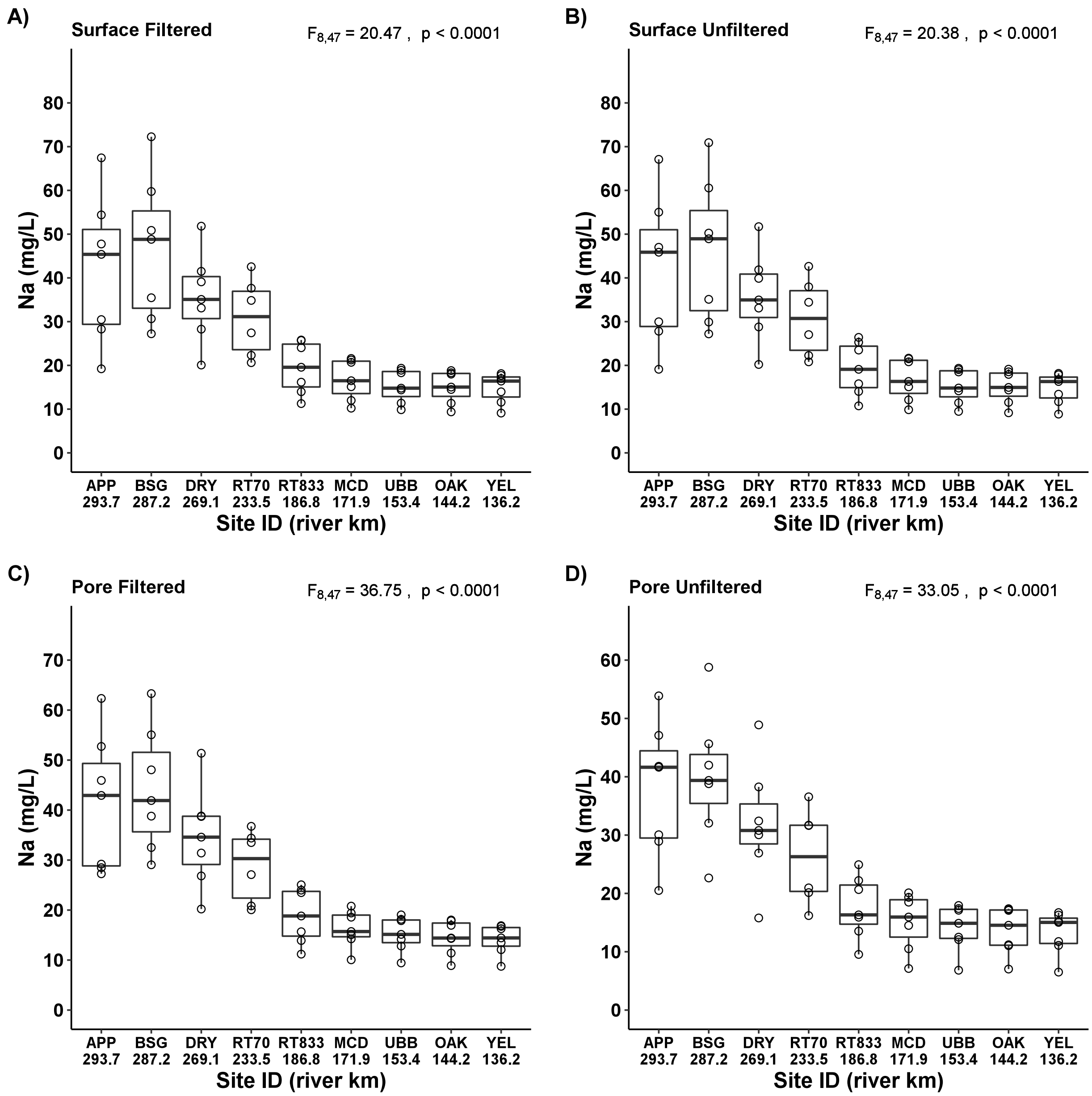

B)
Pore Filtered
F8,47 = 58.55 , p < 0.0001
Sum of 8 major ions (mg/L)
800
700
600
500
400
300
200
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)


A)
Surface Filtered
F8,47 = 37.63 , p < 0.0001
B)
Surface Unfiltered
F8,47 = 36.77 , p < 0.0001
C)
Pore Filtered
F8,47 = 68.12 , p < 0.0001
D)
Pore Unfiltered
F8,47 = 9.59 , p < 0.0001
Mg (mg/L)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

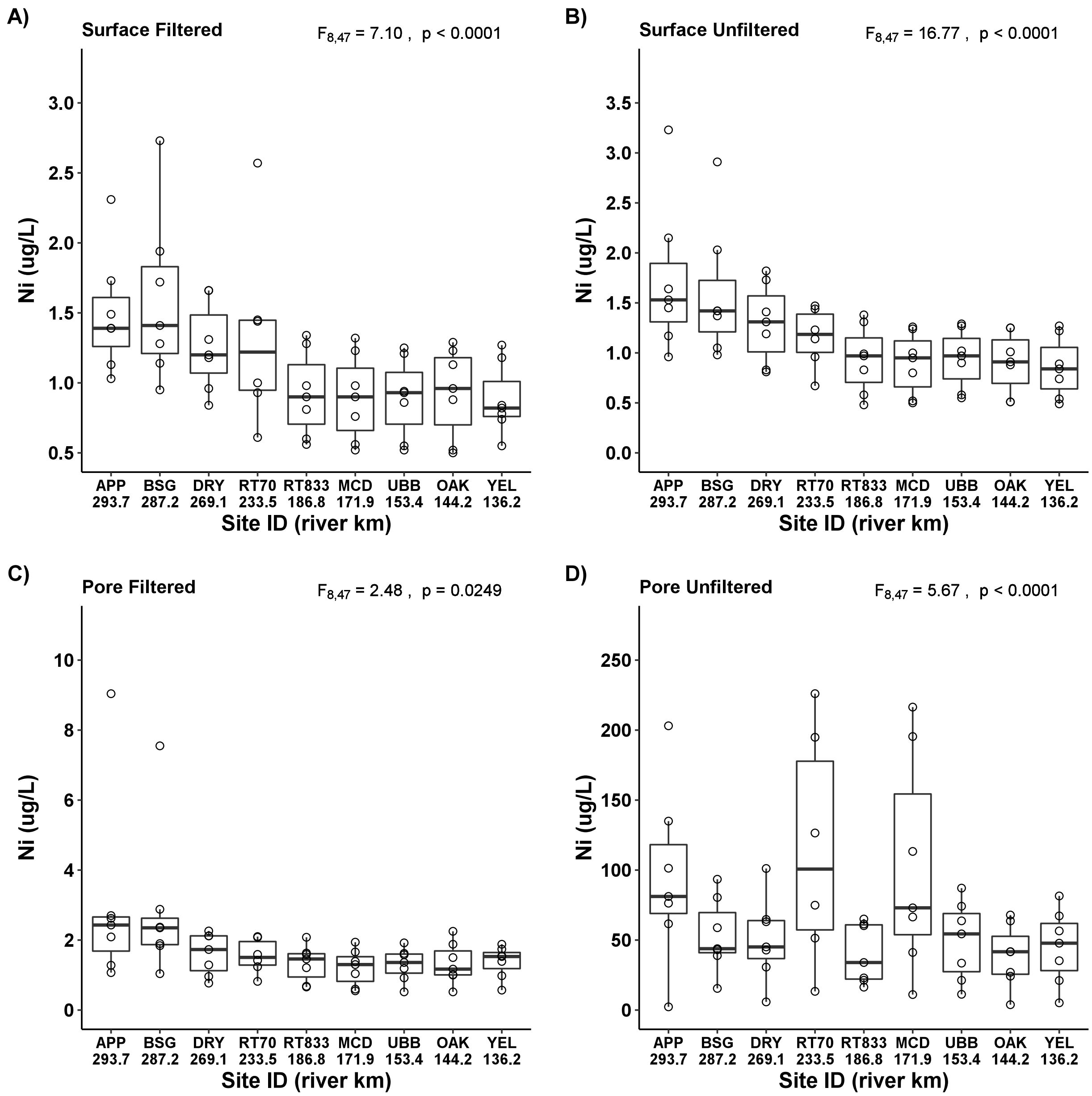

A)
Surface Filtered
$F_{8,47}$ = 18.04 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 1.50 , p = 0.1826
C)
Pore Filtered
$F_{8,47}$ = 1.26 , p = 0.2846
D)
Pore Unfiltered
$F_{8,47}$ = 2.89 , p = 0.0107
Mn (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

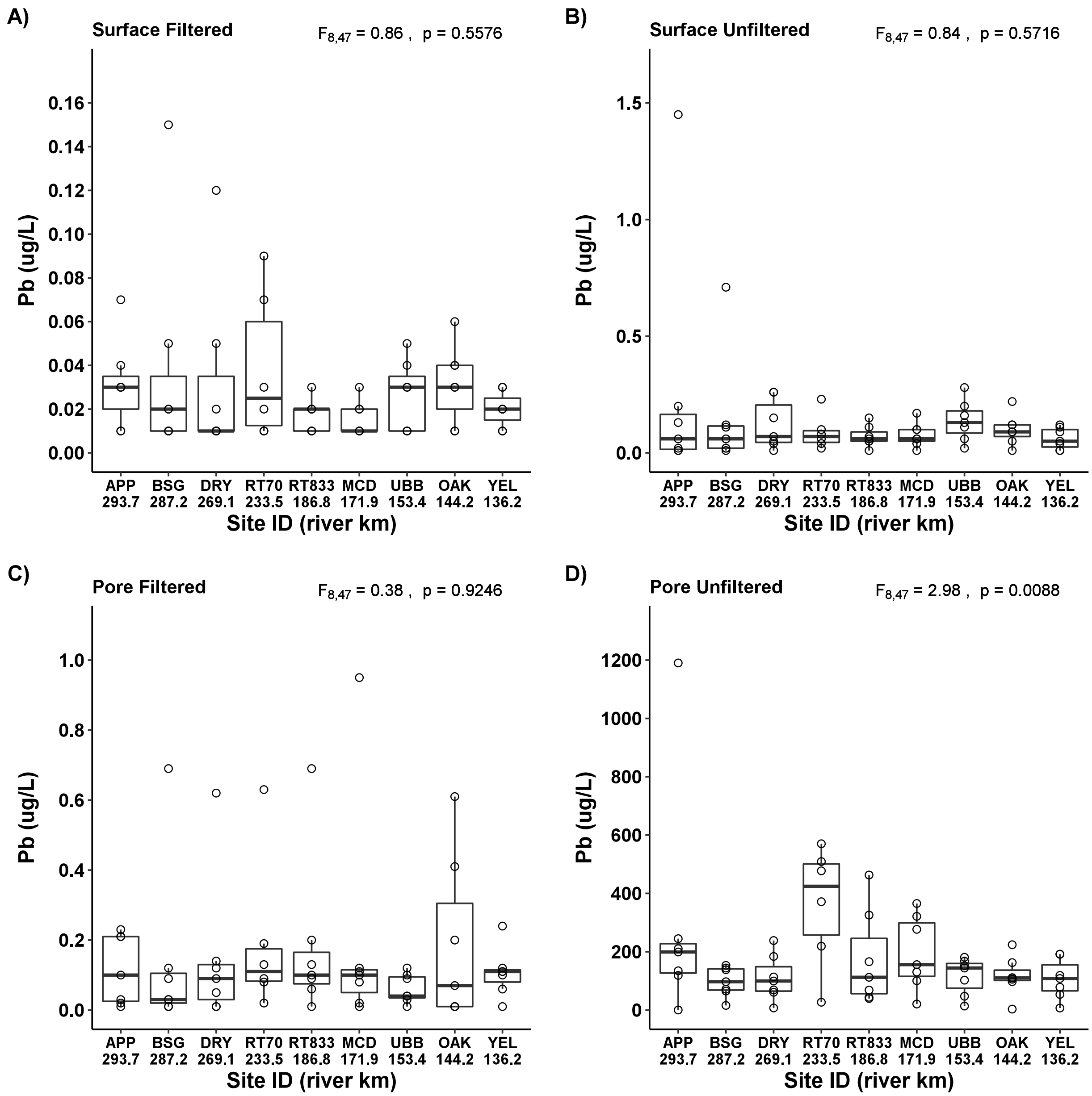


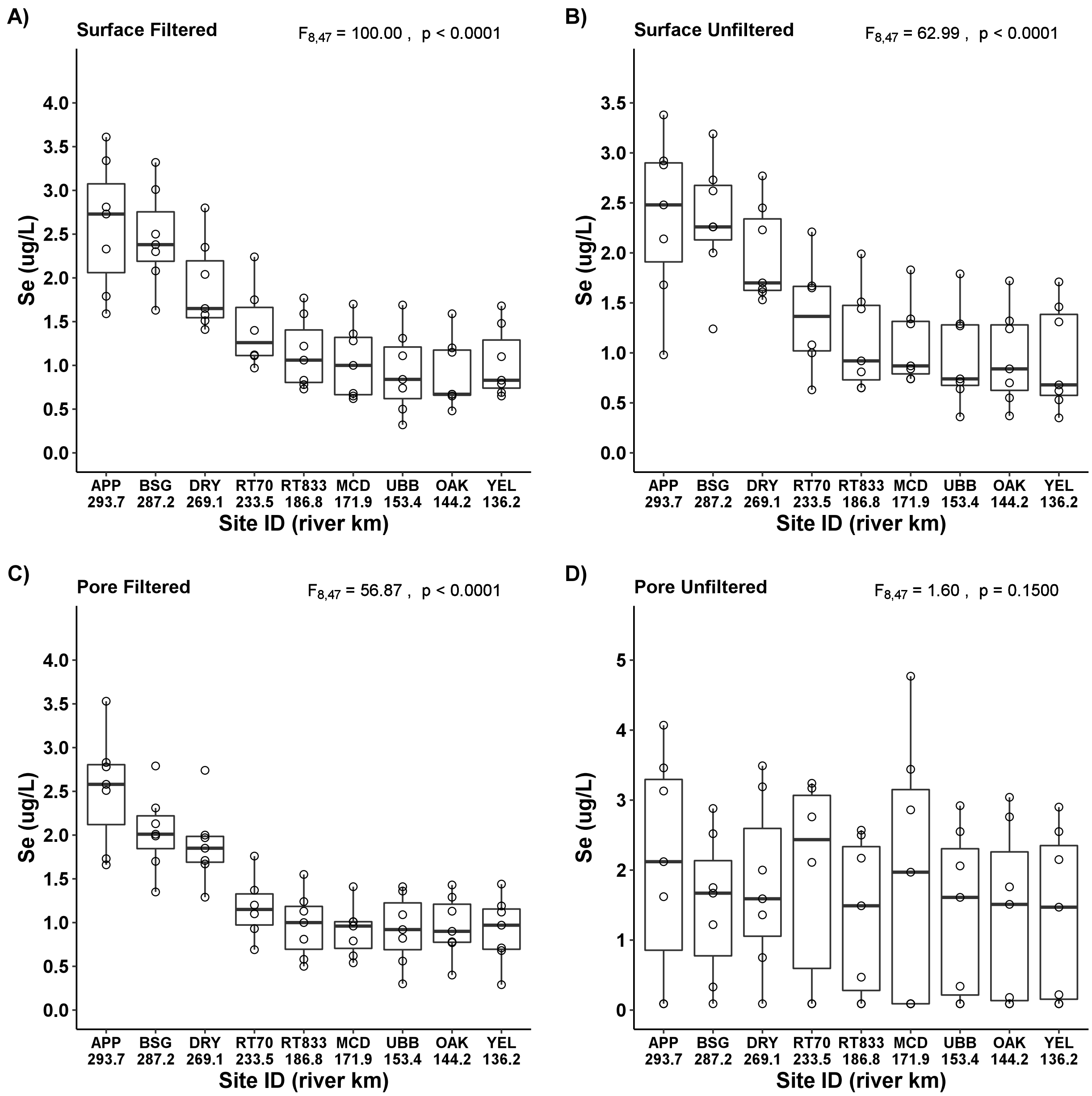
A)
Surface Filtered
$F_{8,47}$ = 5.42 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 0.98 , p = 0.4647
C)
Pore Filtered
$F_{8,47}$ = 10.01 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 1.58 , p = 0.1580
Mo (ug/L)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

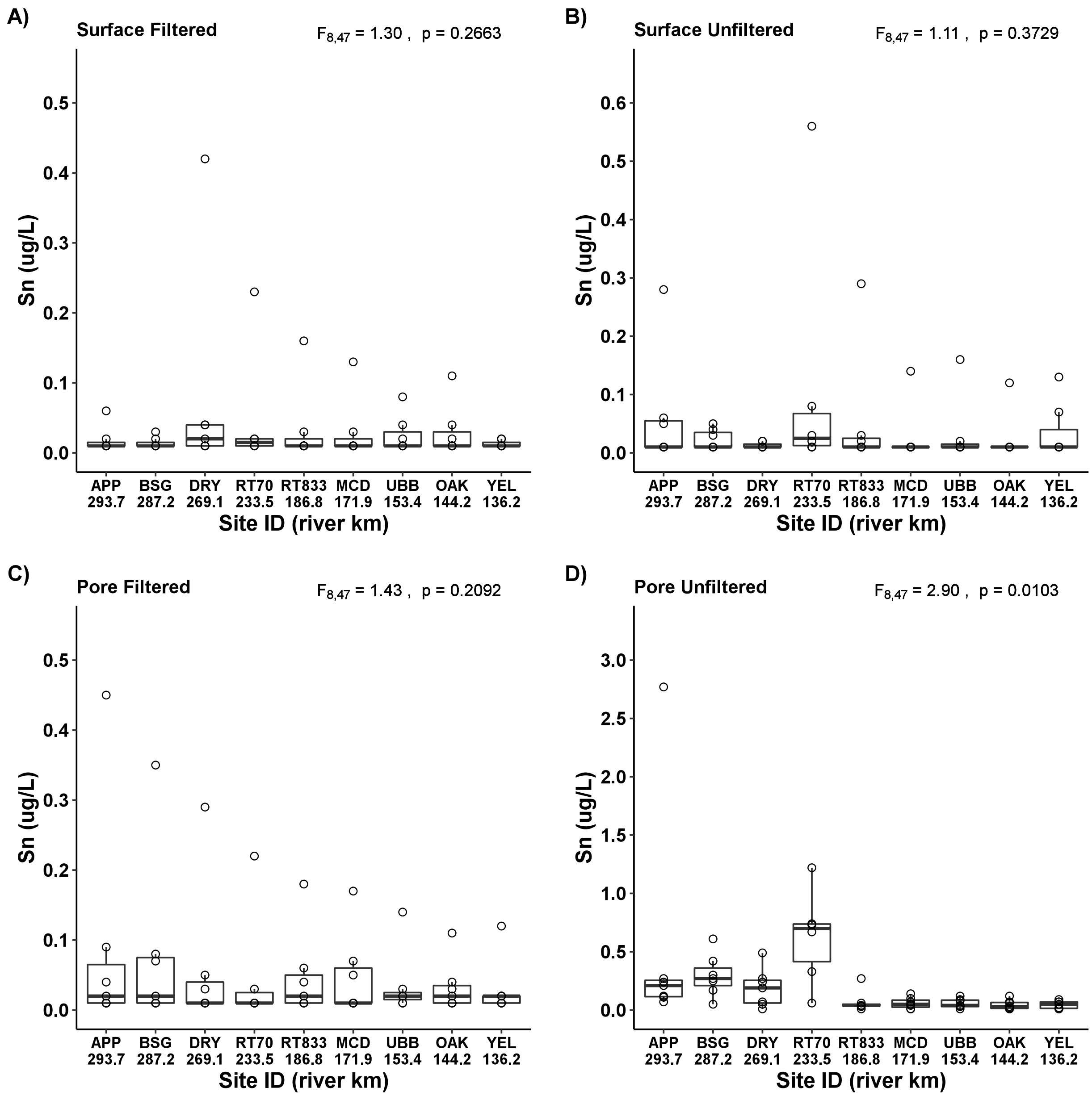


A)
Surface Filtered
$F_{8,47}$ = 20.47 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 20.38 , p < 0.0001
C)
Pore Filtered
$F_{8,47}$ = 36.75 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 33.05 , p < 0.0001
Na (mg/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
F8,47 = 7.10 , p < 0.0001
Ni (ug/L)
0.5
1.0
1.5
2.0
2.5
3.0
B)
Surface Unfiltered
F8,47 = 16.77 , p < 0.0001
Ni (ug/L)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
C)
Pore Filtered
F8,47 = 2.48 , p = 0.0249
Ni (ug/L)
0
2
4
6
8
10
D)
Pore Unfiltered
F8,47 = 5.67 , p < 0.0001
Ni (ug/L)
0
50
100
150
200
250
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

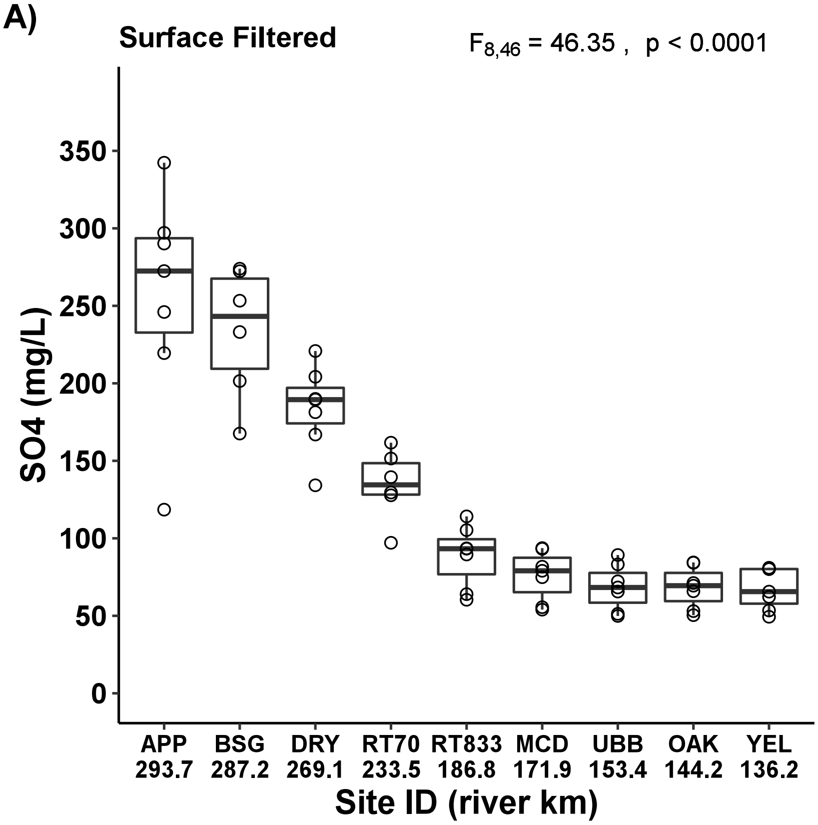

A)
Surface Filtered
$F_{8,47}$ = 0.86 , p = 0.5576
B)
Surface Unfiltered
$F_{8,47}$ = 0.84 , p = 0.5716
C)
Pore Filtered
$F_{8,47}$ = 0.38 , p = 0.9246
D)
Pore Unfiltered
$F_{8,47}$ = 2.98 , p = 0.0088
Pb (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
$F_{8,47}$ = 100.00 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 62.99 , p < 0.0001
C)
Pore Filtered
$F_{8,47}$ = 56.87 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 1.60 , p = 0.1500
Se (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

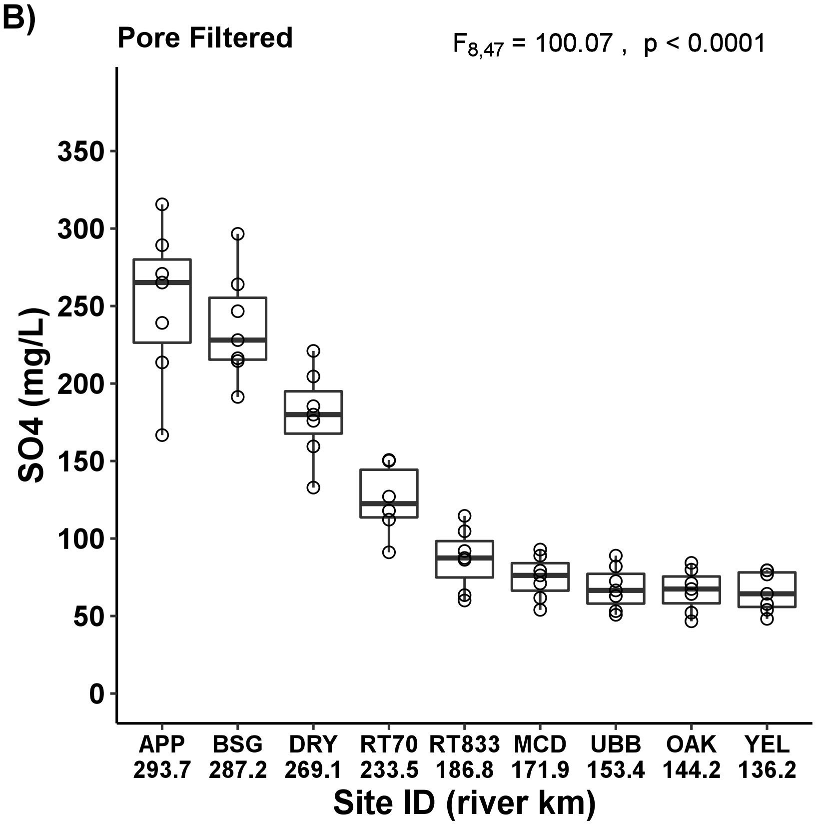


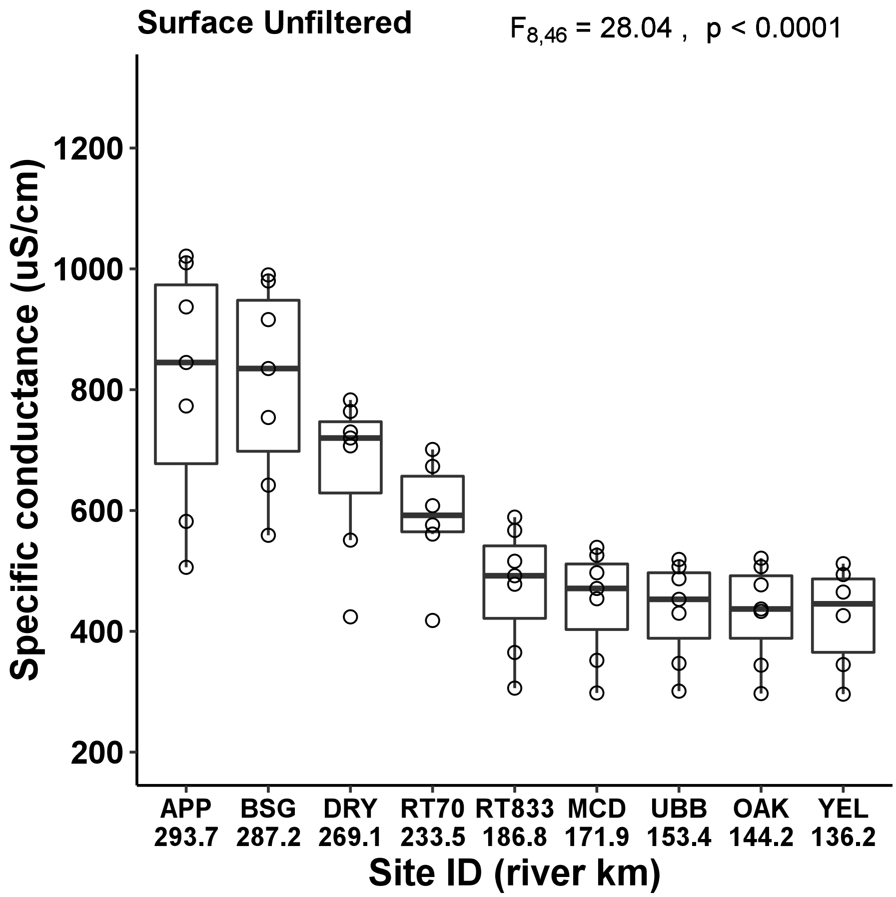
A)
Surface Filtered
F8,47 = 1.30 , p = 0.2663
B)
Surface Unfiltered
F8,47 = 1.11 , p = 0.3729
C)
Pore Filtered
F8,47 = 1.43 , p = 0.2092
D)
Pore Unfiltered
F8,47 = 2.90 , p = 0.0103
Sn (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

A)

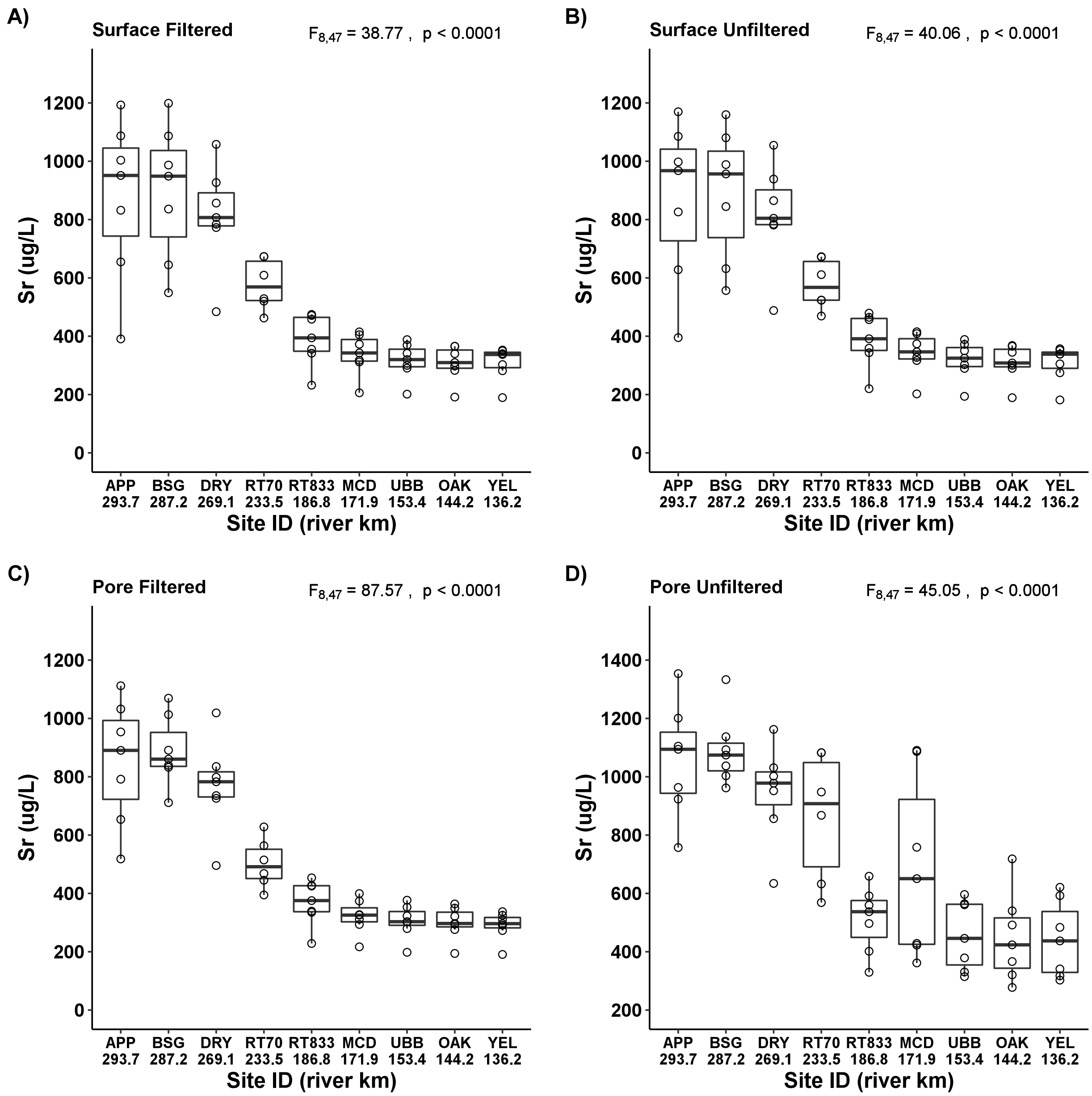

Surface Filtered
F8,46 = 46.35 , p < 0.0001
SO4 (mg/L)
350
300
250
200
150
100
50
0
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

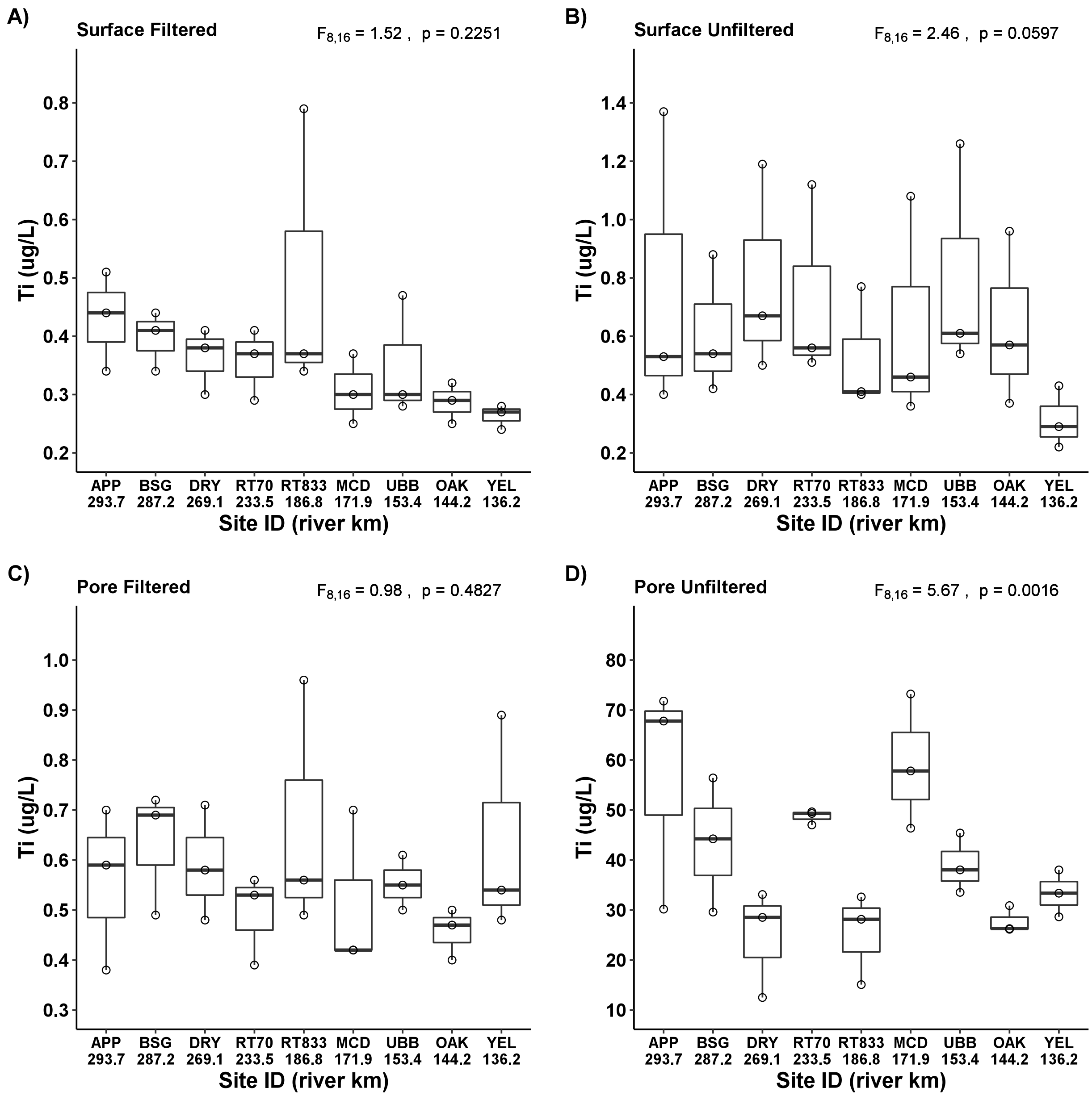
B)

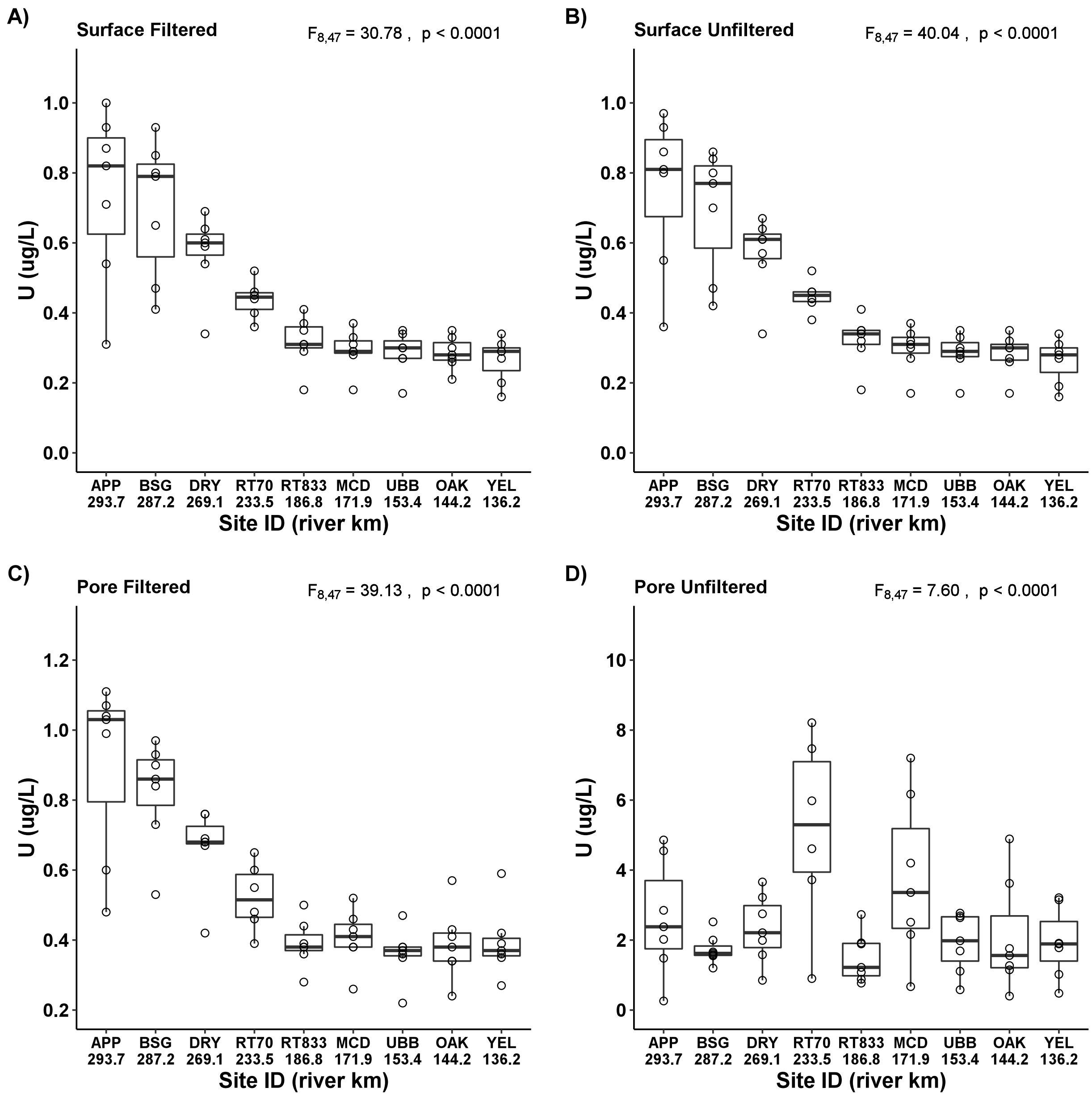

Pore Filtered
F8,47 = 100.07 , p < 0.0001
SO4 (mg/L)
350
300
250
200
150
100
50
0
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)



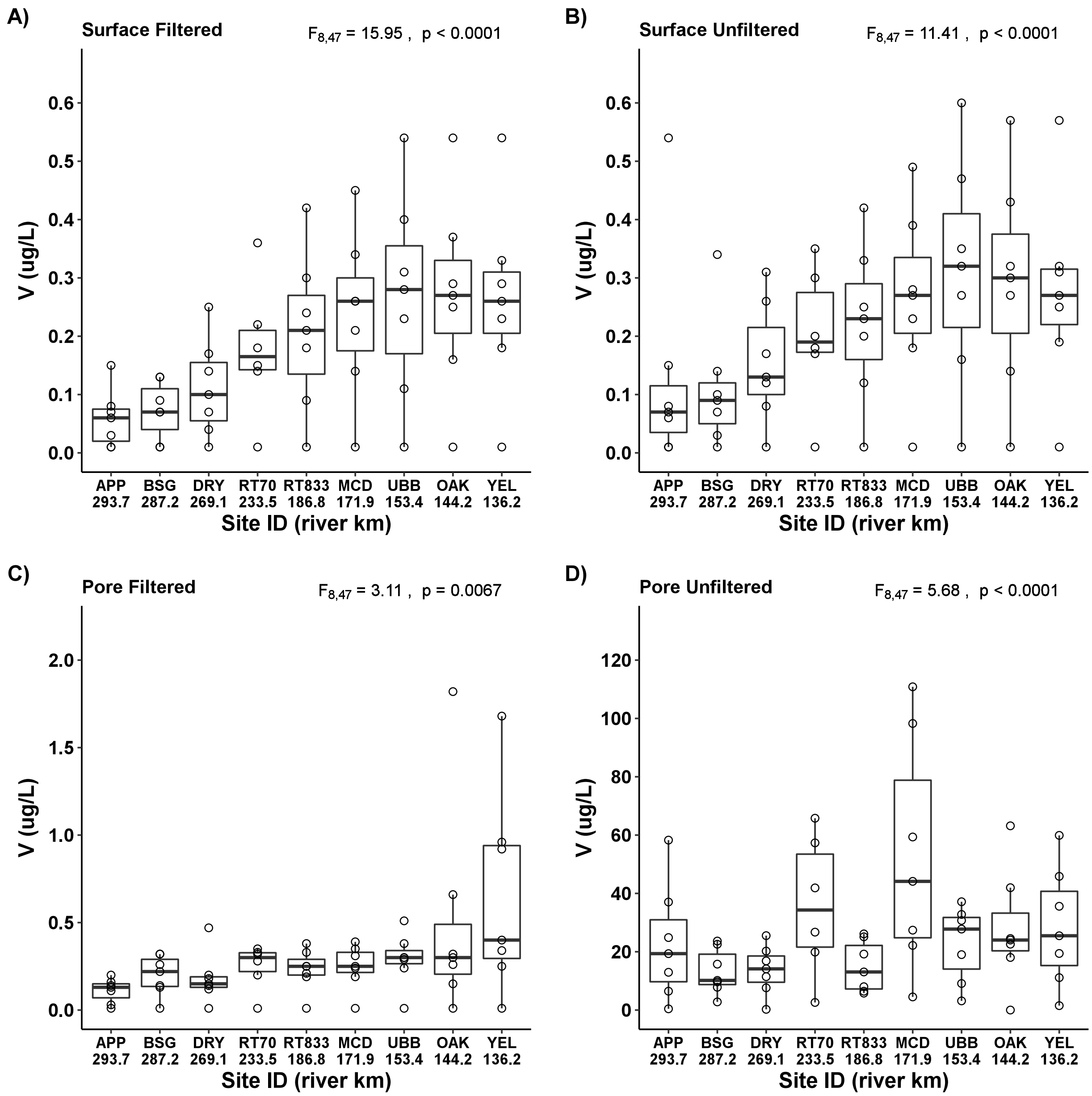
Surface Unfiltered
F8,46 = 28.04 , p < 0.0001
Specific conductance (uS/cm)
1200
1000
800
600
400
200
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

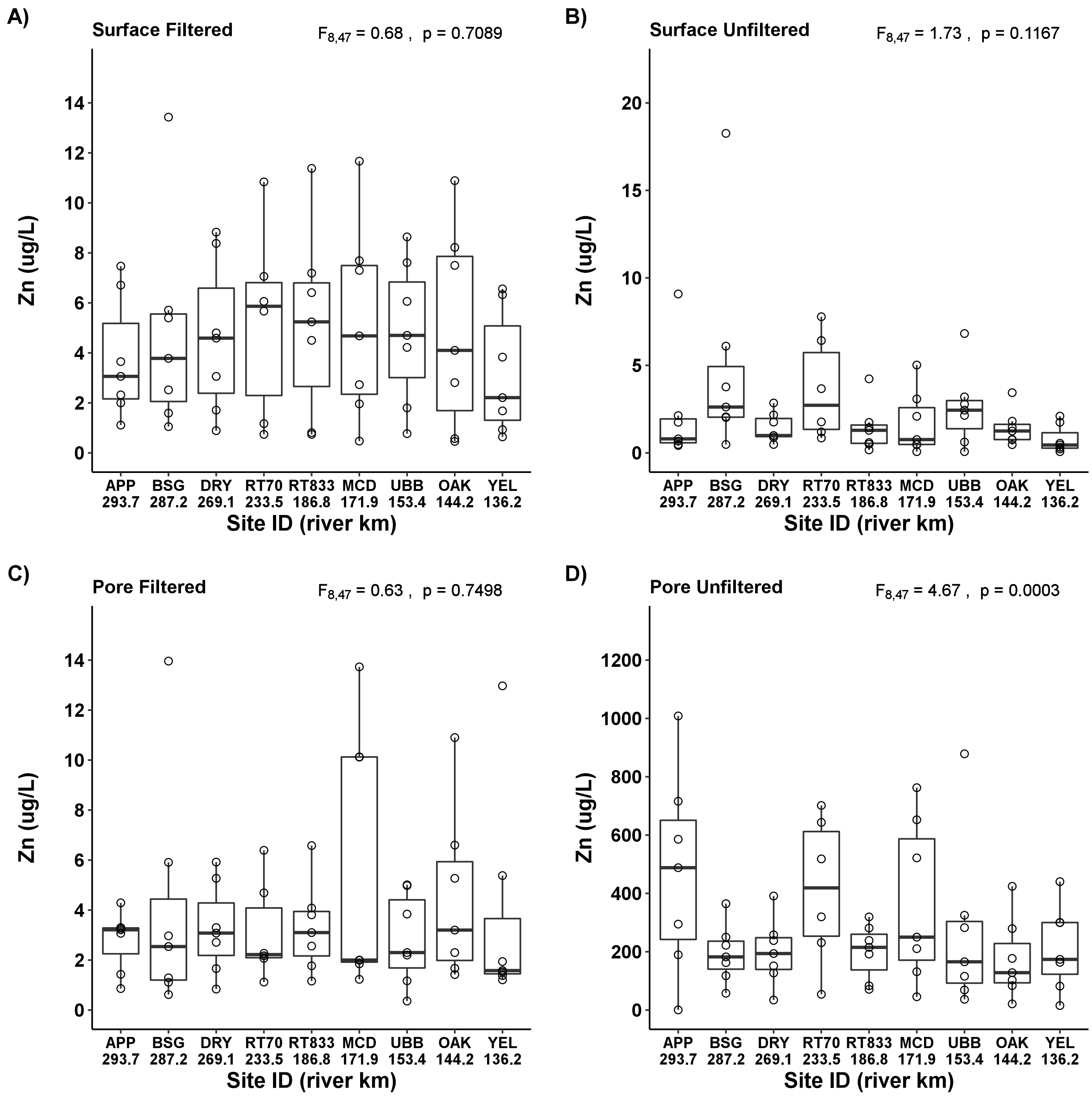

A)
Surface Filtered
$F_{8,47}$ = 38.77 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 40.06 , p < 0.0001
C)
Pore Filtered
$F_{8,47}$ = 87.57 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 45.05 , p < 0.0001
Sr (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
F8,16 = 1.52 , p = 0.2251
B)
Surface Unfiltered
F8,16 = 2.46 , p = 0.0597
C)
Pore Filtered
F8,16 = 0.98 , p = 0.4827
D)
Pore Unfiltered
F8,16 = 5.67 , p = 0.0016
Ti (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2



A)
Surface Filtered
F8,47 = 30.78 , p < 0.0001
B)
Surface Unfiltered
F8,47 = 40.04 , p < 0.0001
C)
Pore Filtered
F8,47 = 39.13 , p < 0.0001
D)
Pore Unfiltered
F8,47 = 7.60 , p < 0.0001
U (ug/L)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

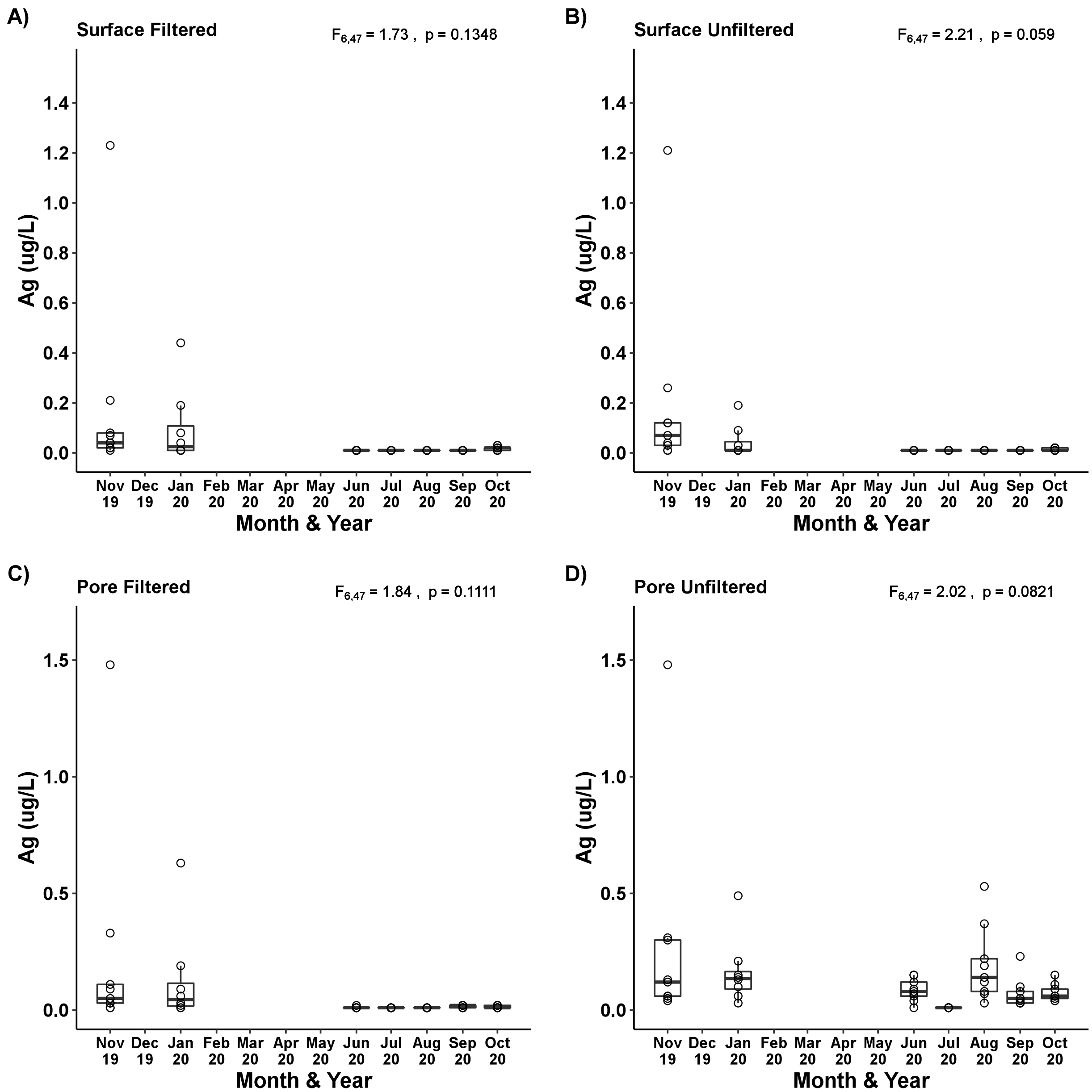

A)
Surface Filtered
F8,47 = 15.95 , p < 0.0001
B)
Surface Unfiltered
F8,47 = 11.41 , p < 0.0001
C)
Pore Filtered
F8,47 = 3.11 , p = 0.0067
D)
Pore Unfiltered
F8,47 = 5.68 , p < 0.0001
V (ug/L)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

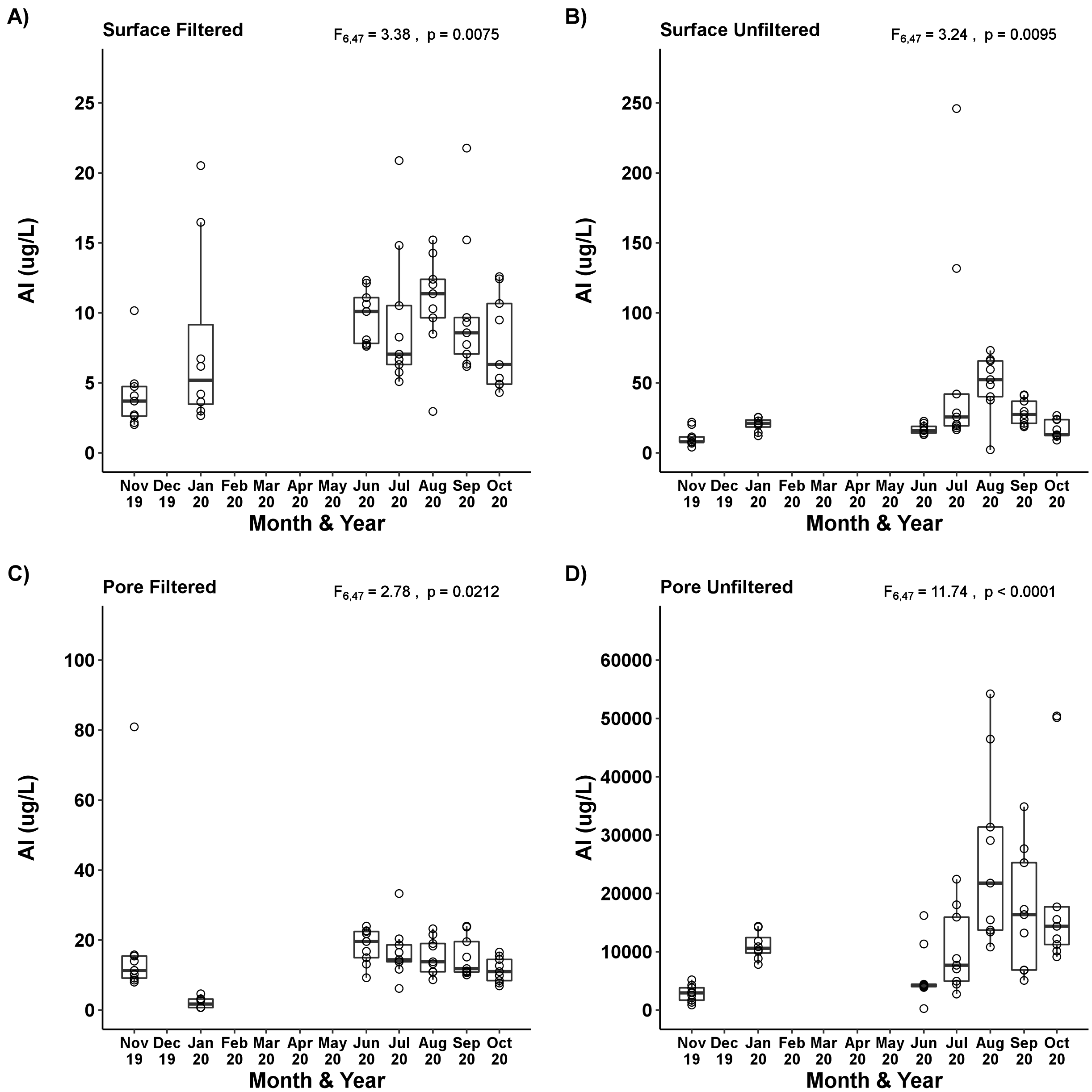

A)
Surface Filtered
F8,47 = 0.68 , p = 0.7089
B)
Surface Unfiltered
F8,47 = 1.73 , p = 0.1167
C)
Pore Filtered
F8,47 = 0.63 , p = 0.7498
D)
Pore Unfiltered
F8,47 = 4.67 , p = 0.0003
Zn (ug/L)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

APPENDIX B – TEMPORAL MIXED MODEL BOXPLOTS: ION CONCENTRATION BY SAMPLE TYPE

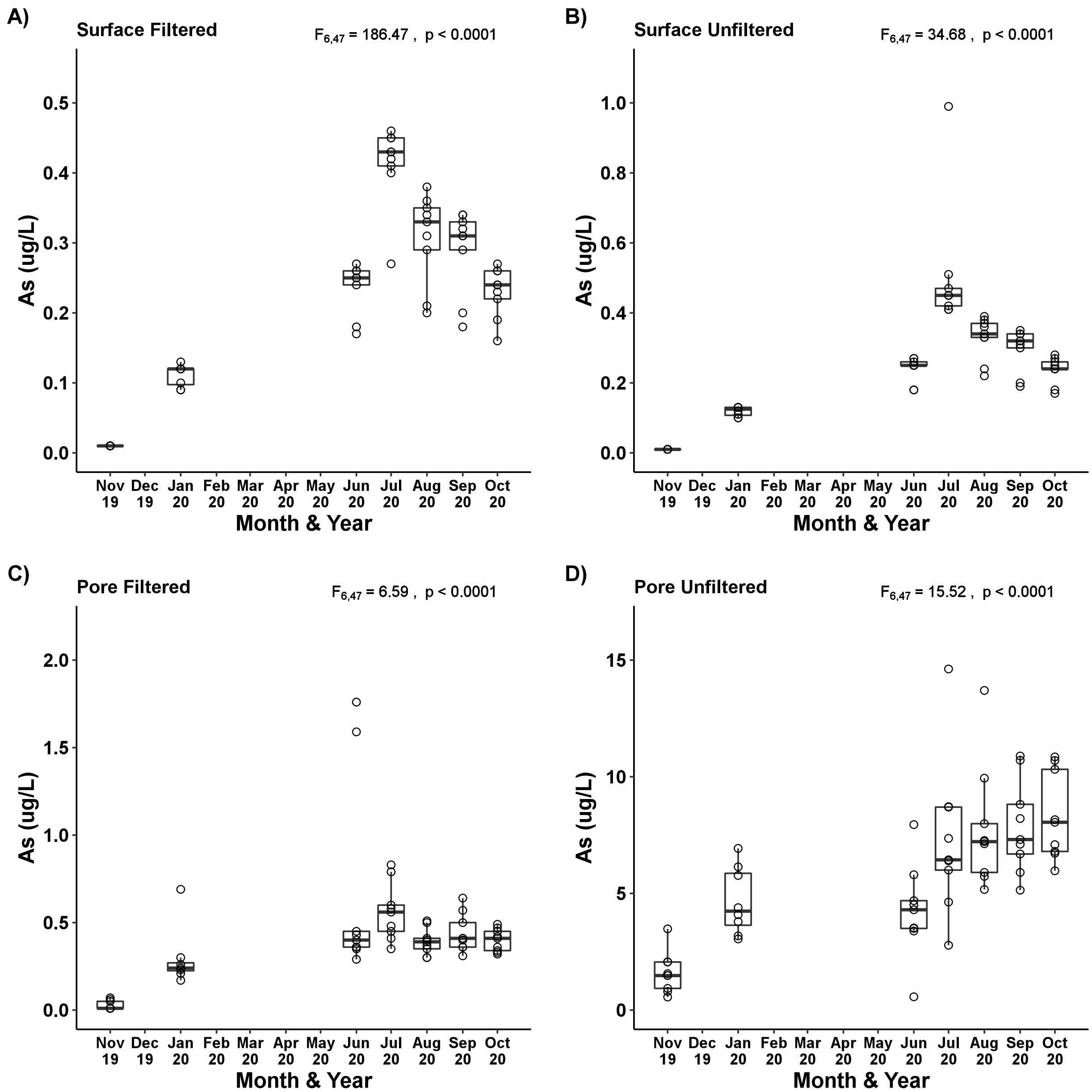
These models evaluate differences in ion concentrations among sampling dates, with sampling site as a random effect to account for samples being collected from multiple sites during each of the 12 sampling months of the study period.

Each page addresses a single ion, with up to four boxplots representing the up to four types of samples collected: Filtered and Unfiltered Surface Water, as well as Filtered and Unfiltered Pore Water. Open circles are individual observations, with observations from up to nine sites per sampling month. The vertical axis indicates the ion and units of concentration; note that axis range is independent among panels. The horizontal axis indicates month and year when the samples were collected. On the upper-right border of each plot are Wald test F-statistics and p-values for overall month-wise effects.

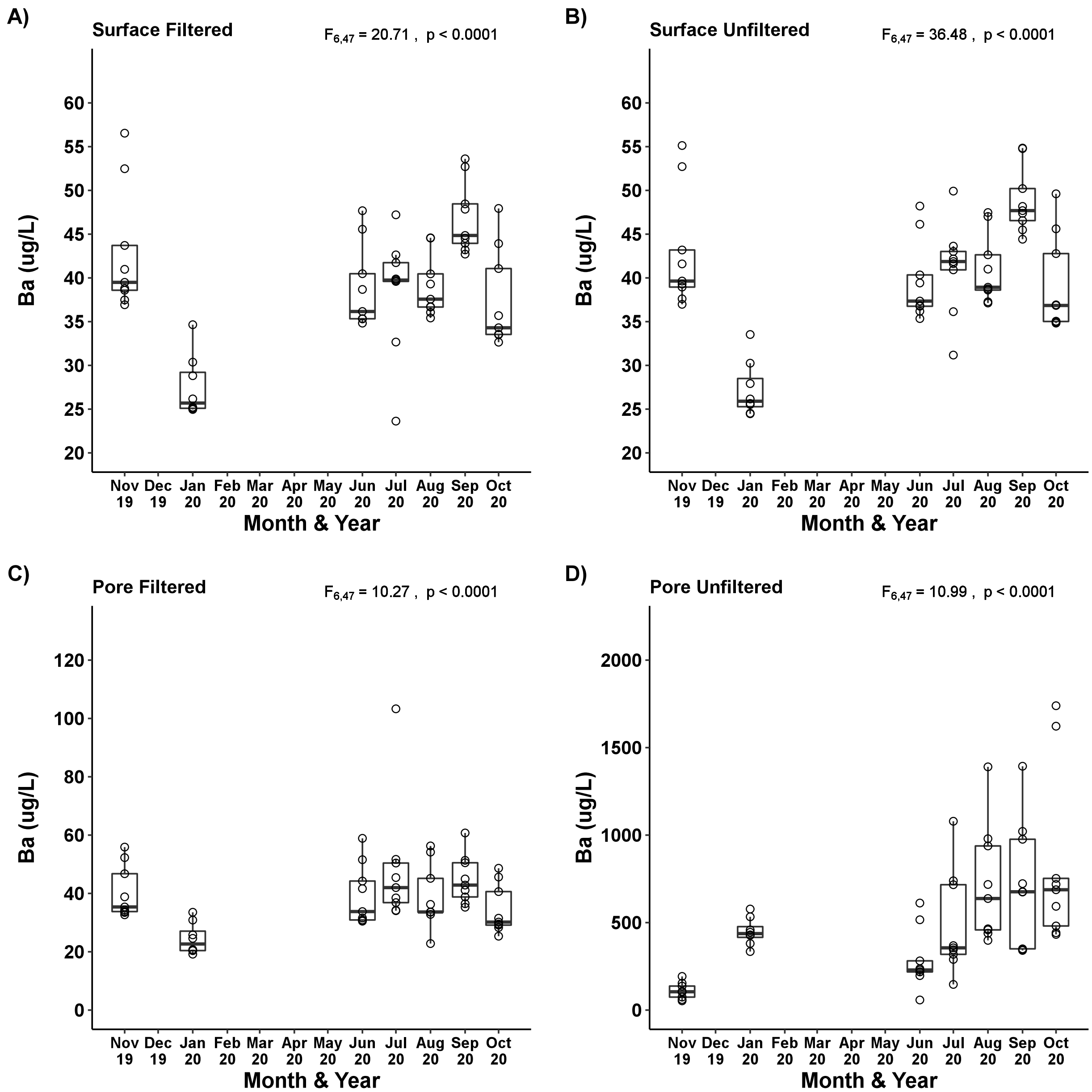

A)
Surface Filtered
F6,47 = 1.73 , p = 0.1348
B)
Surface Unfiltered
F6,47 = 2.21 , p = 0.059
C)
Pore Filtered
F6,47 = 1.84 , p = 0.1111
D)
Pore Unfiltered
F6,47 = 2.02 , p = 0.0821
Ag (ug/L)
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year

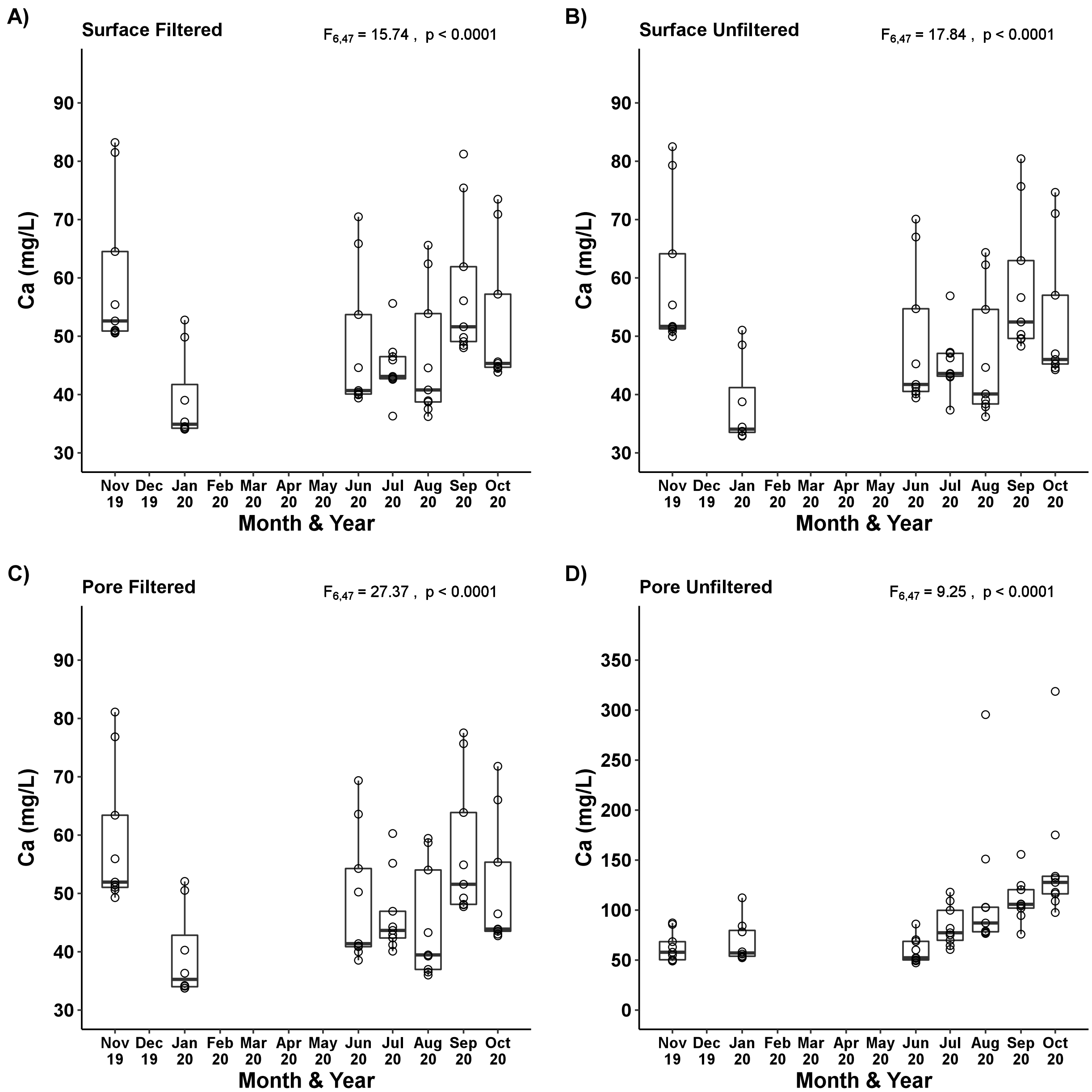


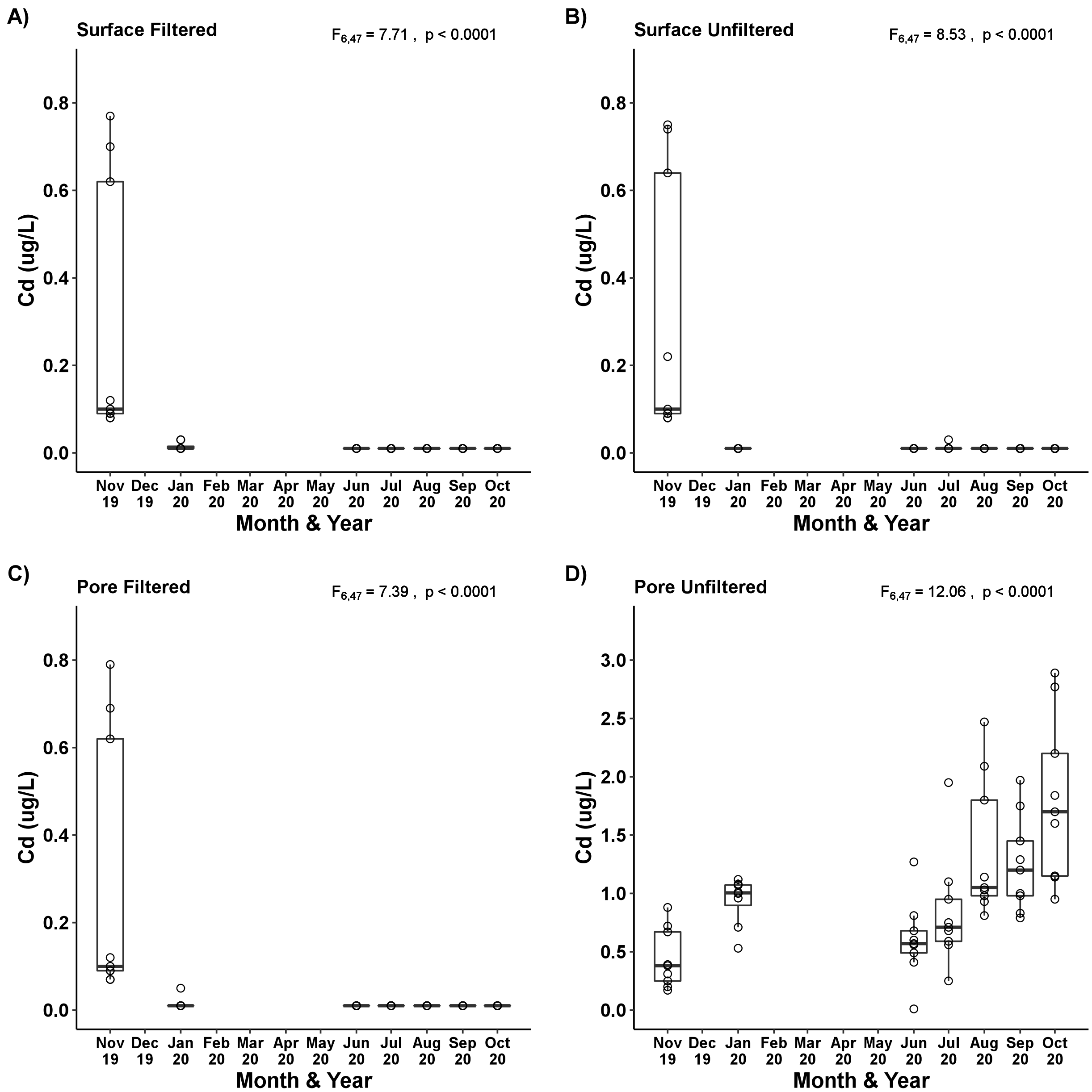
A)
Surface Filtered
F6,47 = 3.38 , p = 0.0075
B)
Surface Unfiltered
F6,47 = 3.24 , p = 0.0095
C)
Pore Filtered
F6,47 = 2.78 , p = 0.0212
D)
Pore Unfiltered
F6,47 = 11.74 , p < 0.0001
Al (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20



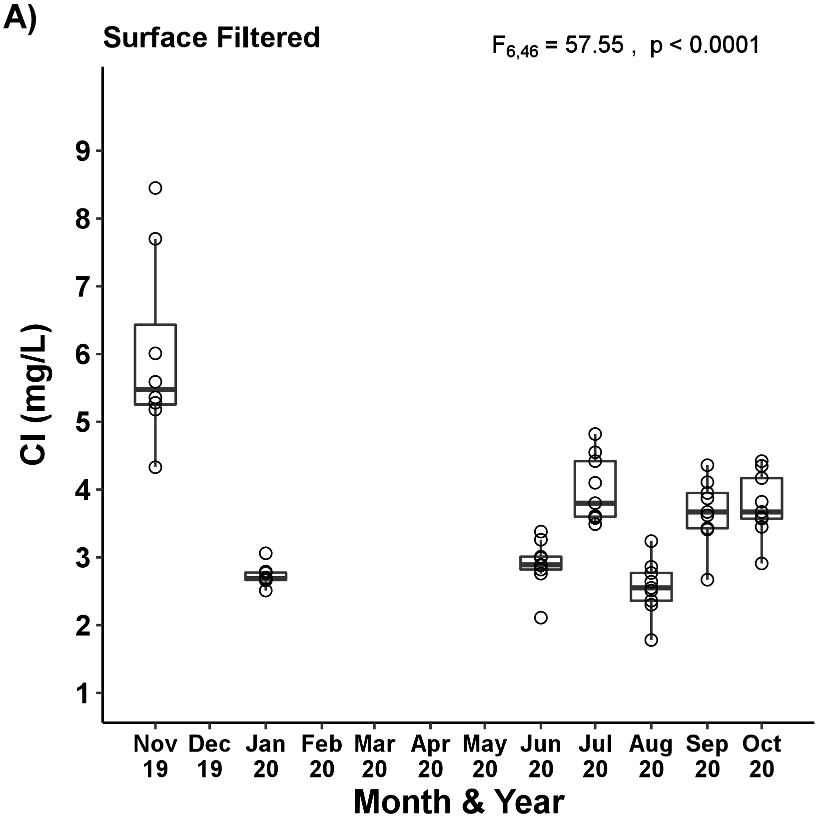
A)
Surface Filtered
$F_{6,47}$ = 186.47 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 34.68 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 6.59 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 15.52 , p < 0.0001
As (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20


A)
Surface Filtered
$F_{6,47}$ = 20.71 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 36.48 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 10.27 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 10.99 , p < 0.0001
Ba (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

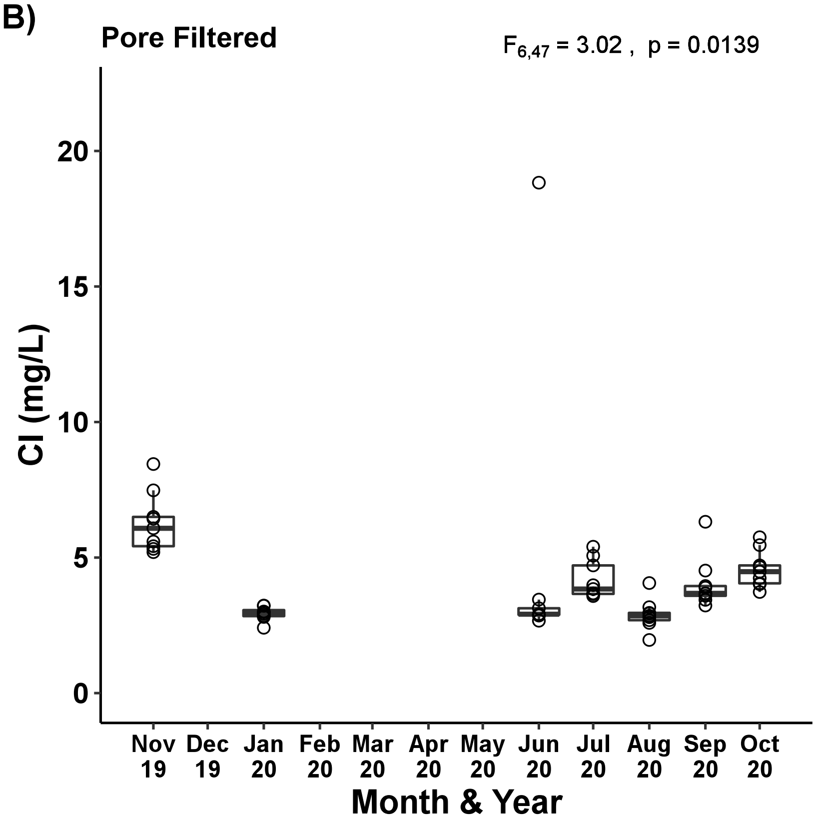

A)
Surface Filtered
$F_{6,47}$ = 15.74 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 17.84 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 27.37 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 9.25 , p < 0.0001
Ca (mg/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

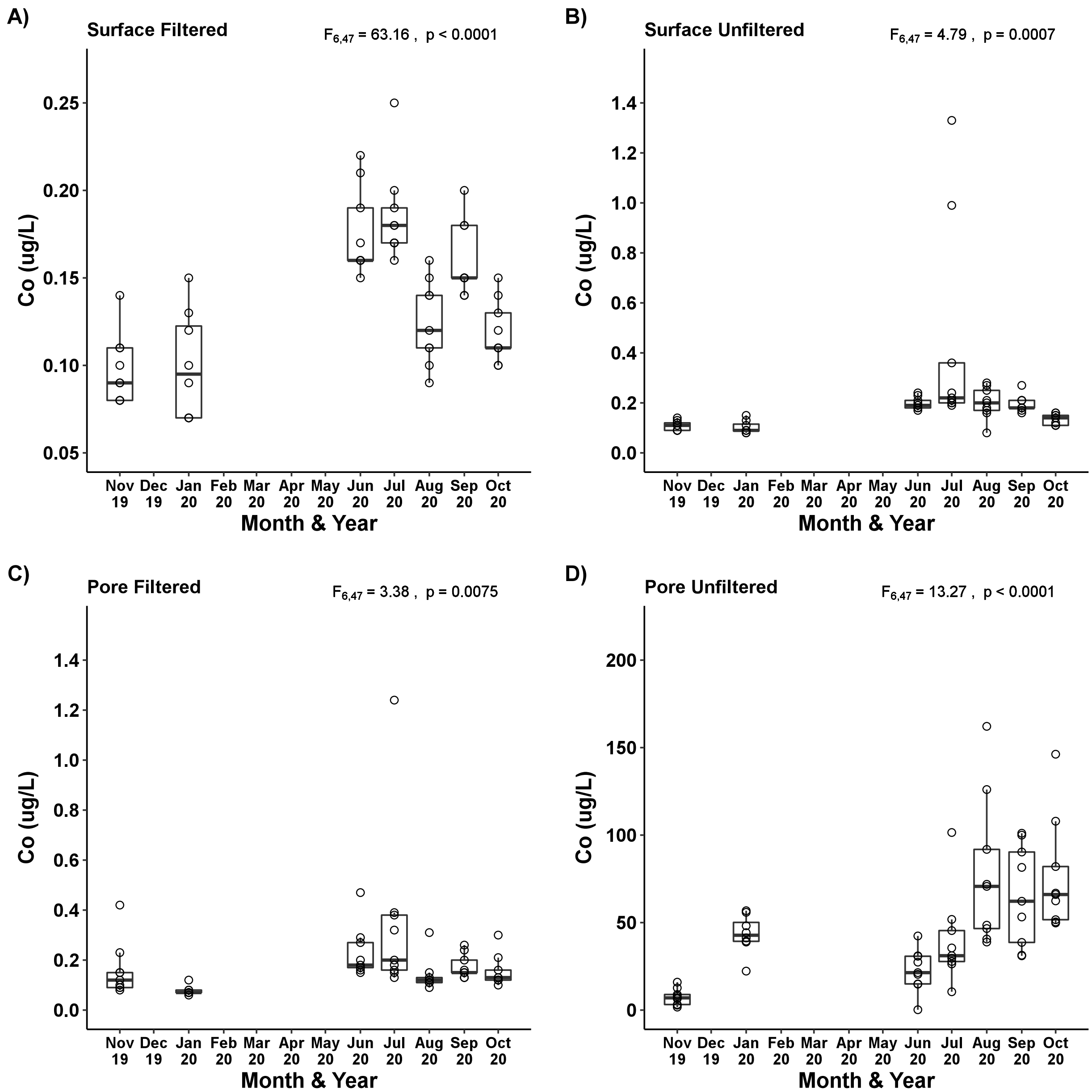

A)
Surface Filtered
$F_{6,47}$ = 7.71 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 8.53 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 7.39 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 12.06 , p < 0.0001
Cd (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

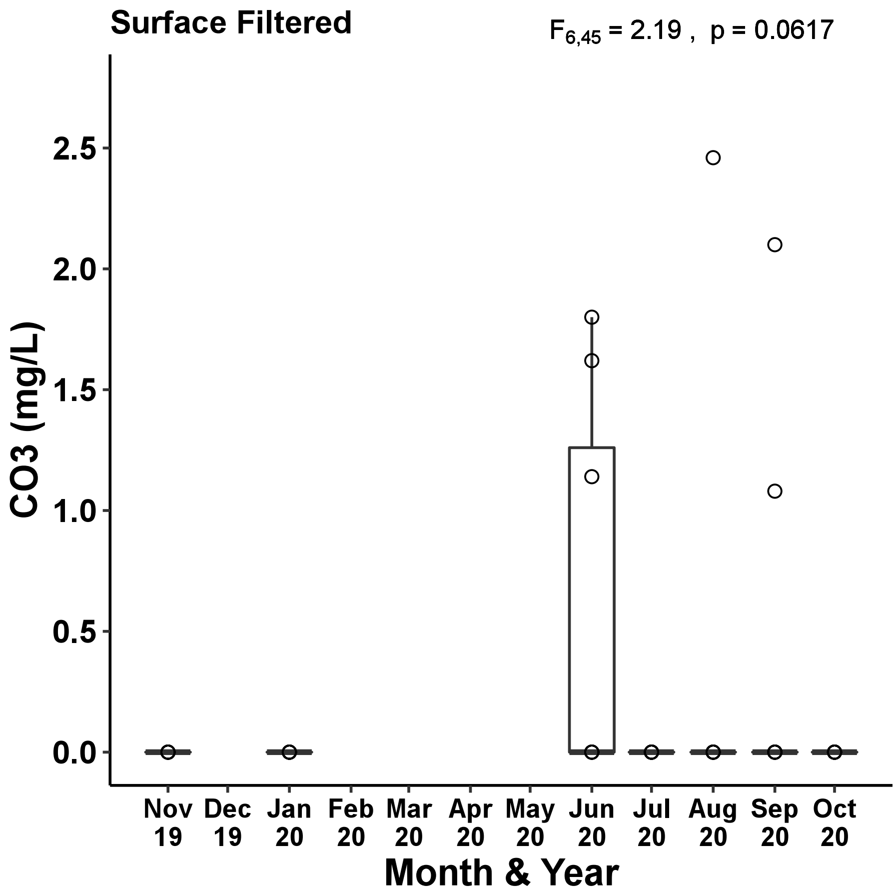
A)


Surface Filtered
$F_{6,46}$ = 57.55 , p < 0.0001
Cl (mg/L)
9
8
7
6
5
4
3
2
1
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

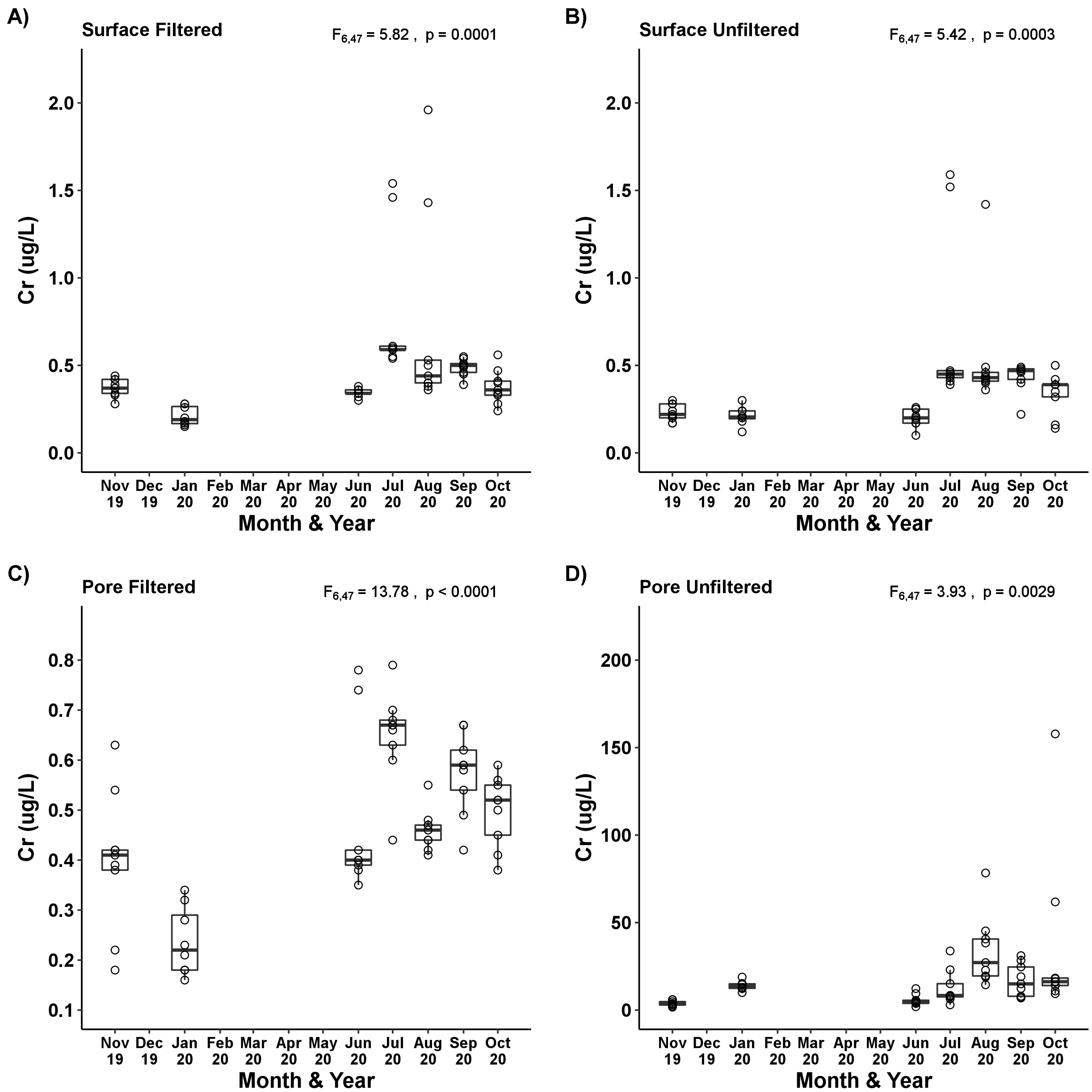
B)


Pore Filtered
$F_{6,47}$ = 3.02 , p = 0.0139
Cl (mg/L)
20
15
10
5
0
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

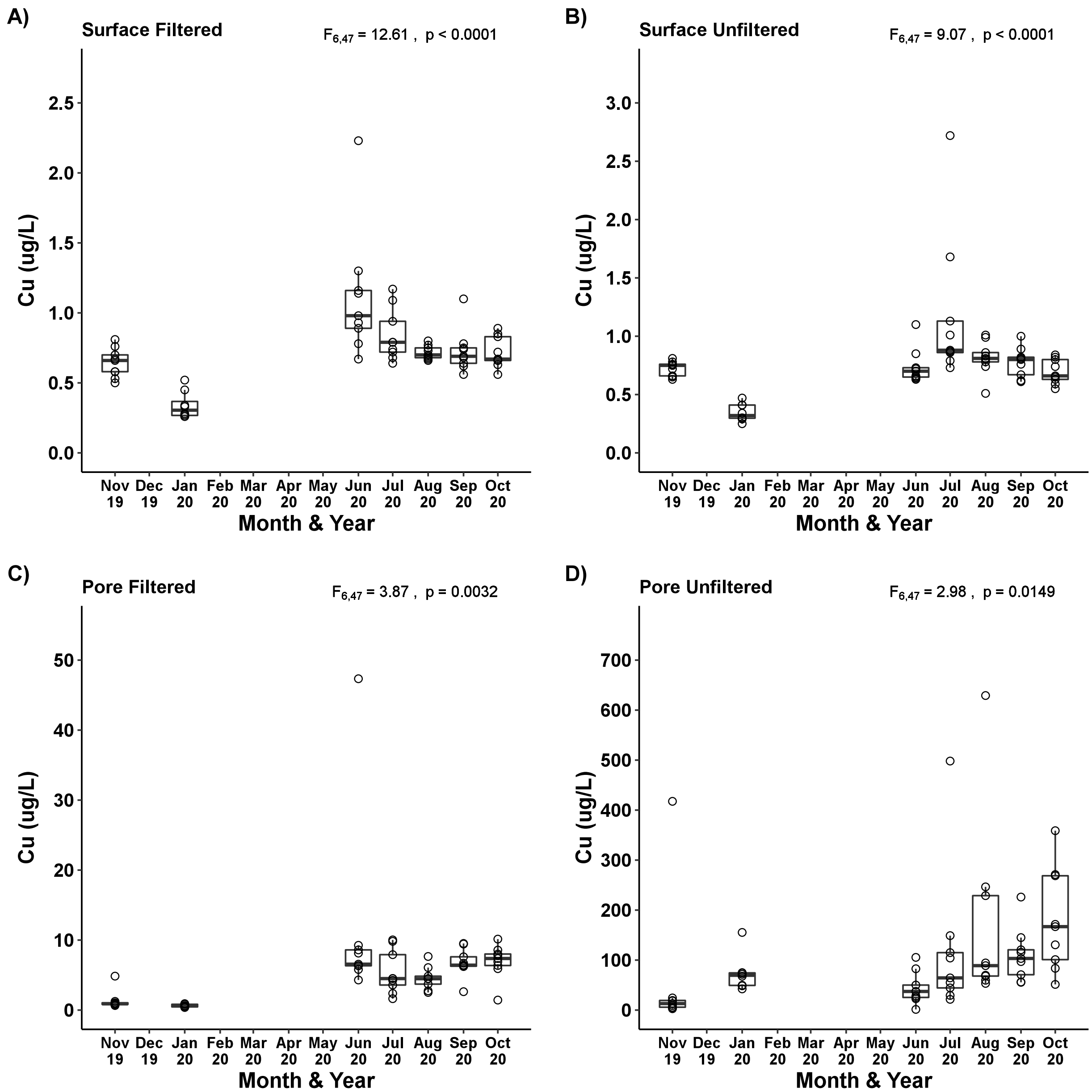

A)
Surface Filtered
F6,47 = 63.16 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 4.79 , p = 0.0007
C)
Pore Filtered
F6,47 = 3.38 , p = 0.0075
D)
Pore Unfiltered
F6,47 = 13.27 , p < 0.0001
Co (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20



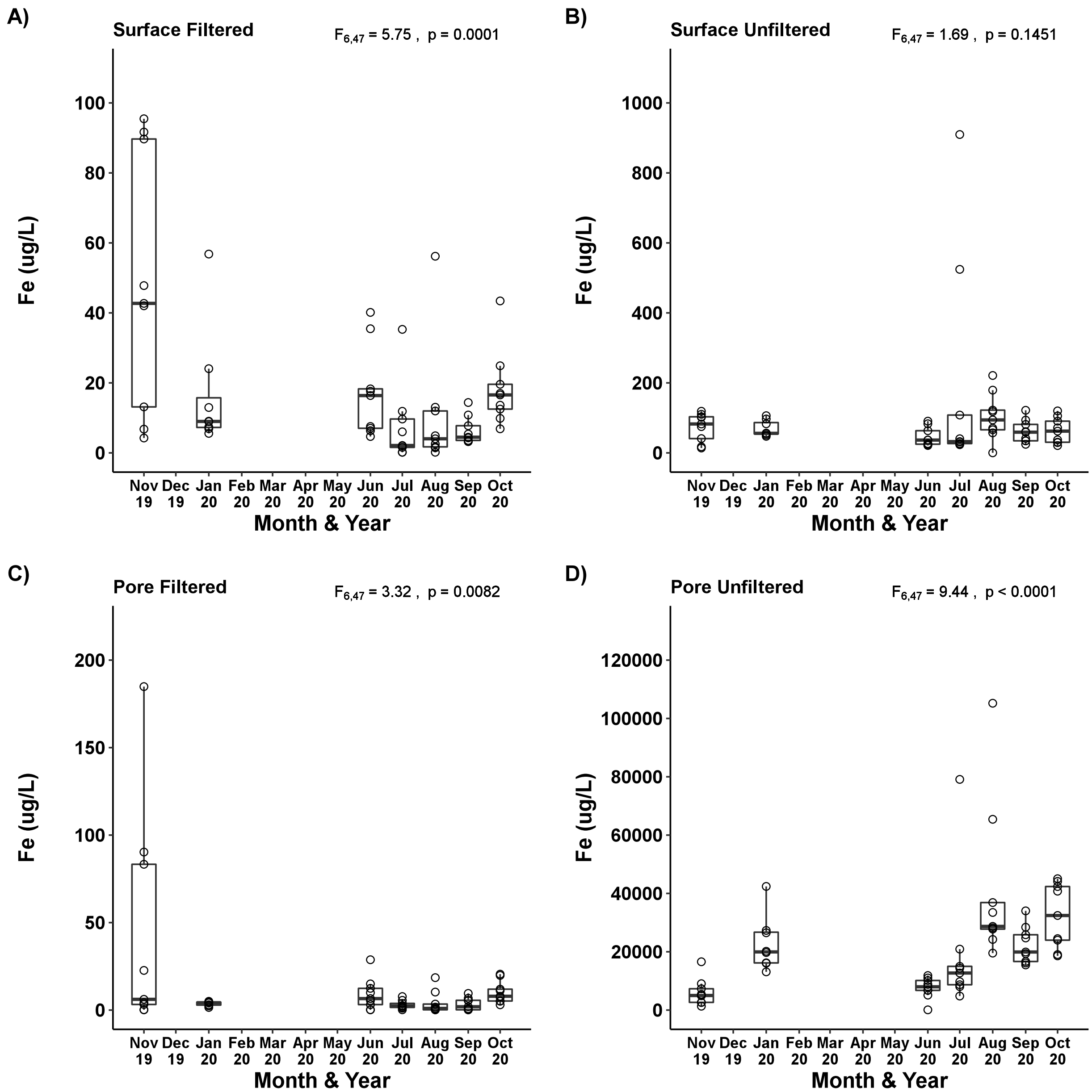
Surface Filtered
F6,45 = 2.19 , p = 0.0617
CO3 (mg/L)
2.5
2.0
1.5
1.0
0.5
0.0
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

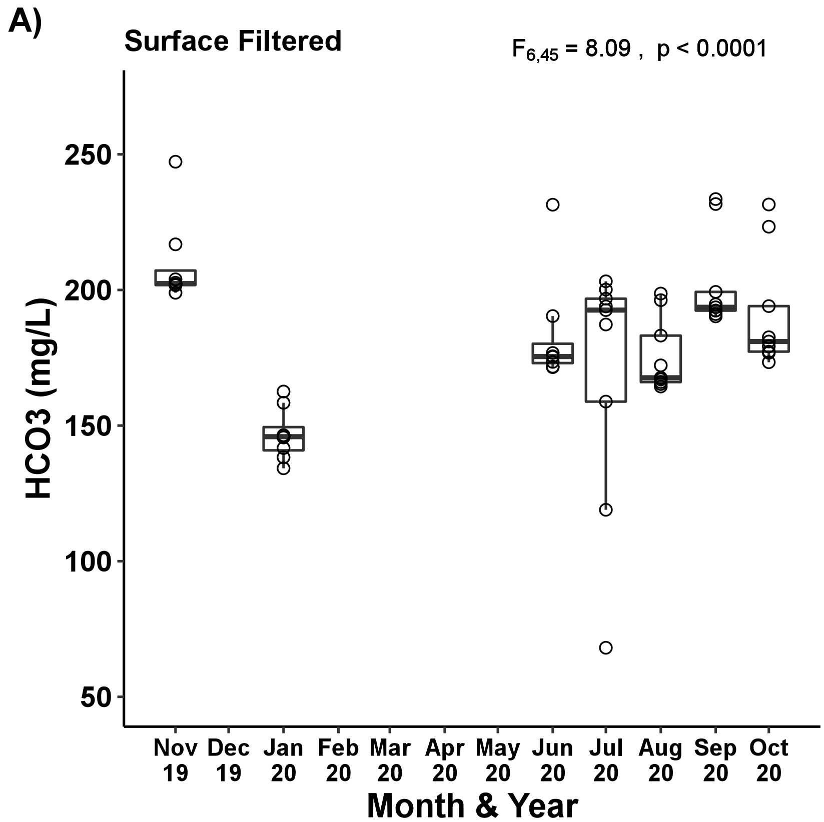


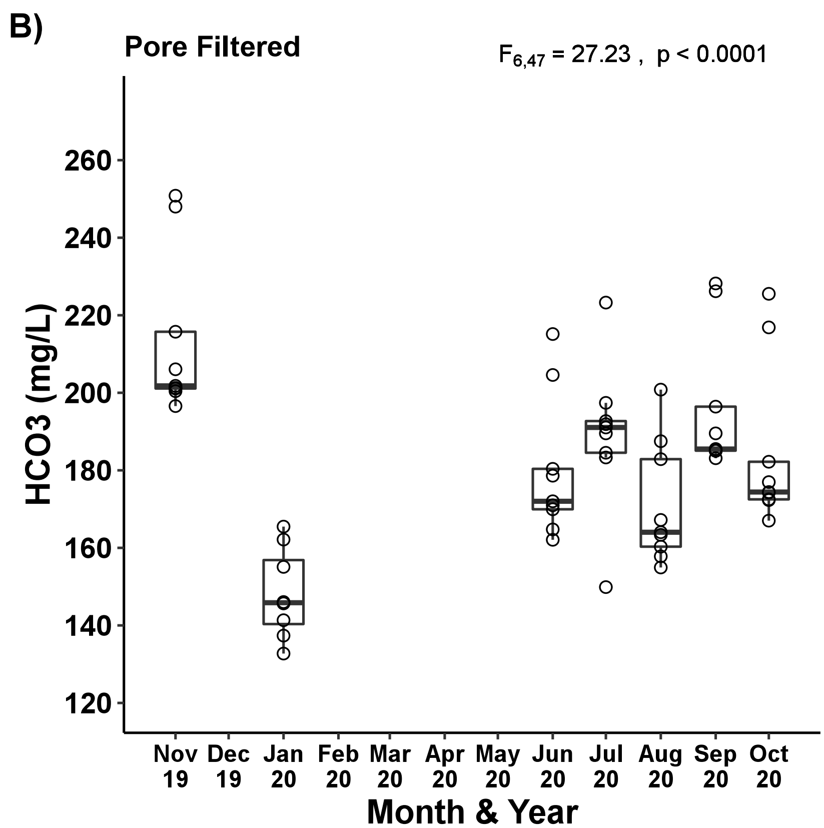
A)
Surface Filtered
$F_{6,47}$ = 5.82 , p = 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 5.42 , p = 0.0003
C)
Pore Filtered
$F_{6,47}$ = 13.78 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 3.93 , p = 0.0029
Cr (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

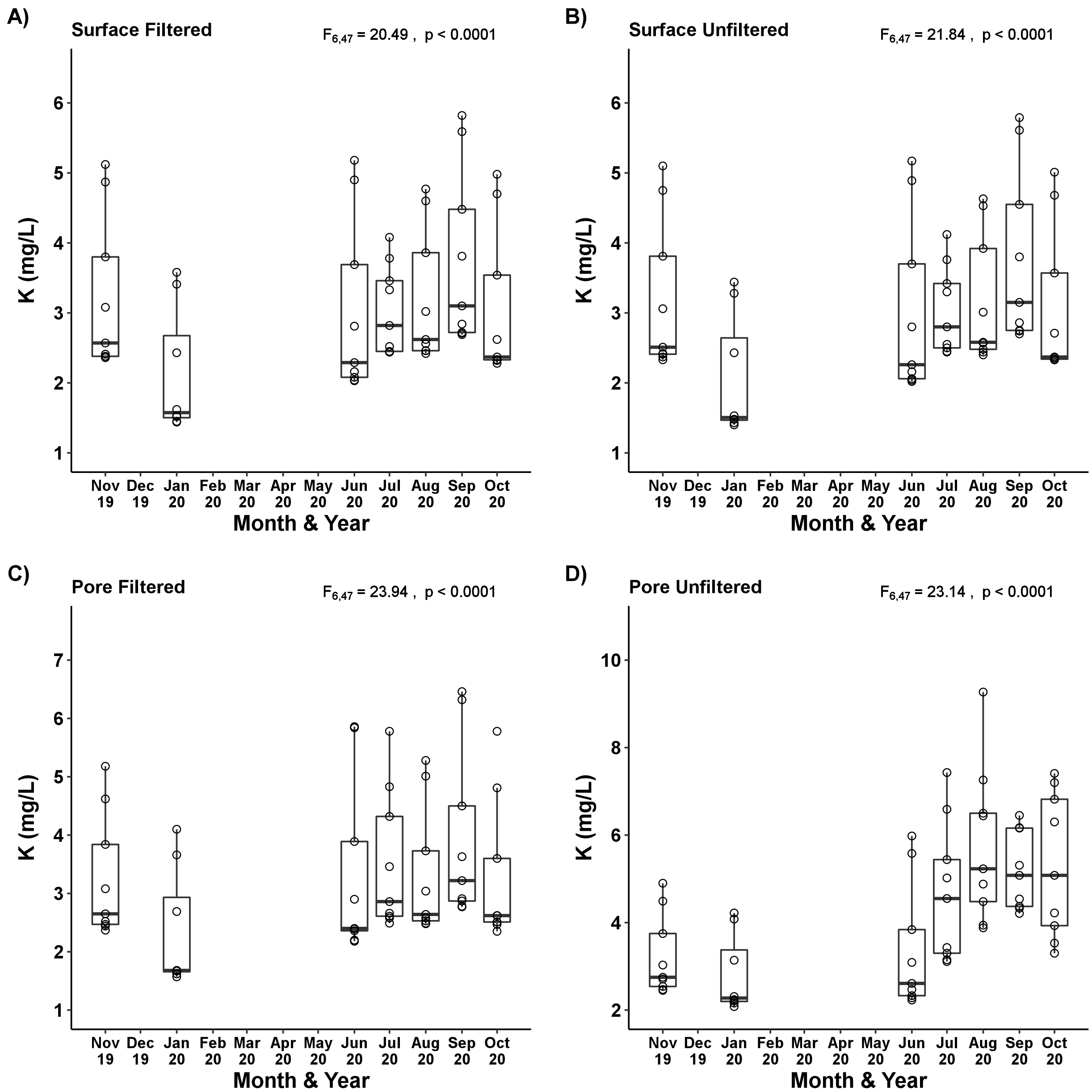


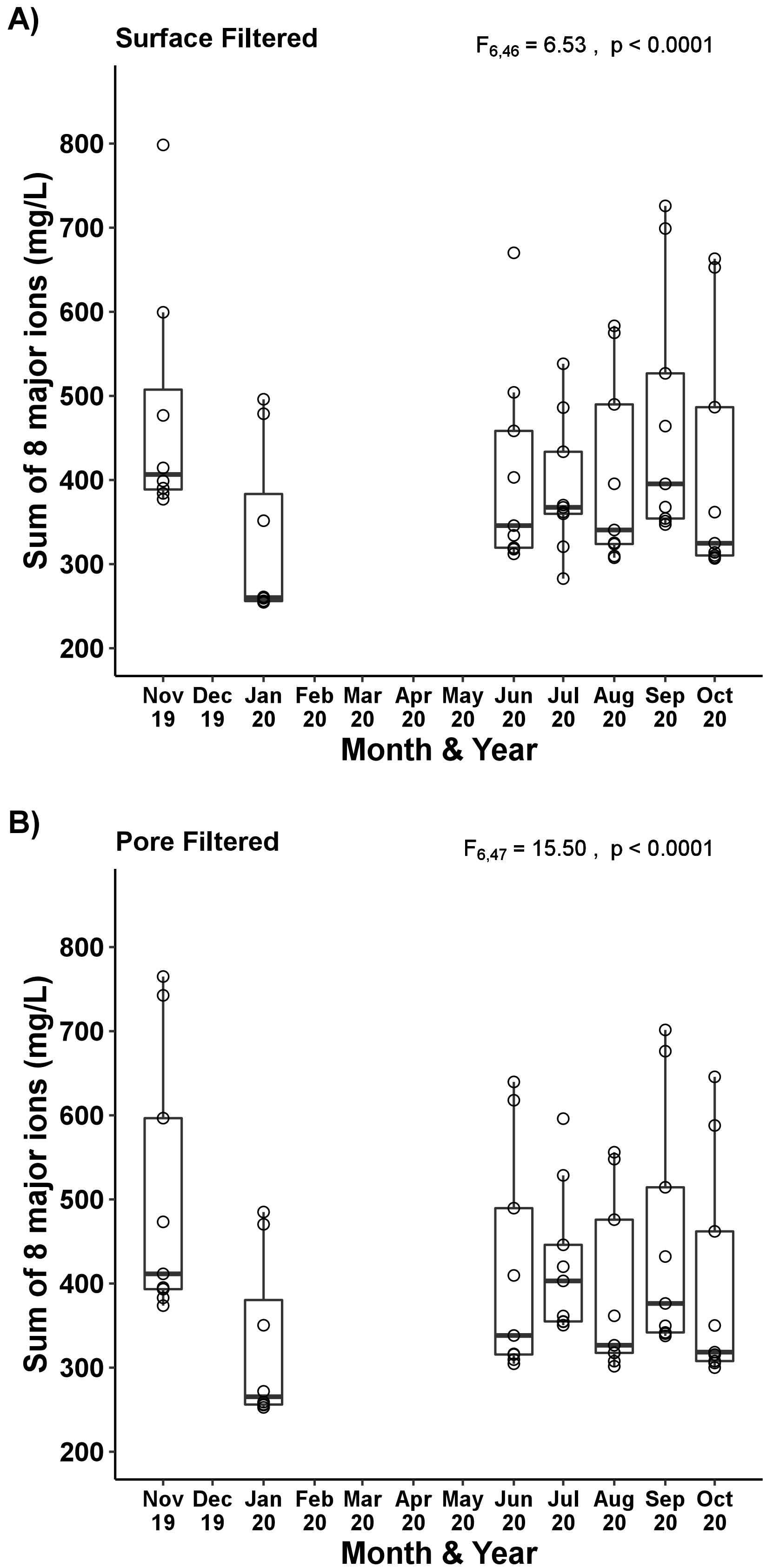
A)
Surface Filtered
F6,47 = 12.61 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 9.07 , p < 0.0001
C)
Pore Filtered
F6,47 = 3.87 , p = 0.0032
D)
Pore Unfiltered
F6,47 = 2.98 , p = 0.0149
Cu (ug/L)
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year

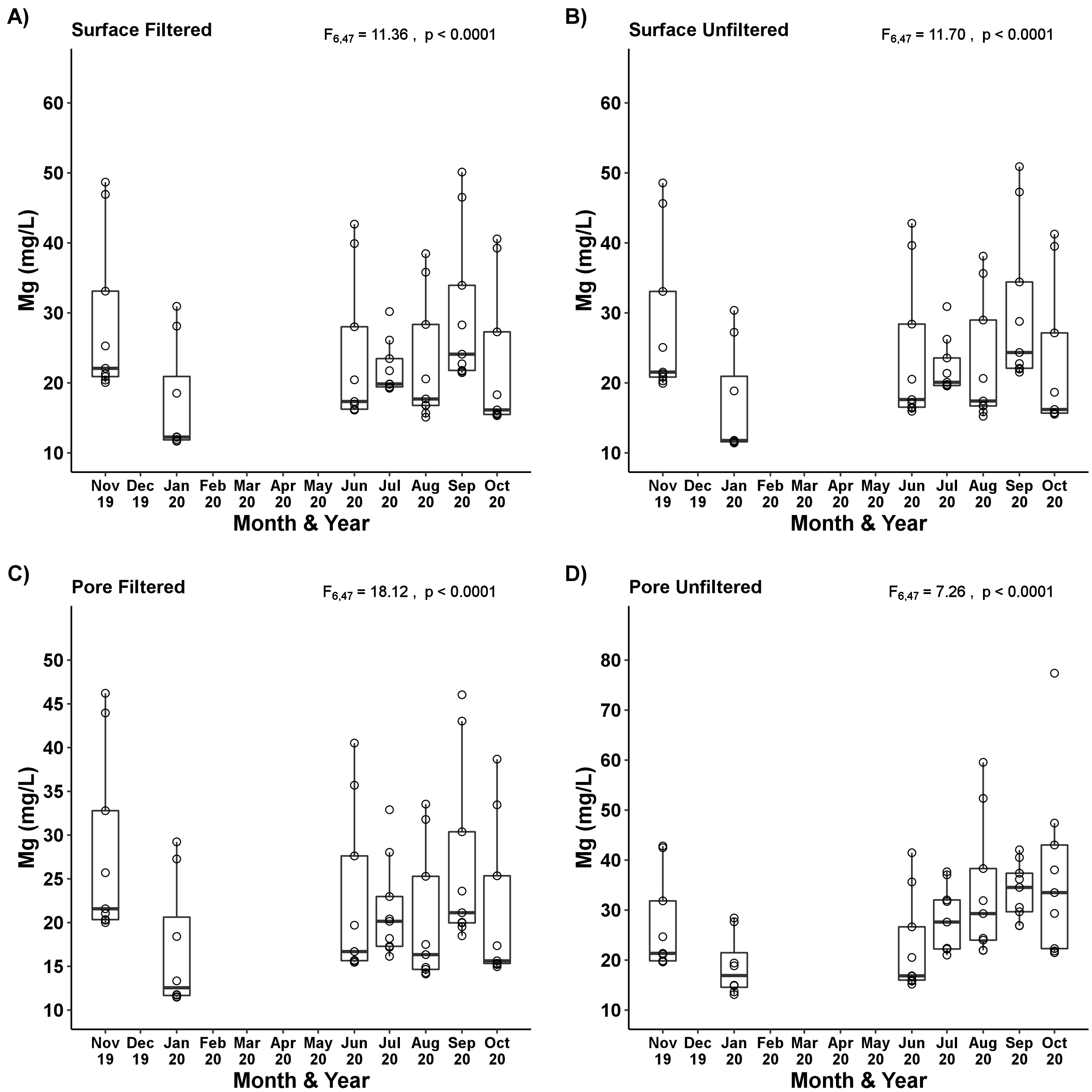

A)
Surface Filtered
F6,47 = 5.75 , p = 0.0001
B)
Surface Unfiltered
F6,47 = 1.69 , p = 0.1451
C)
Pore Filtered
F6,47 = 3.32 , p = 0.0082
D)
Pore Unfiltered
F6,47 = 9.44 , p < 0.0001
Fe (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
0
20
40
60
80
100
200
400
600
800
1000
50
150
20000
40000
60000
80000
100000
120000

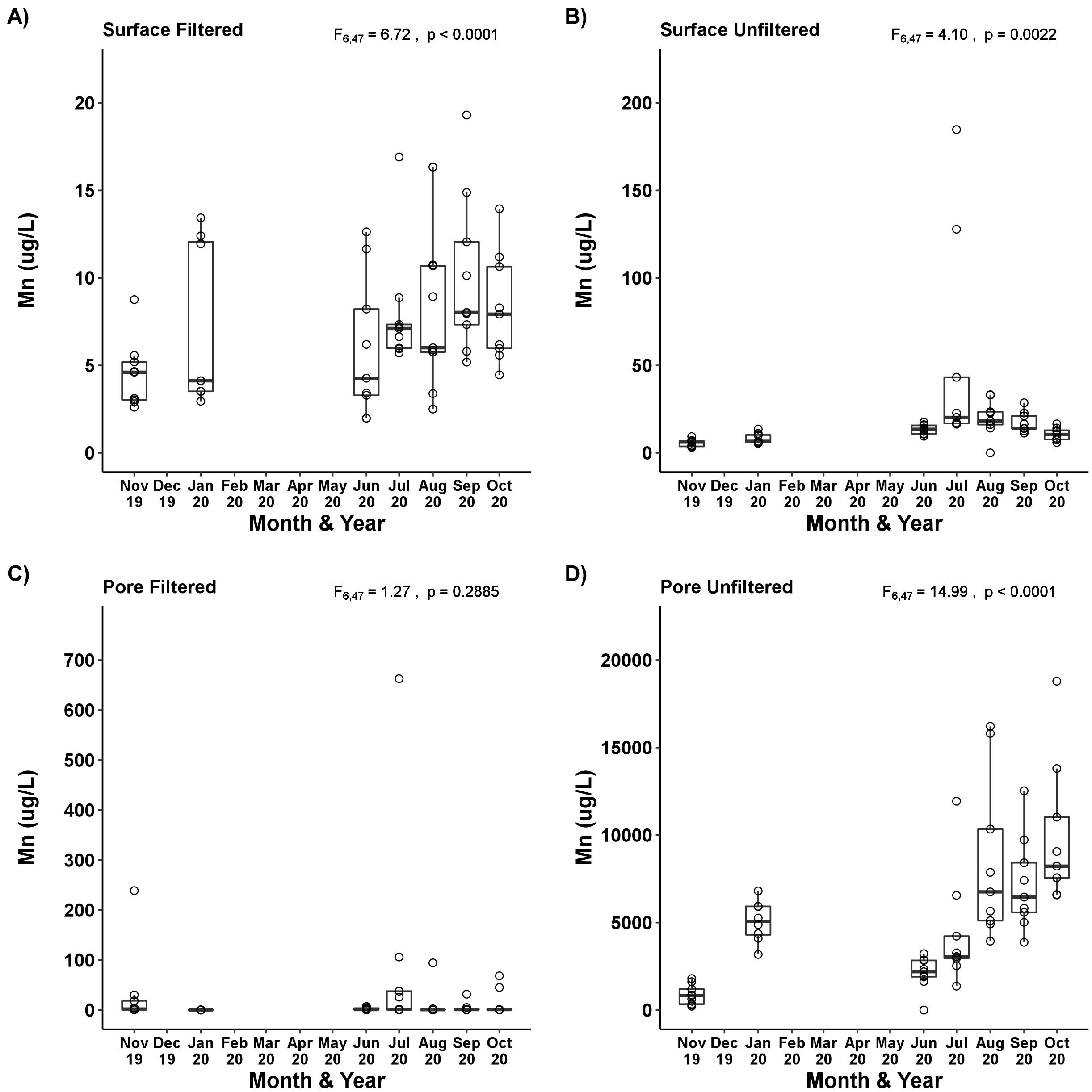

A)
Surface Filtered
$F_{6,45}$ = 8.09 , p < 0.0001
HCO3 (mg/L)
250
200
150
100
50
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year


B)
Pore Filtered
$F_{6,47}$ = 27.23 , p < 0.0001
HCO3 (mg/L)
260
240
220
200
180
160
140
120
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

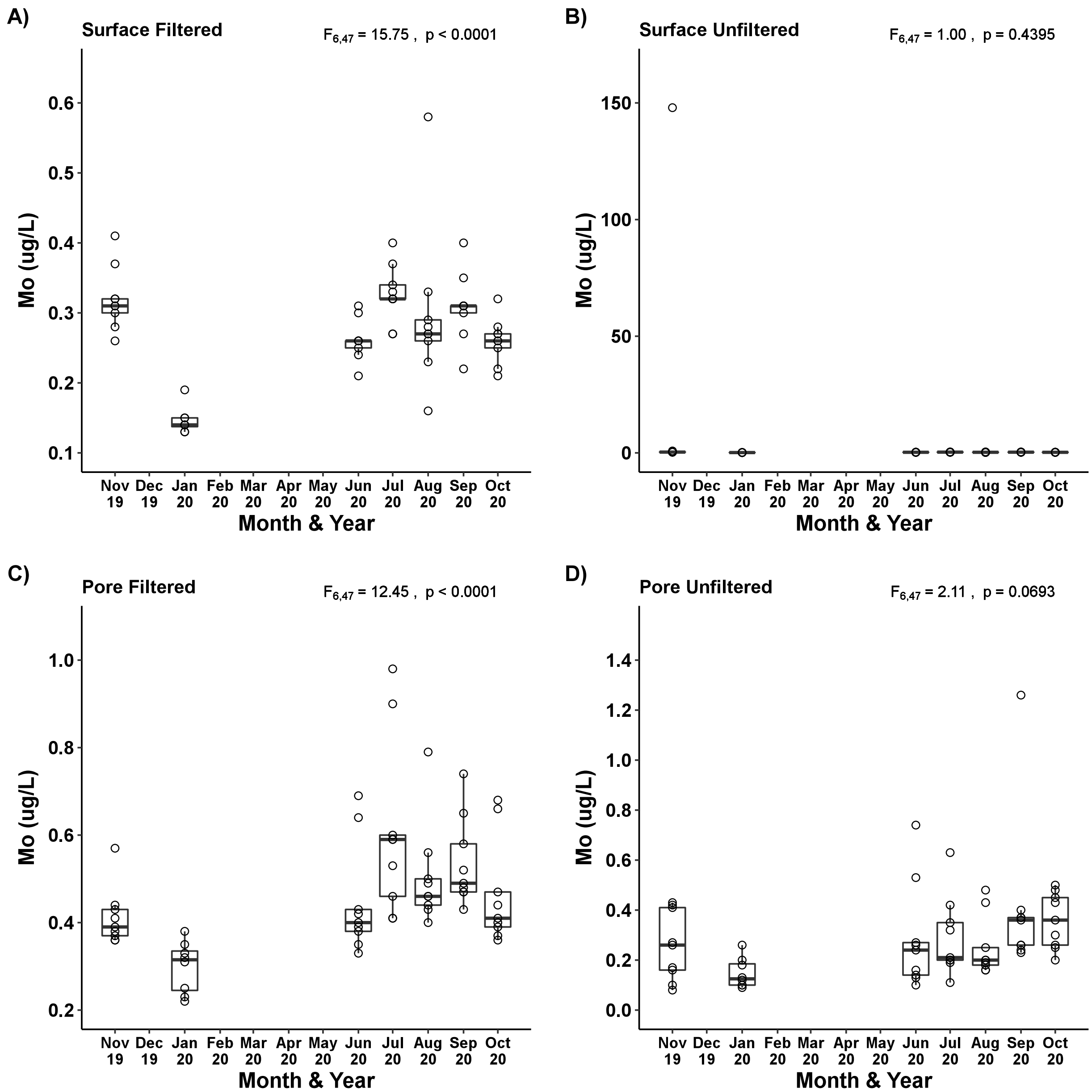

A)
Surface Filtered
F6,47 = 20.49 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 21.84 , p < 0.0001
C)
Pore Filtered
F6,47 = 23.94 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 23.14 , p < 0.0001
K (mg/L)
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year

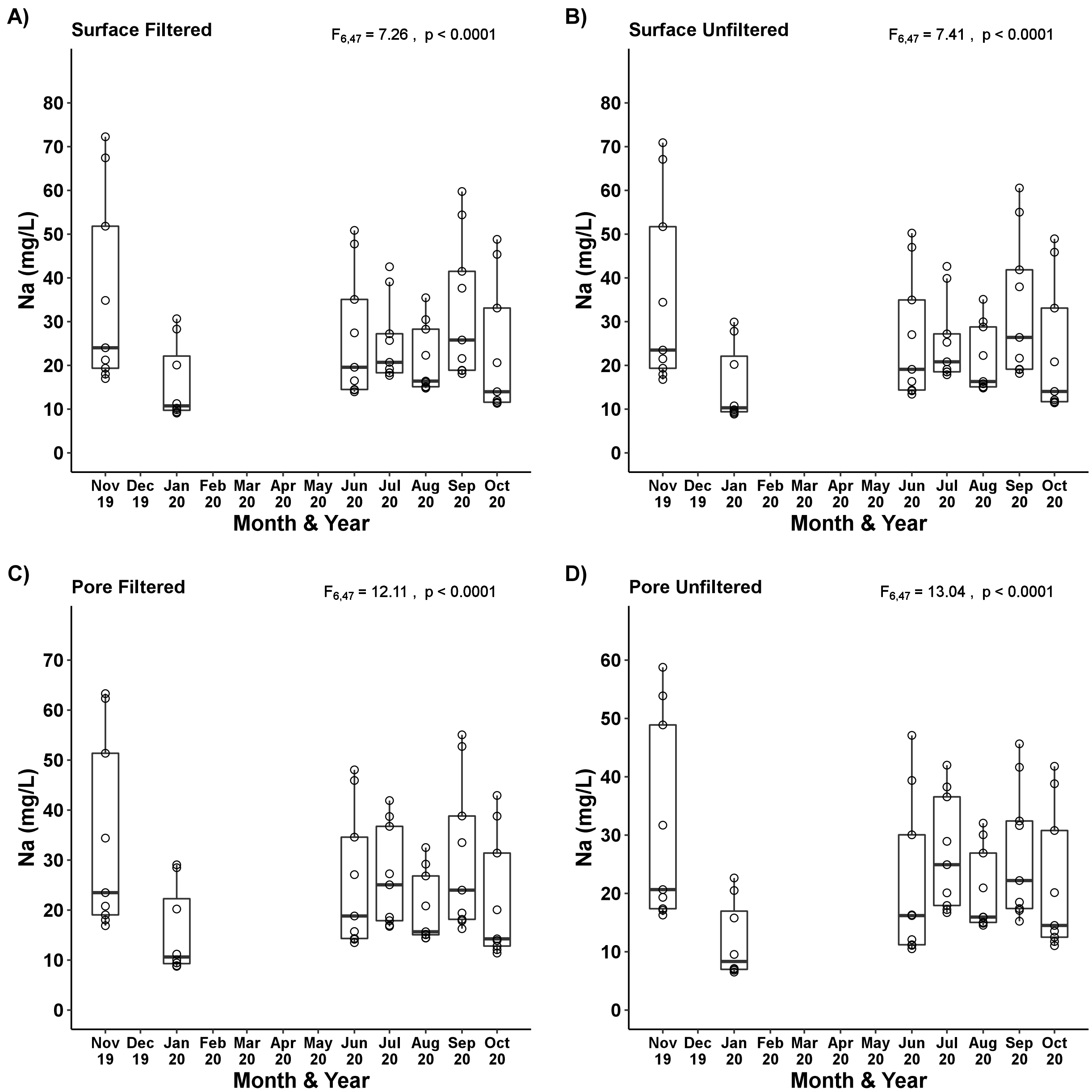

A)
Surface Filtered
F6,46 = 6.53 , p < 0.0001
Sum of 8 major ions (mg/L)
200
300
400
500
600
700
800
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year
B)
Pore Filtered
F6,47 = 15.50 , p < 0.0001
Sum of 8 major ions (mg/L)
200
300
400
500
600
700
800
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

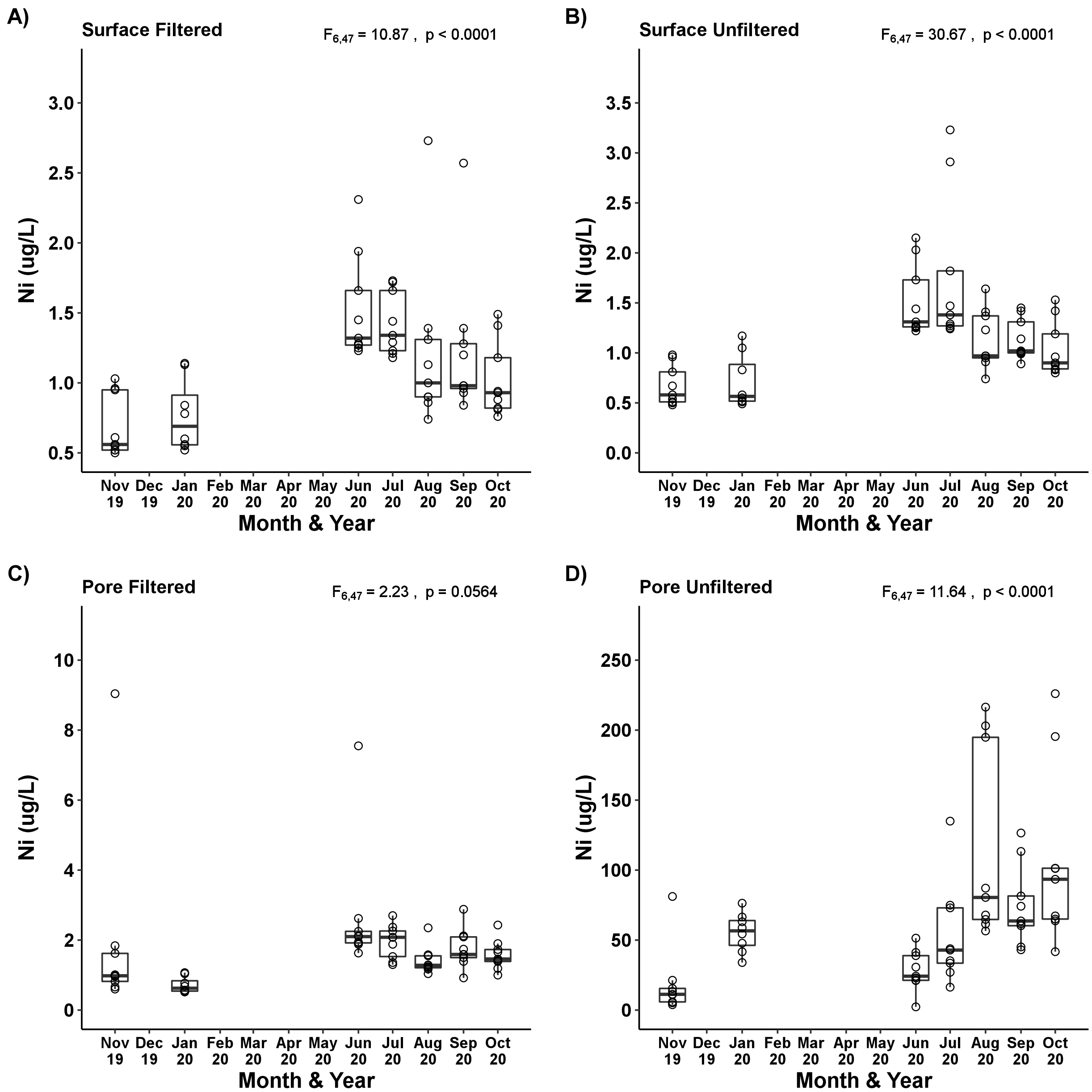

A)
Surface Filtered
$F_{6,47}$ = 11.36 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 11.70 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 18.12 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 7.26 , p < 0.0001
Mg (mg/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

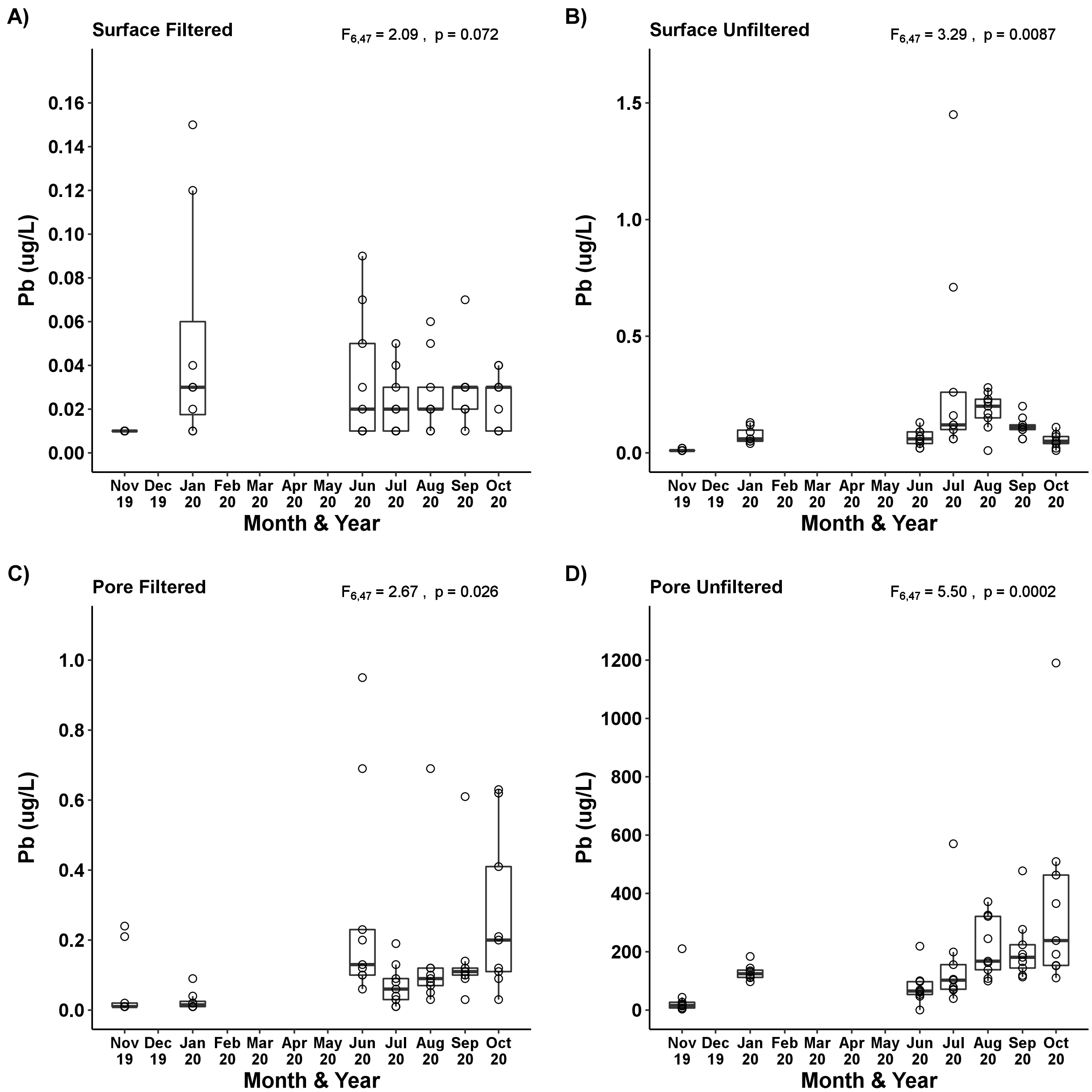


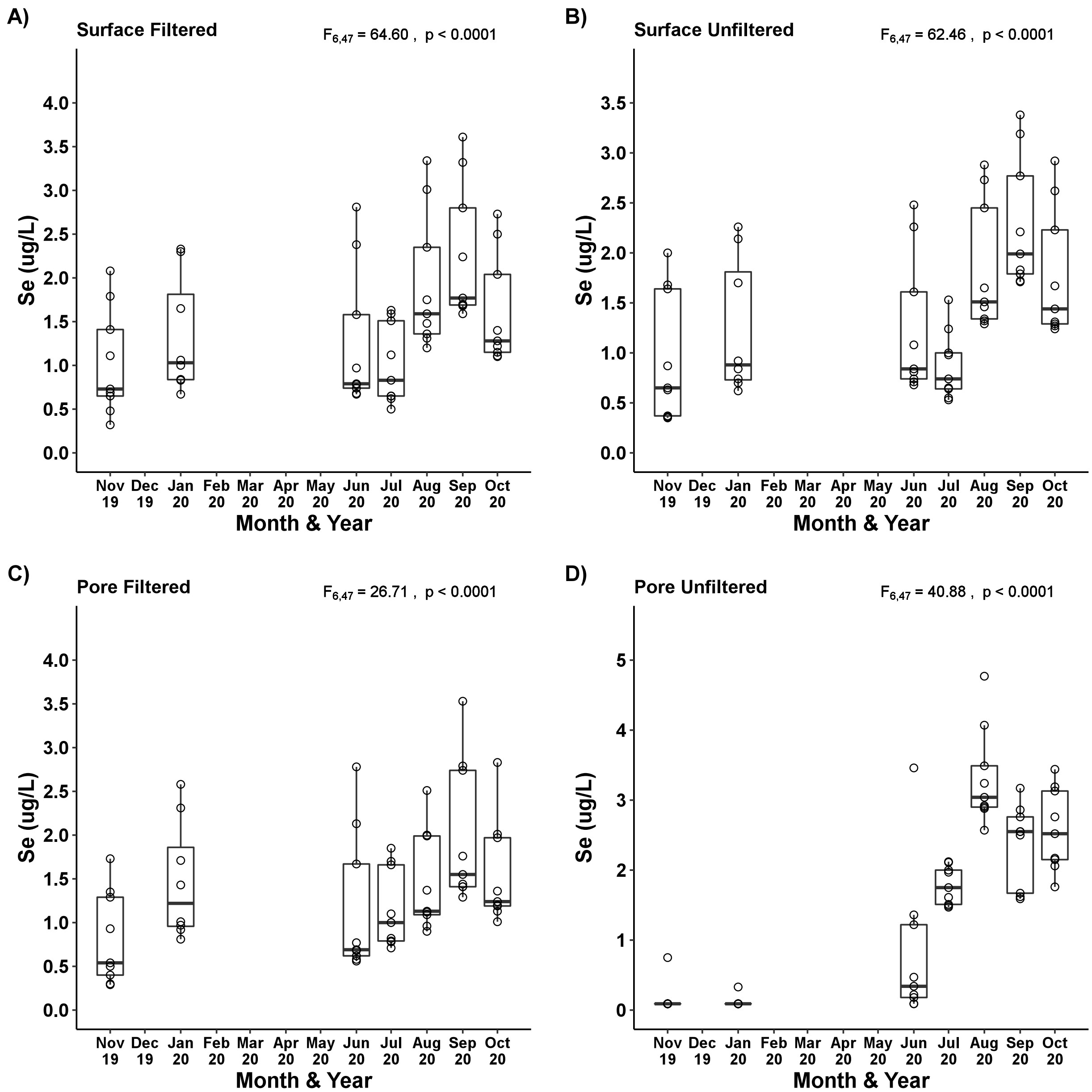
A)
Surface Filtered
F6,47 = 6.72 , p < 0.0001
Mn (ug/L)
Month & Year
B)
Surface Unfiltered
F6,47 = 4.10 , p = 0.0022
C)
Pore Filtered
F6,47 = 1.27 , p = 0.2885
D)
Pore Unfiltered
F6,47 = 14.99 , p < 0.0001
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

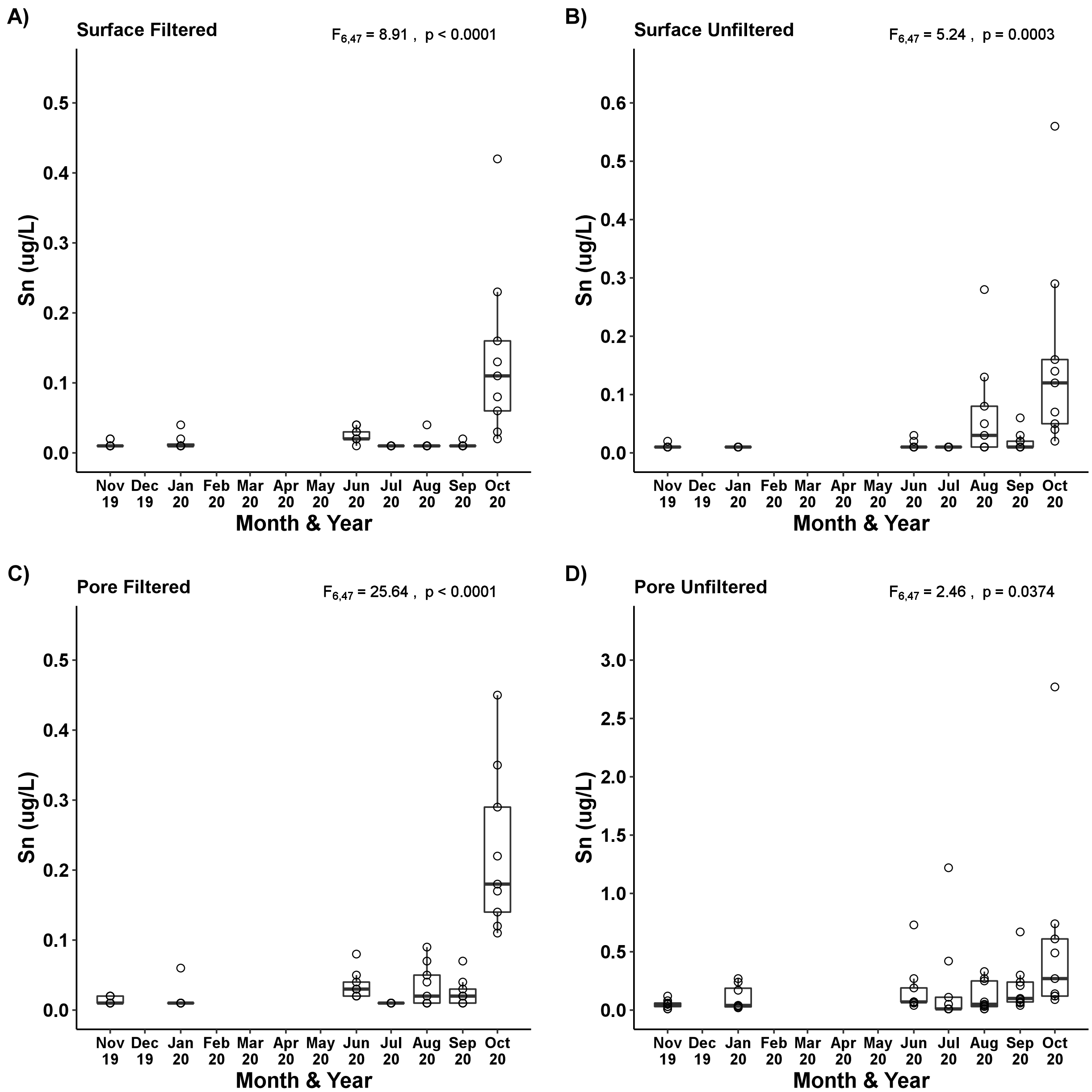

A)
Surface Filtered
$F_{6,47}$ = 15.75 , p < 0.0001
Mo (ug/L)
0.1 0.2 0.3 0.4 0.5 0.6
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year
B)
Surface Unfiltered
$F_{6,47}$ = 1.00 , p = 0.4395
Mo (ug/L)
0 50 100 150
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year
C)
Pore Filtered
$F_{6,47}$ = 12.45 , p < 0.0001
Mo (ug/L)
0.2 0.4 0.6 0.8 1.0
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year
D)
Pore Unfiltered
$F_{6,47}$ = 2.11 , p = 0.0693
Mo (ug/L)
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year


A)
Surface Filtered
$F_{6,47}$ = 7.26 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 7.41 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 12.11 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 13.04 , p < 0.0001
Na (mg/L)
Nov 19, Dec 19, Jan 20, Feb 20, Mar 20, Apr 20, May 20, Jun 20, Jul 20, Aug 20, Sep 20, Oct 20
Month & Year

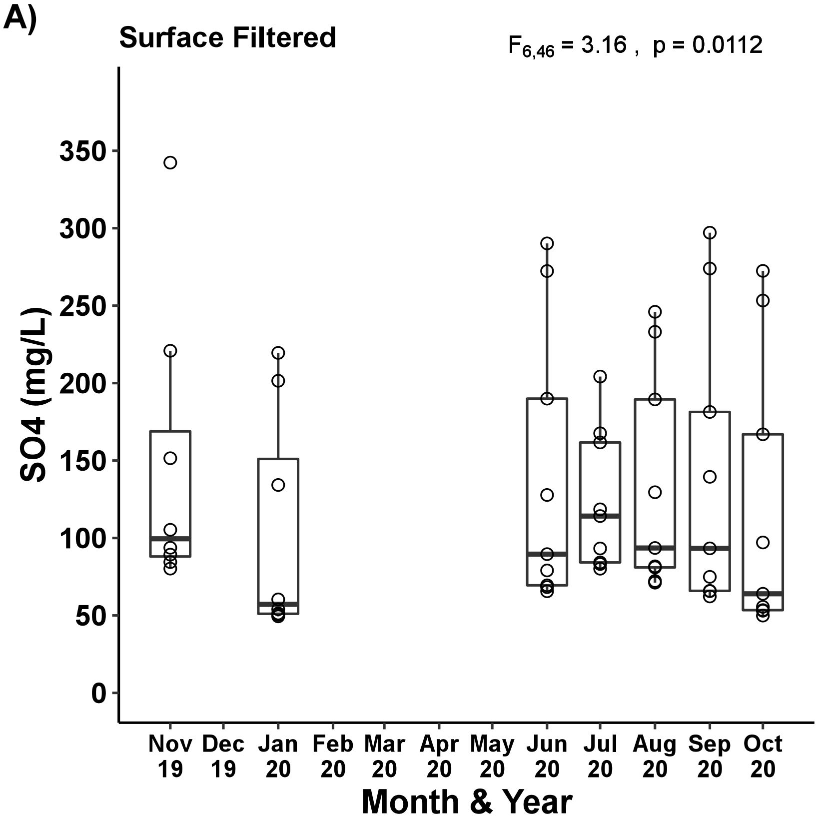

A)
Surface Filtered
F6,47 = 10.87 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 30.67 , p < 0.0001
C)
Pore Filtered
F6,47 = 2.23 , p = 0.0564
D)
Pore Unfiltered
F6,47 = 11.64 , p < 0.0001
Ni (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20


A)
Surface Filtered
F6,47 = 2.09 , p = 0.072
Pb (ug/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
B)
Surface Unfiltered
F6,47 = 3.29 , p = 0.0087
Pb (ug/L)
0.0
0.5
1.0
1.5
C)
Pore Filtered
F6,47 = 2.67 , p = 0.026
Pb (ug/L)
0.0
0.2
0.4
0.6
0.8
1.0
D)
Pore Unfiltered
F6,47 = 5.50 , p = 0.0002
Pb (ug/L)
0
200
400
600
800
1000
1200
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

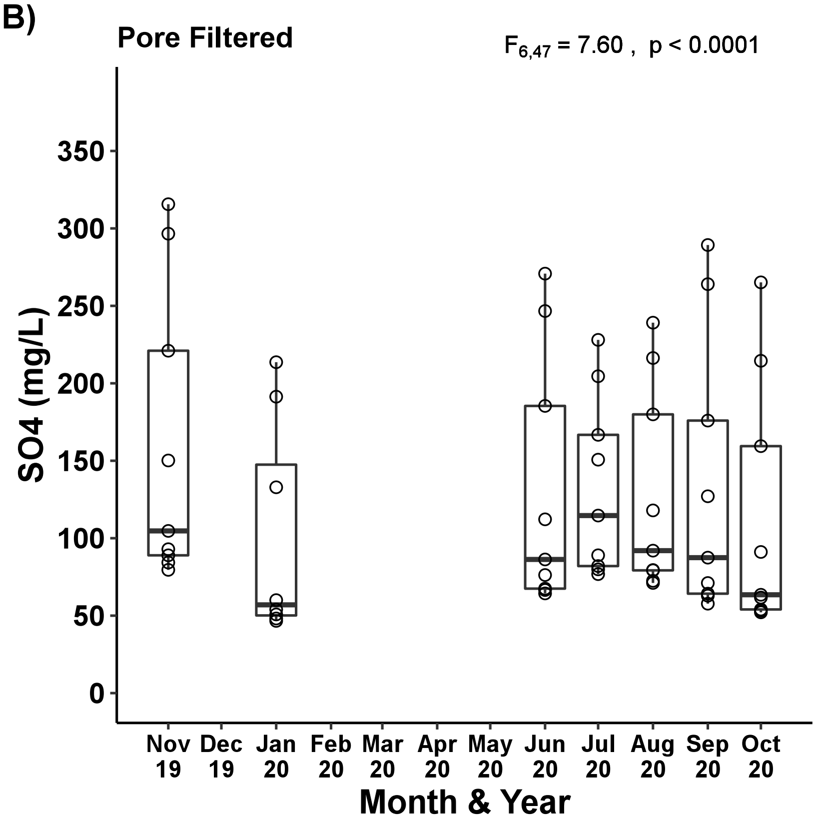

A)
Surface Filtered
F6,47 = 64.60 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 62.46 , p < 0.0001
C)
Pore Filtered
F6,47 = 26.71 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 40.88 , p < 0.0001
Se (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

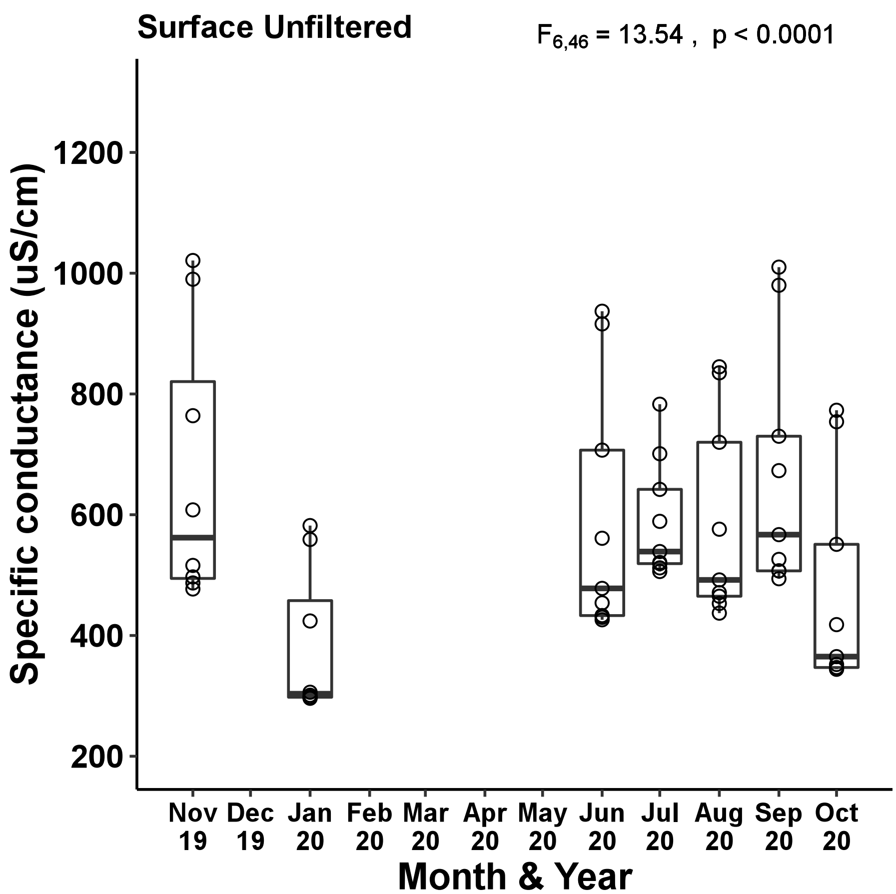

A)
Surface Filtered
$F_{6,47}$ = 8.91 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 5.24 , p = 0.0003
C)
Pore Filtered
$F_{6,47}$ = 25.64 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 2.46 , p = 0.0374
Sn (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

A)

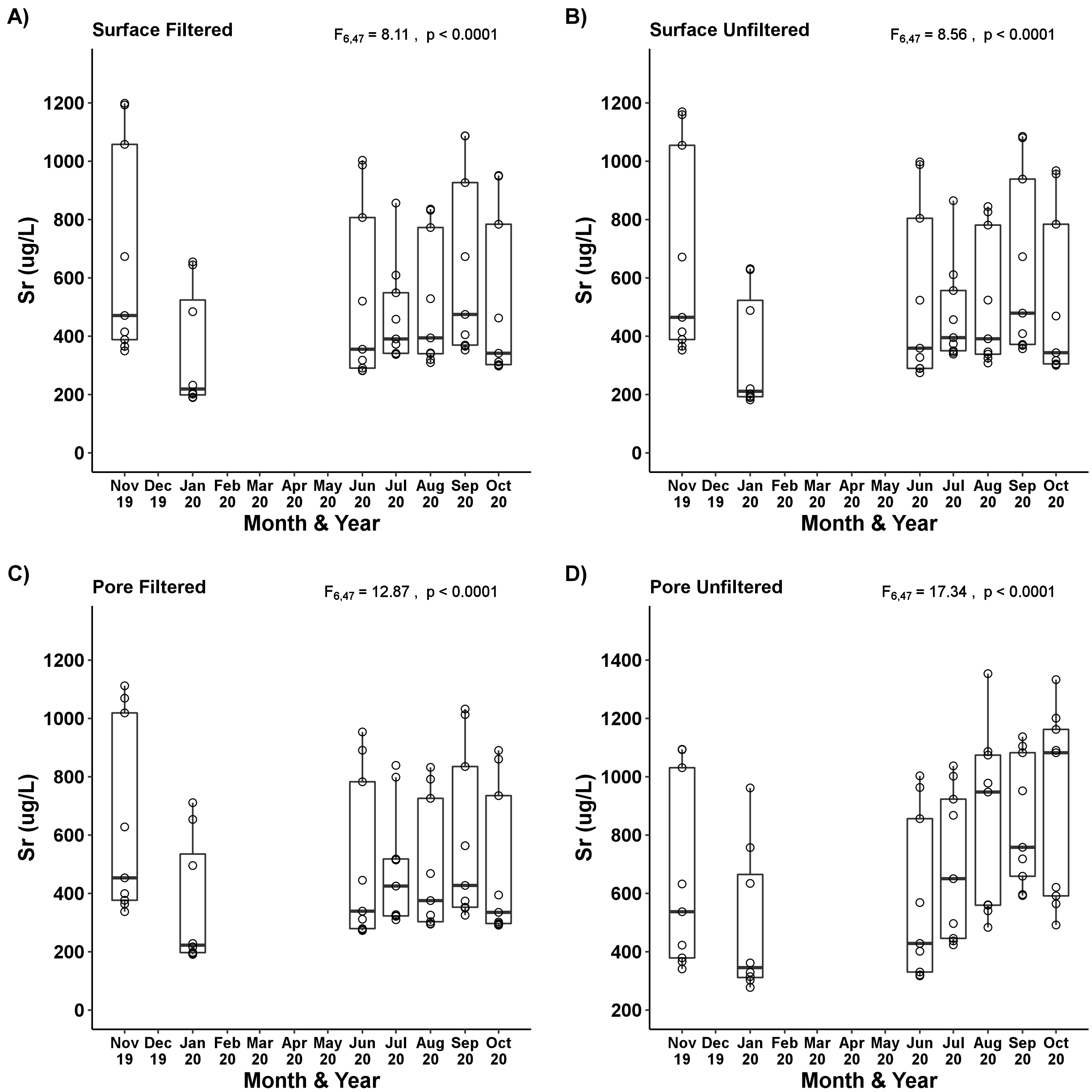

Surface Filtered
F6,46 = 3.16 , p = 0.0112
SO4 (mg/L)
0
50
100
150
200
250
300
350
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

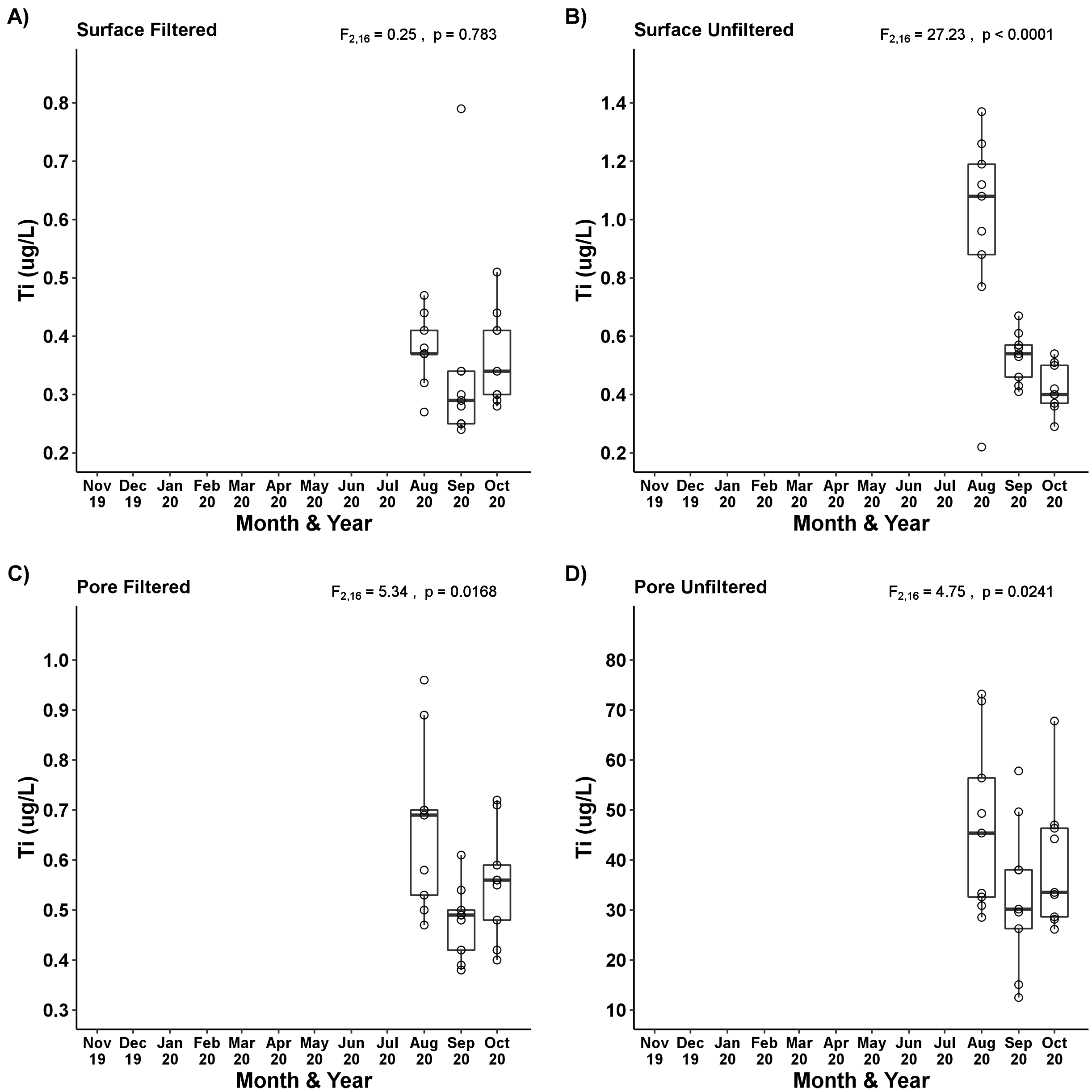
B)


Pore Filtered
F6,47 = 7.60 , p < 0.0001
SO4 (mg/L)
0
50
100
150
200
250
300
350
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

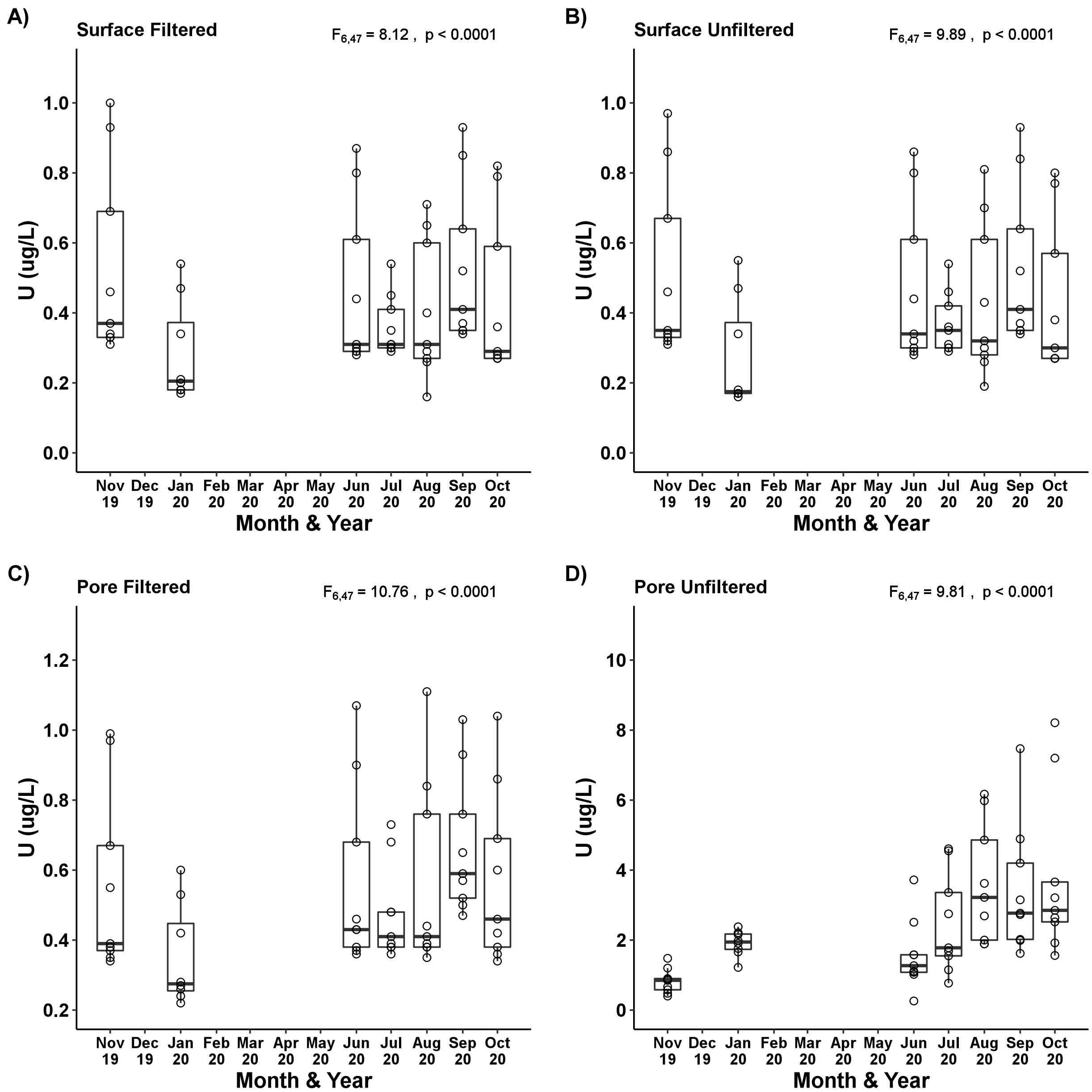


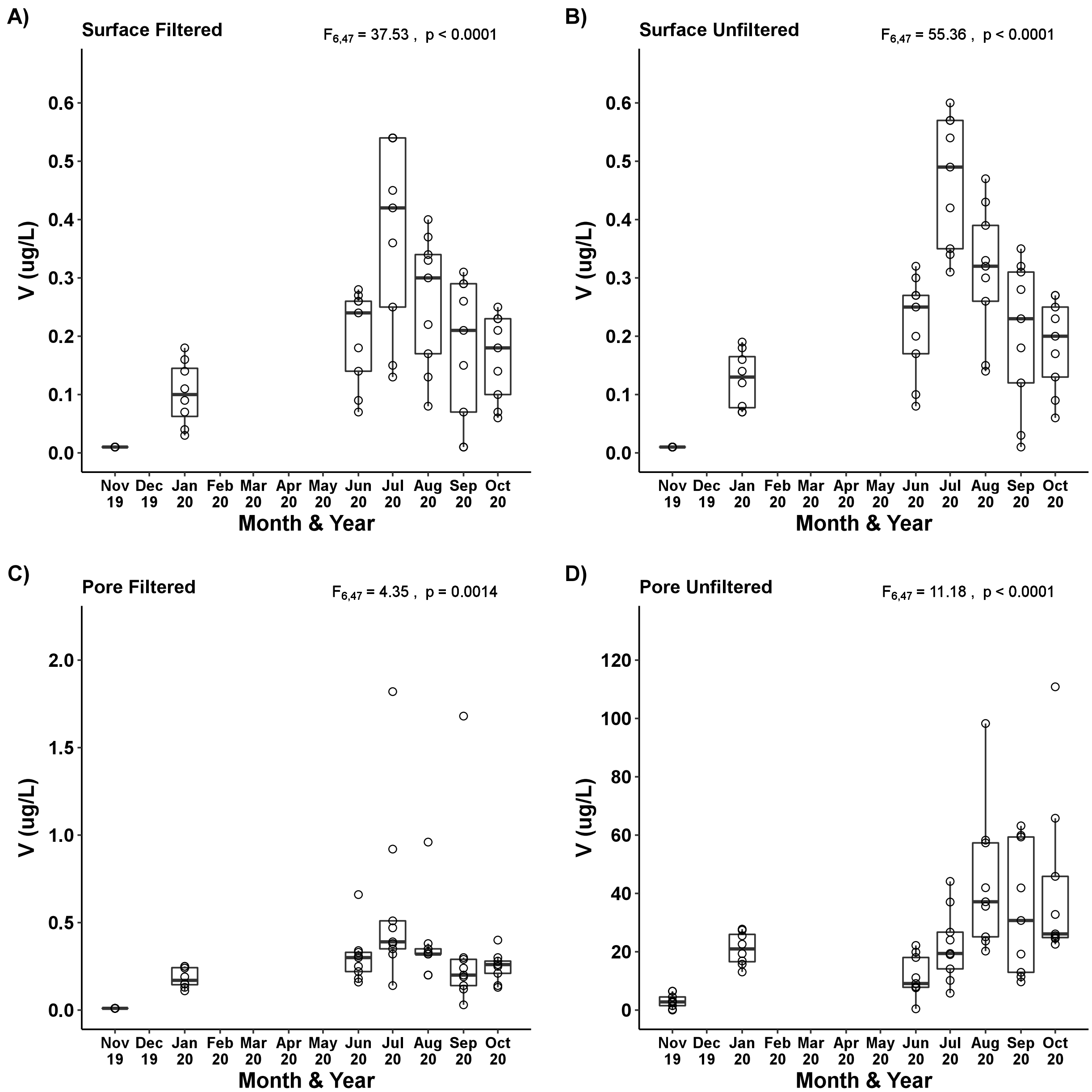
Surface Unfiltered
$F_{6,46}$ = 13.54 , p < 0.0001
Specific conductance (uS/cm)
200
400
600
800
1000
1200
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

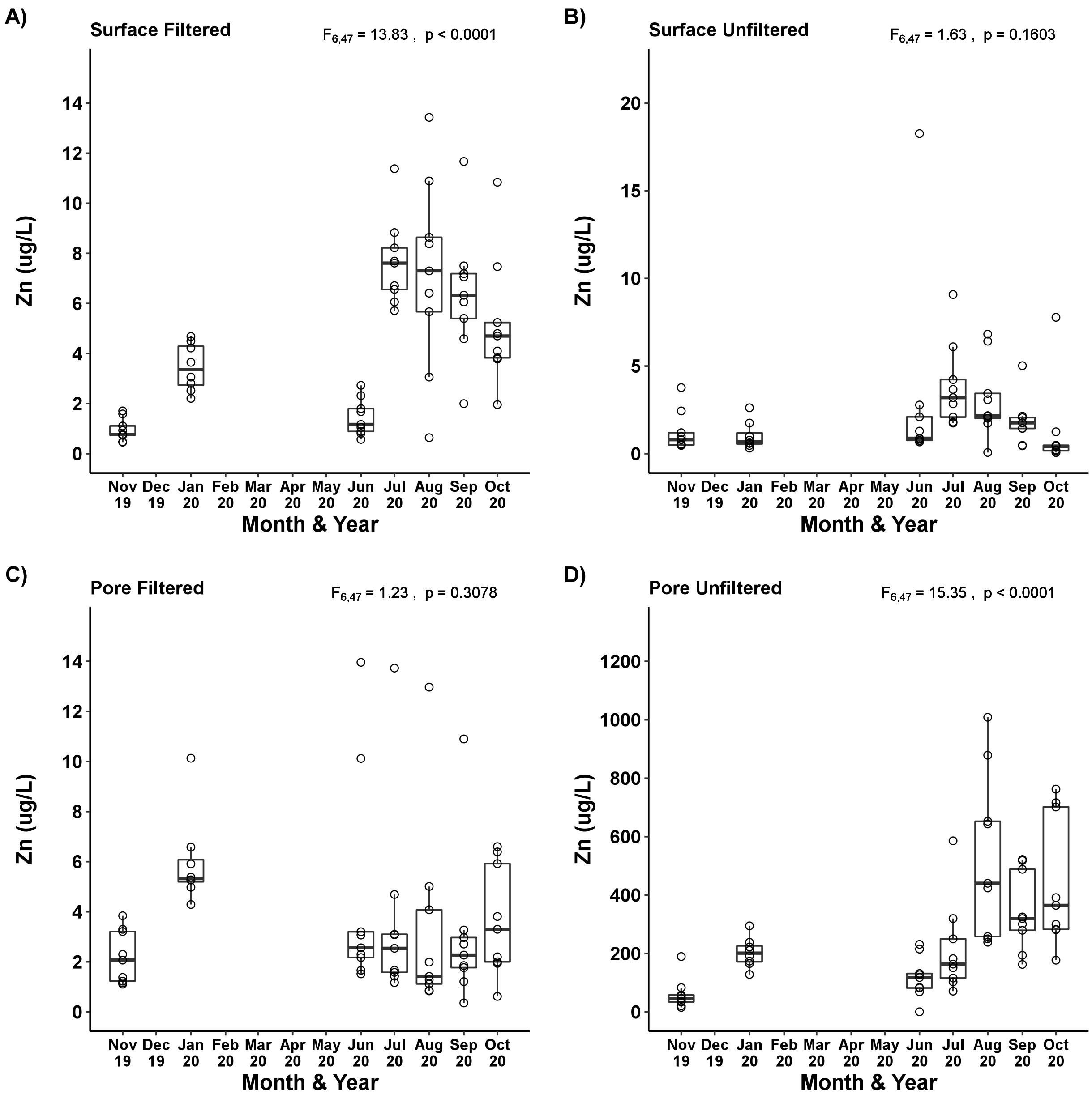

A)
Surface Filtered
F6,47 = 8.11 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 8.56 , p < 0.0001
C)
Pore Filtered
F6,47 = 12.87 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 17.34 , p < 0.0001
Sr (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
0
200
400
600
800
1000
1200
1400



A)
Surface Filtered
$F_{2,16}$ = 0.25 , p = 0.783
B)
Surface Unfiltered
$F_{2,16}$ = 27.23 , p < 0.0001
C)
Pore Filtered
$F_{2,16}$ = 5.34 , p = 0.0168
D)
Pore Unfiltered
$F_{2,16}$ = 4.75 , p = 0.0241
Ti (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20


A)
Surface Filtered
F6,47 = 8.12 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 9.89 , p < 0.0001
C)
Pore Filtered
F6,47 = 10.76 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 9.81 , p < 0.0001
U (ug/L)
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year


A)
Surface Filtered
F6,47 = 37.53 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 55.36 , p < 0.0001
C)
Pore Filtered
F6,47 = 4.35 , p = 0.0014
D)
Pore Unfiltered
F6,47 = 11.18 , p < 0.0001
V (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

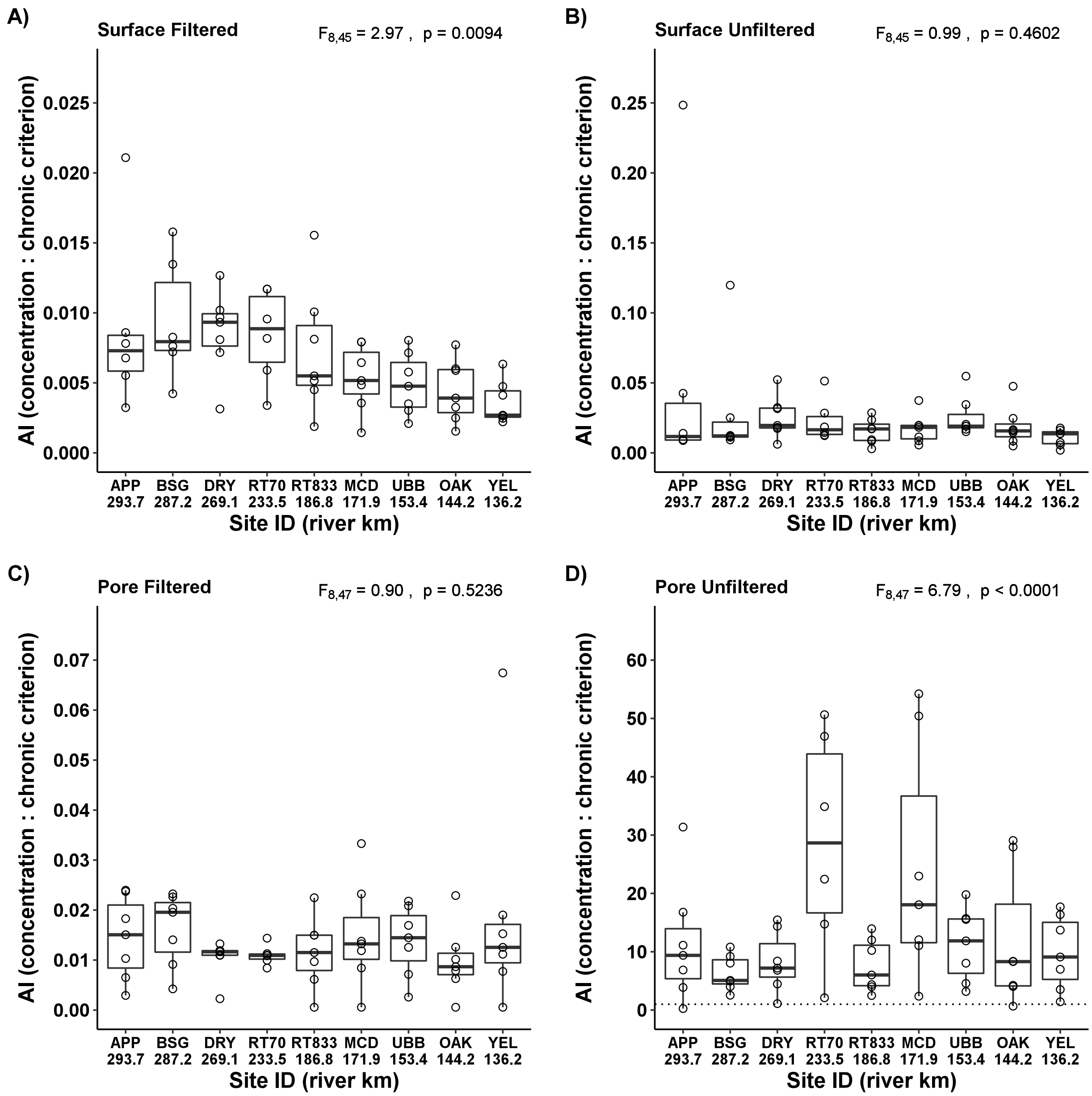

A)
Surface Filtered
$F_{6,47}$ = 13.83 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 1.63 , p = 0.1603
C)
Pore Filtered
$F_{6,47}$ = 1.23 , p = 0.3078
D)
Pore Unfiltered
$F_{6,47}$ = 15.35 , p < 0.0001
Zn (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

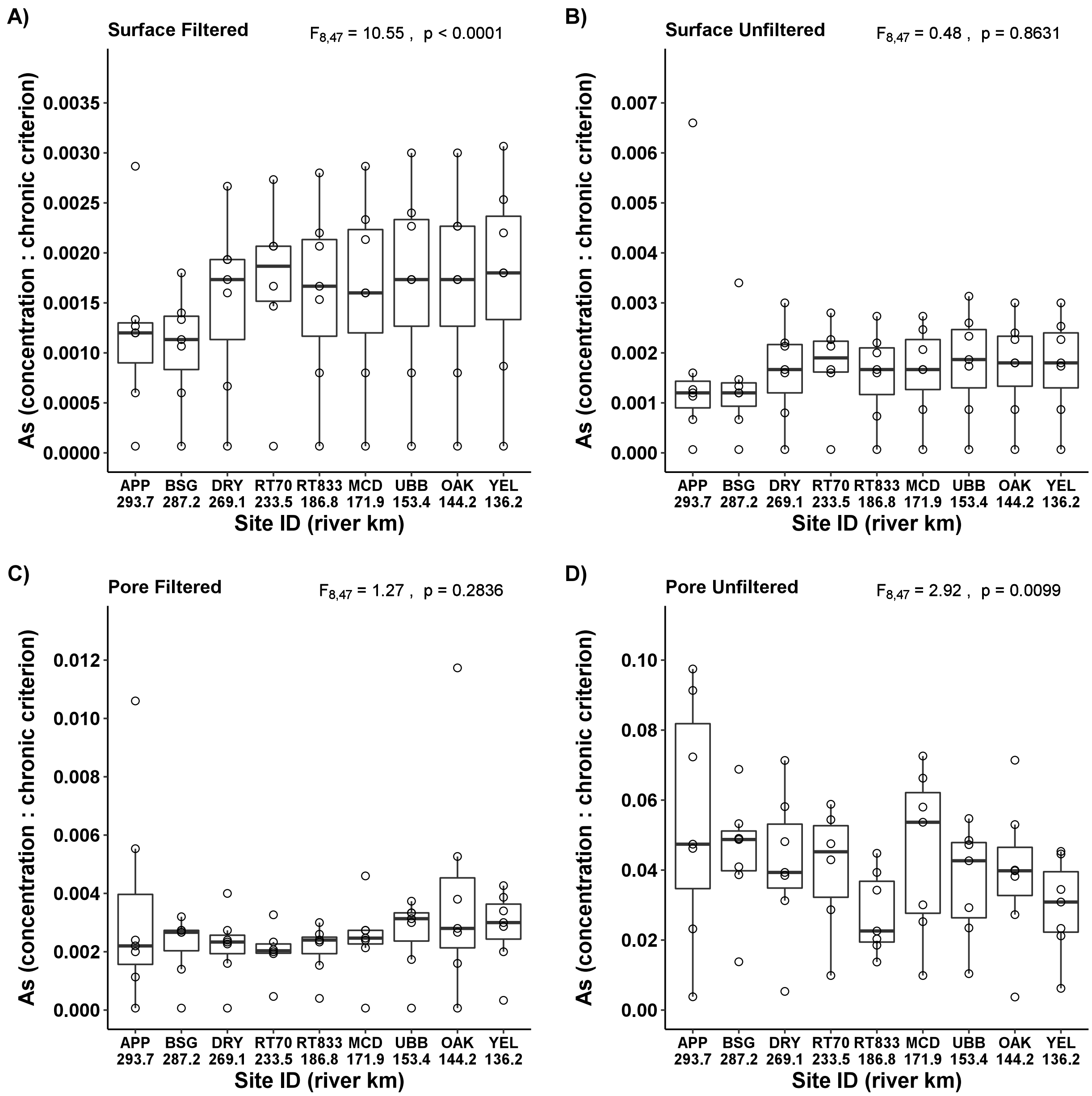
APPENDIX C – SPATIAL MIXED MODEL BOXPLOTS: TRACE ELEMENT CHRONIC CRITERION RATIOS BY SAMPLE TYPE

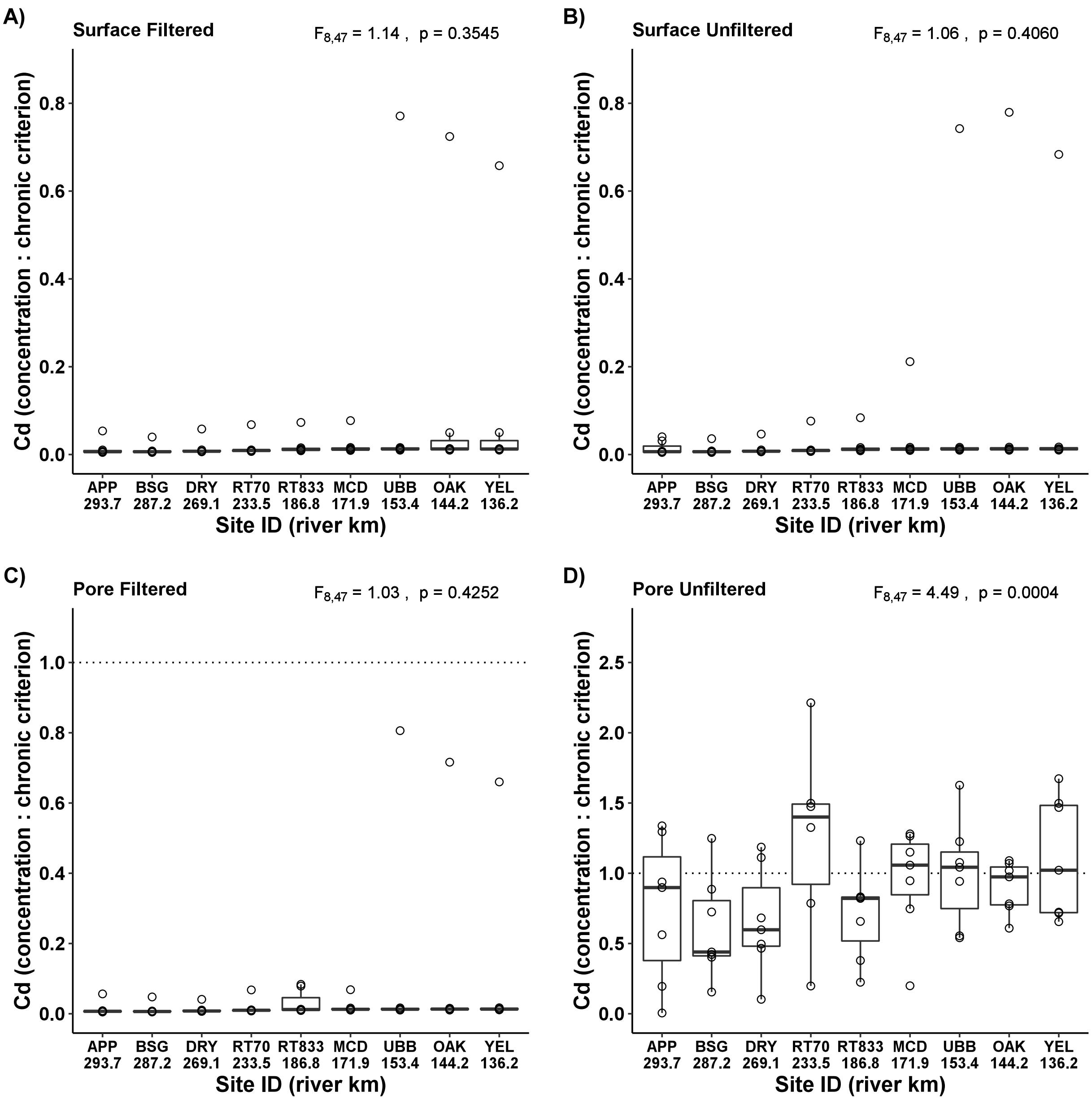
These models evaluate differences in criterion ratios – the ratio of trace-element concentration:chronic criterion – among sampling sites, with sampling date as a random effect to account for multiple samples being collected from each site during the 12-month study period.

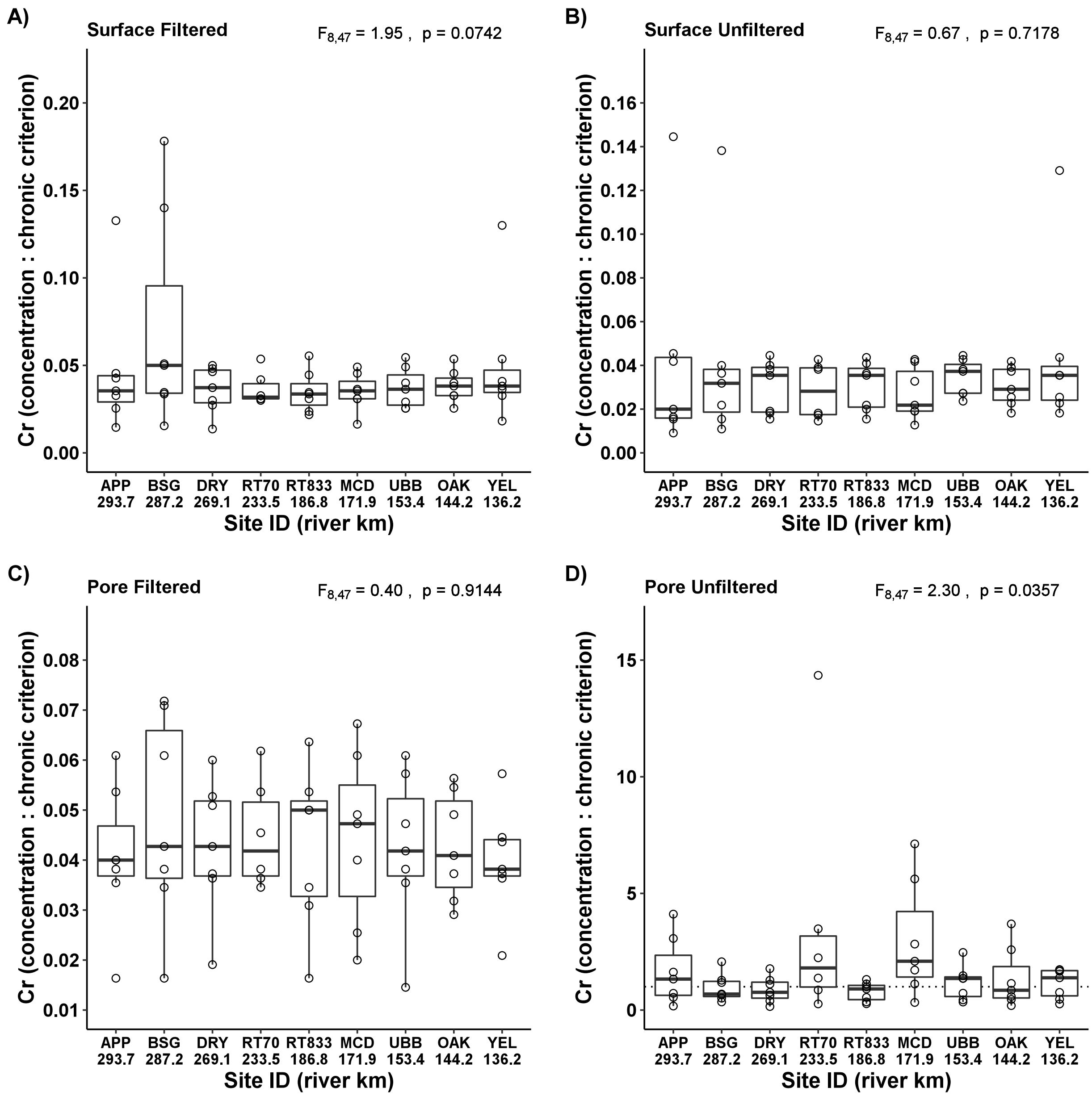
Each page presents results for a single trace element, with four boxplots representing the four models fit, one for each type of sample collected: surface water, filtered (SF); surface water, unfiltered (SU); pore water, filtered (PF); pore water, unfiltered (PU). Open circles are individual observations, with up to seven observations per site measured roughly monthly from November 2019 through October 2020. The horizontal axis indicates the abbreviated identifier and river kilometer of the nine sample locations, arranged moving downriver from left to right from Appalachia, Virginia to near Tazewell, Tennessee. The vertical axis indicates the ratio of trace element concentration to its respective chronic water quality criterion; note that vertical-axis range is independent among boxplots. Criteria are USEPA recommended "dissolved" criteria for freshwater aquatic life, with sample-specific adjustments as appropriate using sample hardness, dissolved organic carbon (DOC), pH, and/or the Biotic Ligand Model (copper). Dotted line indicates ratio of concentration:criterion = 1. On the upper-right border of each boxplot are Wald test F-statistics and p-values for overall site-wise effects.

Criterion ratios were calculated for each of 10 trace elements with chronic water quality criteria for freshwater aquatic life (Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Se, and Zn). Because samples for Cr represent un-speciated, or "total dissolved" Cr, criterion ratios for Cr were calculated using criteria for hexavalent Cr (VI), as an indication of a "worst-case scenario" if all Cr present were of the more-toxic Cr (VI) speciation. For elements other than Cr with criteria that depend on hardness (Cd, Ni, Pb, Zn), criterion ratios are based on criteria calculated for each individual sample, regardless of sample type. For aluminum and copper, criterion ratios are based on criteria calculated for each individual sample but only for filtered samples (SF, PF). Criterion ratios for unfiltered samples (SU, PU) for those elements are based on unfiltered concentrations divided by criteria calculated for the respective filtered sample. This was done because the DOC data needed to calculate Al and Cu criteria were not available for SU or PU samples, as DOC can not be measured on unfiltered samples.

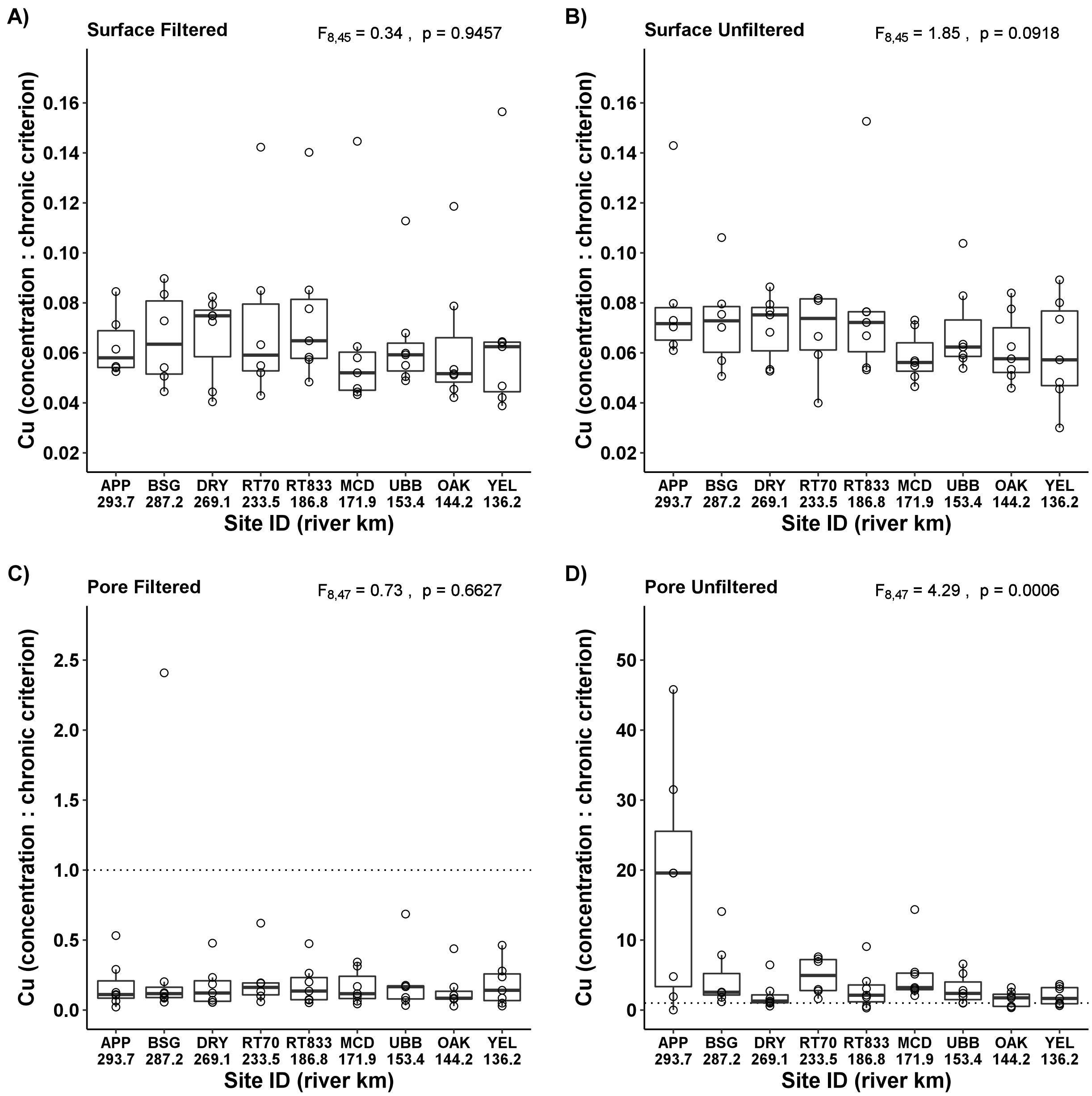

A)
Surface Filtered
F8,45 = 2.97 , p = 0.0094
B)
Surface Unfiltered
F8,45 = 0.99 , p = 0.4602
C)
Pore Filtered
F8,47 = 0.90 , p = 0.5236
D)
Pore Unfiltered
F8,47 = 6.79 , p < 0.0001
AI (concentration : chronic criterion)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

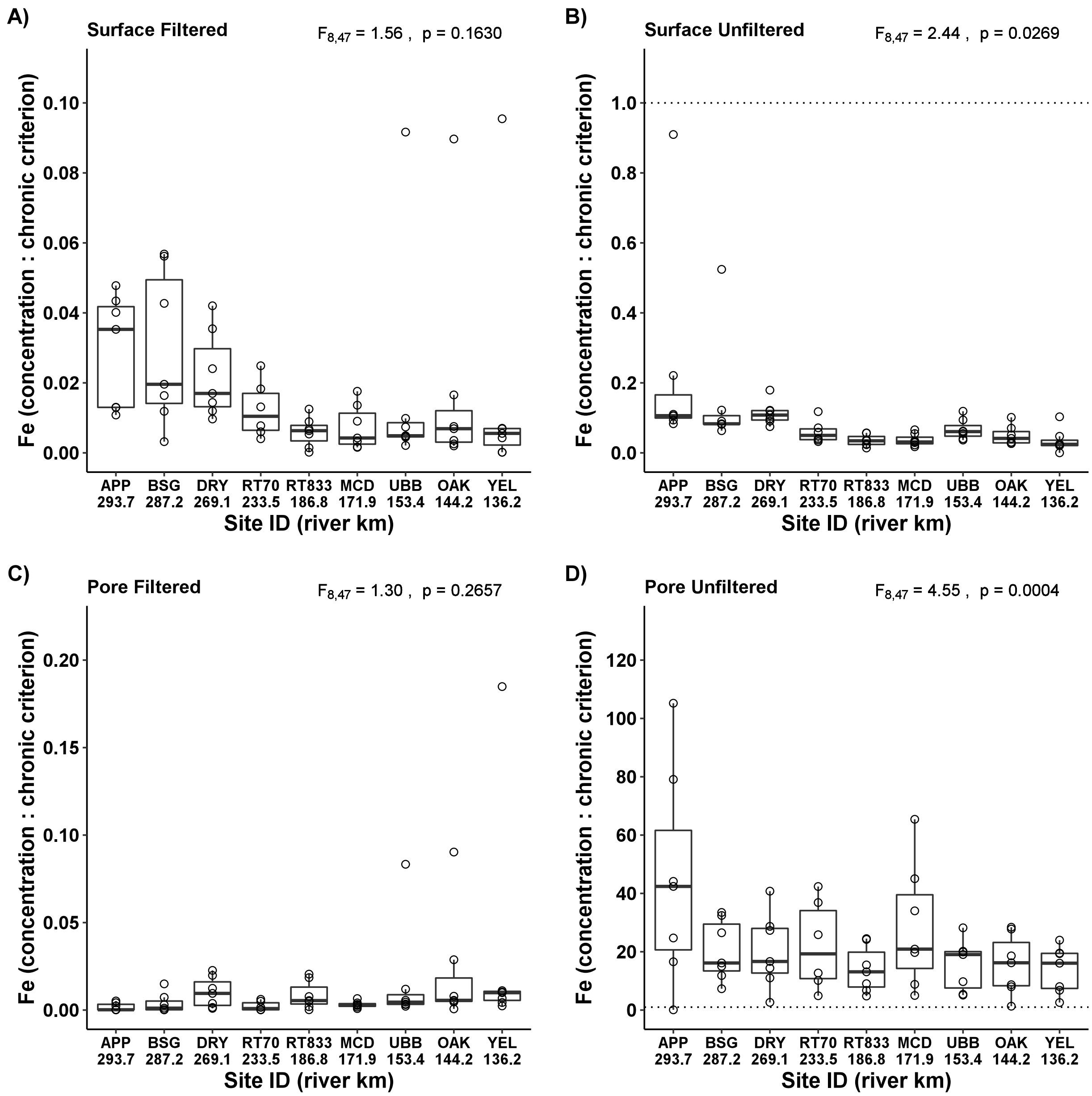

A)
Surface Filtered
$F_{8,47}$ = 10.55 , p < 0.0001
As (concentration : chronic criterion)
0.0000
0.0005
0.0010
0.0015
0.0020
0.0025
0.0030
0.0035
B)
Surface Unfiltered
$F_{8,47}$ = 0.48 , p = 0.8631
0.000
0.001
0.002
0.003
0.004
0.005
0.006
0.007
C)
Pore Filtered
$F_{8,47}$ = 1.27 , p = 0.2836
0.000
0.002
0.004
0.006
0.008
0.010
0.012
D)
Pore Unfiltered
$F_{8,47}$ = 2.92 , p = 0.0099
0.00
0.02
0.04
0.06
0.08
0.10
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

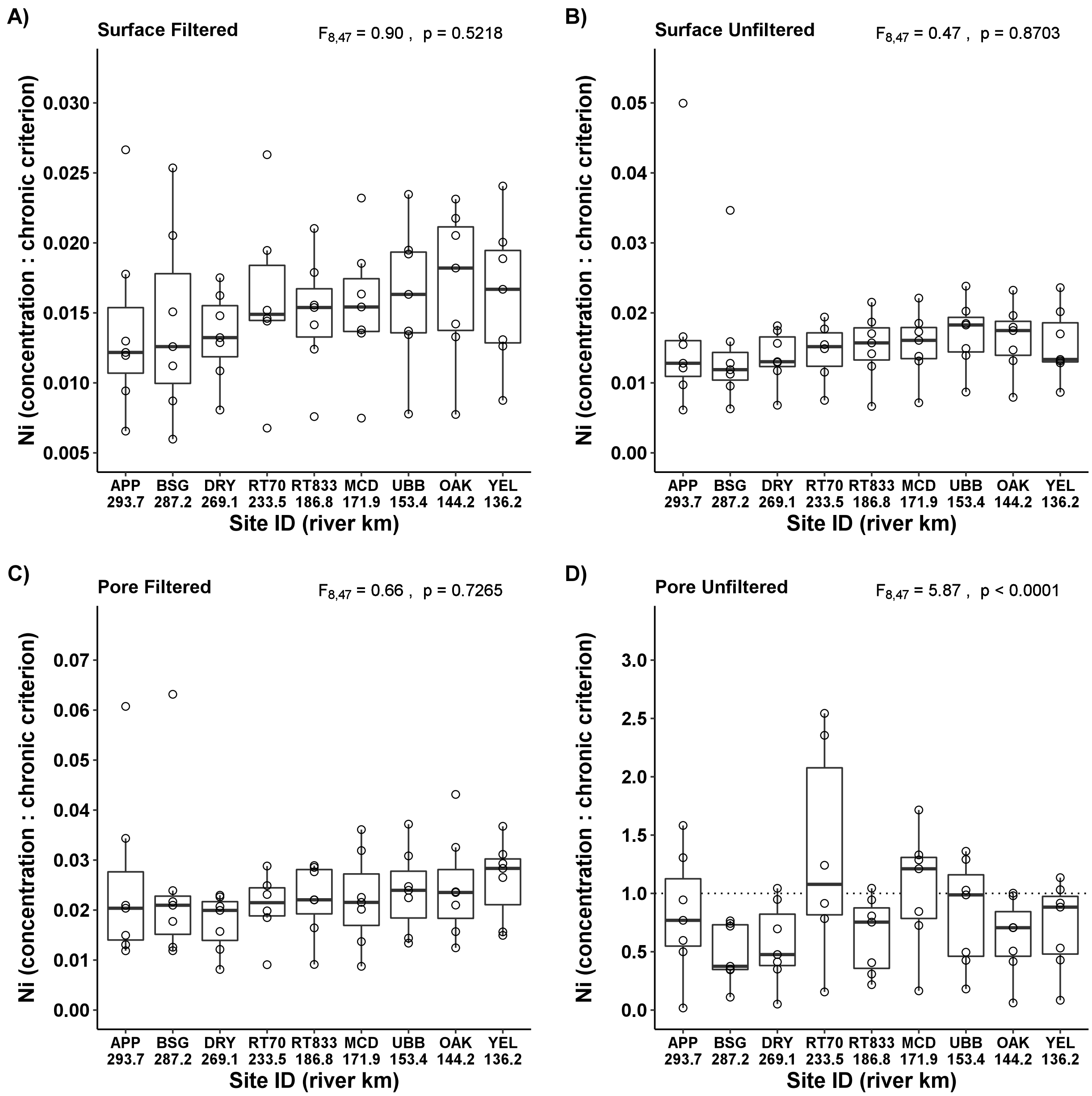

A)
Surface Filtered
$F_{8,47}$ = 1.14 , p = 0.3545
B)
Surface Unfiltered
$F_{8,47}$ = 1.06 , p = 0.4060
C)
Pore Filtered
$F_{8,47}$ = 1.03 , p = 0.4252
D)
Pore Unfiltered
$F_{8,47}$ = 4.49 , p = 0.0004
Cd (concentration : chronic criterion)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

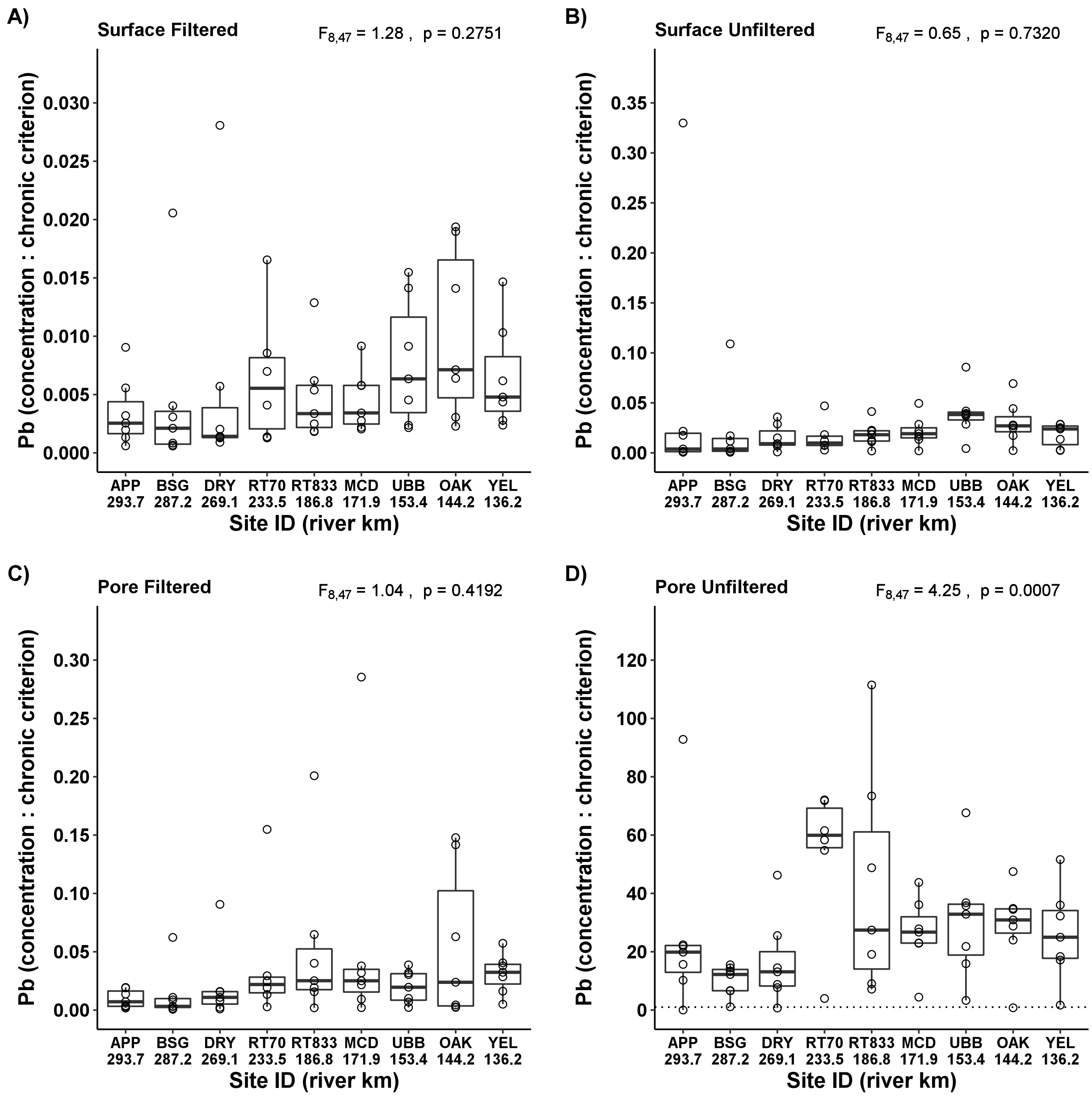


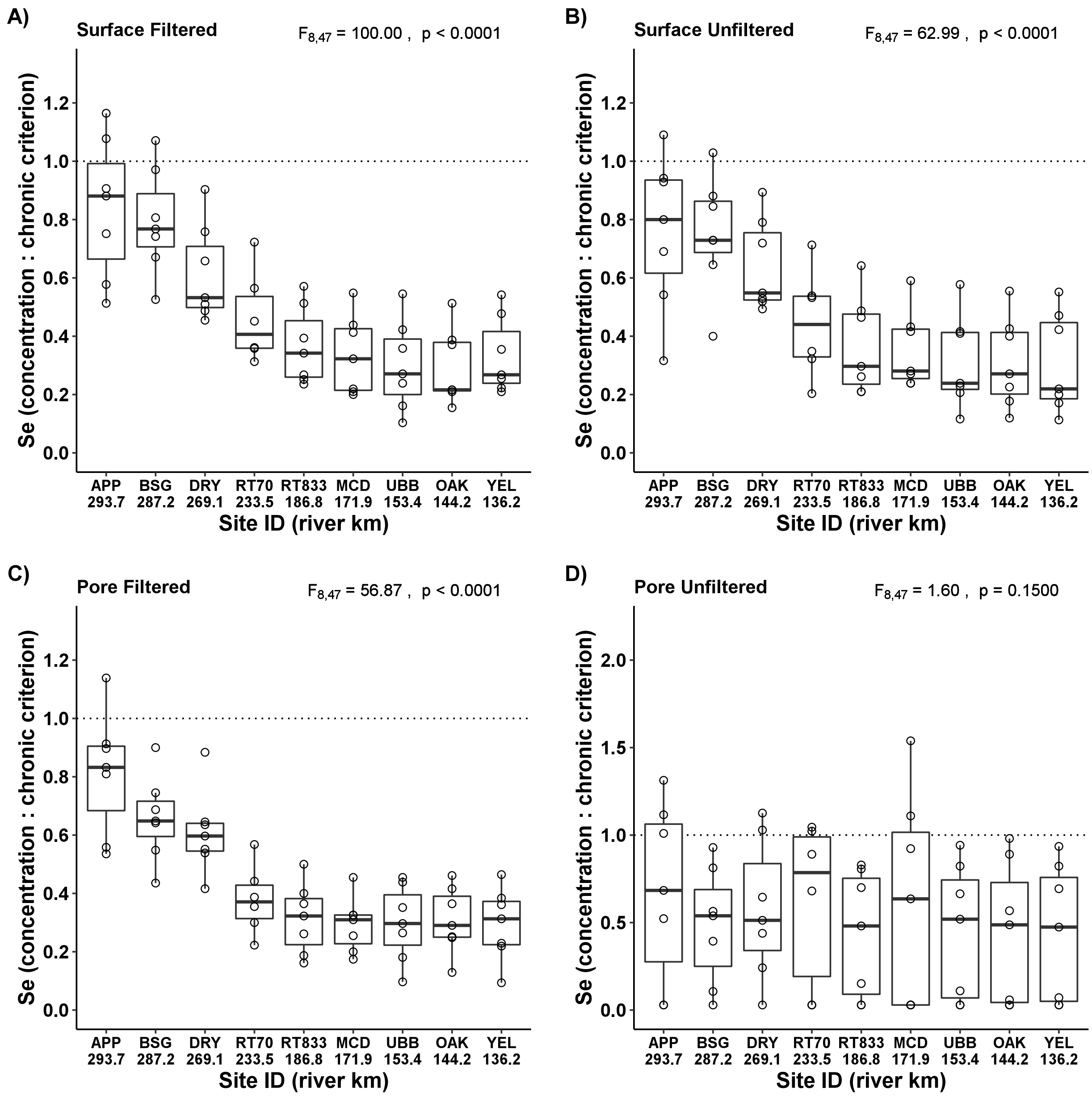
A)
Surface Filtered
F8,47 = 1.95 , p = 0.0742
B)
Surface Unfiltered
F8,47 = 0.67 , p = 0.7178
C)
Pore Filtered
F8,47 = 0.40 , p = 0.9144
D)
Pore Unfiltered
F8,47 = 2.30 , p = 0.0357
Cr (concentration : chronic criterion)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

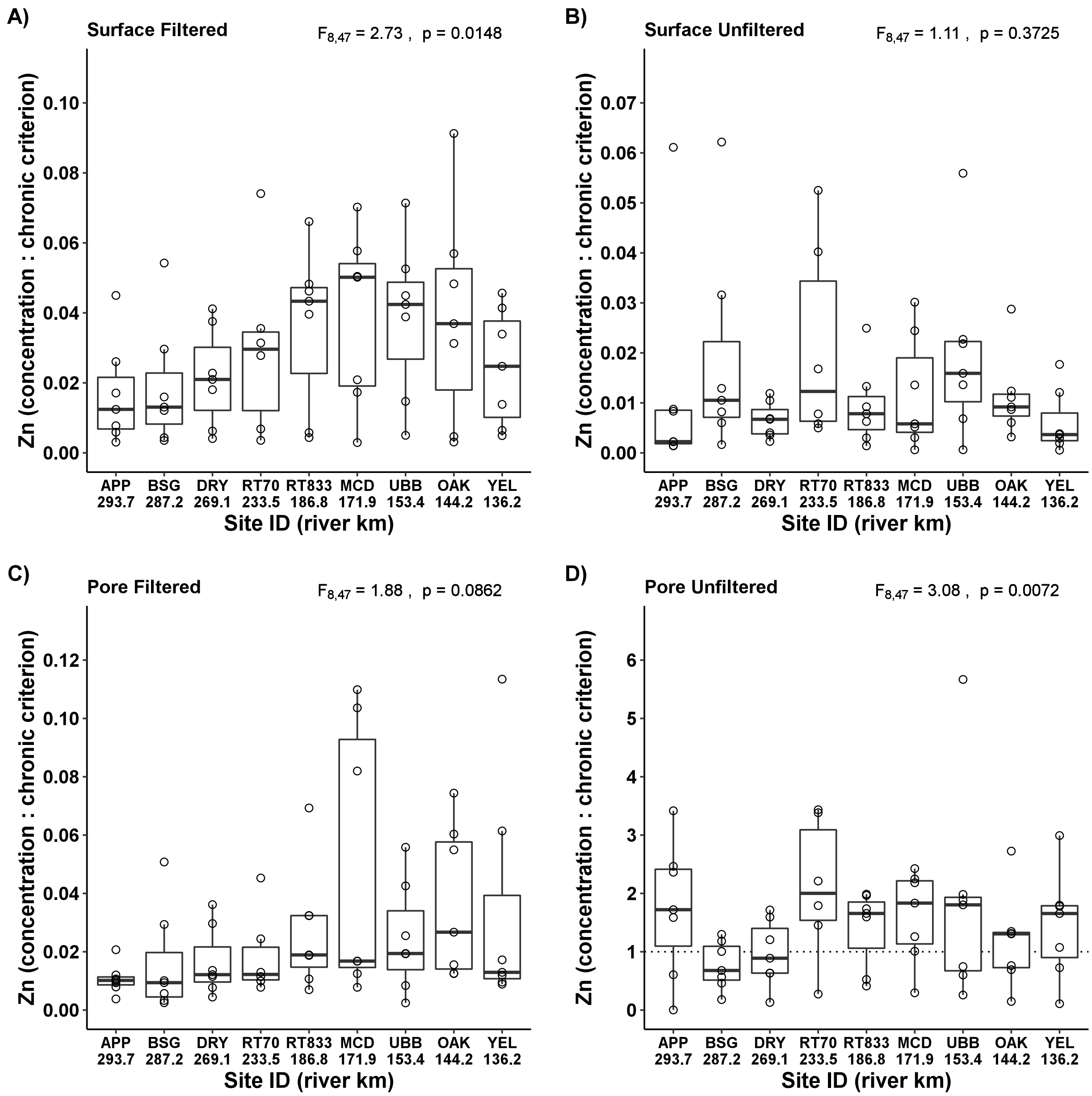

A)
Surface Filtered
F8,45 = 0.34 , p = 0.9457
B)
Surface Unfiltered
F8,45 = 1.85 , p = 0.0918
C)
Pore Filtered
F8,47 = 0.73 , p = 0.6627
D)
Pore Unfiltered
F8,47 = 4.29 , p = 0.0006
Cu (concentration : chronic criterion)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
F8,47 = 1.56 , p = 0.1630
B)
Surface Unfiltered
F8,47 = 2.44 , p = 0.0269
C)
Pore Filtered
F8,47 = 1.30 , p = 0.2657
D)
Pore Unfiltered
F8,47 = 4.55 , p = 0.0004
Fe (concentration : chronic criterion)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
$F_{8,47}$ = 0.90 , p = 0.5218
B)
Surface Unfiltered
$F_{8,47}$ = 0.47 , p = 0.8703
C)
Pore Filtered
$F_{8,47}$ = 0.66 , p = 0.7265
D)
Pore Unfiltered
$F_{8,47}$ = 5.87 , p < 0.0001
Ni (concentration : chronic criterion)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2


A)
Surface Filtered
$F_{8,47}$ = 1.28 , p = 0.2751
B)
Surface Unfiltered
$F_{8,47}$ = 0.65 , p = 0.7320
C)
Pore Filtered
$F_{8,47}$ = 1.04 , p = 0.4192
D)
Pore Unfiltered
$F_{8,47}$ = 4.25 , p = 0.0007
Pb (concentration : chronic criterion)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)


A)
Surface Filtered
$F_{8,47}$ = 100.00 , p < 0.0001
B)
Surface Unfiltered
$F_{8,47}$ = 62.99 , p < 0.0001
C)
Pore Filtered
$F_{8,47}$ = 56.87 , p < 0.0001
D)
Pore Unfiltered
$F_{8,47}$ = 1.60 , p = 0.1500
Se (concentration : chronic criterion)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2
Site ID (river km)

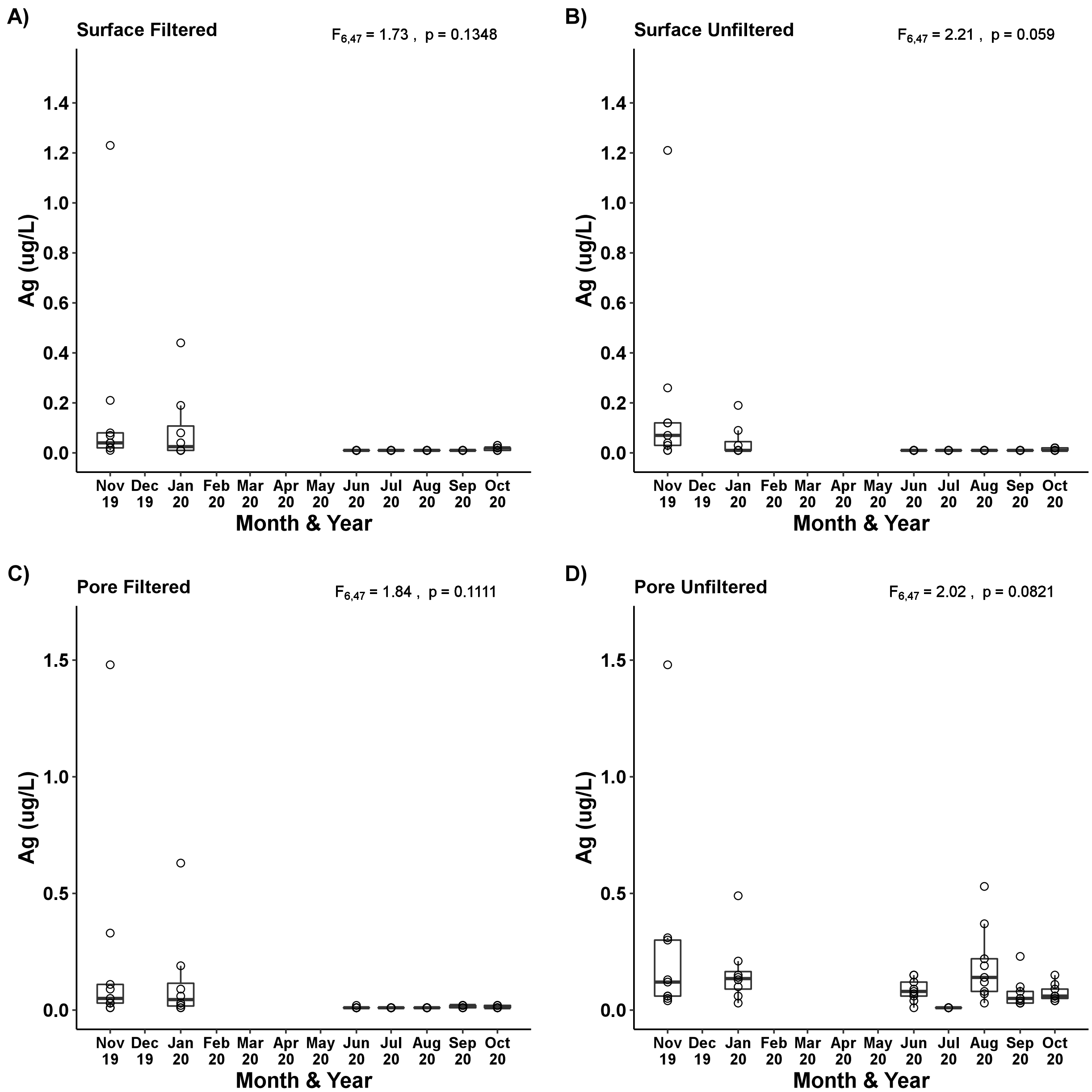


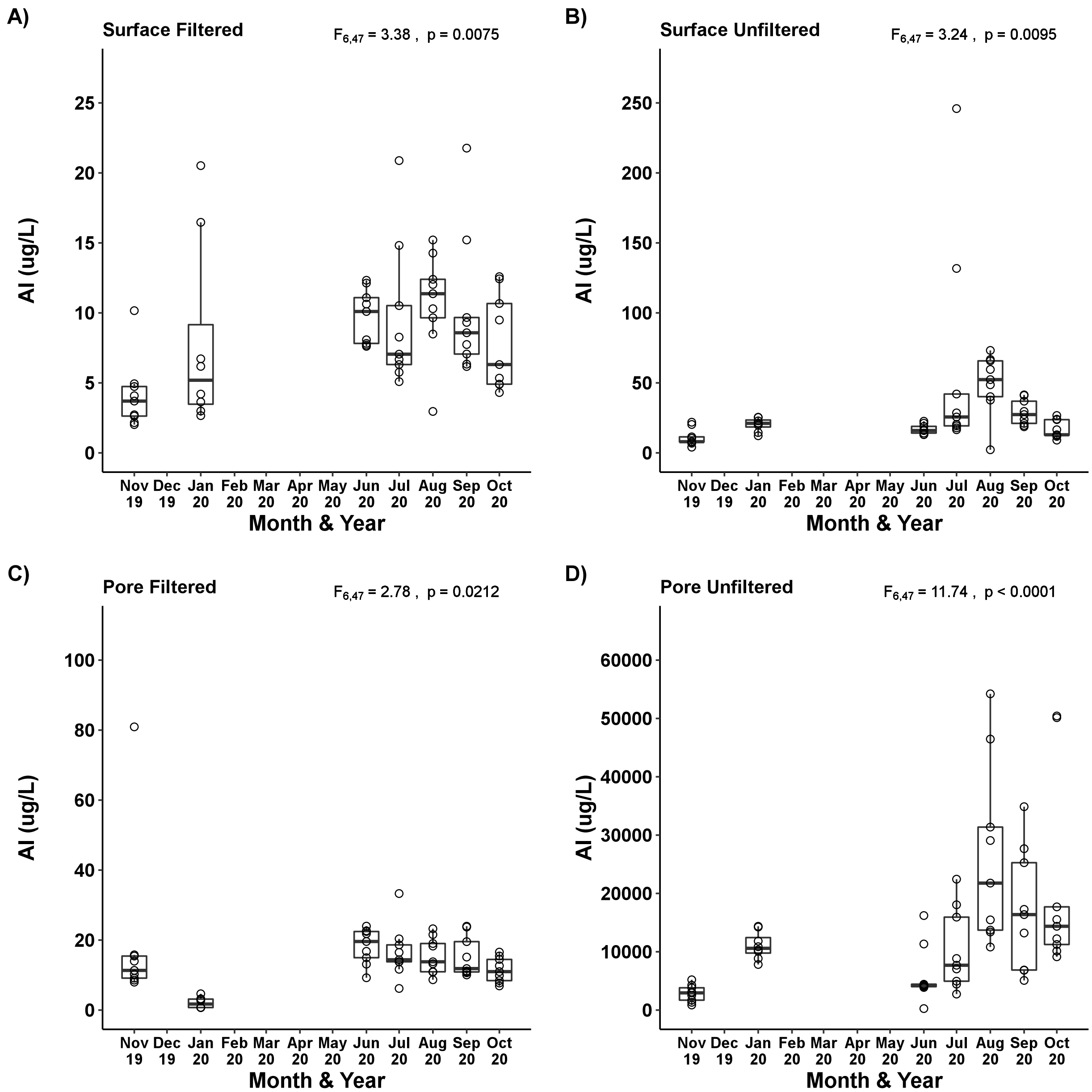
A)
Surface Filtered
$F_{8,47}$ = 2.73 , p = 0.0148
B)
Surface Unfiltered
$F_{8,47}$ = 1.11 , p = 0.3725
C)
Pore Filtered
$F_{8,47}$ = 1.88 , p = 0.0862
D)
Pore Unfiltered
$F_{8,47}$ = 3.08 , p = 0.0072
Zn (concentration : chronic criterion)
Site ID (river km)
APP 293.7
BSG 287.2
DRY 269.1
RT70 233.5
RT833 186.8
MCD 171.9
UBB 153.4
OAK 144.2
YEL 136.2

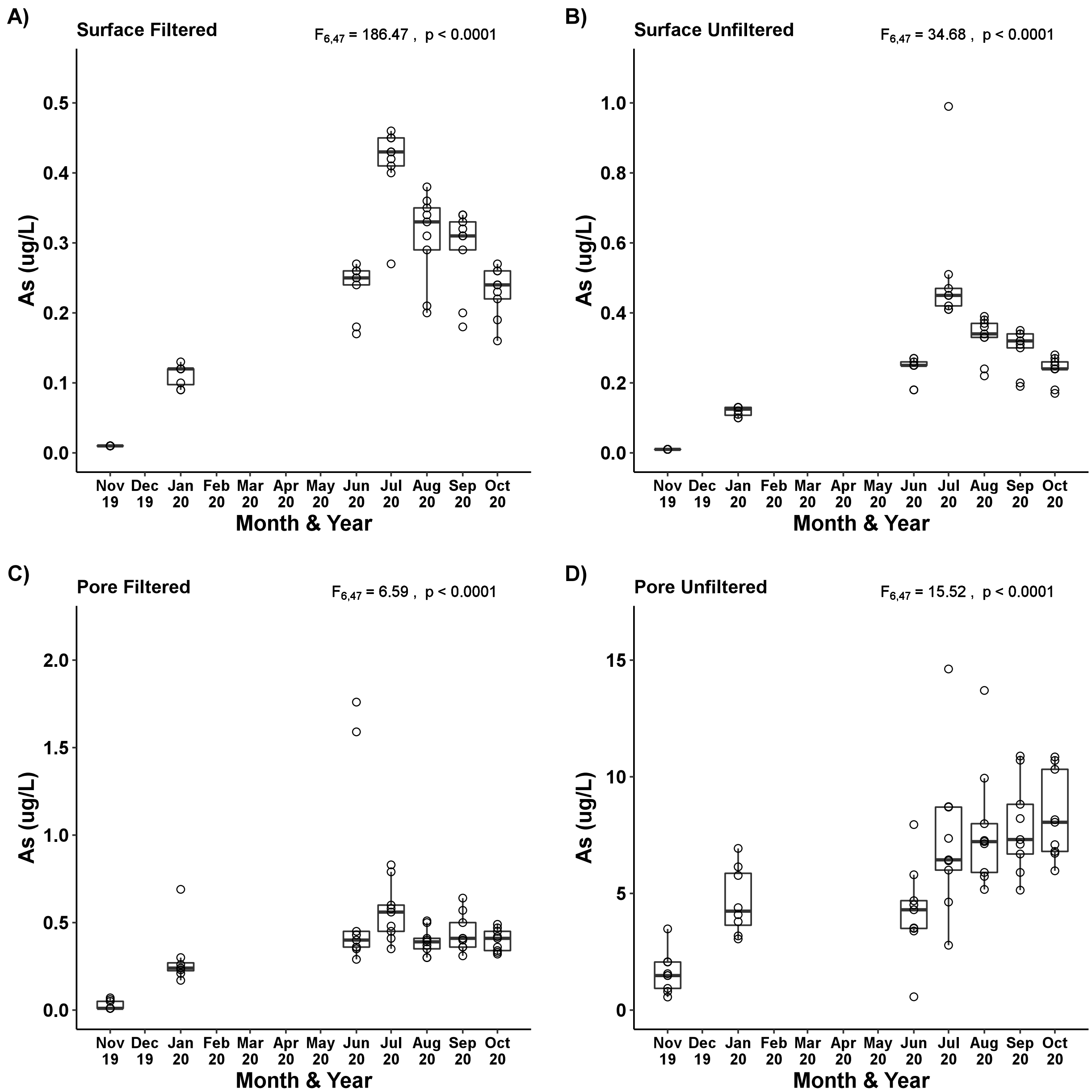
APPENDIX D – TEMPORAL MIXED MODEL BOXPLOTS: TRACE ELEMENT CHRONIC CRITERION RATIOS BY SAMPLE TYPE

These models evaluate differences in ion concentrations among sampling dates, with sampling site as a random effect to account for samples being collected from multiple sites during each sampling month of the study period.

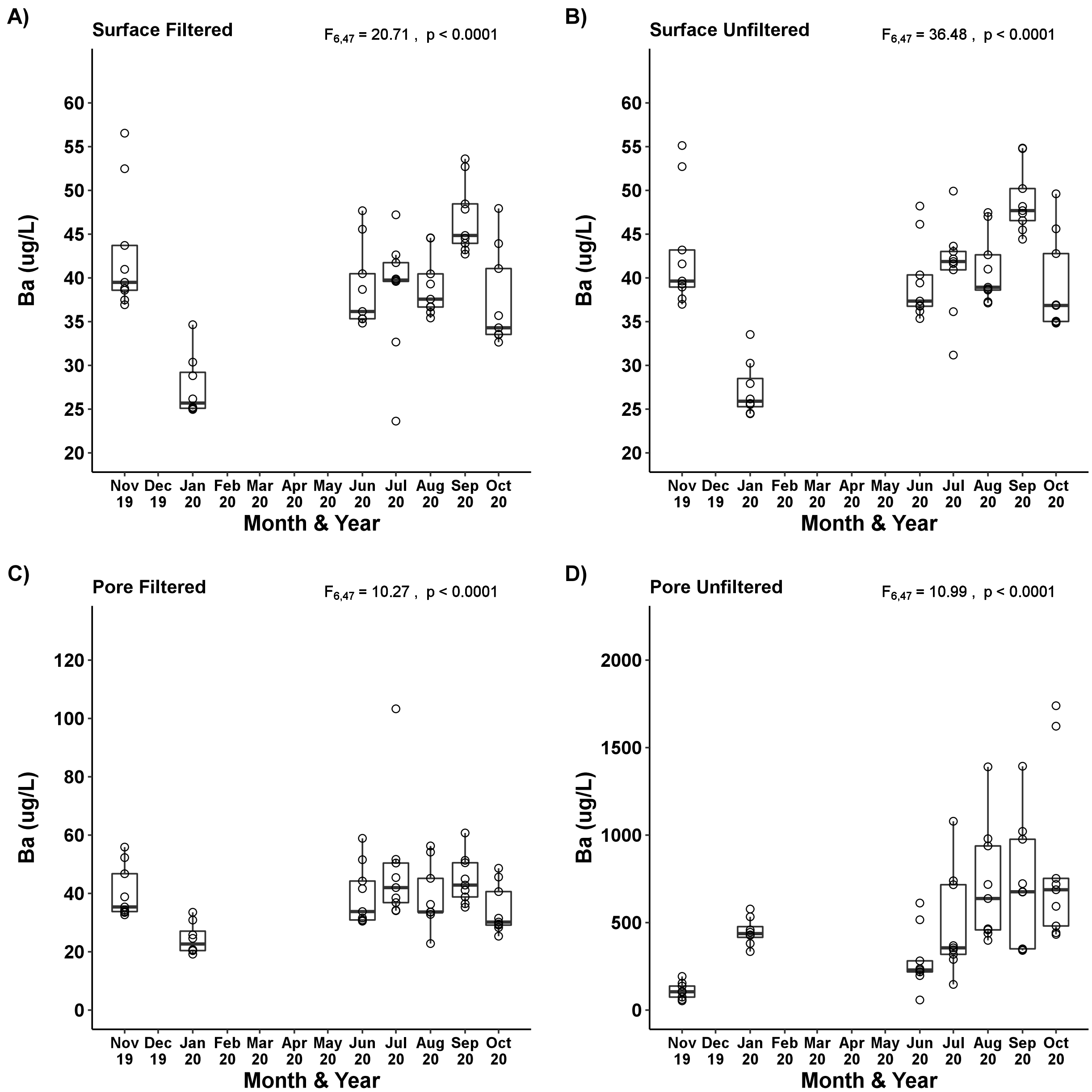
Each page addresses a single ion, with up to four boxplots representing the up to four types of samples collected: Filtered and Unfiltered Surface Water, as well as Filtered and Unfiltered Pore Water. Open circles are individual observations, with observations from up to nine sites per sampling month. The vertical axis indicates the ion and units of concentration; note that axis range is independent among panels. The horizontal axis indicates month and year when the samples were collected. On the upper-right border of each plot are Wald test F-statistics and p-values for overall month-wise effects.

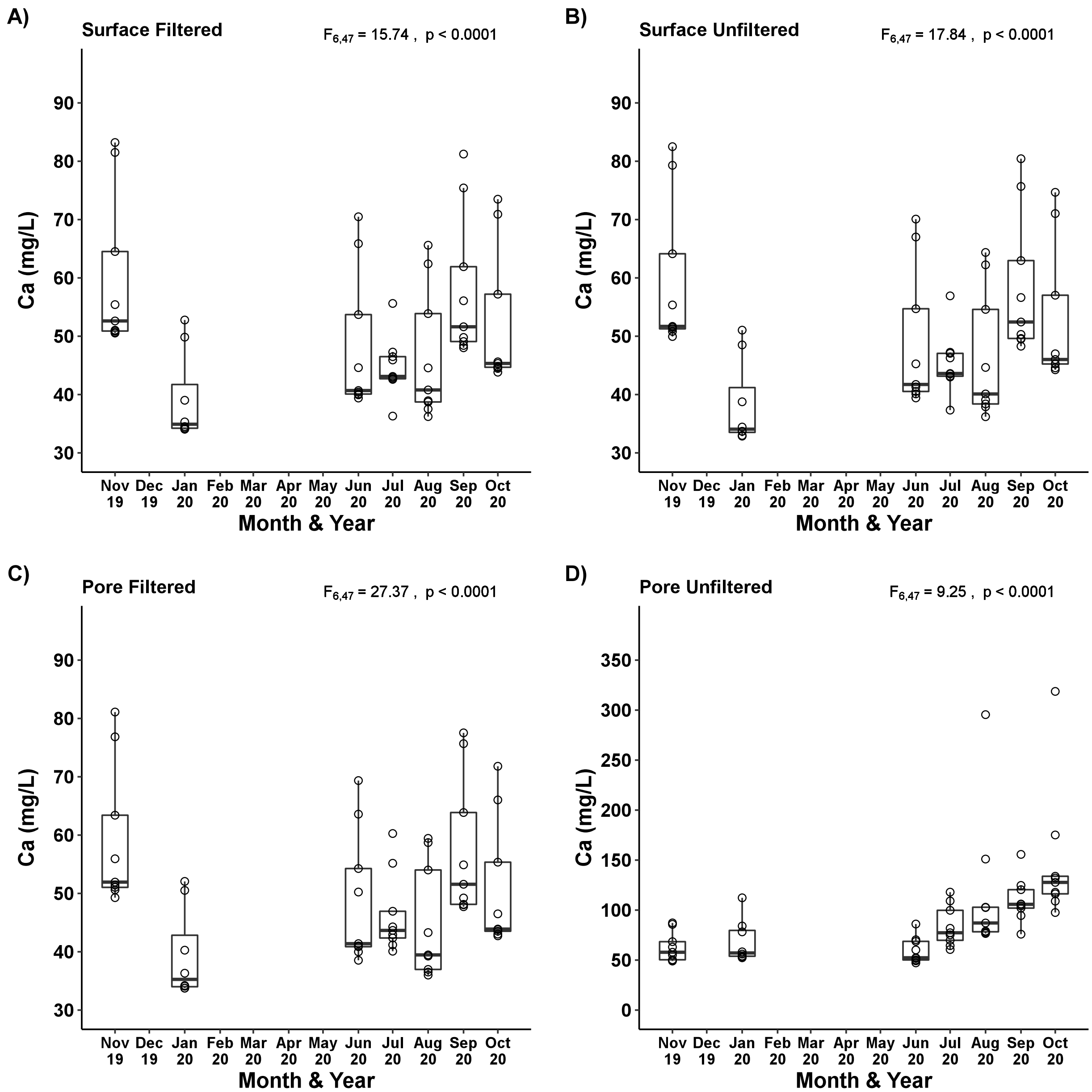

A)
Surface Filtered
F6,47 = 1.73 , p = 0.1348
B)
Surface Unfiltered
F6,47 = 2.21 , p = 0.059
C)
Pore Filtered
F6,47 = 1.84 , p = 0.1111
D)
Pore Unfiltered
F6,47 = 2.02 , p = 0.0821
Ag (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0.5
1.5


A)
Surface Filtered
$F_{6,47}$ = 3.38 , p = 0.0075
B)
Surface Unfiltered
$F_{6,47}$ = 3.24 , p = 0.0095
C)
Pore Filtered
$F_{6,47}$ = 2.78 , p = 0.0212
D)
Pore Unfiltered
$F_{6,47}$ = 11.74 , p < 0.0001
Al (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

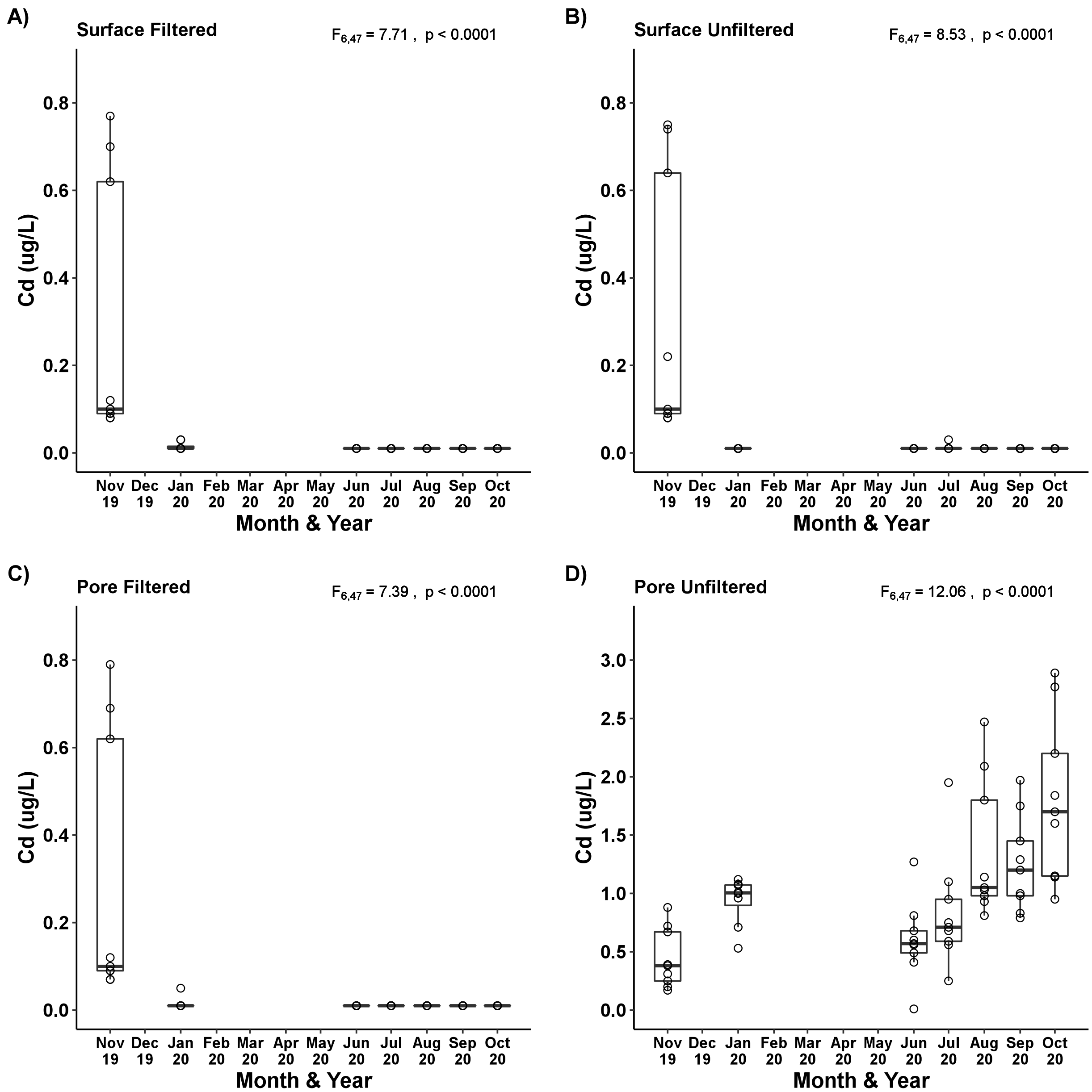


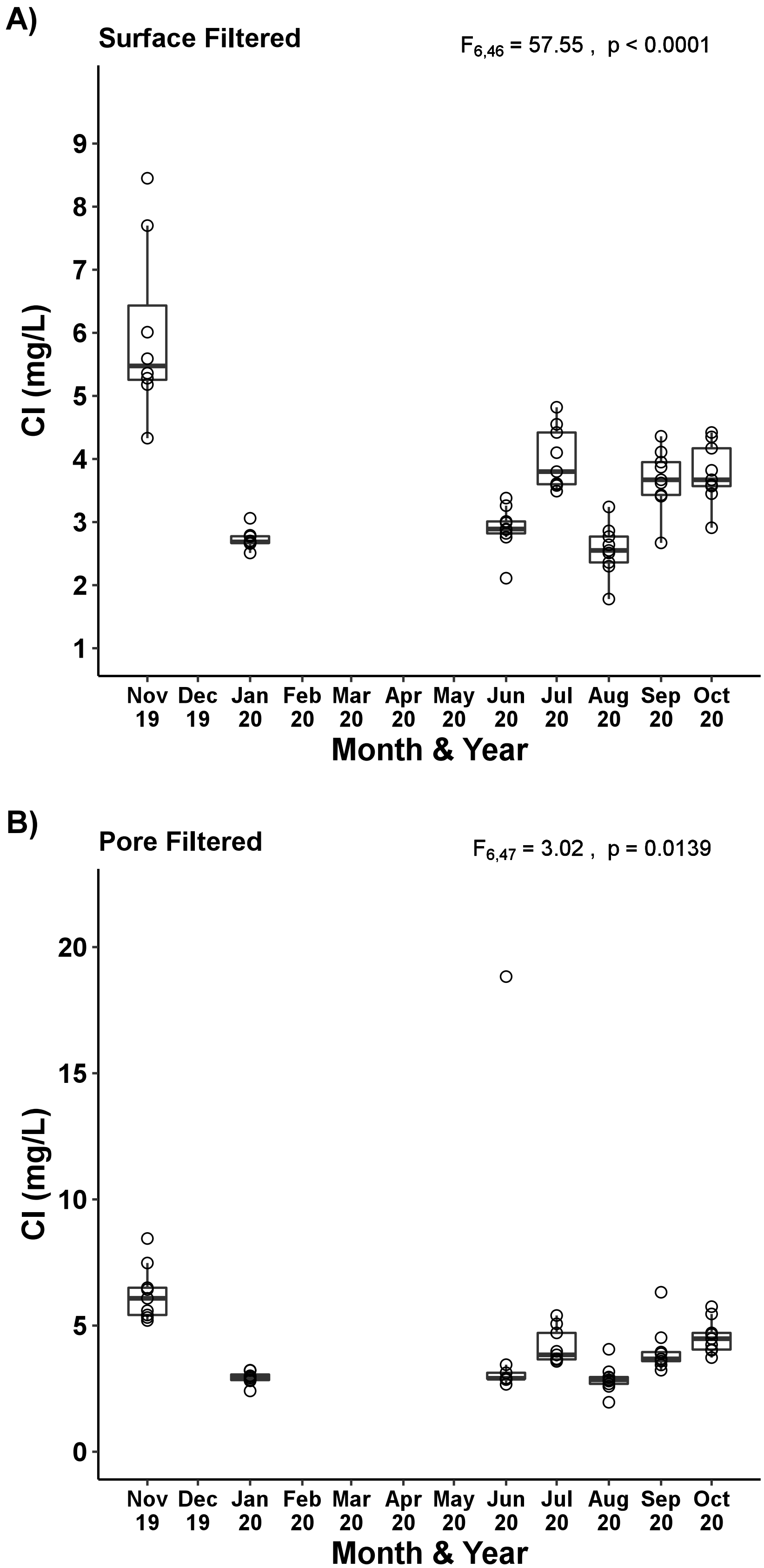
A)
Surface Filtered
F6,47 = 186.47 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 34.68 , p < 0.0001
C)
Pore Filtered
F6,47 = 6.59 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 15.52 , p < 0.0001
As (ug/L)
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

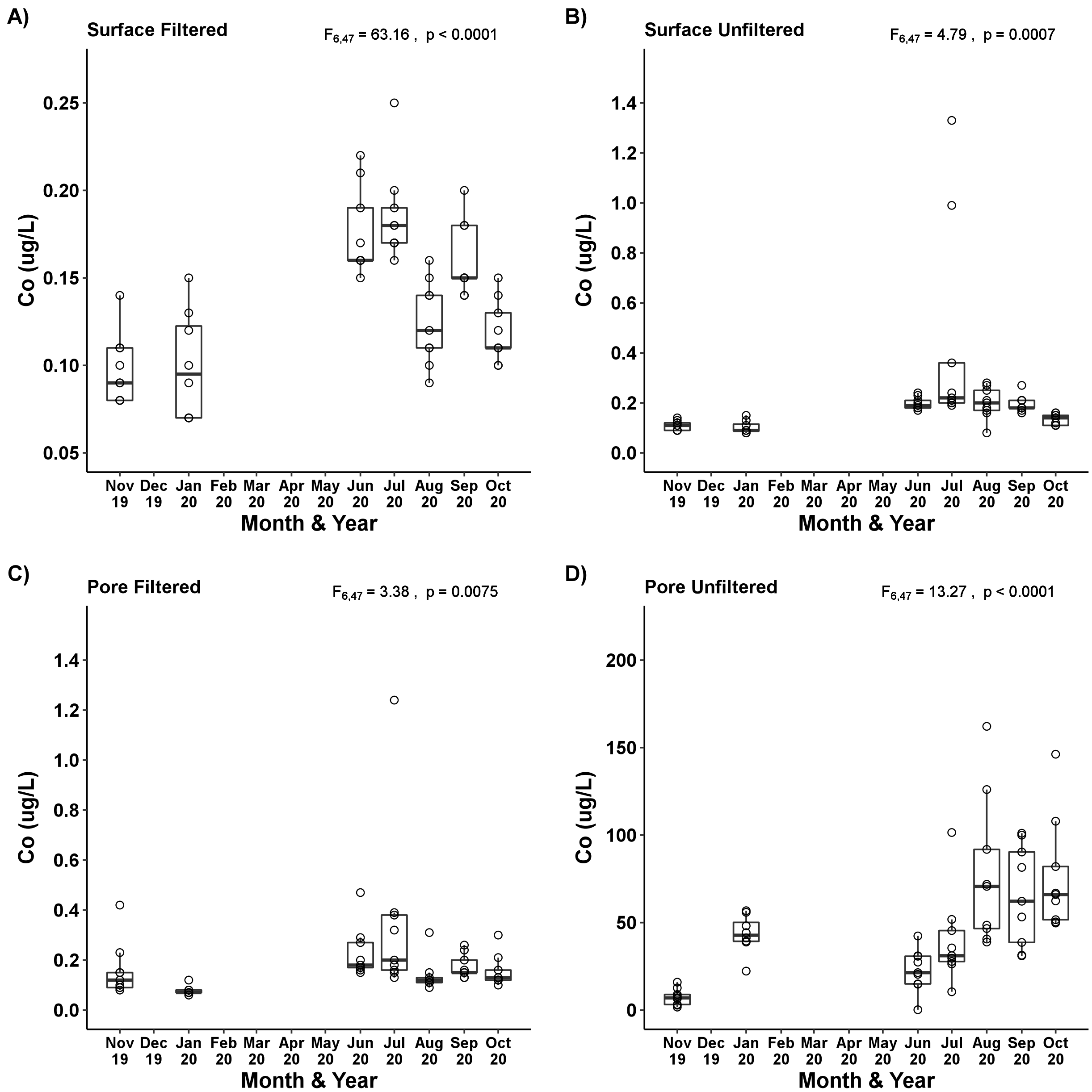

A)
Surface Filtered
$F_{6,47}$ = 20.71 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 36.48 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 10.27 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 10.99 , p < 0.0001
Ba (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

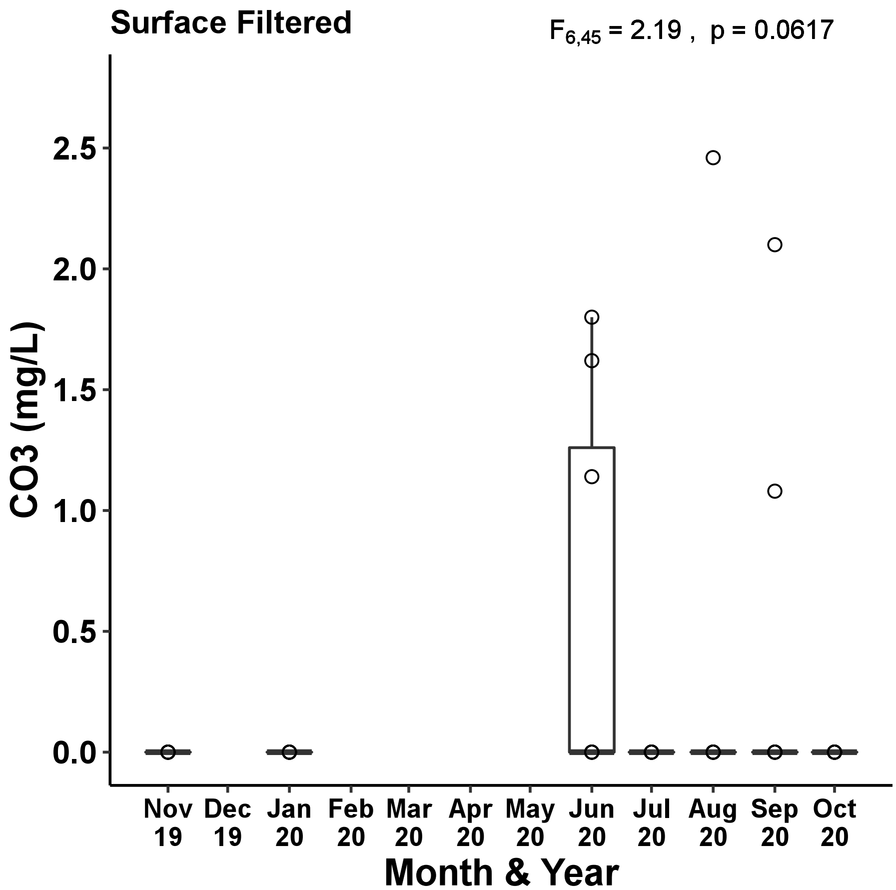


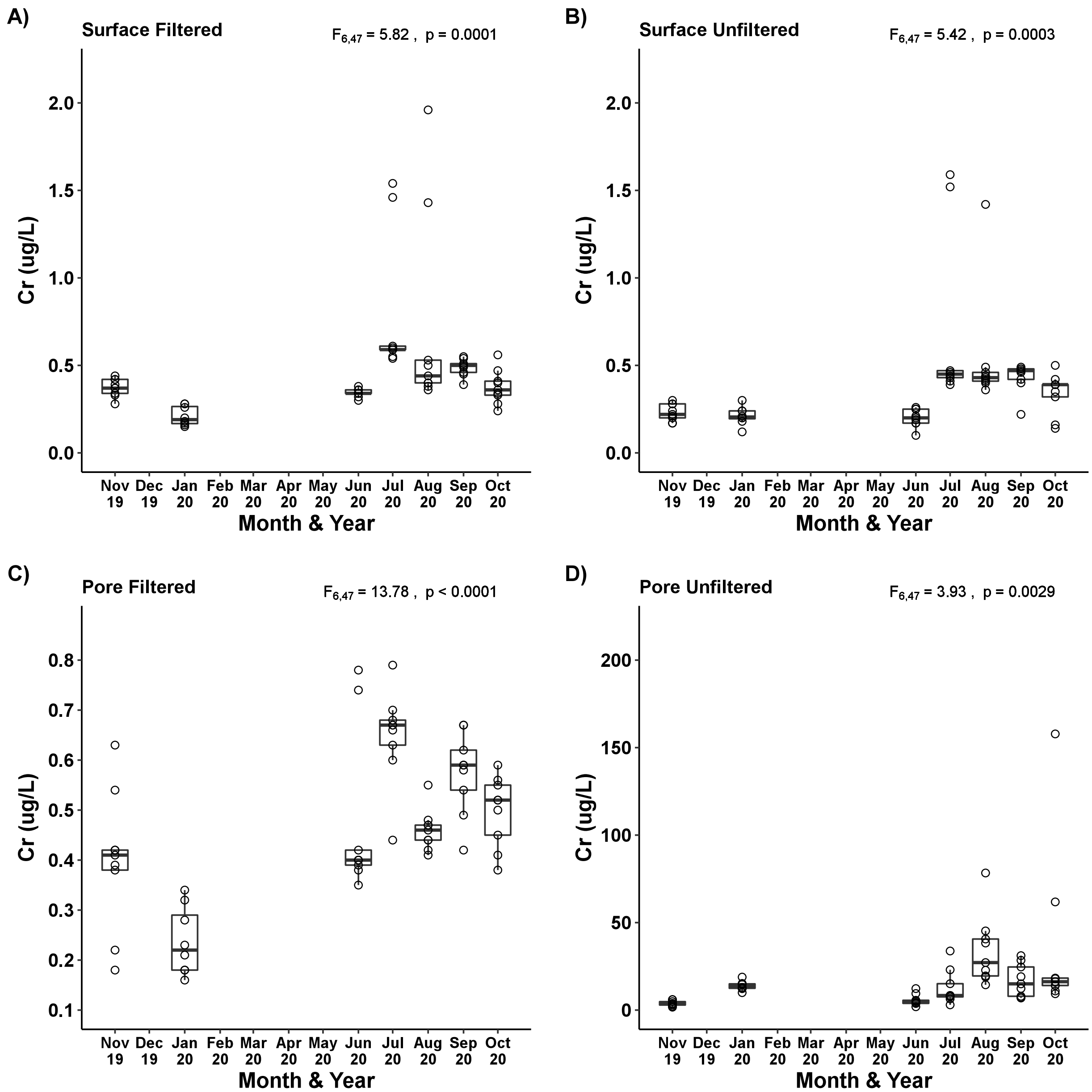
A)
Surface Filtered
$F_{6,47}$ = 15.74 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 17.84 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 27.37 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 9.25 , p < 0.0001
Ca (mg/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20


A)
Surface Filtered
F6,47 = 7.71 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 8.53 , p < 0.0001
C)
Pore Filtered
F6,47 = 7.39 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 12.06 , p < 0.0001
Cd (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

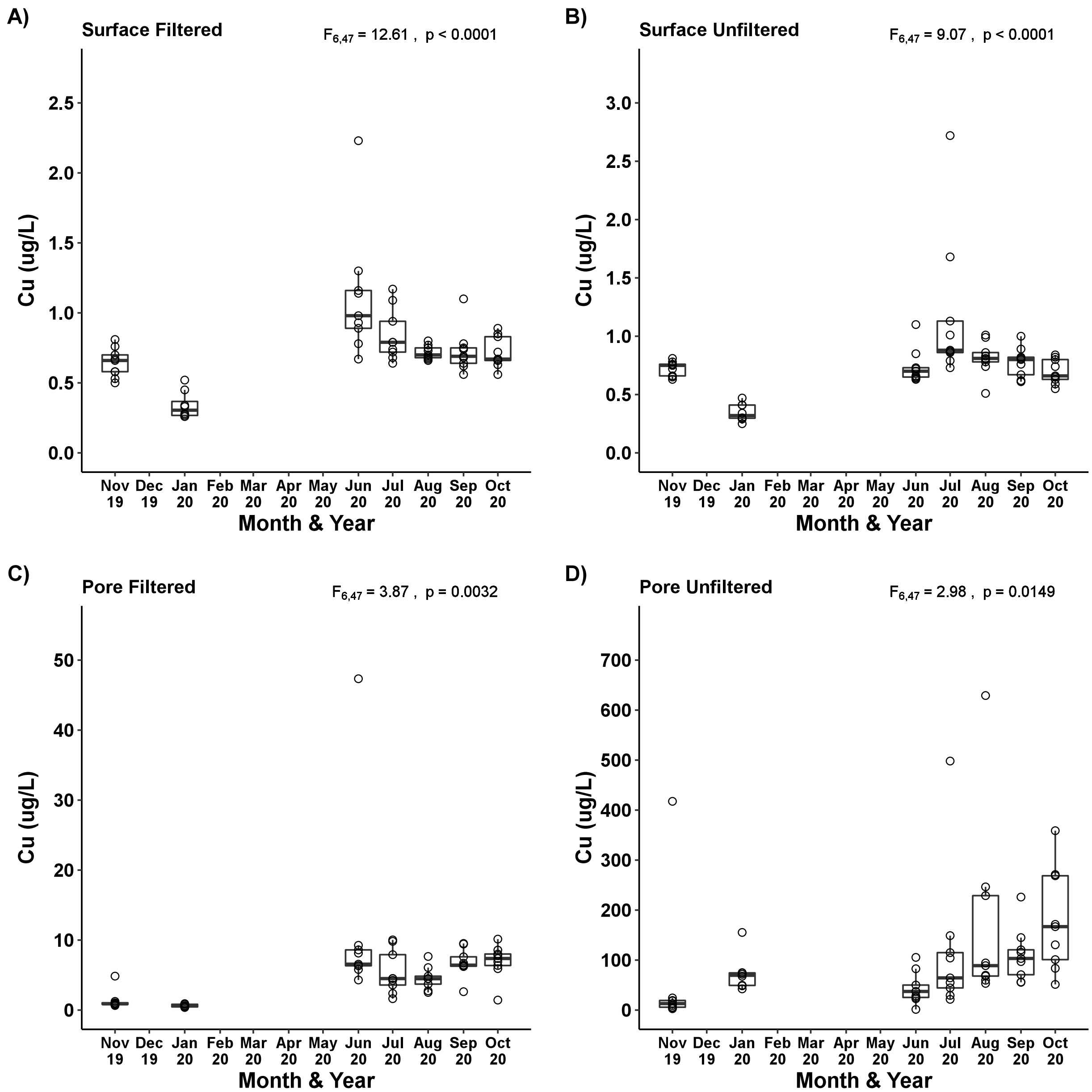

A)
Surface Filtered
F6,46 = 57.55 , p < 0.0001
Cl (mg/L)
1
2
3
4
5
6
7
8
9
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year
B)
Pore Filtered
F6,47 = 3.02 , p = 0.0139
Cl (mg/L)
0
5
10
15
20
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

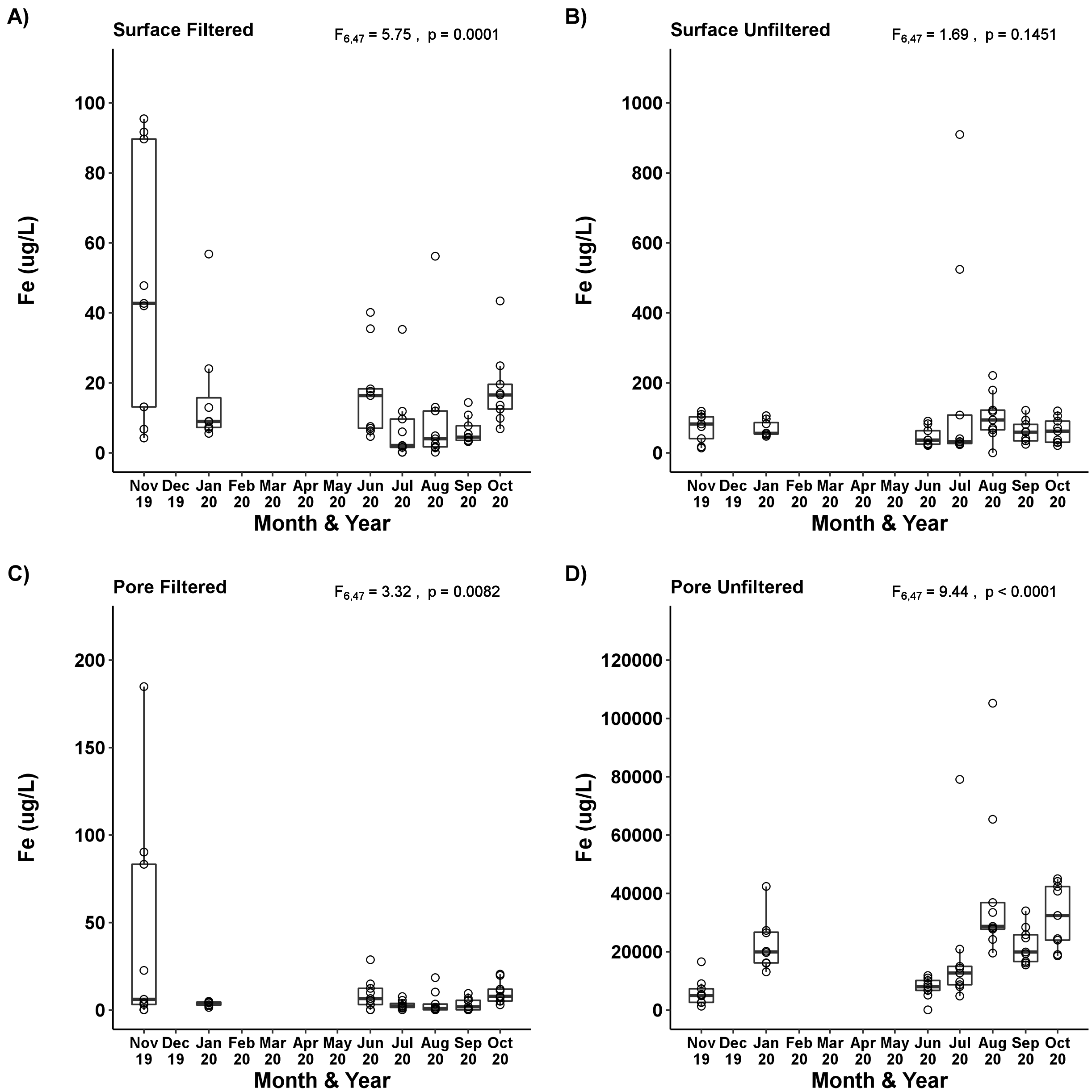

A)
Surface Filtered
F6,47 = 63.16 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 4.79 , p = 0.0007
C)
Pore Filtered
F6,47 = 3.38 , p = 0.0075
D)
Pore Unfiltered
F6,47 = 13.27 , p < 0.0001
Co (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20


Surface Filtered
F6,45 = 2.19 , p = 0.0617
CO3 (mg/L)
2.5
2.0
1.5
1.0
0.5
0.0
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year



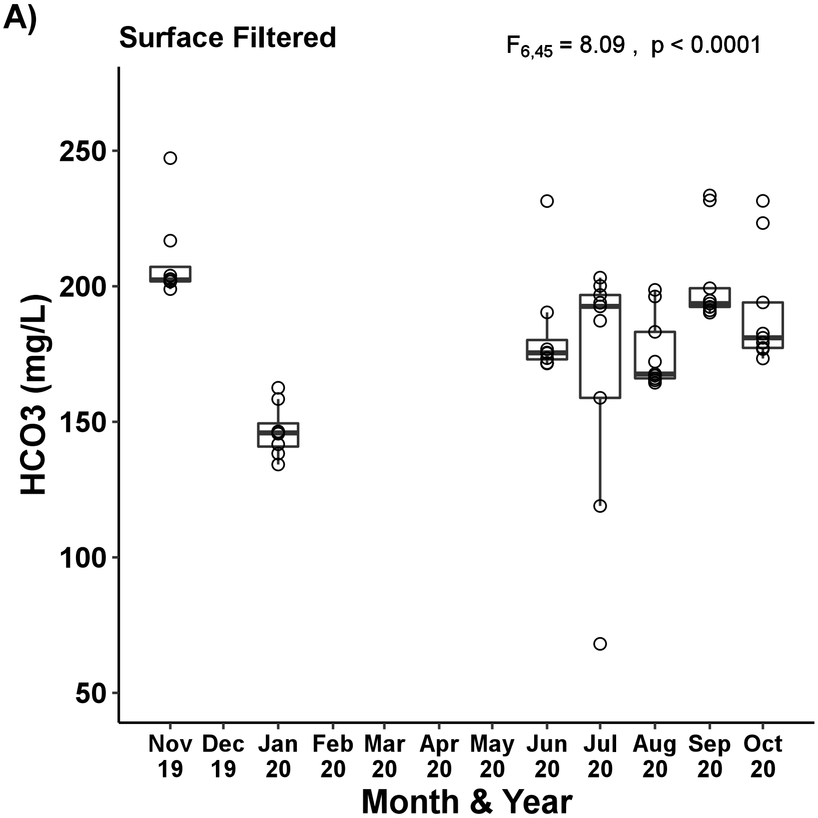
A)
Surface Filtered
$F_{6,47}$ = 5.82 , p = 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 5.42 , p = 0.0003
C)
Pore Filtered
$F_{6,47}$ = 13.78 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 3.93 , p = 0.0029
Cr (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20


A)
Surface Filtered
$F_{6,47}$ = 12.61 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 9.07 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 3.87 , p = 0.0032
D)
Pore Unfiltered
$F_{6,47}$ = 2.98 , p = 0.0149
Cu (ug/L)
Month & Year
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20

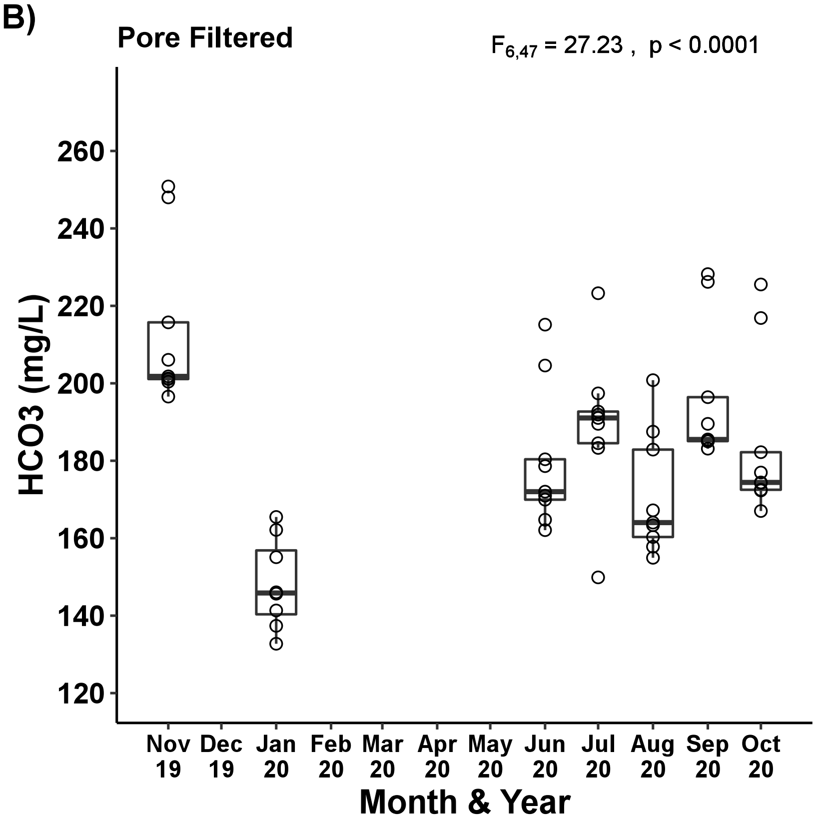


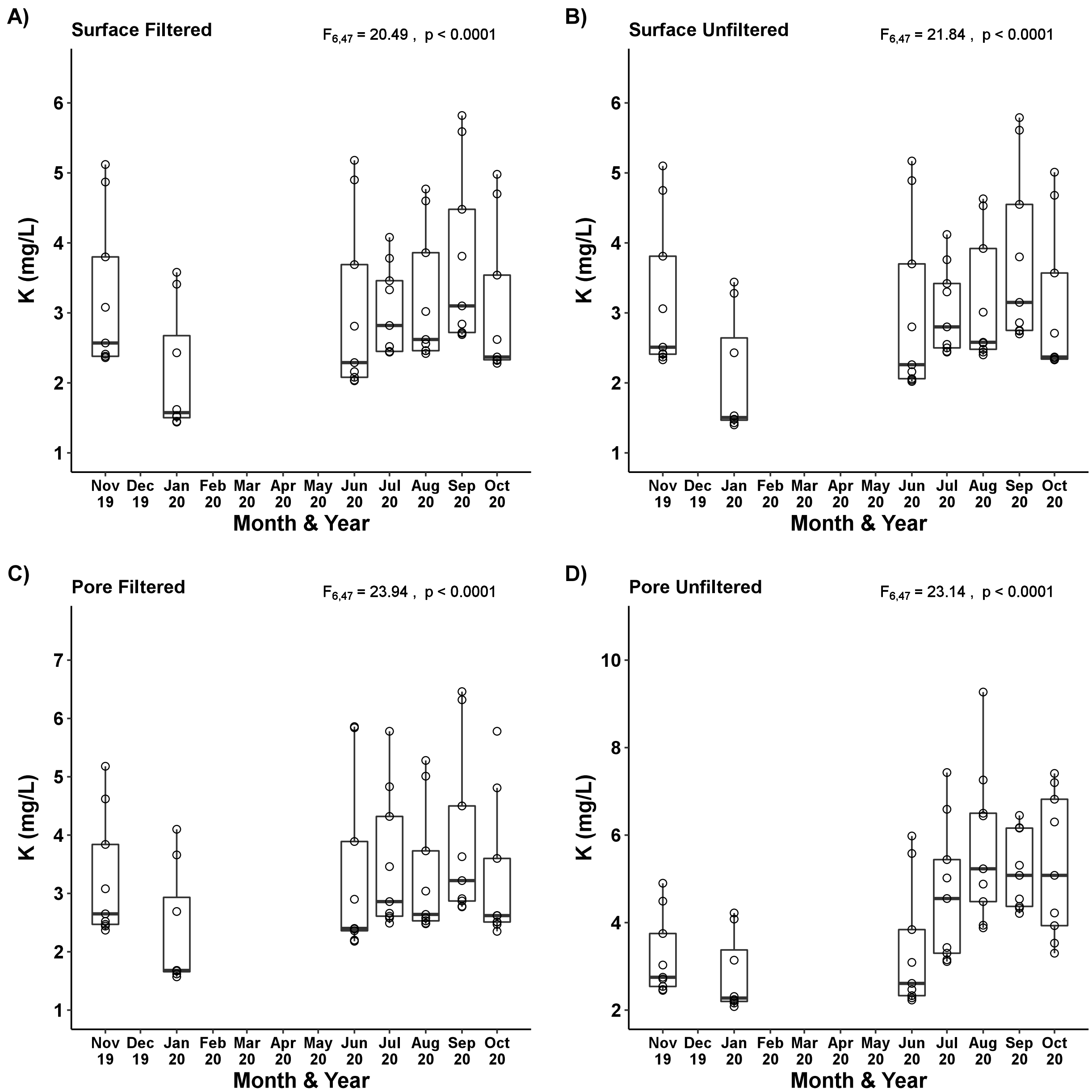
A)
Surface Filtered
$F_{6,47}$ = 5.75 , p = 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 1.69 , p = 0.1451
C)
Pore Filtered
$F_{6,47}$ = 3.32 , p = 0.0082
D)
Pore Unfiltered
$F_{6,47}$ = 9.44 , p < 0.0001
Fe (ug/L)
Month & Year
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20

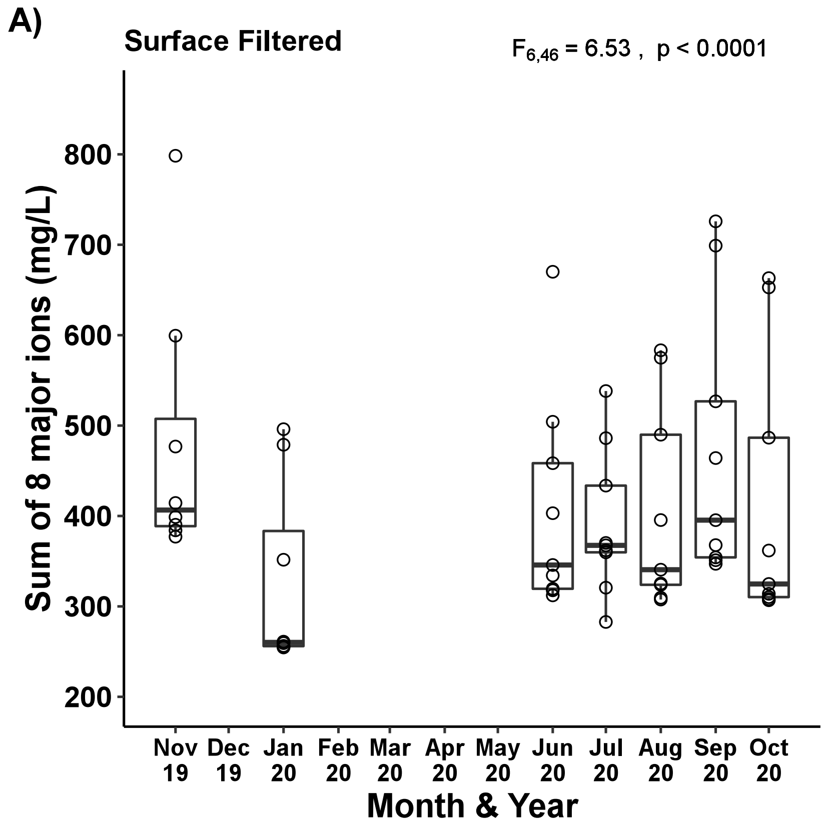
A)

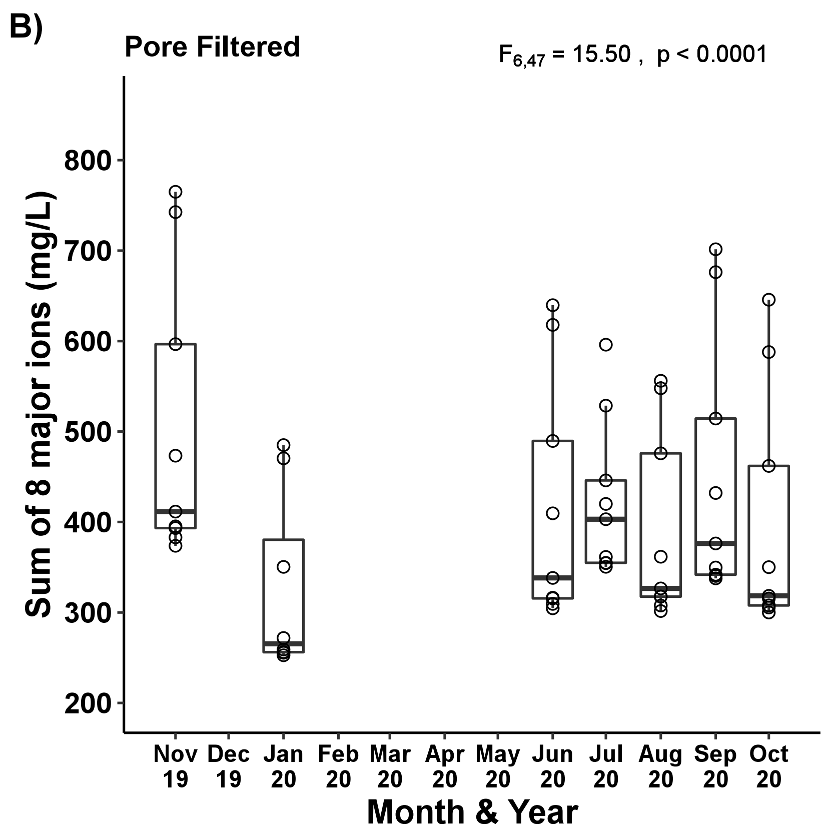

Surface Filtered
$F_{6,45}$ = 8.09 , p < 0.0001
HCO3 (mg/L)
250
200
150
100
50
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

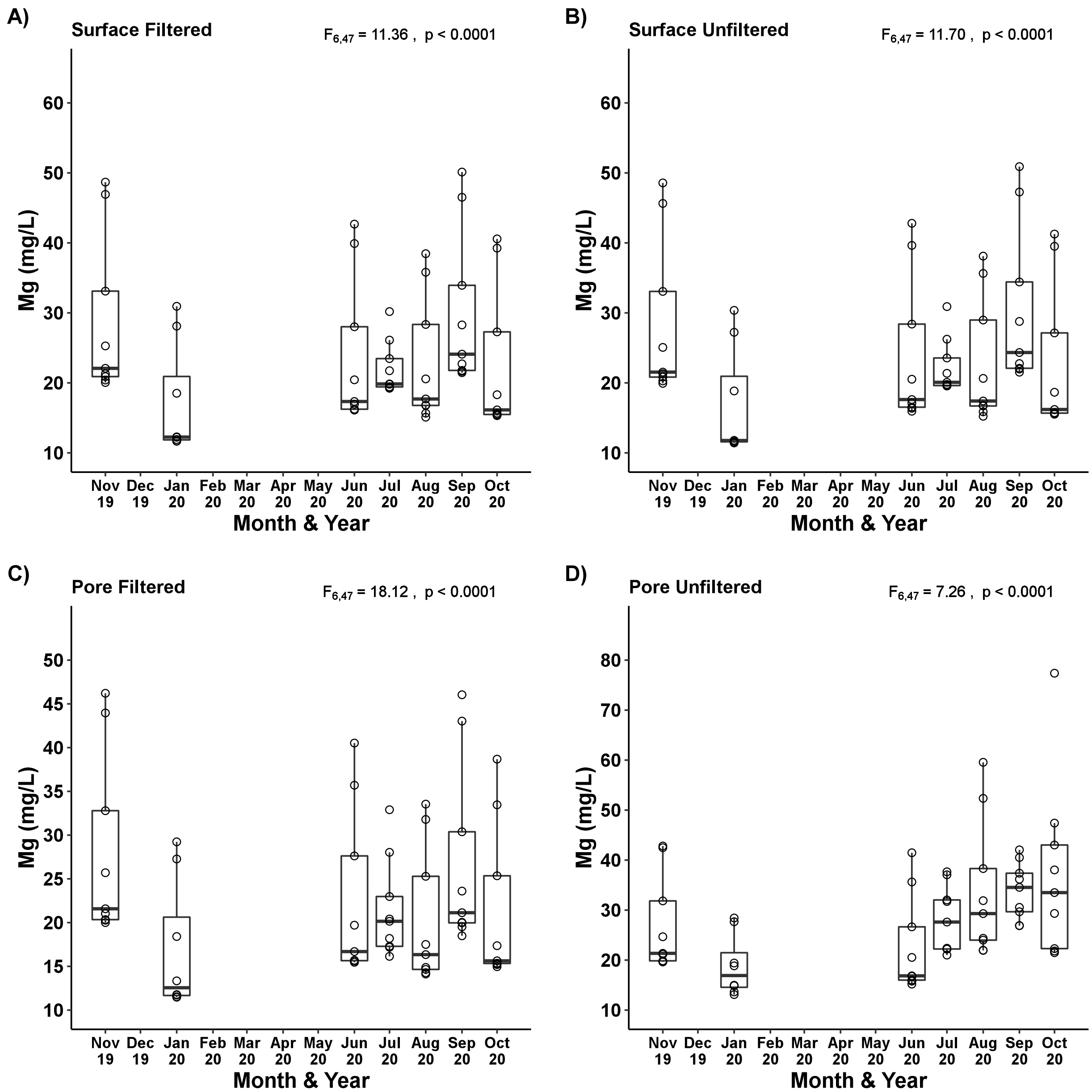
B)

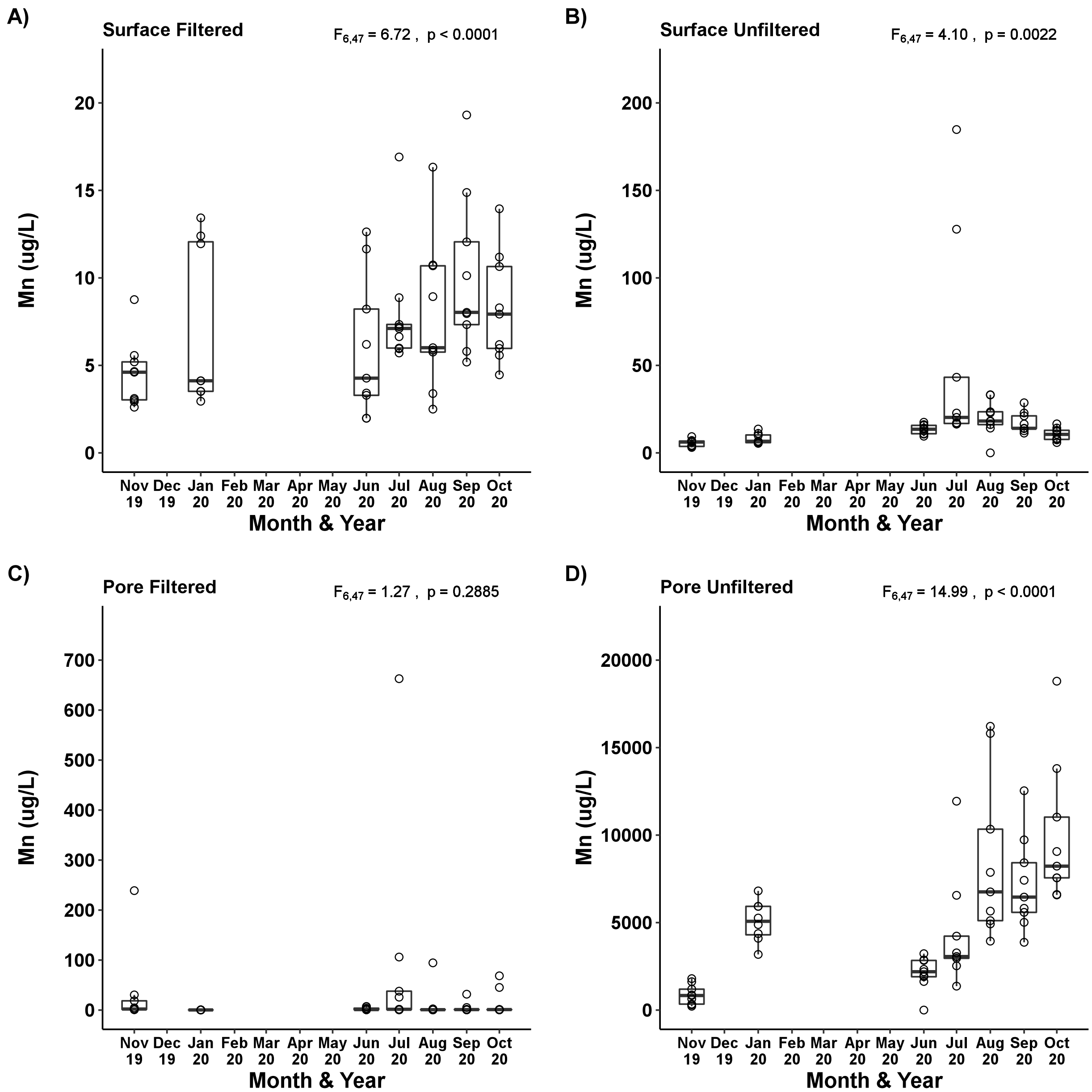

Pore Filtered
$F_{6,47}$ = 27.23 , p < 0.0001
HCO3 (mg/L)
260
240
220
200
180
160
140
120
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

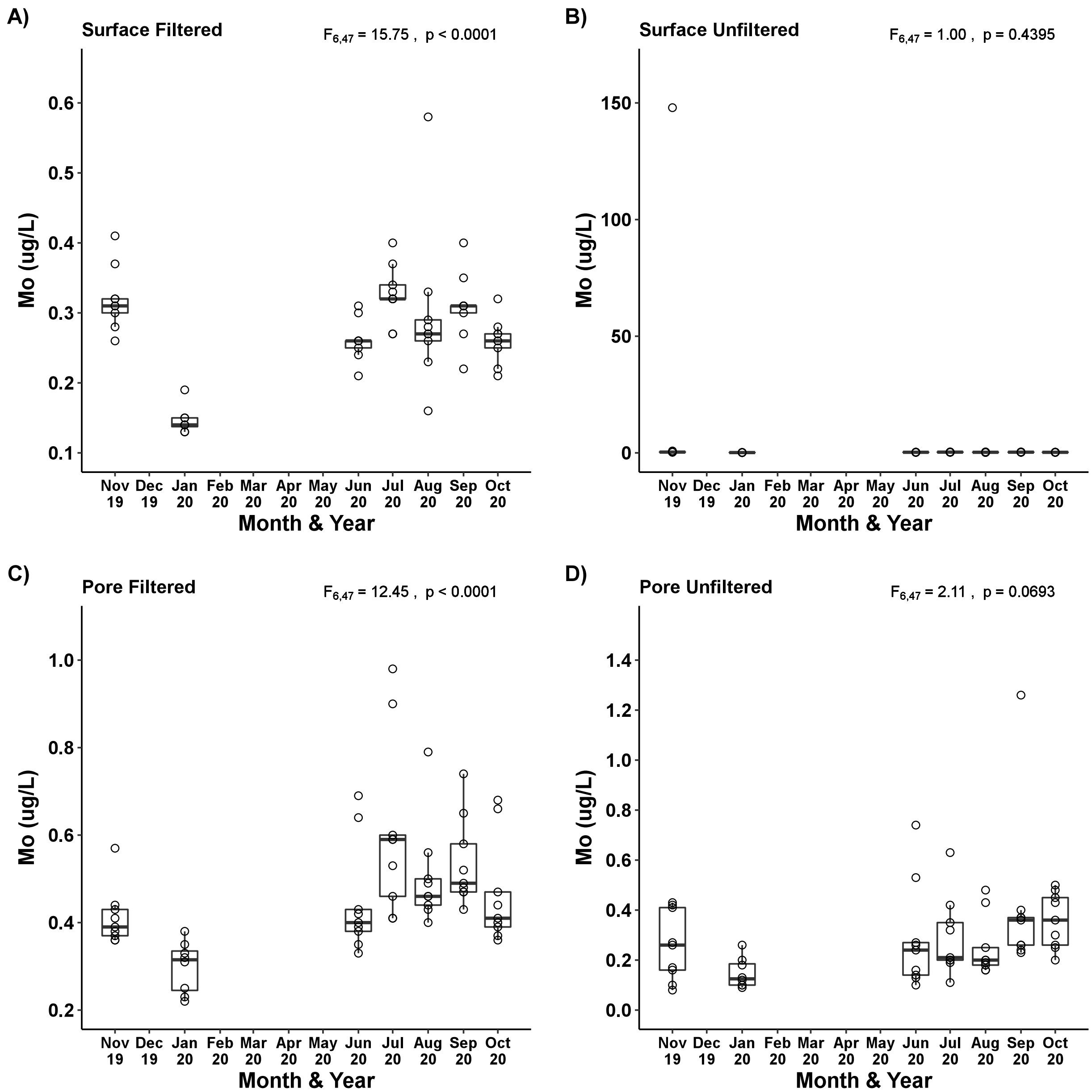

A)
Surface Filtered
F6,47 = 20.49 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 21.84 , p < 0.0001
C)
Pore Filtered
F6,47 = 23.94 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 23.14 , p < 0.0001
K (mg/L)
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year


A)
Surface Filtered
$F_{6,46} = 6.53$, $p < 0.0001$
Sum of 8 major ions (mg/L)
800
700
600
500
400
300
200
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

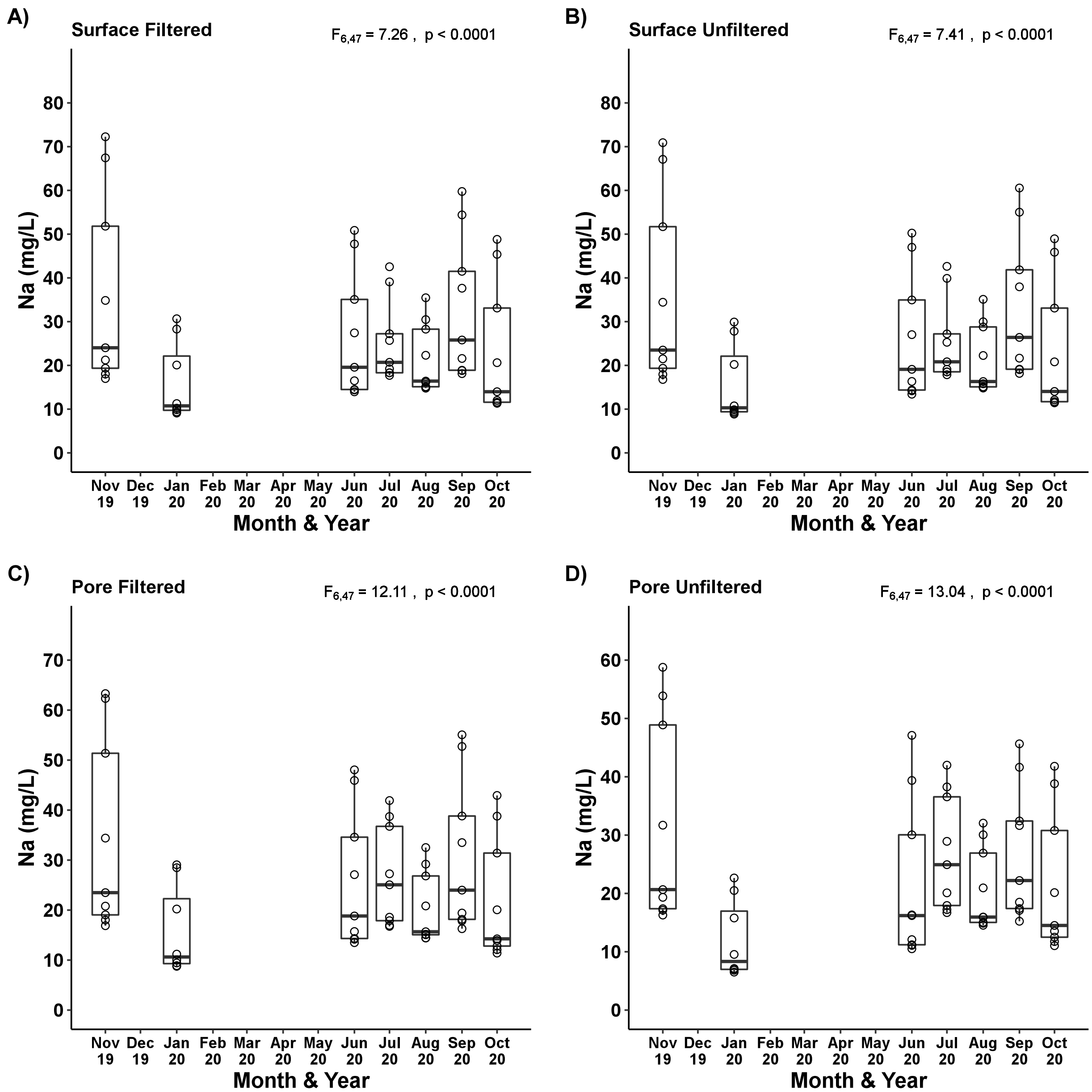

B)
Pore Filtered
$F_{6,47} = 15.50$, $p < 0.0001$
Sum of 8 major ions (mg/L)
800
700
600
500
400
300
200
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year


A)
Surface Filtered
$F_{6,47}$ = 11.36 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 11.70 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 18.12 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 7.26 , p < 0.0001
Mg (mg/L)
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

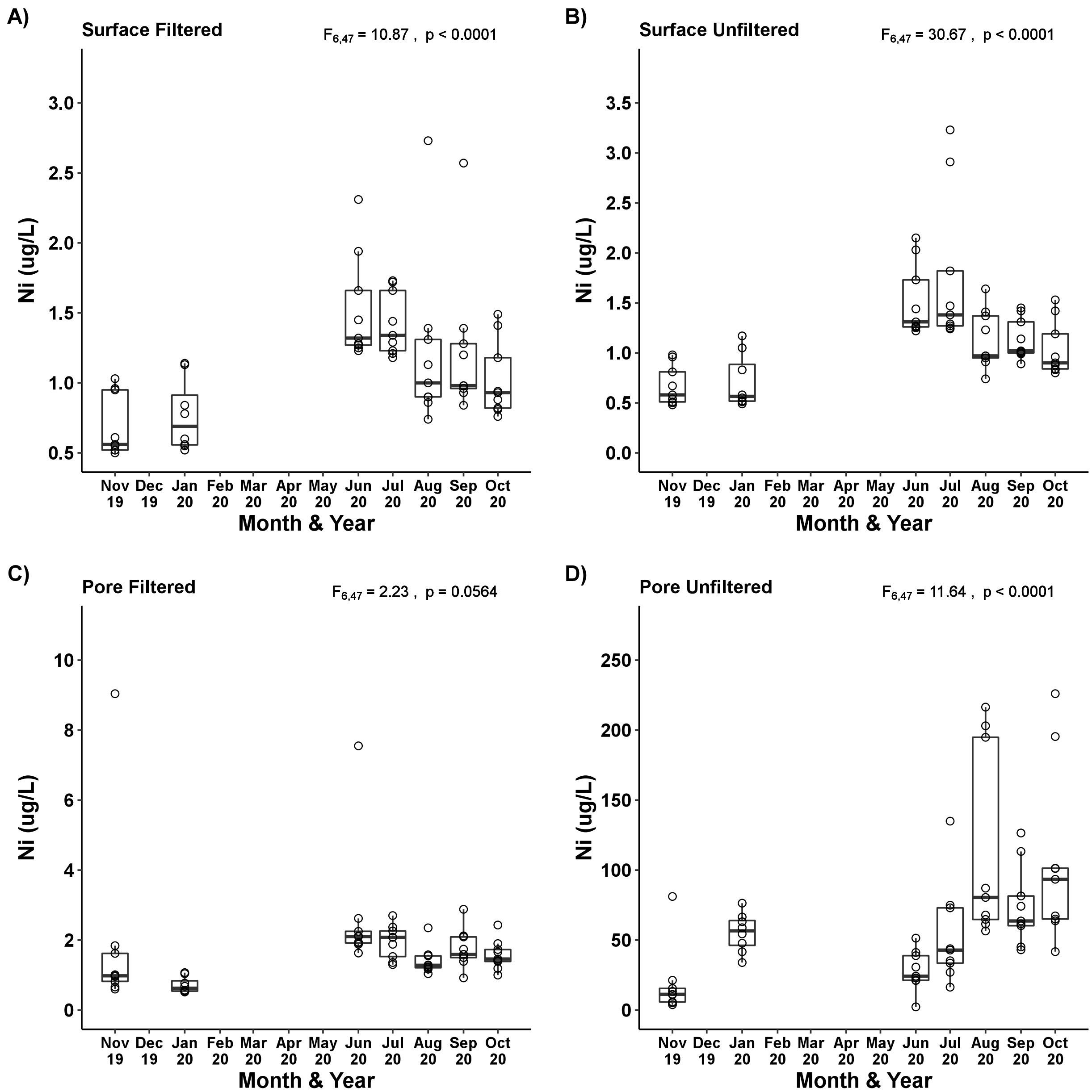

A)
Surface Filtered
F6,47 = 6.72 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 4.10 , p = 0.0022
C)
Pore Filtered
F6,47 = 1.27 , p = 0.2885
D)
Pore Unfiltered
F6,47 = 14.99 , p < 0.0001
Mn (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

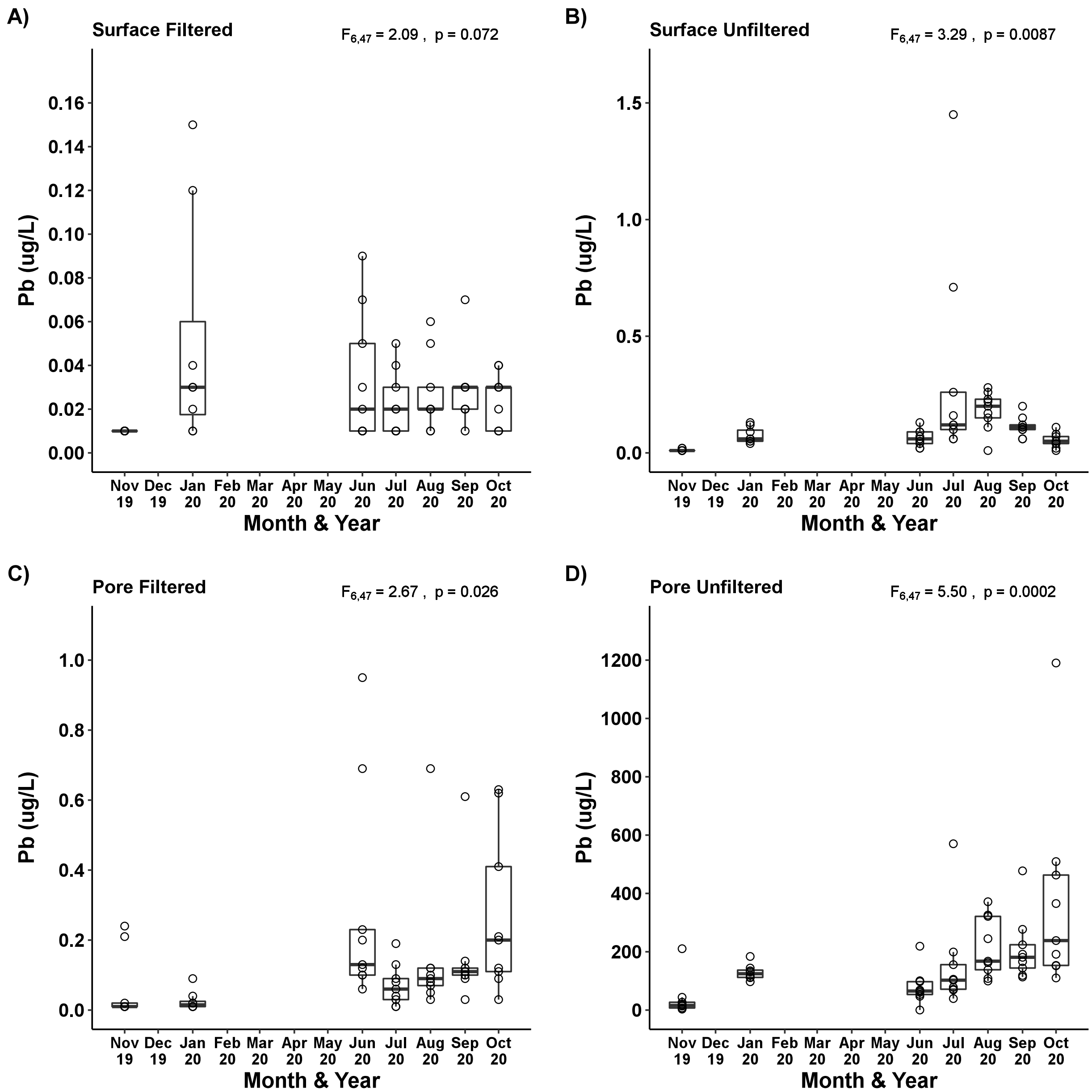


A)
Surface Filtered
F6,47 = 15.75 , p < 0.0001
Mo (ug/L)
Month & Year
B)
Surface Unfiltered
F6,47 = 1.00 , p = 0.4395
C)
Pore Filtered
F6,47 = 12.45 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 2.11 , p = 0.0693
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

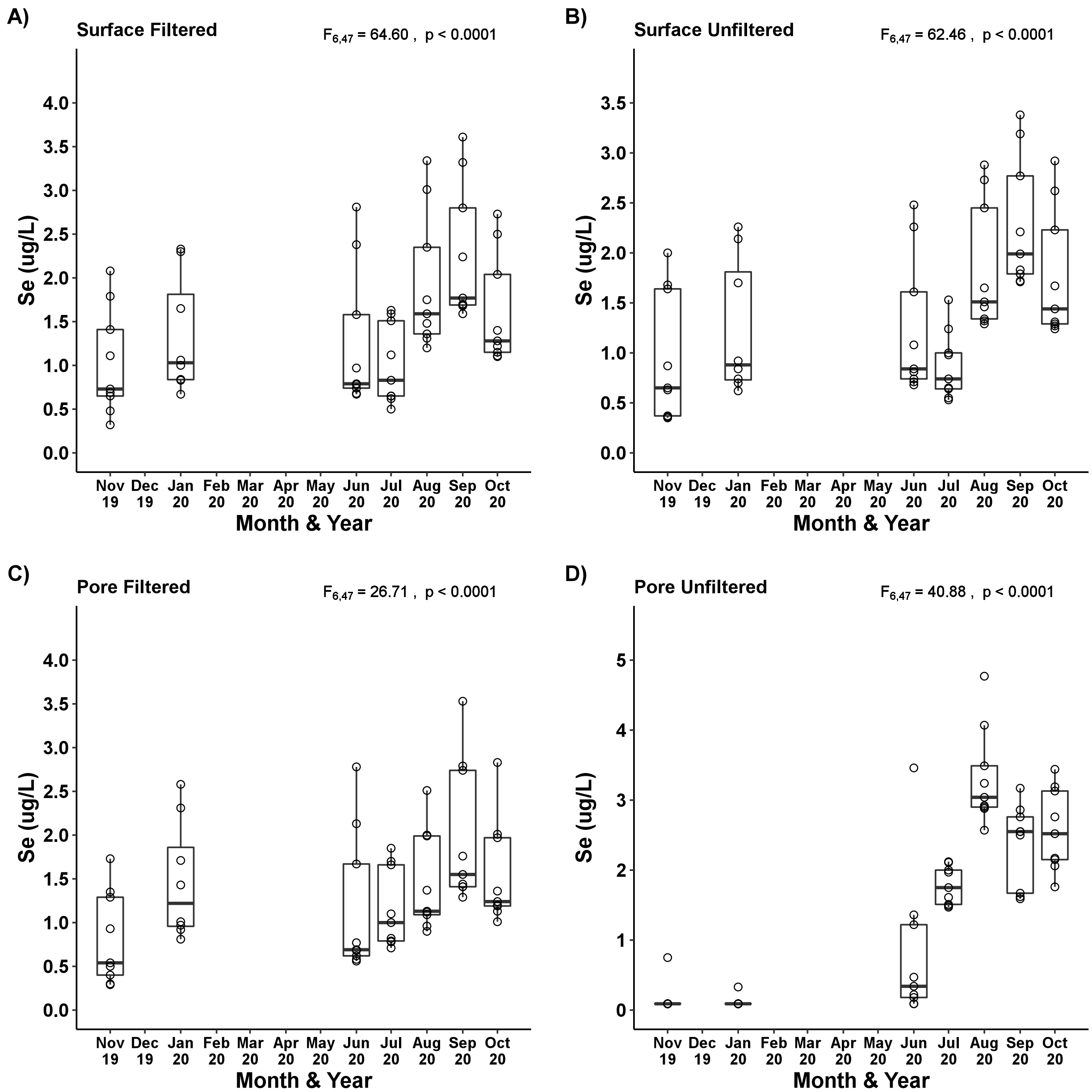


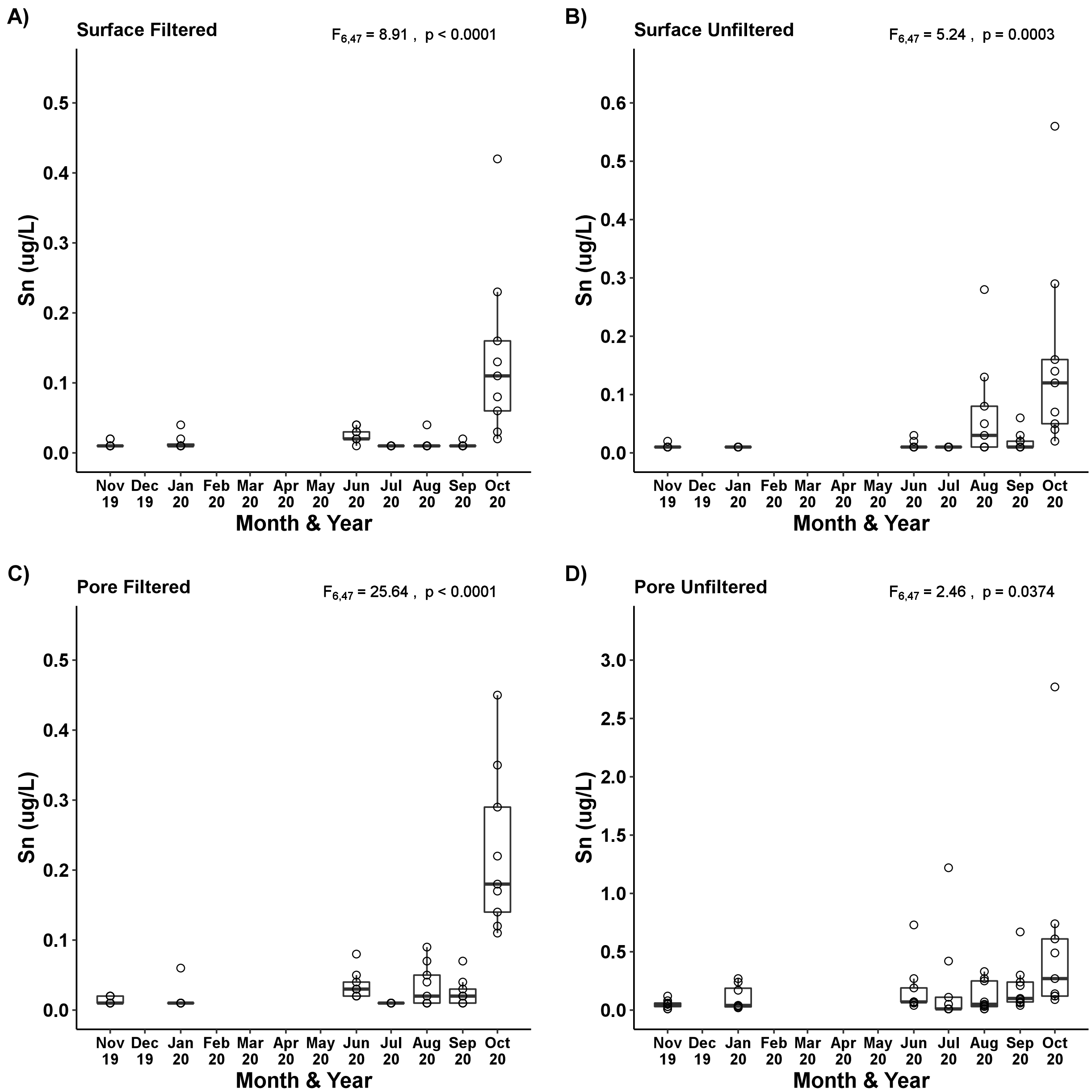
A)
Surface Filtered
F6,47 = 7.26 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 7.41 , p < 0.0001
C)
Pore Filtered
F6,47 = 12.11 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 13.04 , p < 0.0001
Na (mg/L)
Nov 19 Dec 19 Jan 20 Feb 20 Mar 20 Apr 20 May 20 Jun 20 Jul 20 Aug 20 Sep 20 Oct 20
Month & Year


A)
Surface Filtered
F6,47 = 10.87 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 30.67 , p < 0.0001
C)
Pore Filtered
F6,47 = 2.23 , p = 0.0564
D)
Pore Unfiltered
F6,47 = 11.64 , p < 0.0001
Ni (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20



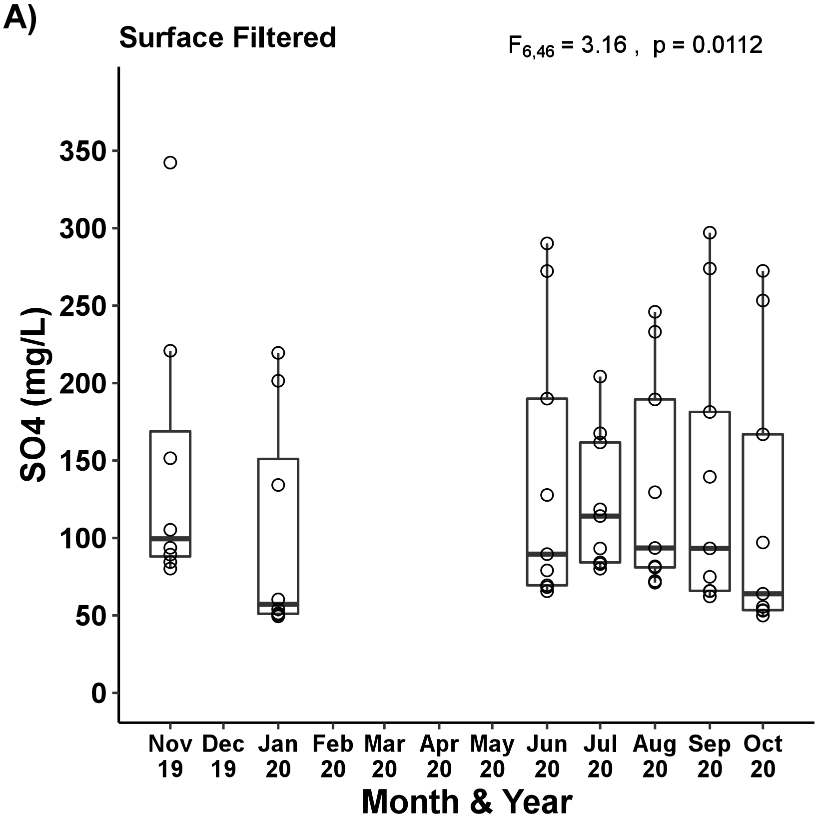
A)
Surface Filtered
F6,47 = 2.09 , p = 0.072
B)
Surface Unfiltered
F6,47 = 3.29 , p = 0.0087
C)
Pore Filtered
F6,47 = 2.67 , p = 0.026
D)
Pore Unfiltered
F6,47 = 5.50 , p = 0.0002
Pb (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20


A)
Surface Filtered
F6,47 = 64.60 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 62.46 , p < 0.0001
C)
Pore Filtered
F6,47 = 26.71 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 40.88 , p < 0.0001
Se (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

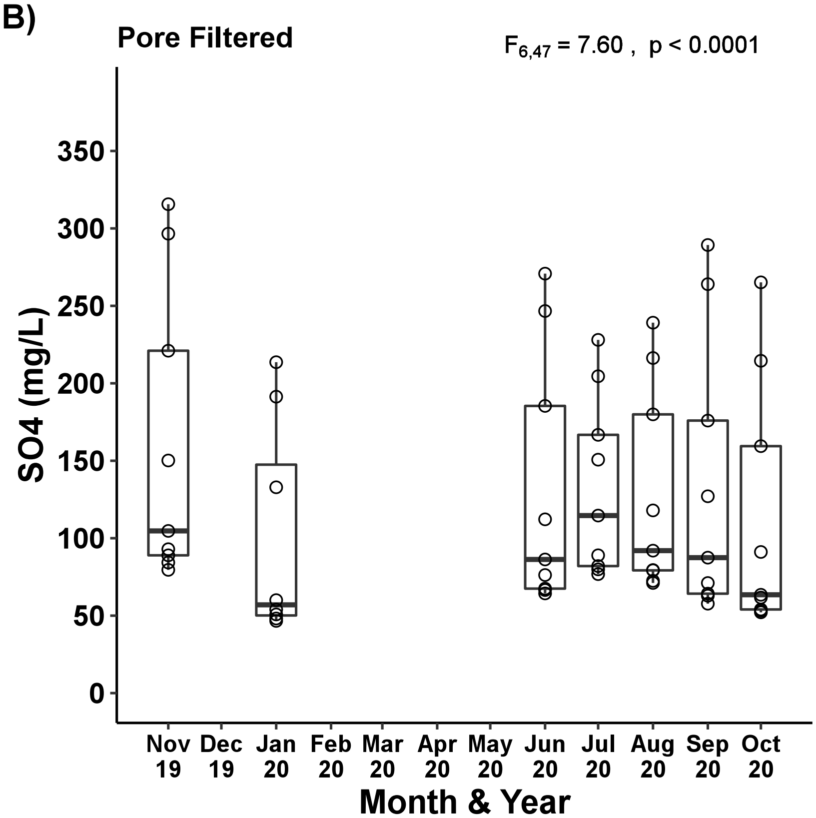


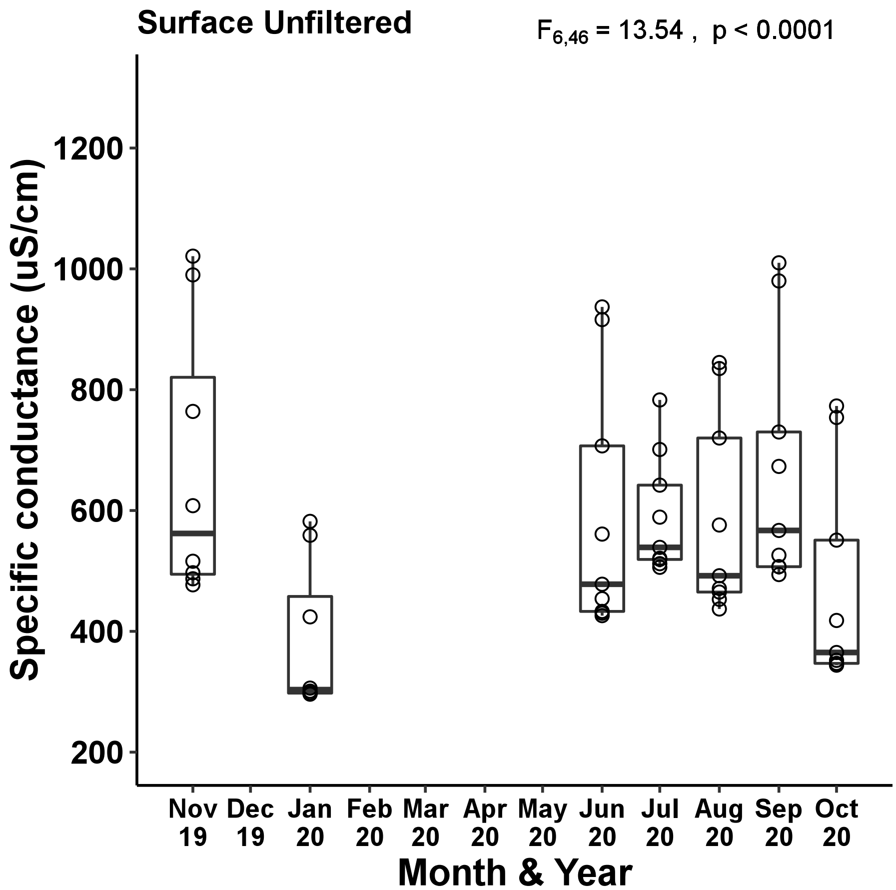
A)
Surface Filtered
F6,47 = 8.91 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 5.24 , p = 0.0003
C)
Pore Filtered
F6,47 = 25.64 , p < 0.0001
D)
Pore Unfiltered
F6,47 = 2.46 , p = 0.0374
Sn (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

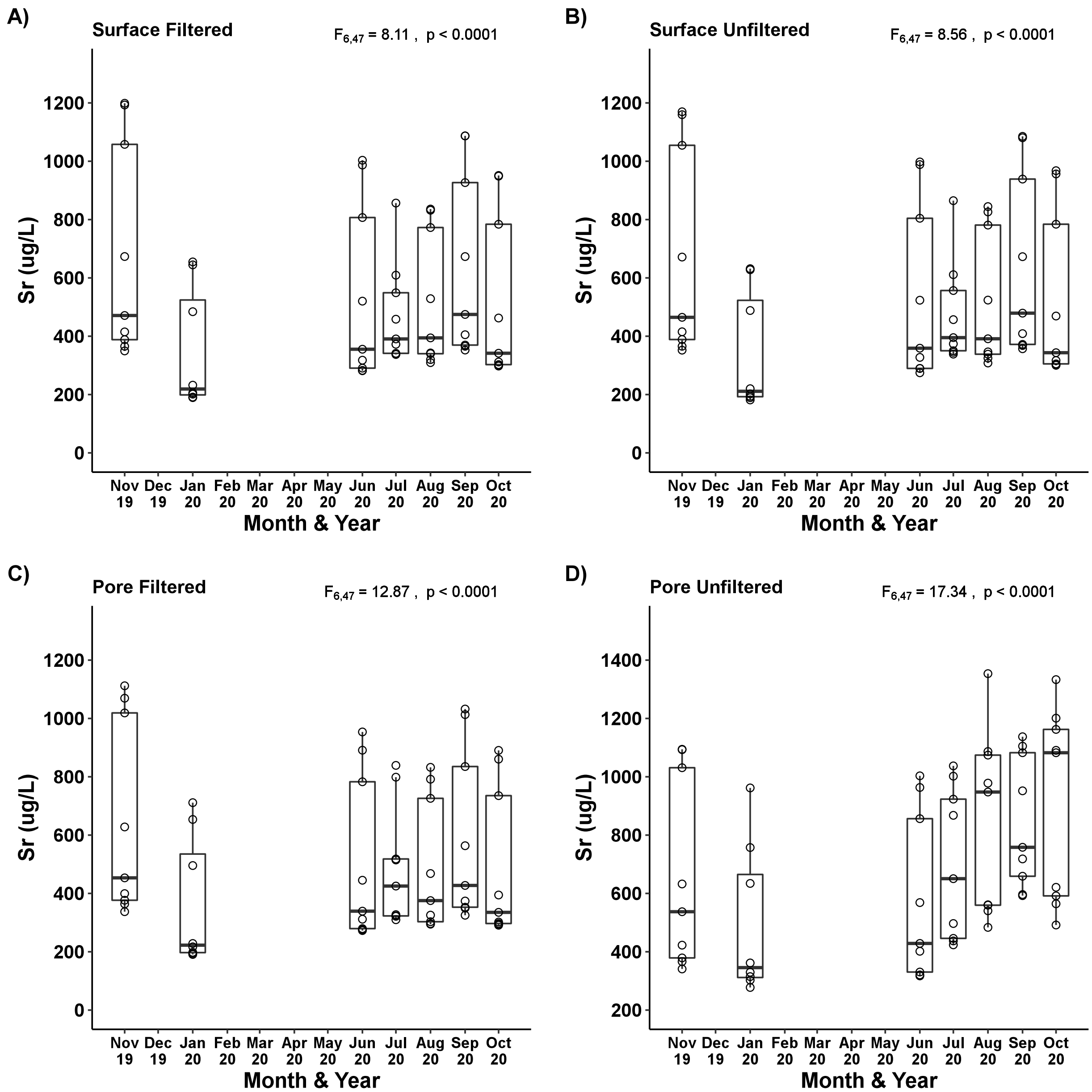
A)

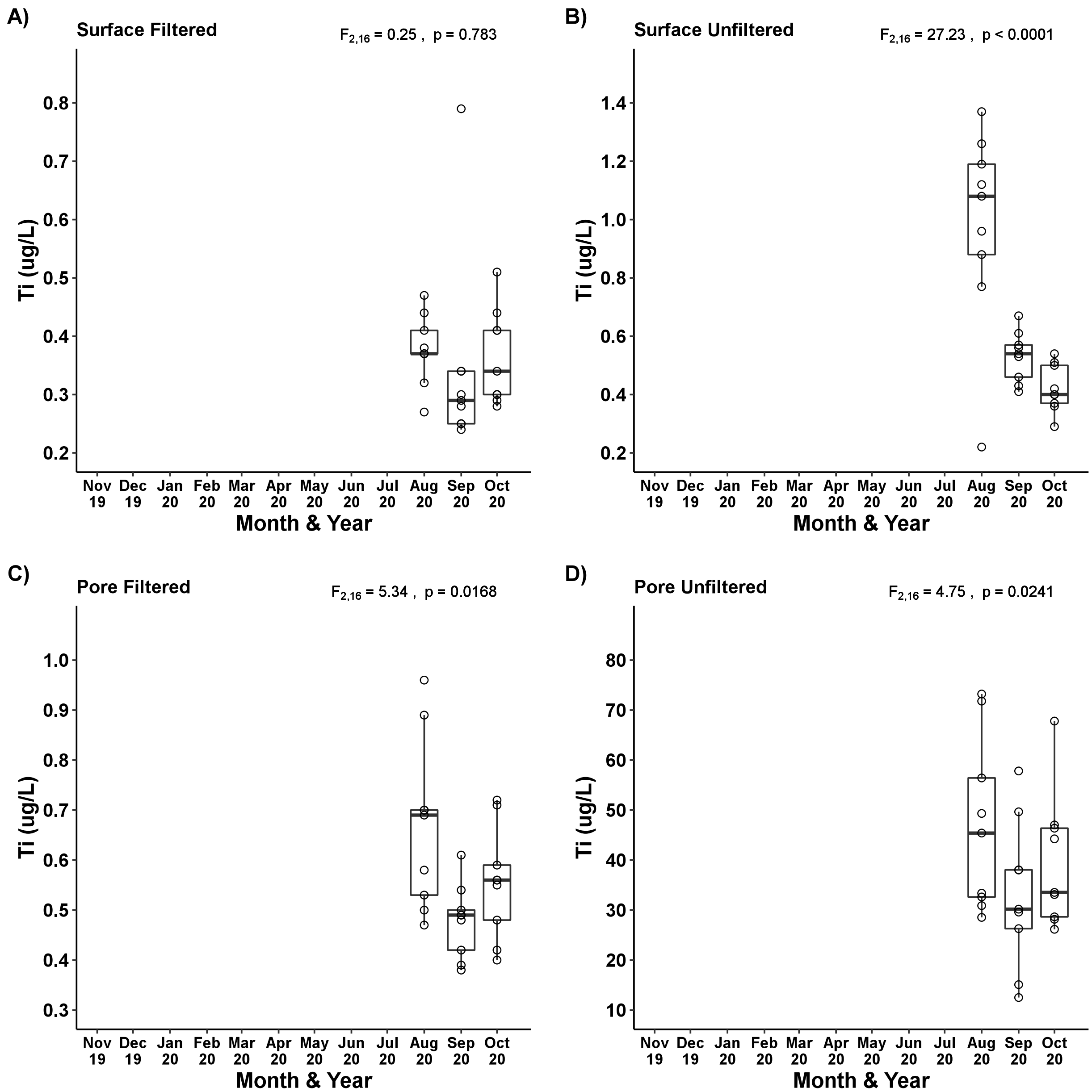

Surface Filtered
$F_{6,46}$ = 3.16 , p = 0.0112
SO4 (mg/L)
0
50
100
150
200
250
300
350
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

B)

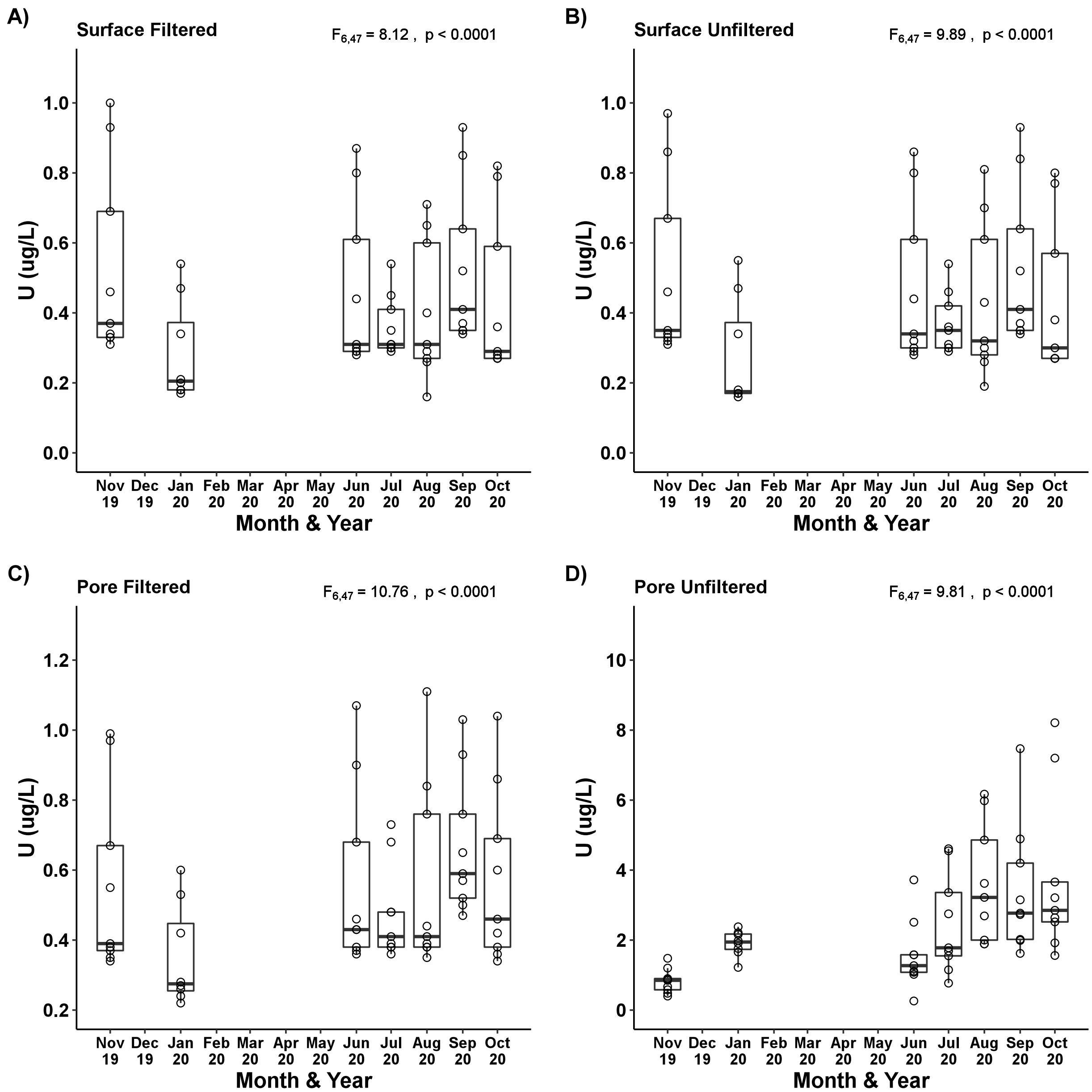

Pore Filtered
$F_{6,47}$ = 7.60 , p < 0.0001
SO4 (mg/L)
0
50
100
150
200
250
300
350
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

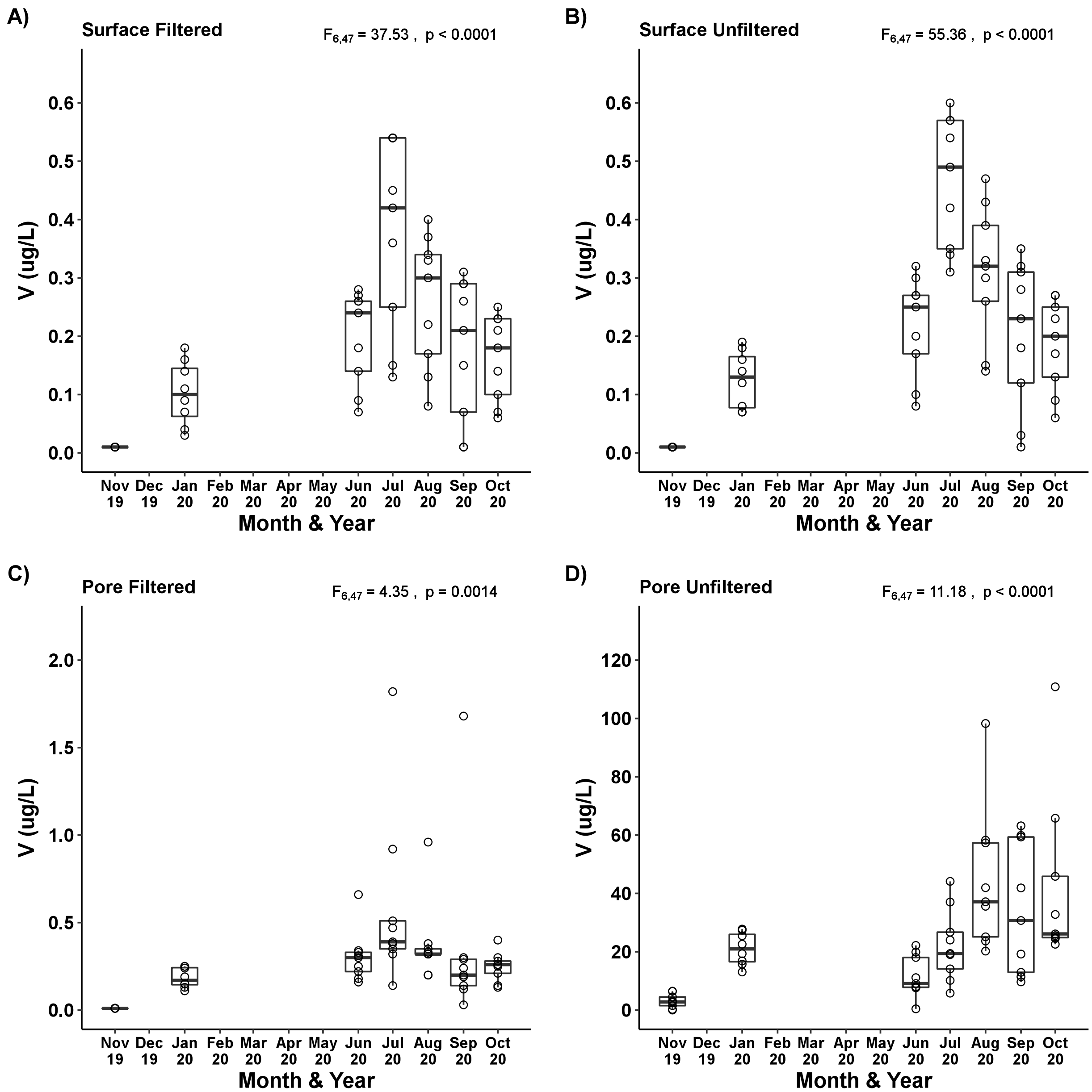

Surface Unfiltered
F6,46 = 13.54 , p < 0.0001
Specific conductance (uS/cm)
1200
1000
800
600
400
200
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20
Month & Year

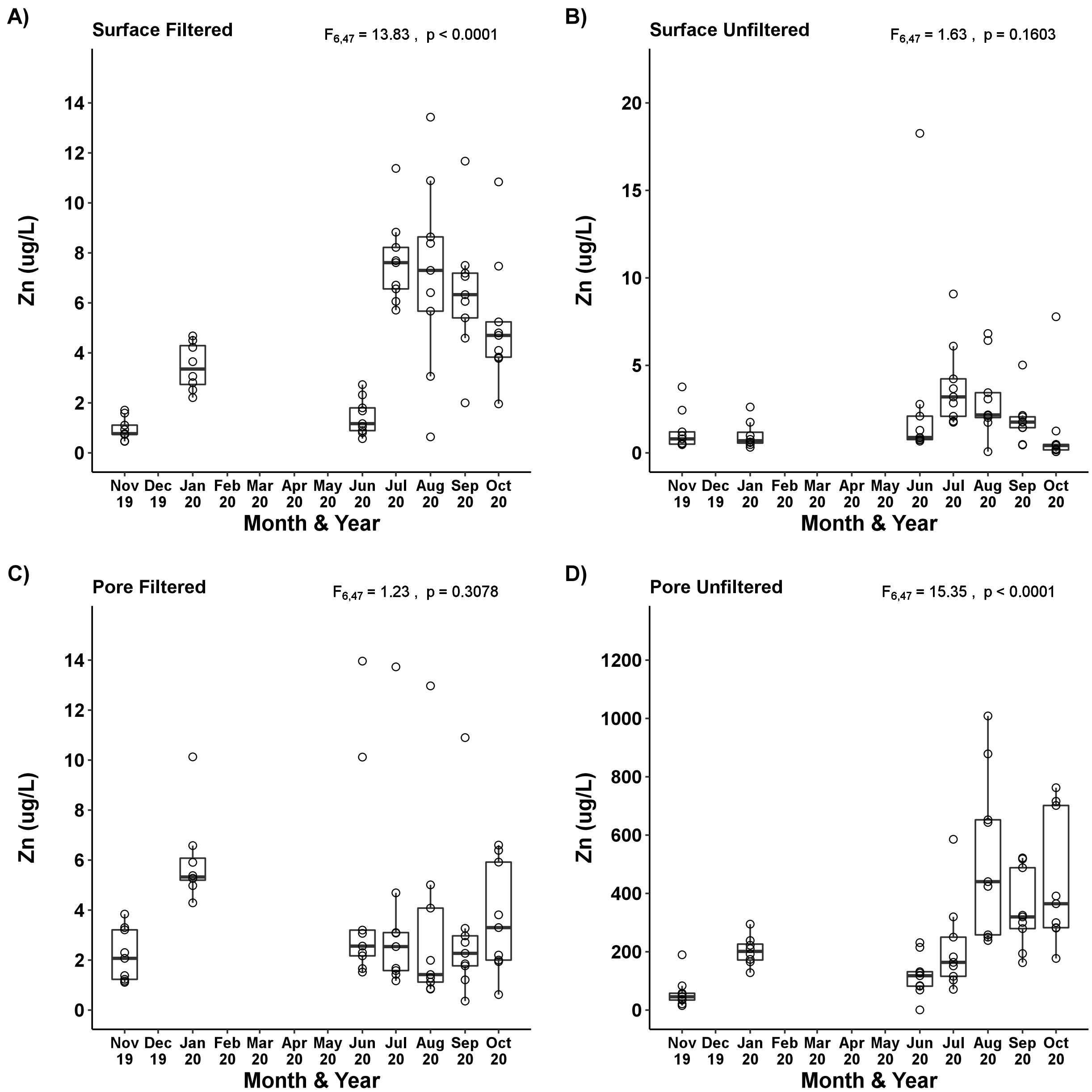

A)
Surface Filtered
$F_{6,47}$ = 8.11 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 8.56 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 12.87 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 17.34 , p < 0.0001
Sr (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20



A)
Surface Filtered
$F_{2,16}$ = 0.25 , p = 0.783
Ti (ug/L)
Month & Year
B)
Surface Unfiltered
$F_{2,16}$ = 27.23 , p < 0.0001
Ti (ug/L)
Month & Year
C)
Pore Filtered
$F_{2,16}$ = 5.34 , p = 0.0168
Ti (ug/L)
Month & Year
D)
Pore Unfiltered
$F_{2,16}$ = 4.75 , p = 0.0241
Ti (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

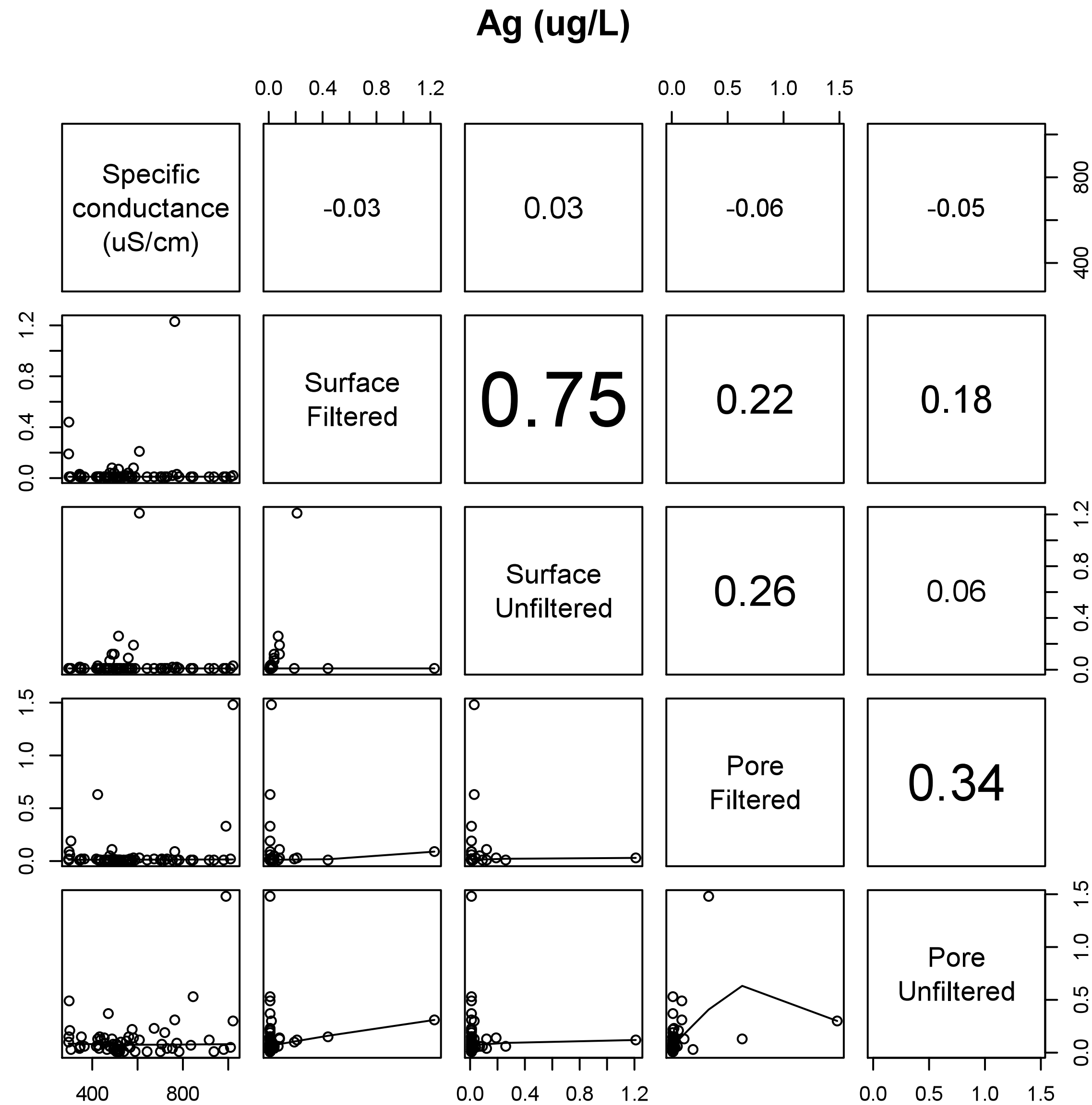

A)
Surface Filtered
$F_{6,47}$ = 8.12 , p < 0.0001
B)
Surface Unfiltered
$F_{6,47}$ = 9.89 , p < 0.0001
C)
Pore Filtered
$F_{6,47}$ = 10.76 , p < 0.0001
D)
Pore Unfiltered
$F_{6,47}$ = 9.81 , p < 0.0001
U (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

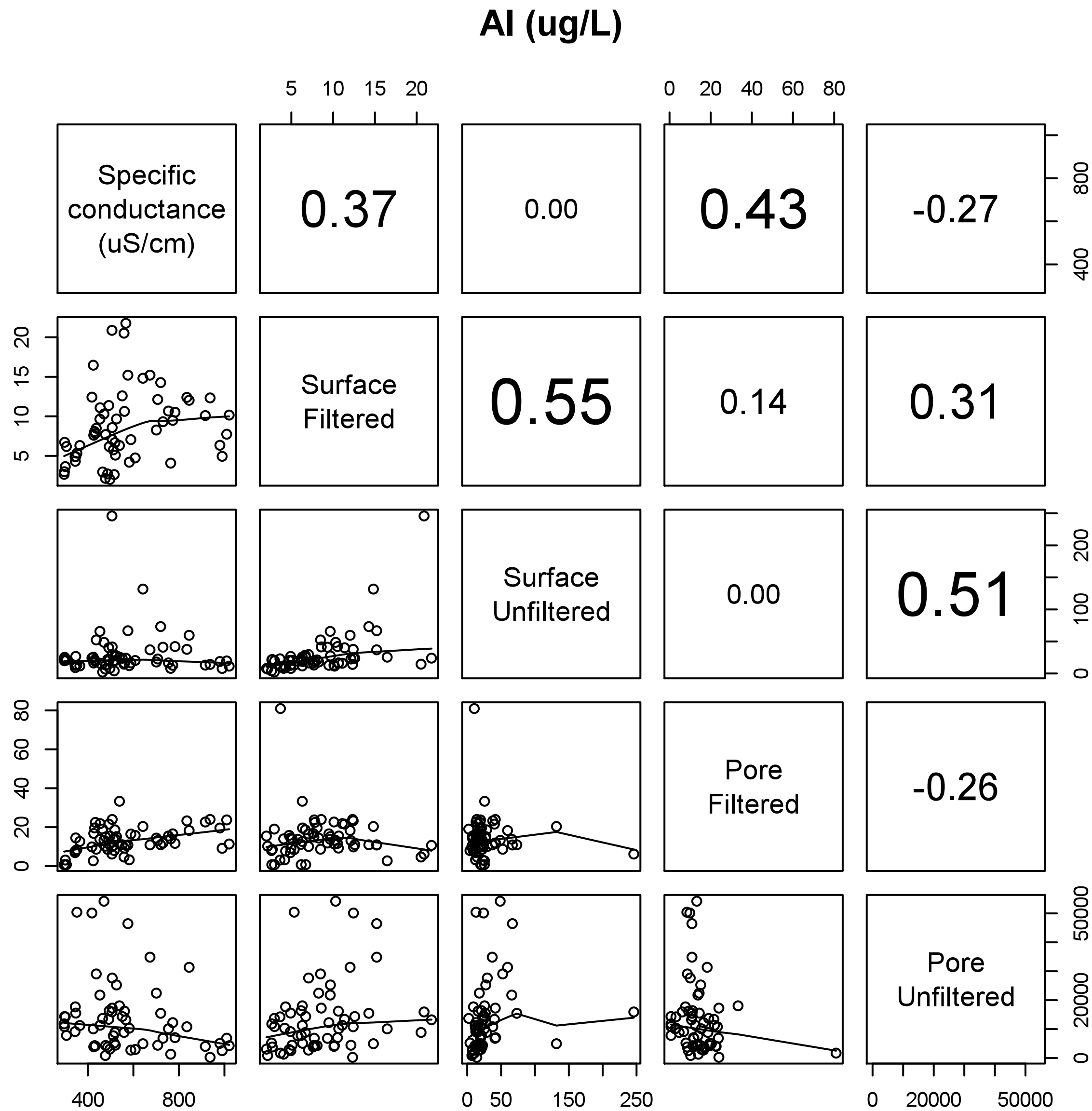

A)
Surface Filtered
F6,47 = 37.53 , p < 0.0001
V (ug/L)
Month & Year
B)
Surface Unfiltered
F6,47 = 55.36 , p < 0.0001
V (ug/L)
Month & Year
C)
Pore Filtered
F6,47 = 4.35 , p = 0.0014
V (ug/L)
Month & Year
D)
Pore Unfiltered
F6,47 = 11.18 , p < 0.0001
V (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

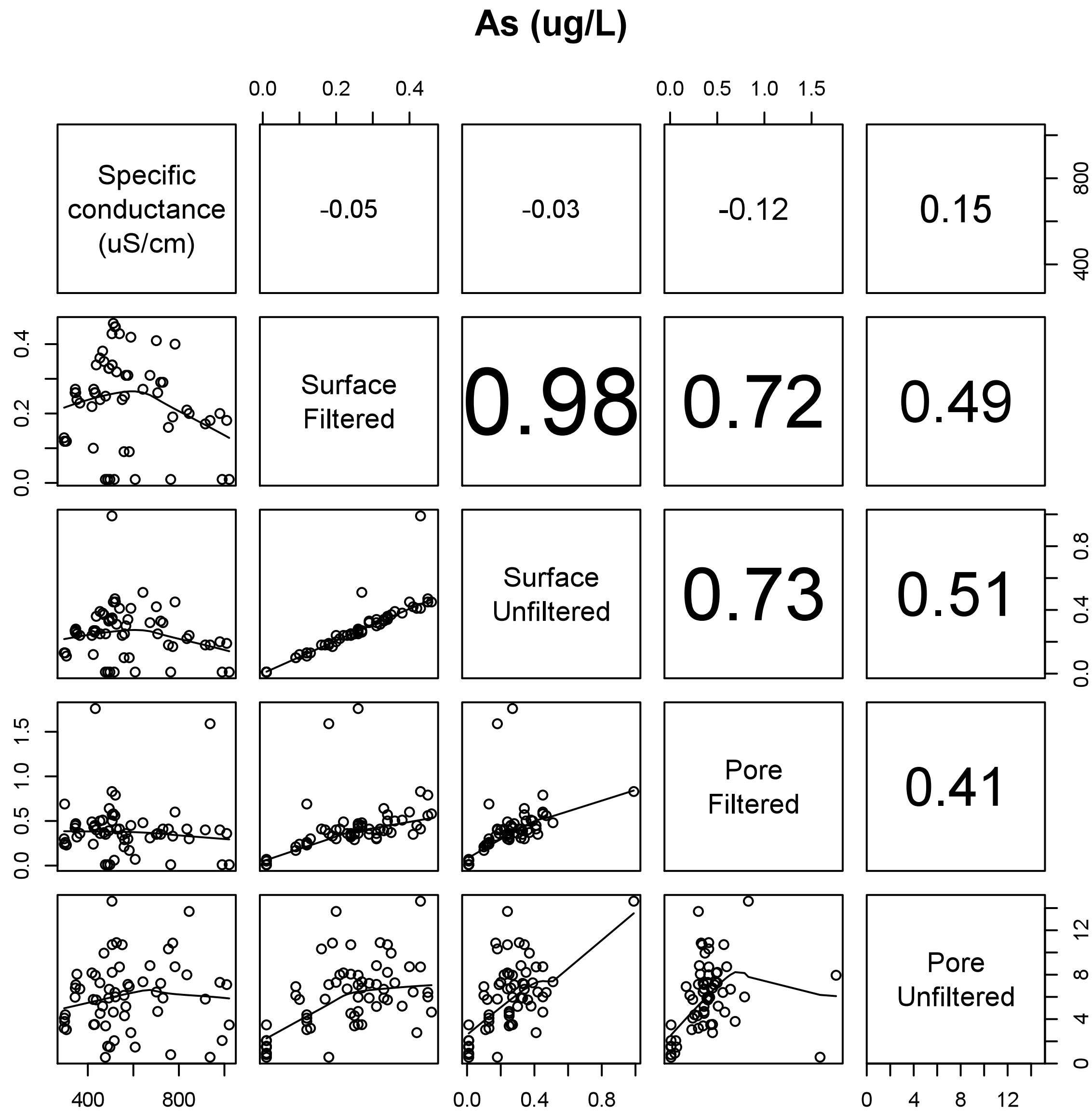

A)
Surface Filtered
F6,47 = 13.83 , p < 0.0001
B)
Surface Unfiltered
F6,47 = 1.63 , p = 0.1603
C)
Pore Filtered
F6,47 = 1.23 , p = 0.3078
D)
Pore Unfiltered
F6,47 = 15.35 , p < 0.0001
Zn (ug/L)
Month & Year
Nov 19
Dec 19
Jan 20
Feb 20
Mar 20
Apr 20
May 20
Jun 20
Jul 20
Aug 20
Sep 20
Oct 20

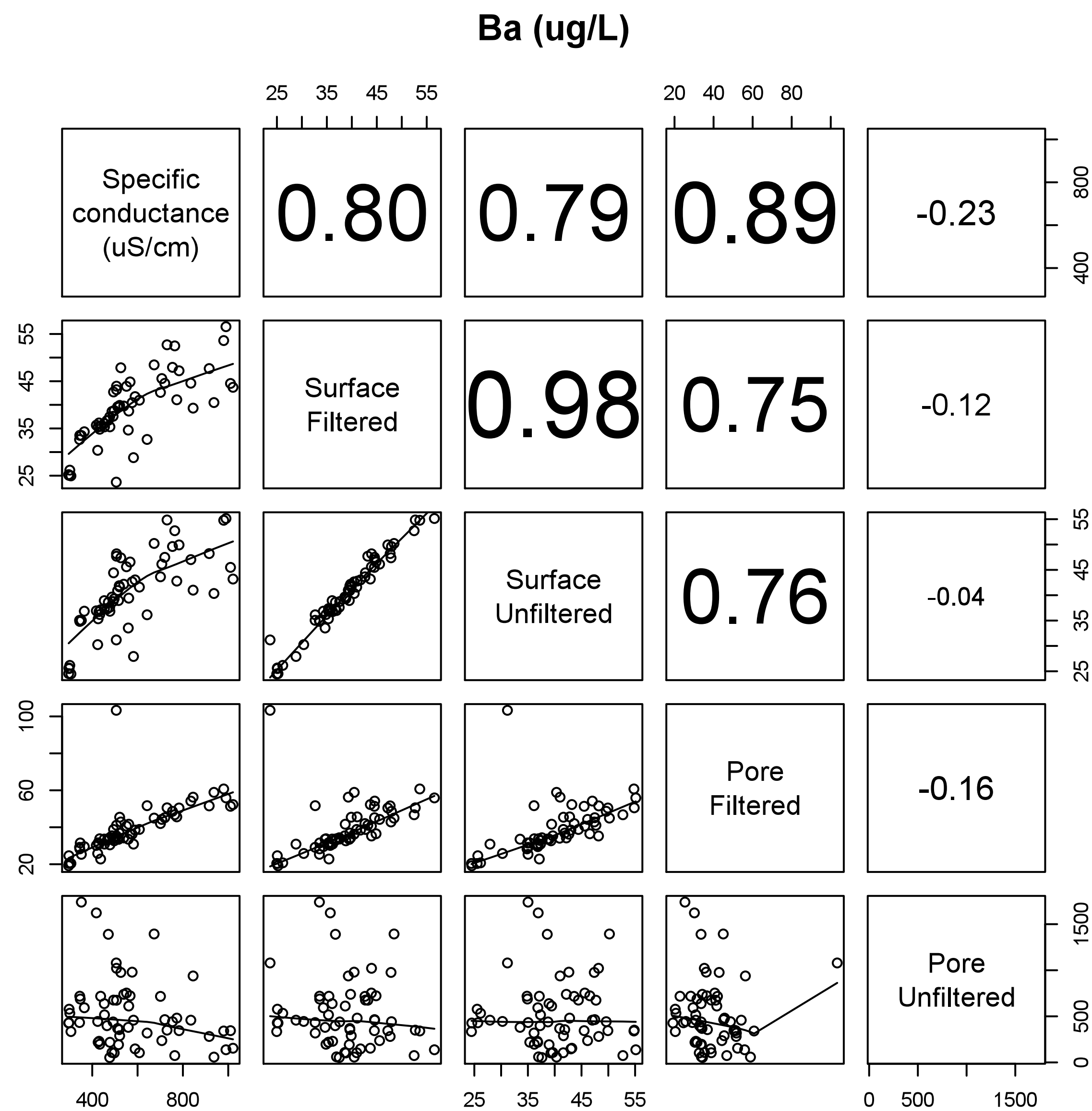
APPENDIX E – SCATTERPLOT MATRIX OF ION CONCENTRATION BY SAMPLE-TYPE PAIR

These scatterplots show overall relationships between surface water and pore water ion concentrations. Specific conductance of unfiltered surface water is included, as an indicator of water-column aggregate ion concentration. Scatterplots include LOWESS smoothed line and pairwise Spearman rank correlation coefficients (larger numerals correspond to larger coefficients).

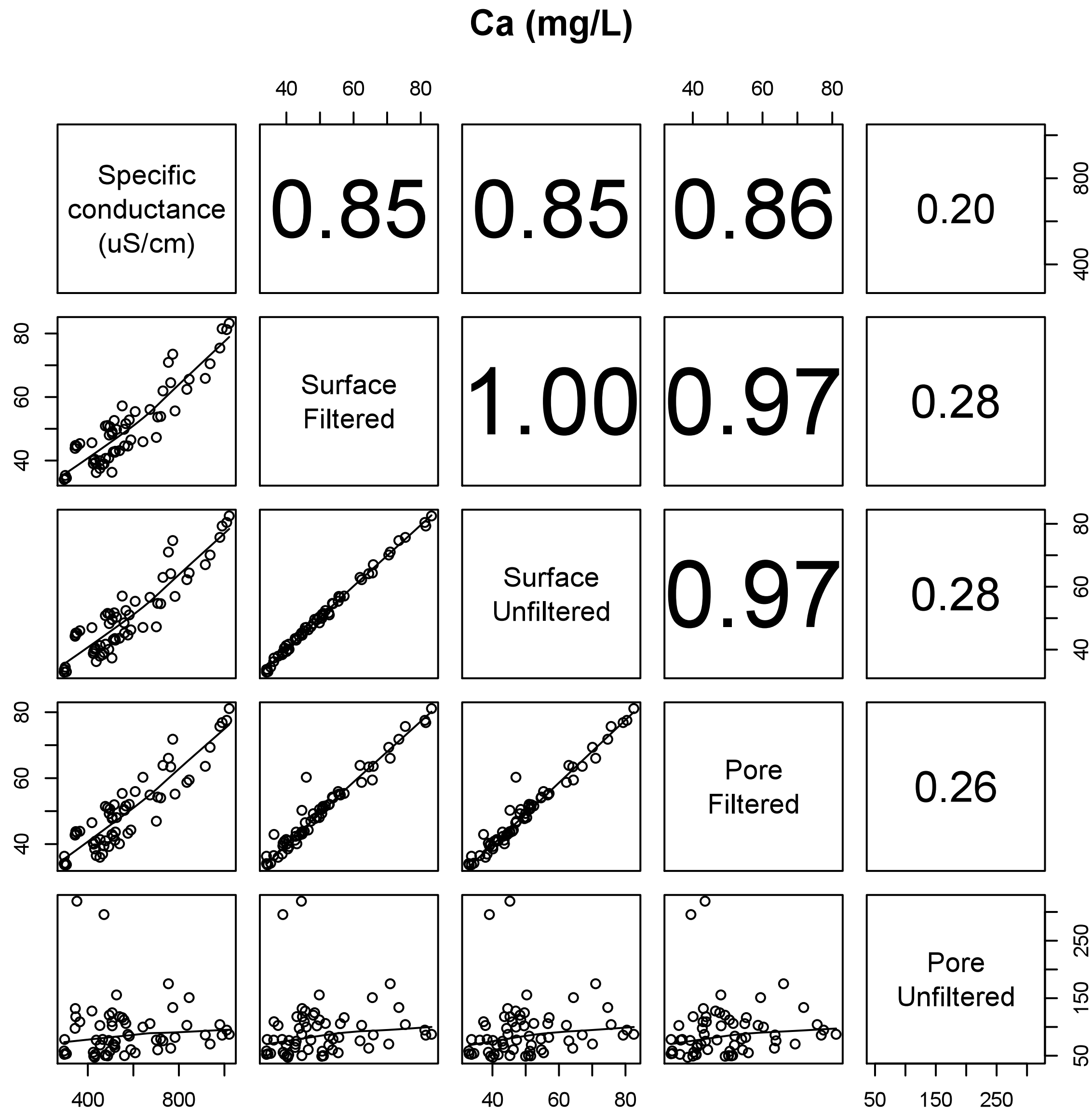

Ag (ug/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
-0.03
0.03
-0.06
-0.05
0.75
0.22
0.18
0.26
0.06
0.34


Al (ug/L)
Specific conductance (uS/cm)
0.37
0.00
0.43
-0.27
Surface Filtered
0.55
0.14
0.31
Surface Unfiltered
0.00
0.51
Pore Filtered
-0.26
Pore Unfiltered
5 10 15 20
0 20 40 60 80
400 800
0 50 150 250
0 20000 50000
0 100 200
0 20 40 60 80
0 20000 50000

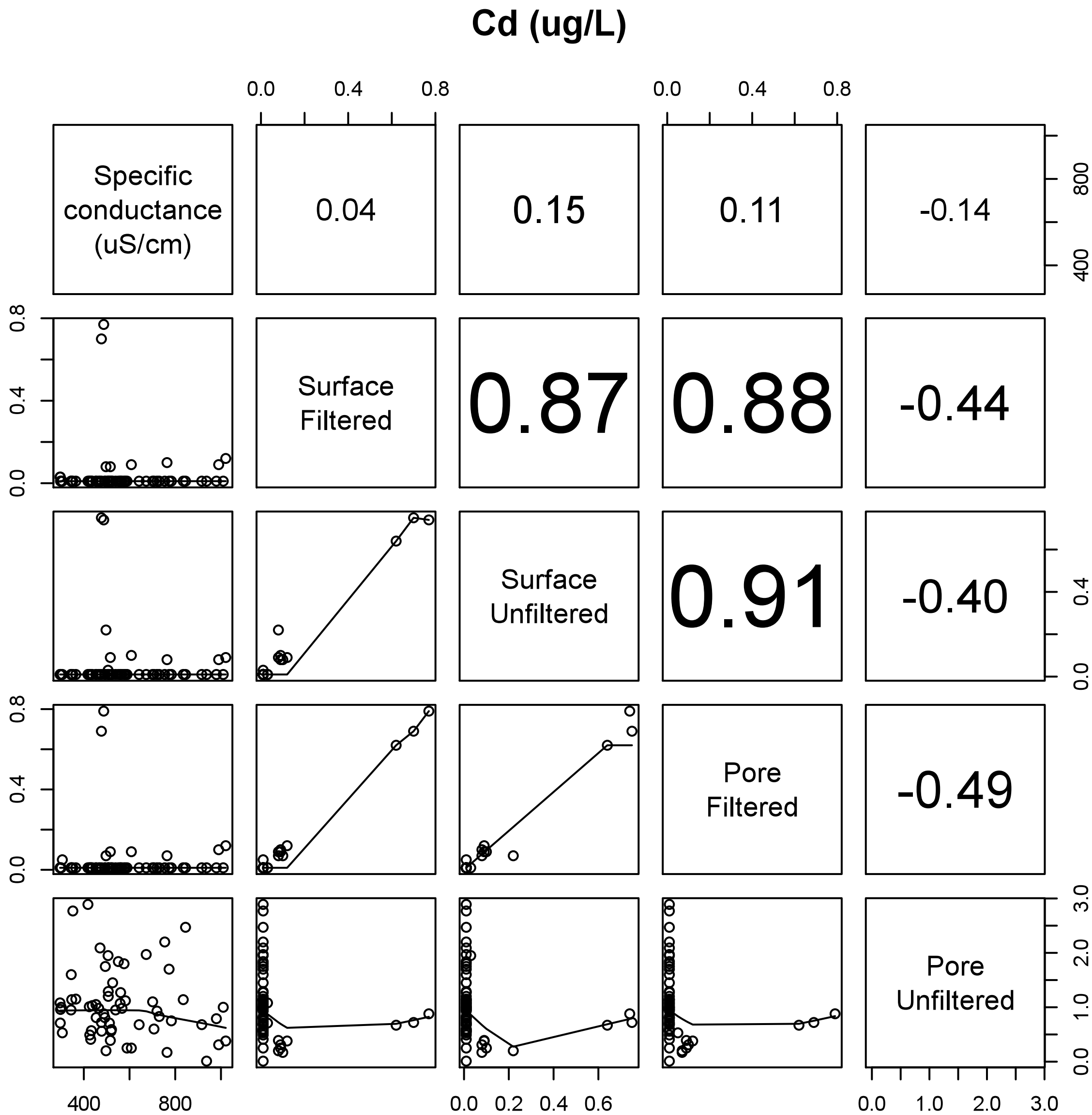

As (ug/L)
Specific conductance (uS/cm)
-0.05
-0.03
-0.12
0.15
Surface Filtered
0.98
0.72
0.49
Surface Unfiltered
0.73
0.51
Pore Filtered
0.41
Pore Unfiltered

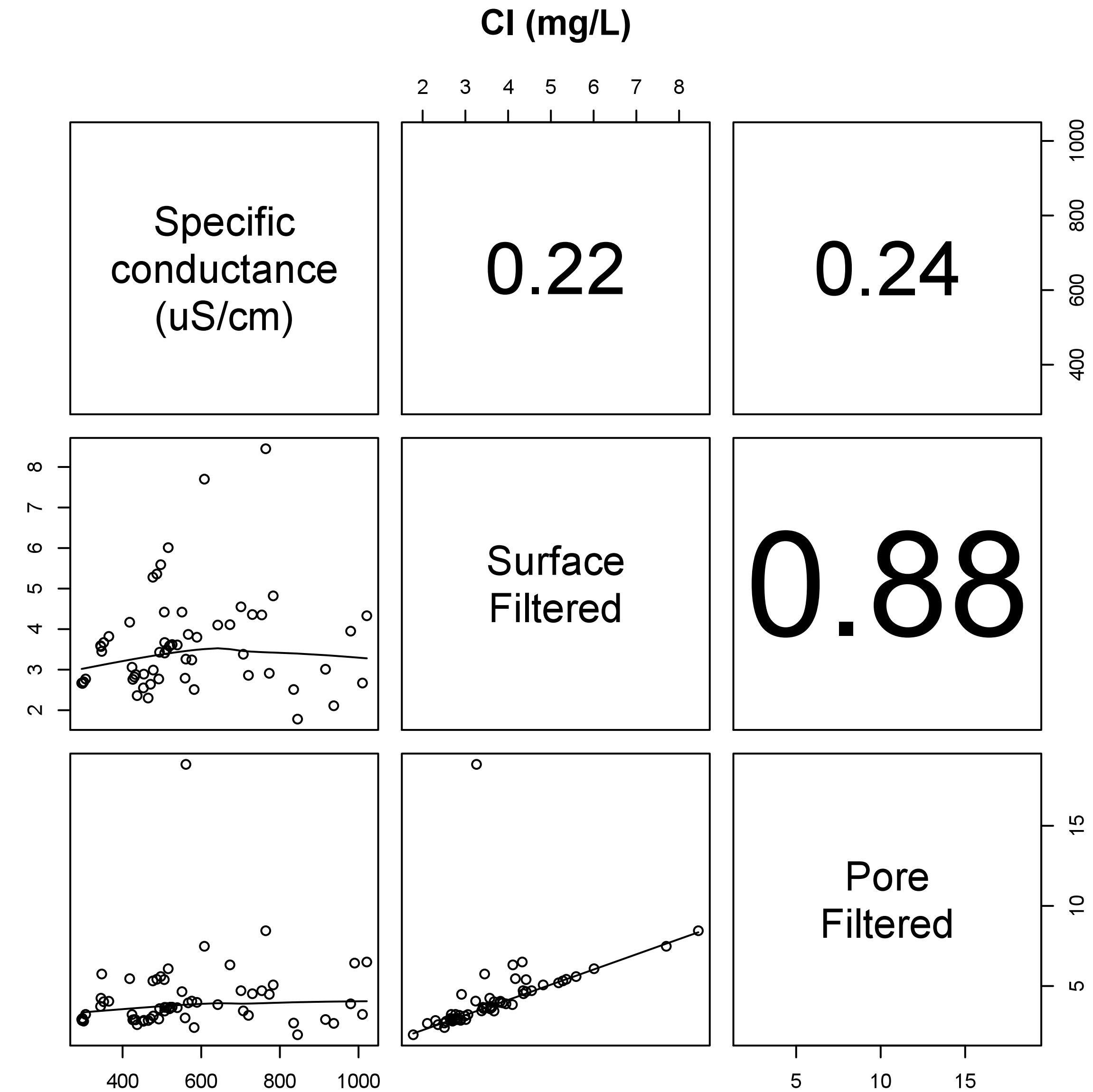


Ba (ug/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.80
0.79
0.89
-0.23
0.98
0.75
-0.12
0.76
-0.04
-0.16

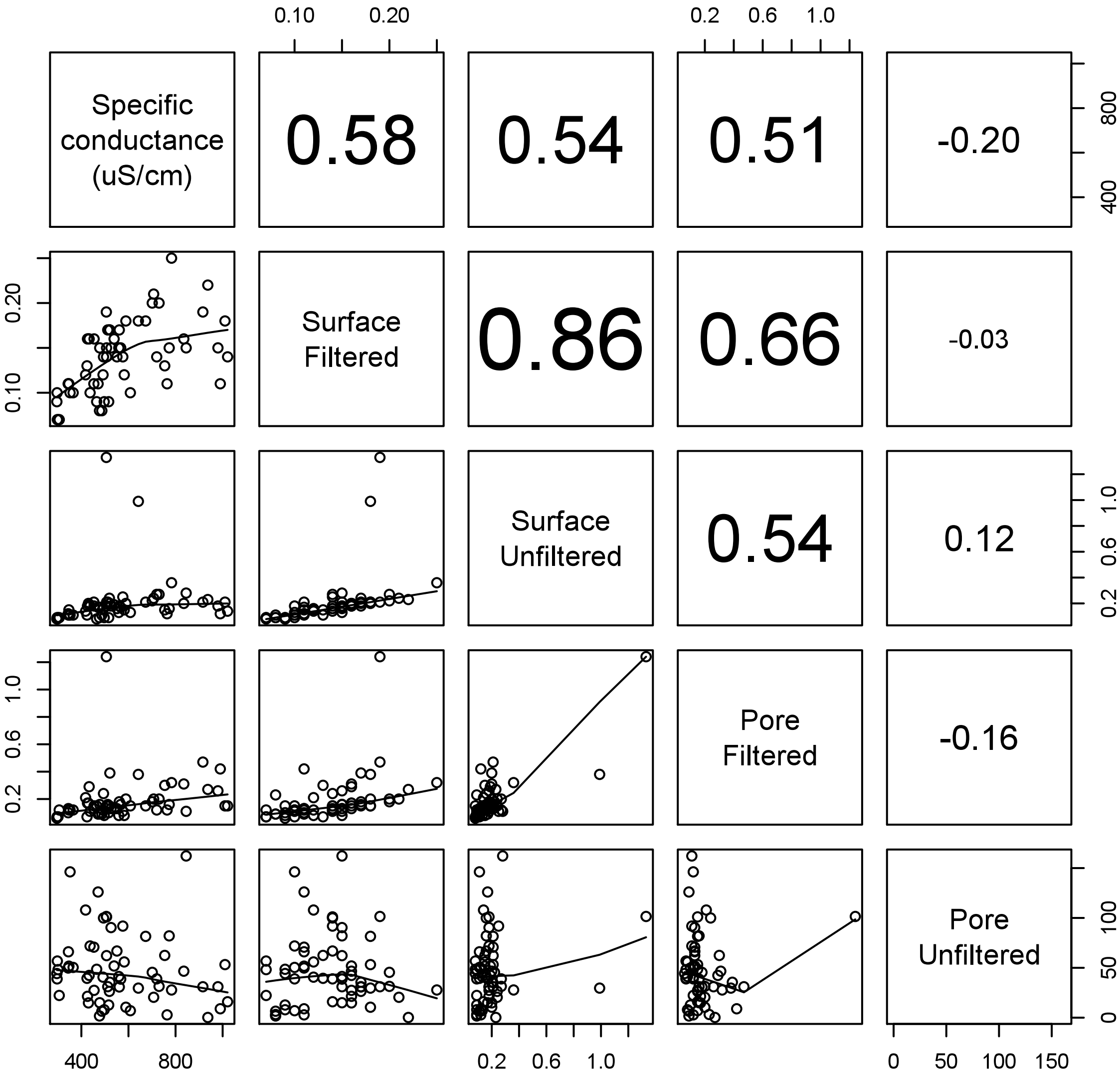


Ca (mg/L)
Specific conductance (uS/cm)
0.85
0.85
0.86
0.20
Surface Filtered
1.00
0.97
0.28
Surface Unfiltered
0.97
0.28
Pore Filtered
0.26
Pore Unfiltered

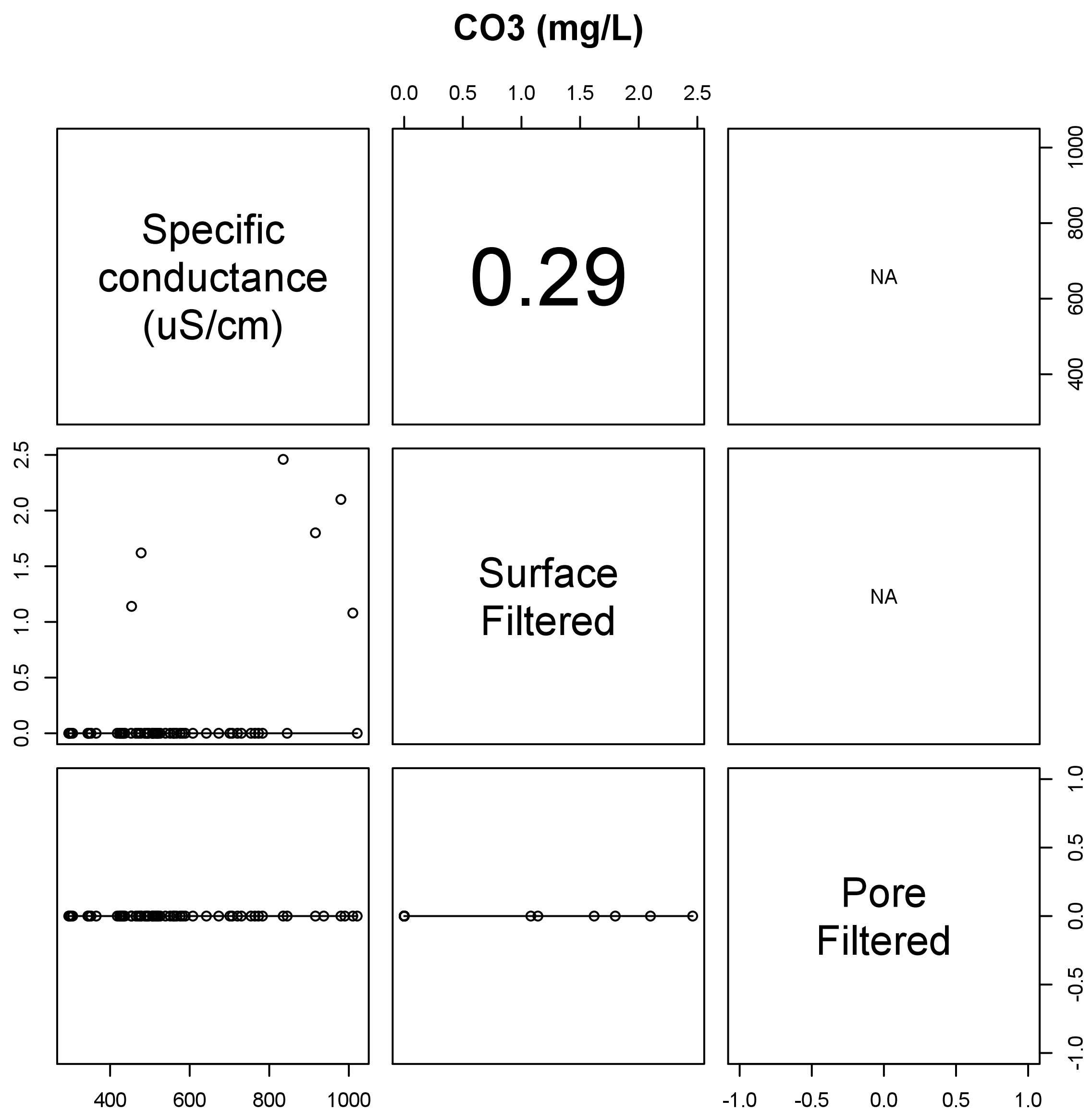

Cd (ug/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.04
0.15
0.11
-0.14
0.87
0.88
-0.44
0.91
-0.40
-0.49

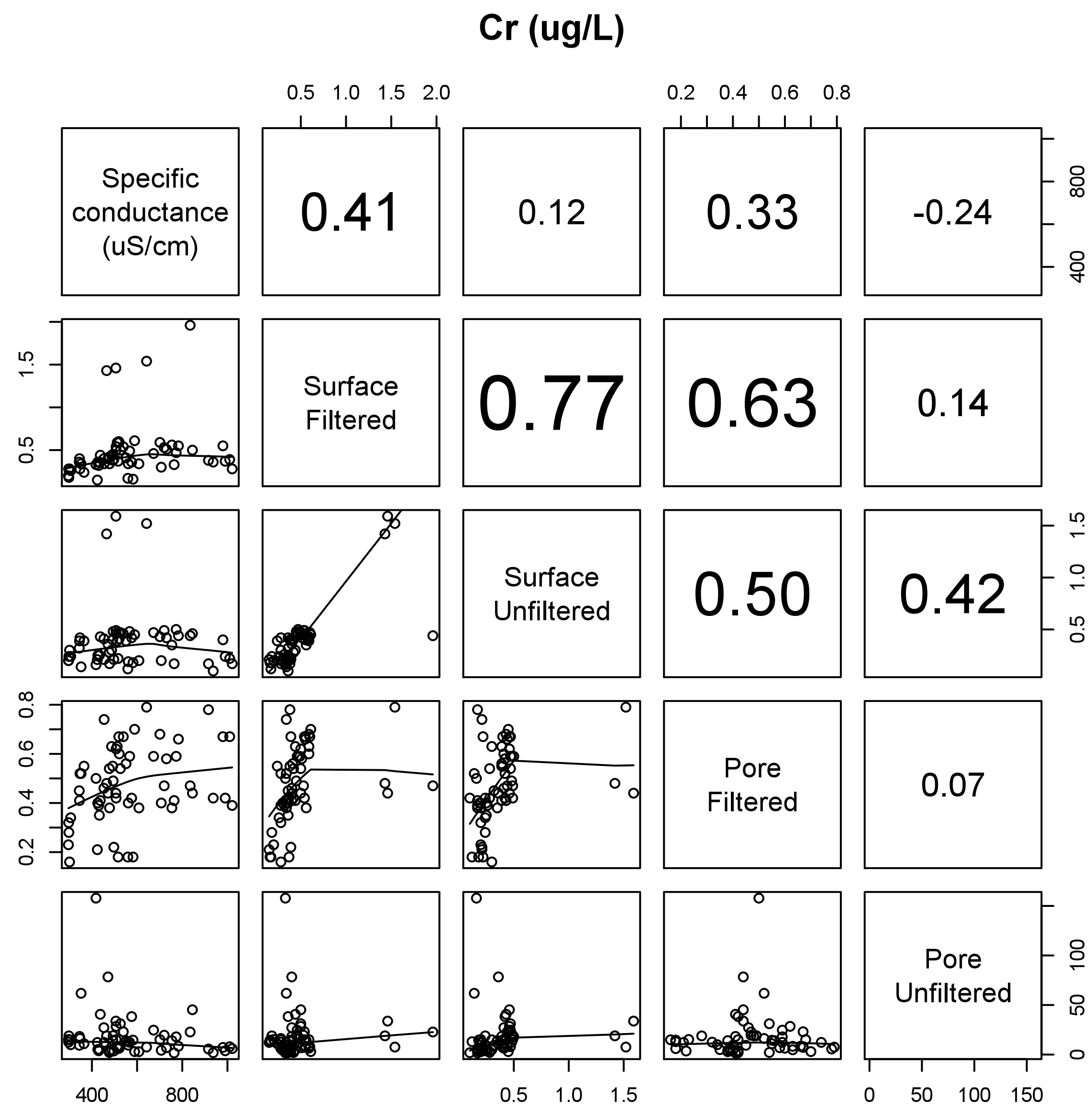

Cl (mg/L)
Specific conductance (uS/cm)
0.22
0.24
Surface Filtered
0.88
Pore Filtered
2 3 4 5 6 7 8
400 600 800 1000
5 10 15

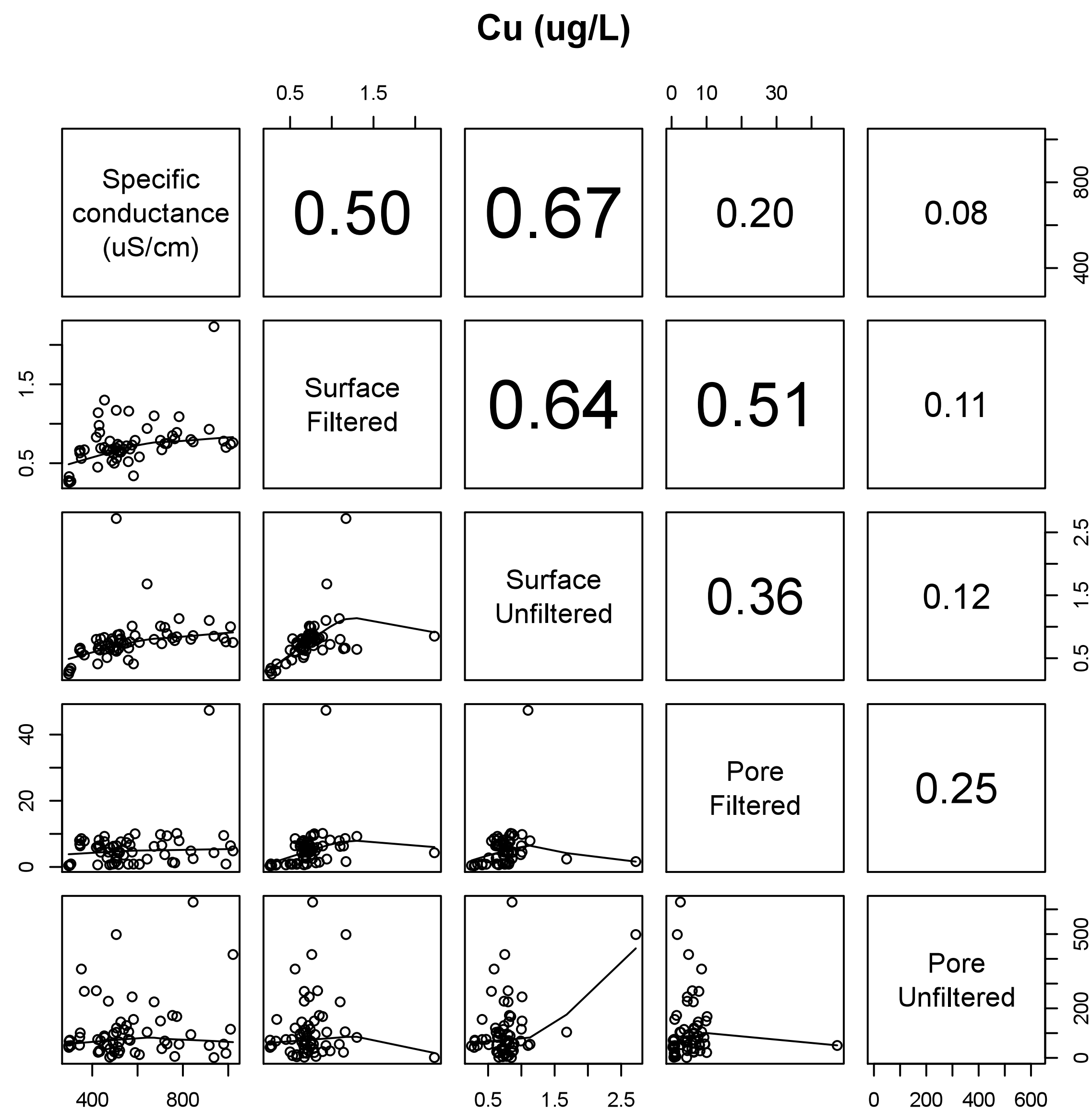
Co (ug/L)

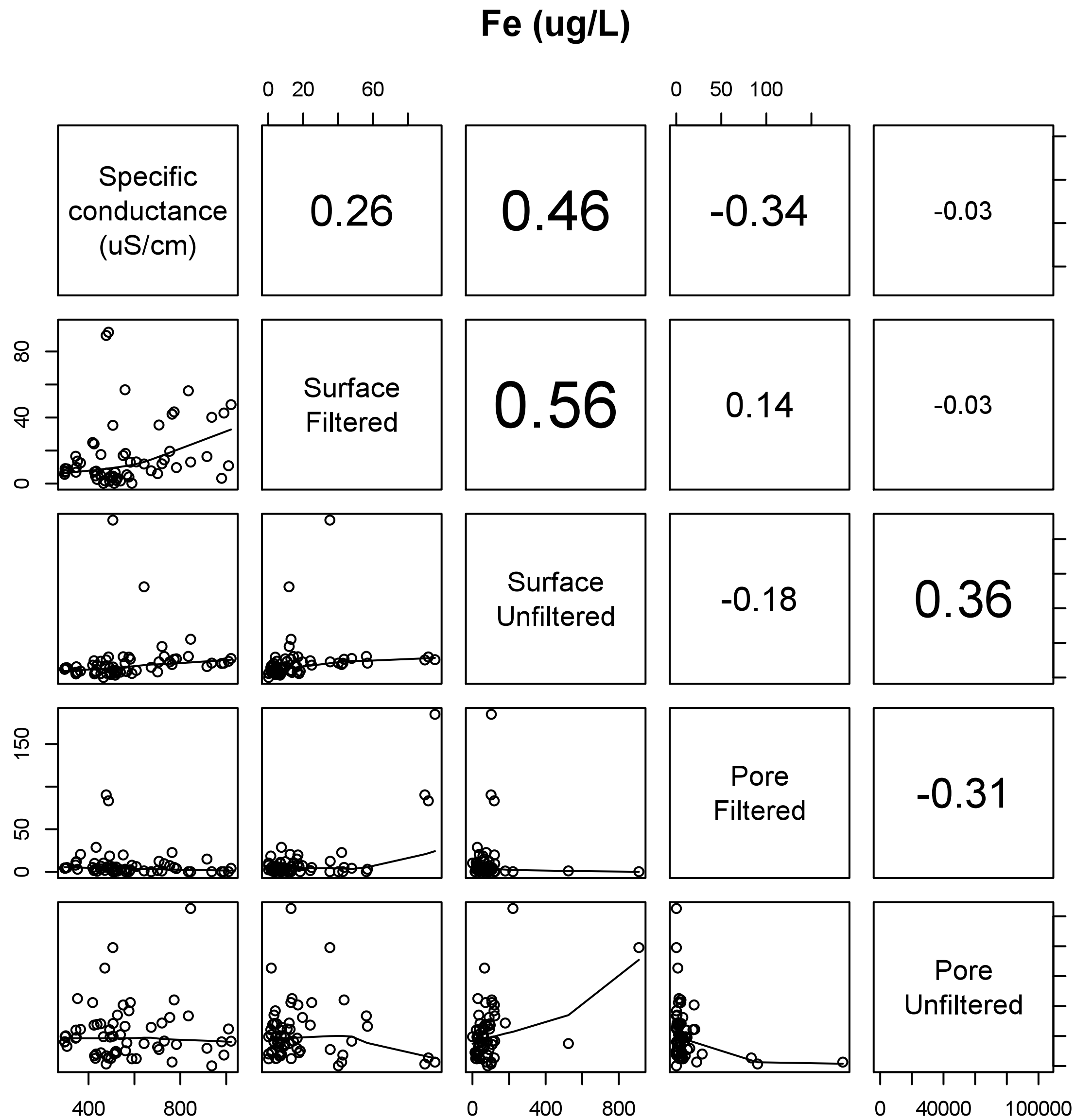


Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.58
0.54
0.51
-0.20
0.86
0.66
-0.03
0.54
0.12
-0.16

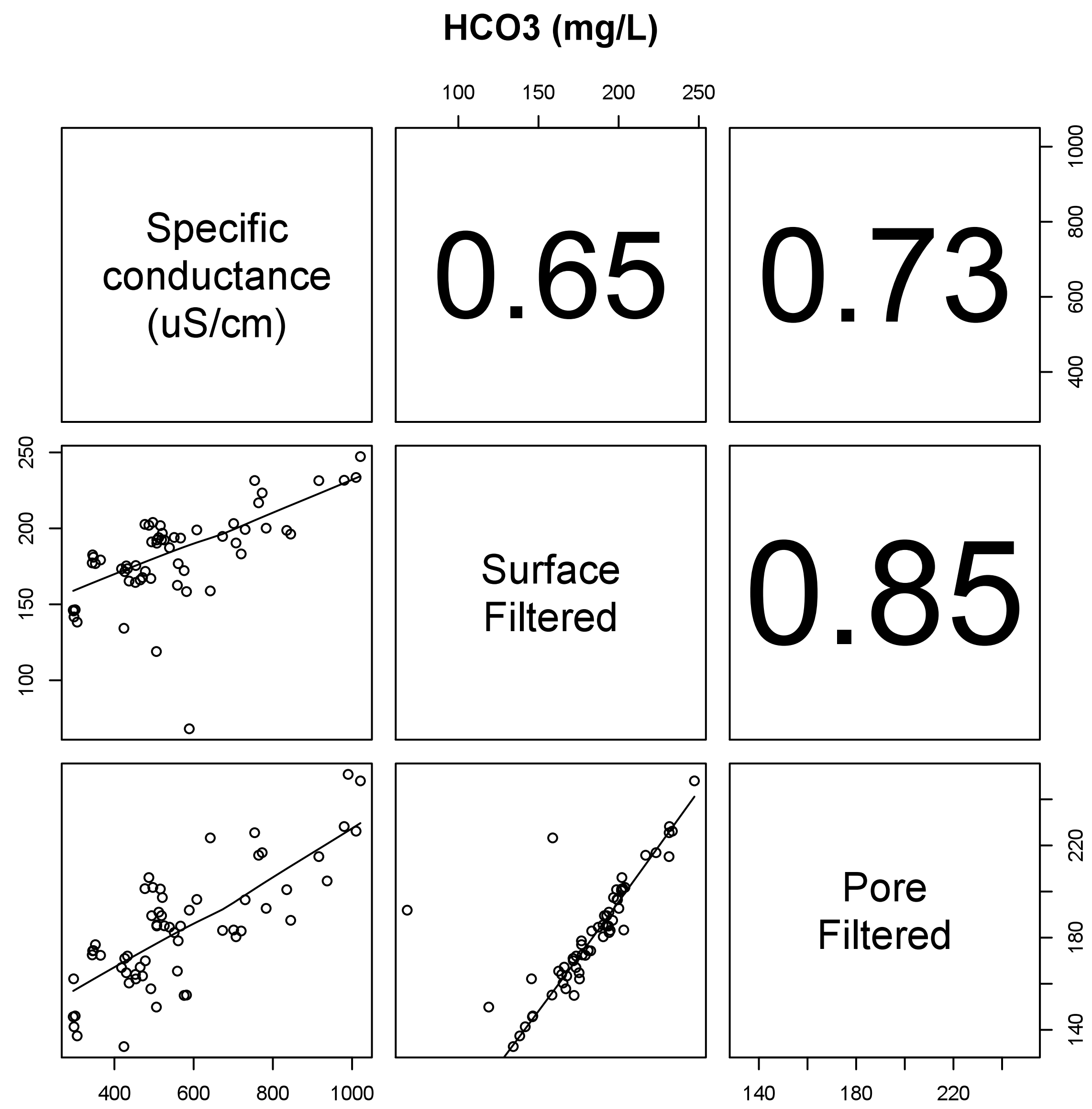

CO3 (mg/L)
0.0 0.5 1.0 1.5 2.0 2.5
Specific conductance (uS/cm)
0.29
NA
1000 800 600 400
2.5 2.0 1.5 1.0 0.5 0.0
Surface Filtered
NA
Pore Filtered
1.0 0.5 0.0 -0.5 -1.0
400 600 800 1000
-1.0 -0.5 0.0 0.5 1.0


Cr (ug/L)
Specific conductance (uS/cm)
0.41
0.12
0.33
-0.24
Surface Filtered
0.77
0.63
0.14
Surface Unfiltered
0.50
0.42
Pore Filtered
0.07
Pore Unfiltered

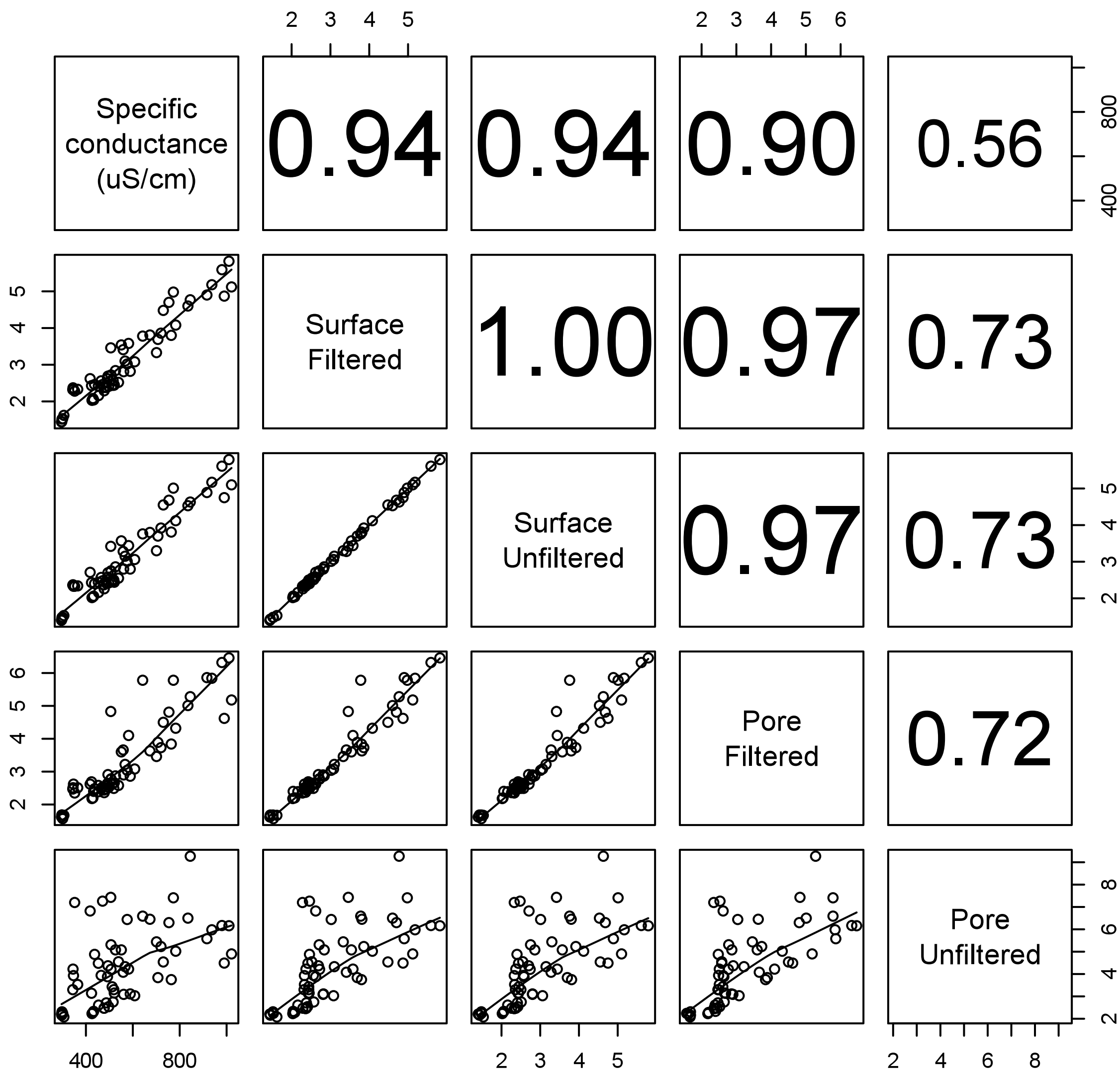

Cu (ug/L)
Specific conductance (uS/cm)
0.50
0.67
0.20
0.08
Surface Filtered
0.64
0.51
0.11
Surface Unfiltered
0.36
0.12
Pore Filtered
0.25
Pore Unfiltered



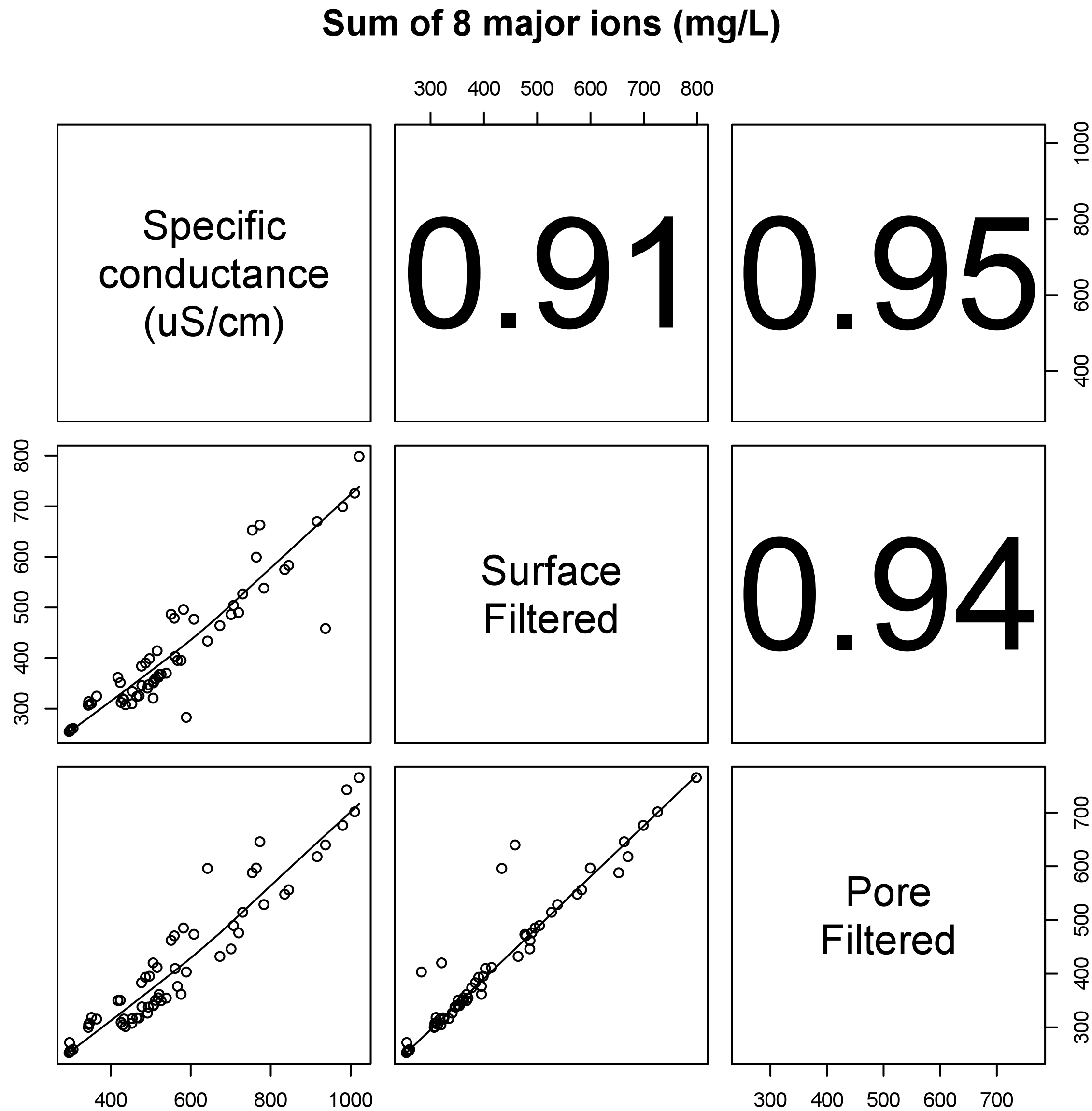
Fe (ug/L)
Specific conductance (uS/cm)
0.26
0.46
-0.34
-0.03
Surface Filtered
0.56
0.14
-0.03
Surface Unfiltered
-0.18
0.36
Pore Filtered
-0.31
Pore Unfiltered

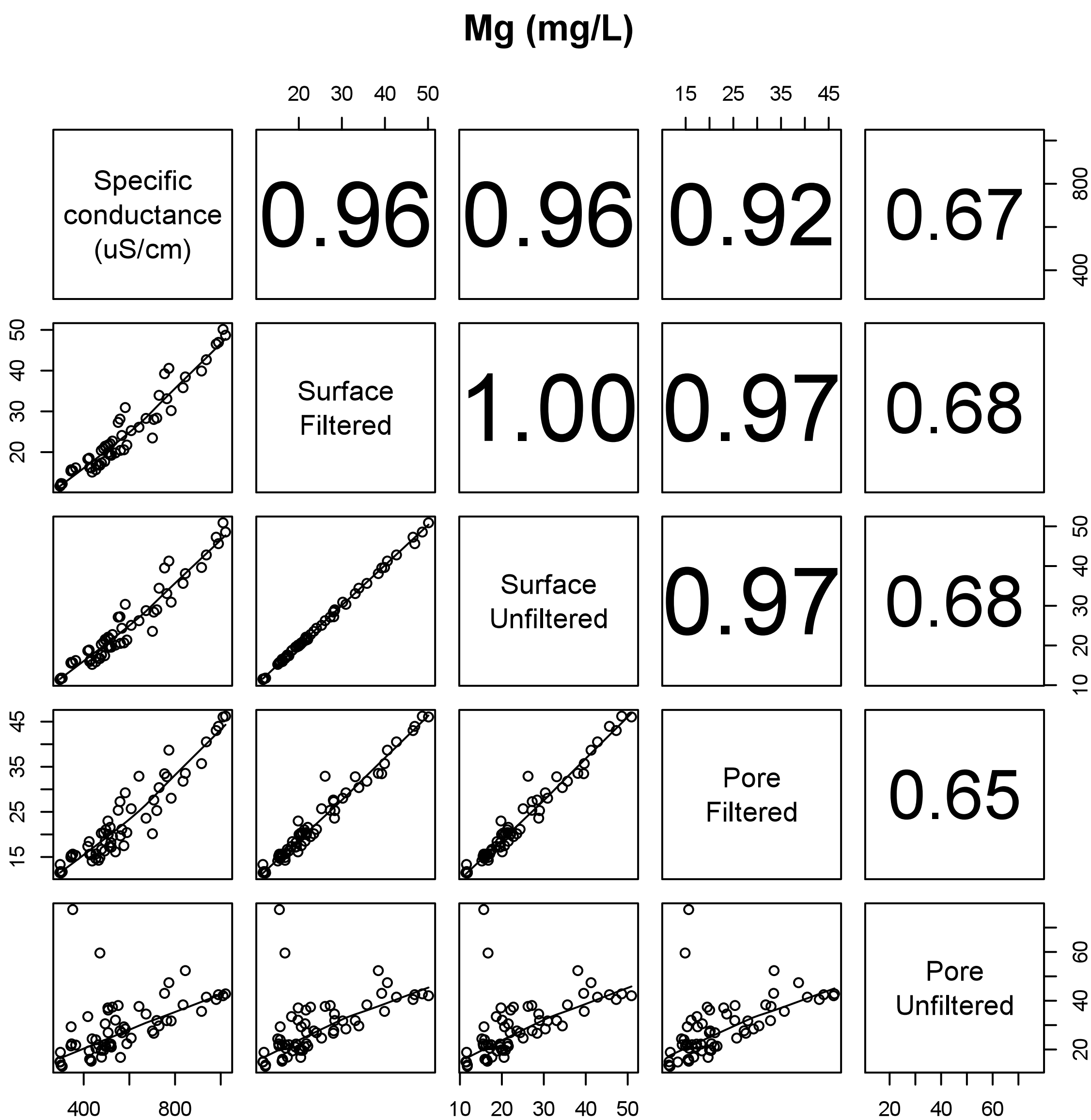

HCO3 (mg/L)
Specific conductance (uS/cm)
0.65
0.73
Surface Filtered
0.85
Pore Filtered
100
150
200
250
1000
800
600
400
250
200
150
100
220
180
140
400
600
800
1000
140
180
220

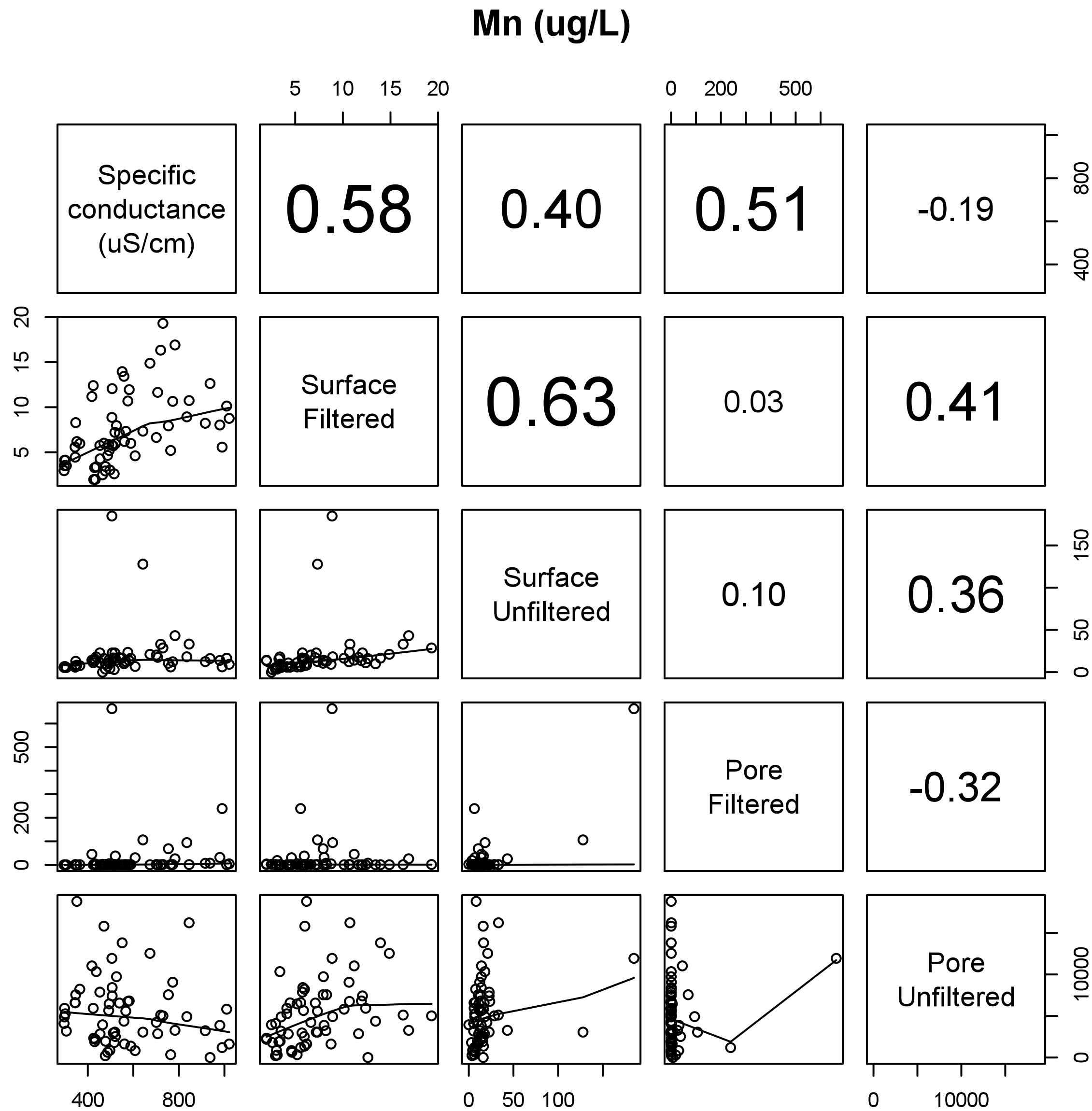
K (mg/L)



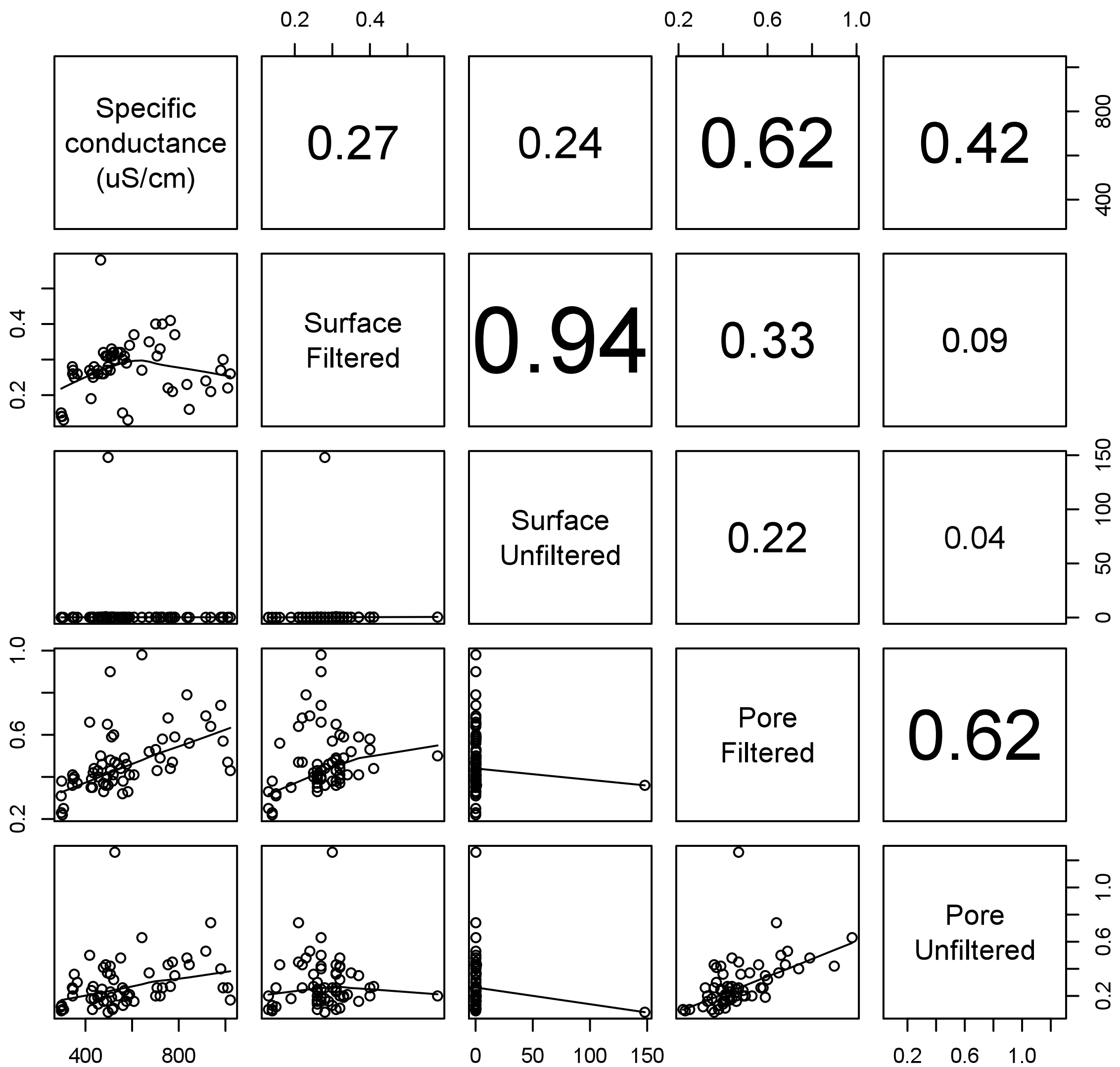
Specific conductance (uS/cm)
0.94
0.94
0.90
0.56
Surface Filtered
1.00
0.97
0.73
Surface Unfiltered
0.97
0.73
Pore Filtered
0.72
Pore Unfiltered
400
800
2
3
4
5
6
8

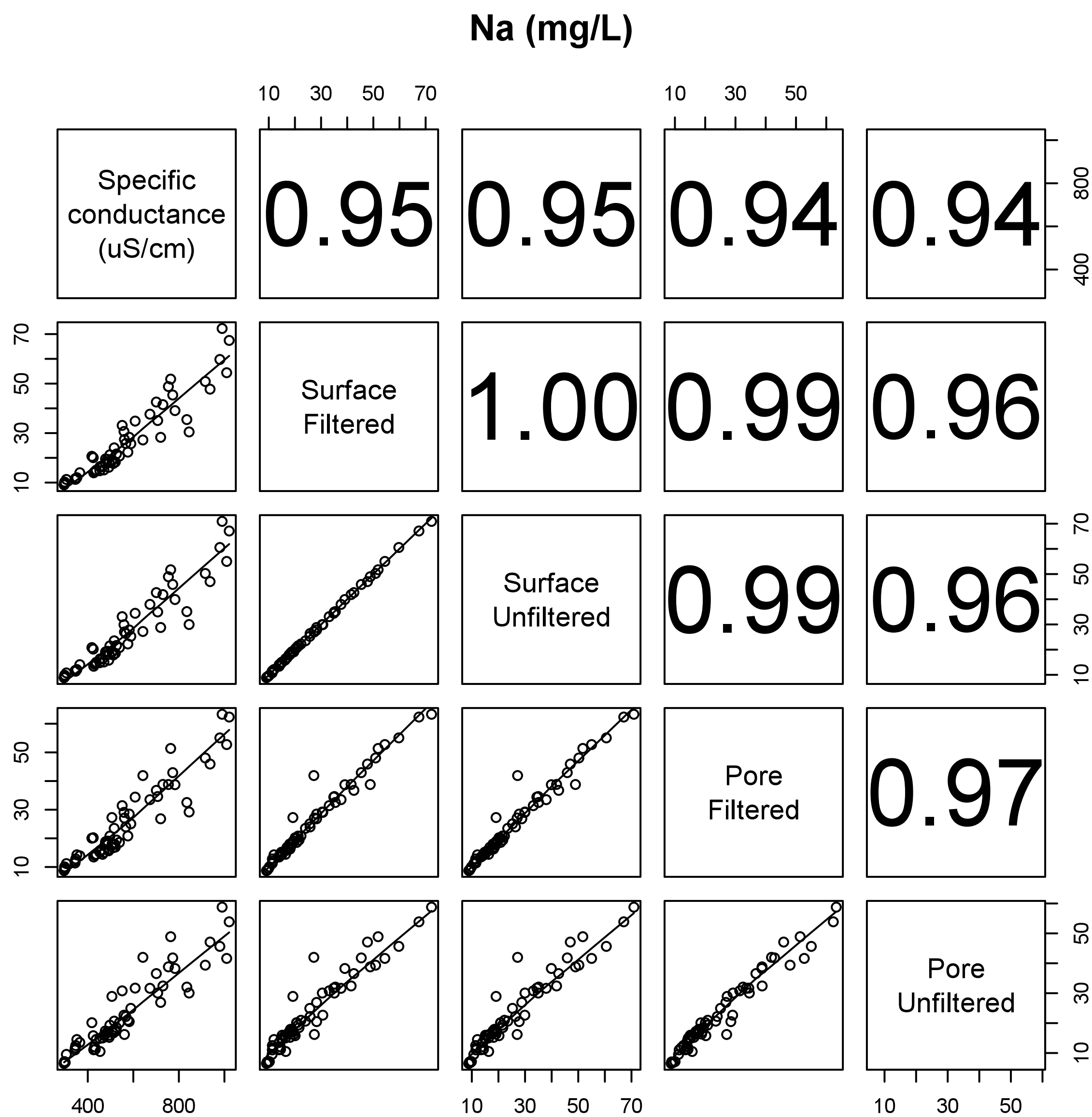

Sum of 8 major ions (mg/L)
Specific conductance (uS/cm)
0.91
0.95
Surface Filtered
0.94
Pore Filtered
300 400 500 600 700 800
1000 800 600 400
800 700 600 500 400 300
700 600 500 400 300
400 600 800 1000
300 400 500 600 700


Mg (mg/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.96
0.96
0.92
0.67
1.00
0.97
0.68
0.97
0.68
0.65


Mn (ug/L)
Specific conductance (uS/cm)
0.58
0.40
0.51
-0.19
Surface Filtered
0.63
0.03
0.41
Surface Unfiltered
0.10
0.36
Pore Filtered
-0.32
Pore Unfiltered
5
10
15
20
0
200
500
400
800
0
50
100
150
10000

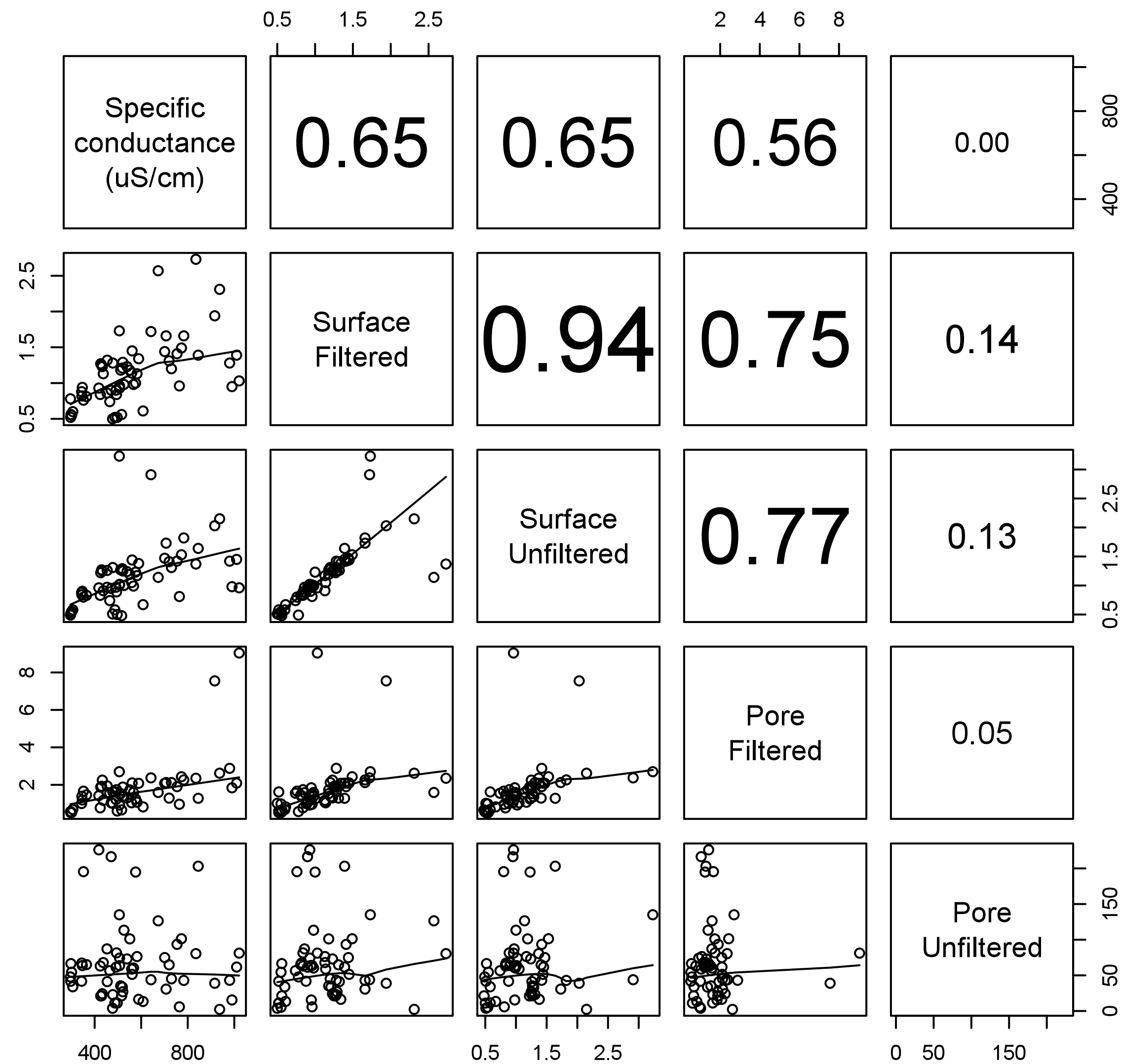
Mo (ug/L)


Specific conductance (uS/cm)
0.27
0.24
0.62
0.42
Surface Filtered
0.94
0.33
0.09
Surface Unfiltered
0.22
0.04
Pore Filtered
0.62
Pore Unfiltered
0.2
0.4
0.6
0.8
1.0
400
800
0
50
100
150
1.2



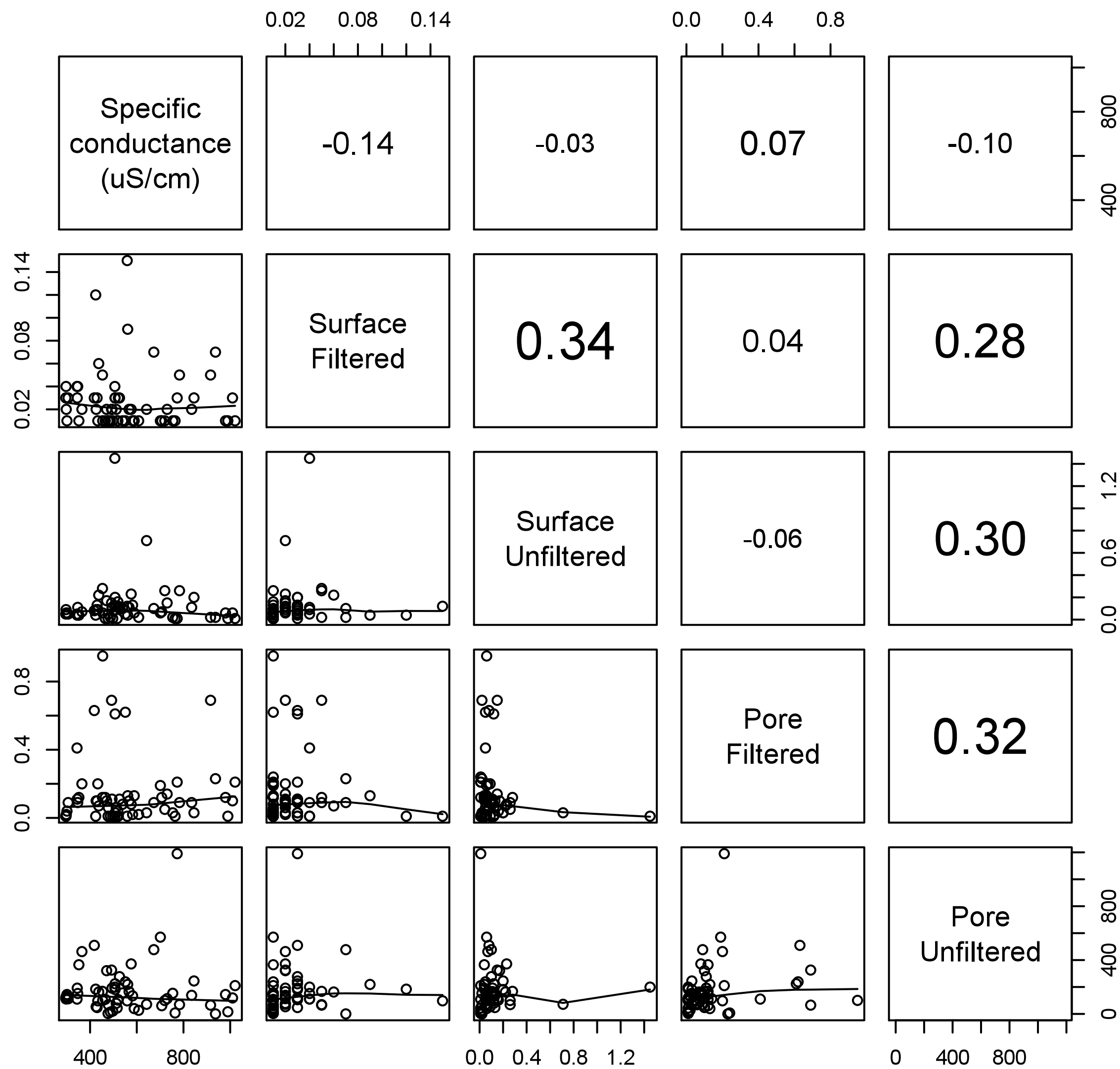
Na (mg/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.95
0.95
0.94
0.94
1.00
0.99
0.96
0.99
0.96
0.97

Ni (ug/L)

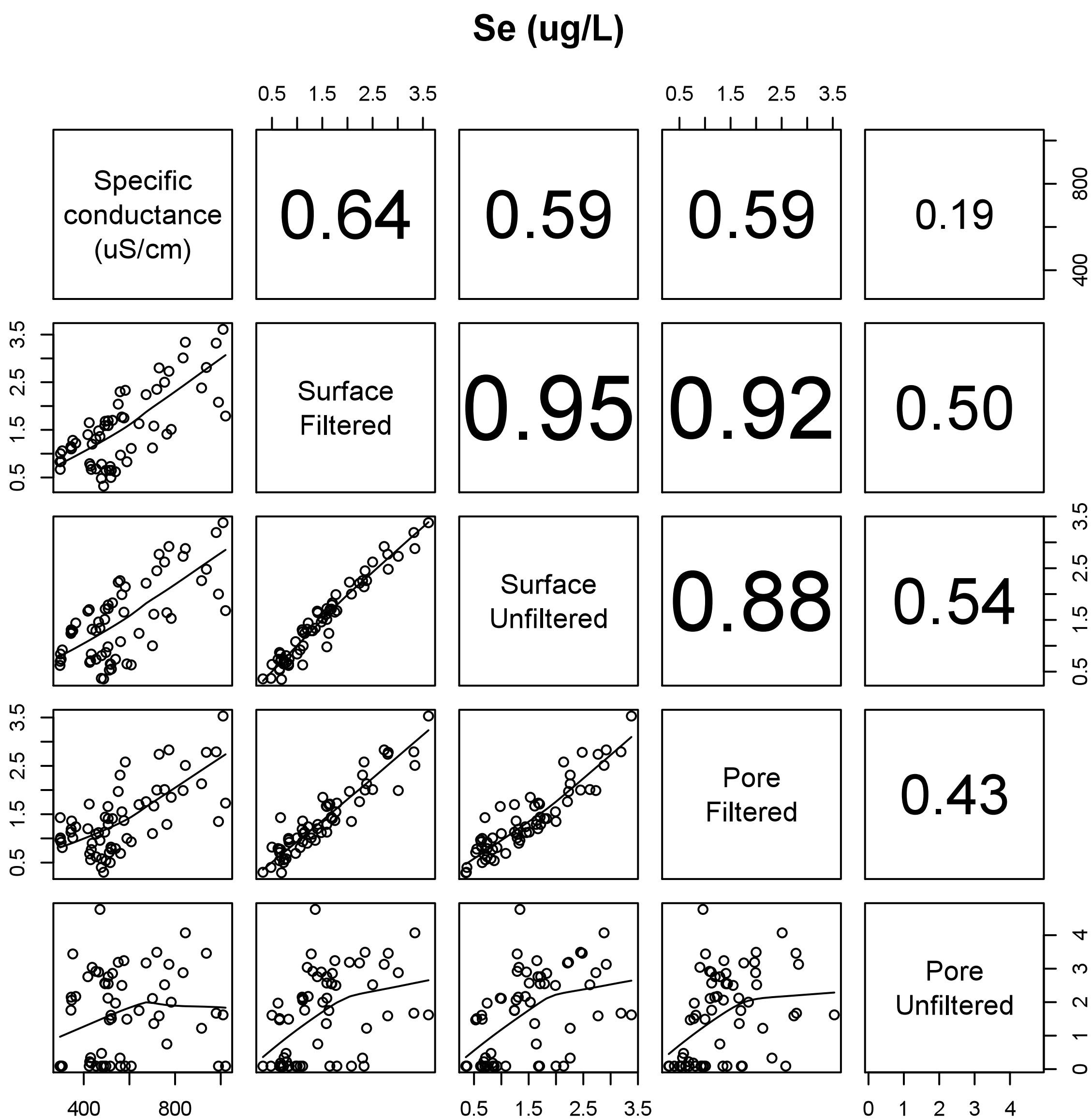


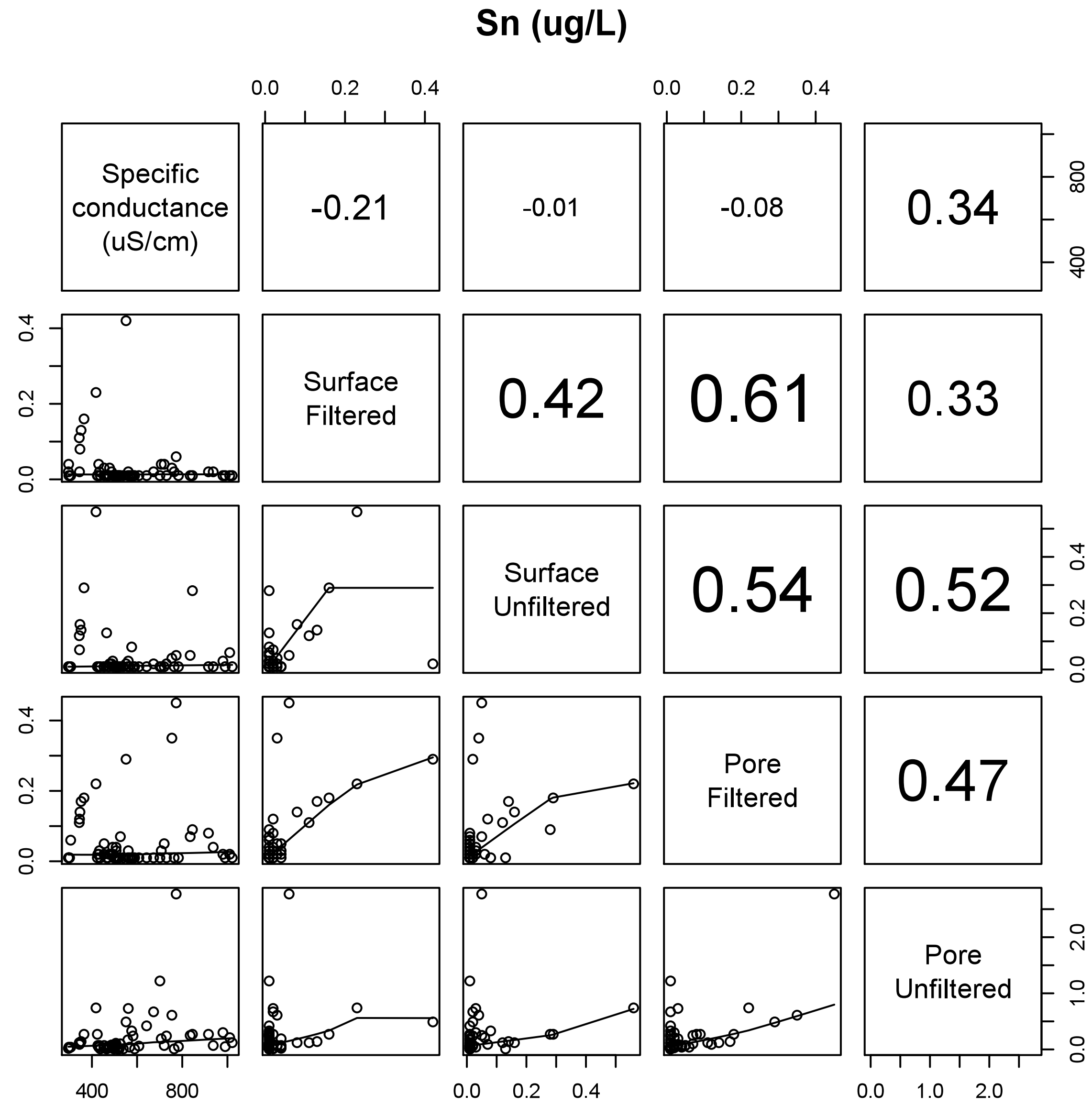
Specific conductance (uS/cm)
0.65
0.65
0.56
0.00
Surface Filtered
0.94
0.75
0.14
Surface Unfiltered
0.77
0.13
Pore Filtered
0.05
Pore Unfiltered

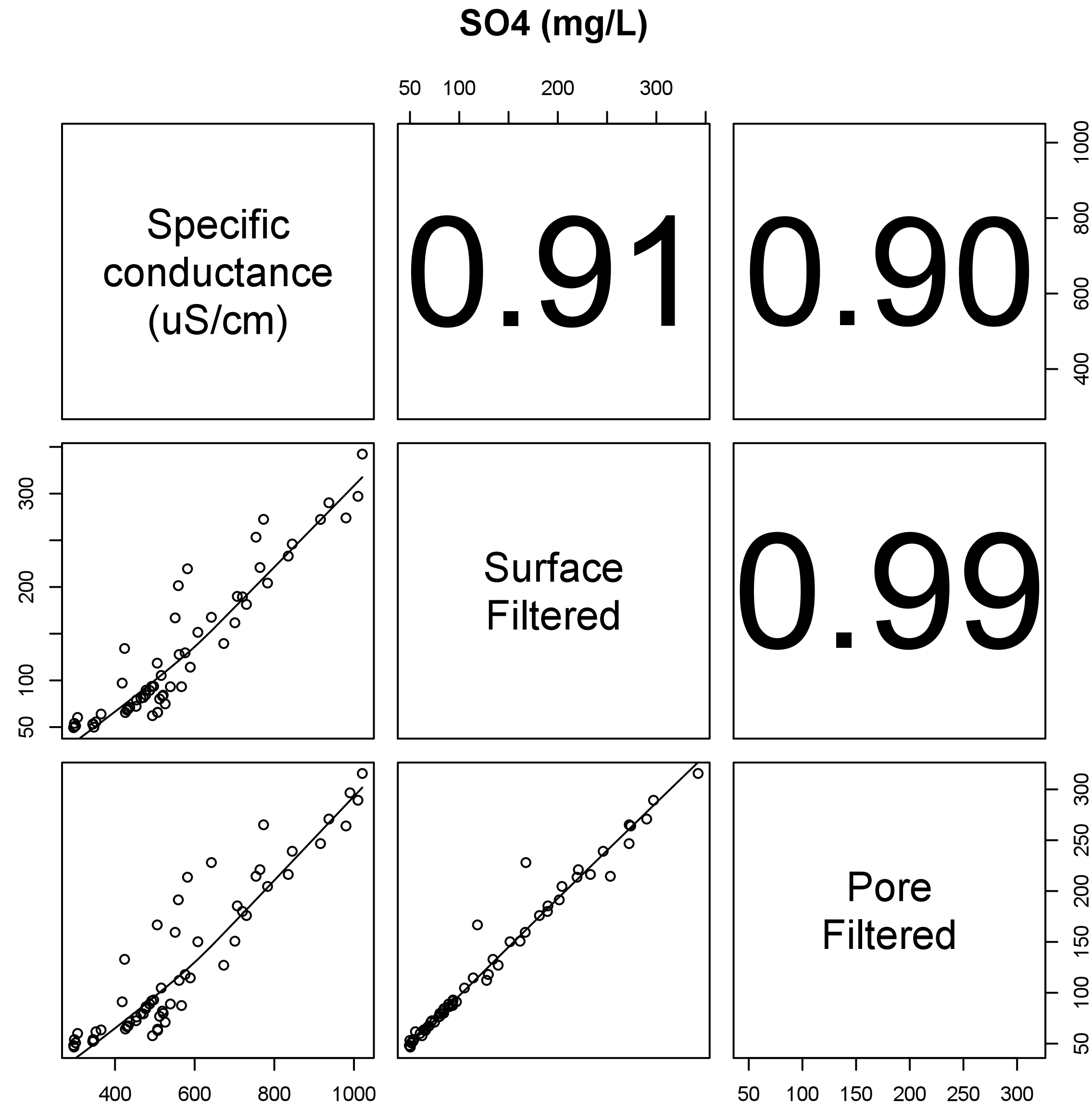
Pb (ug/L)

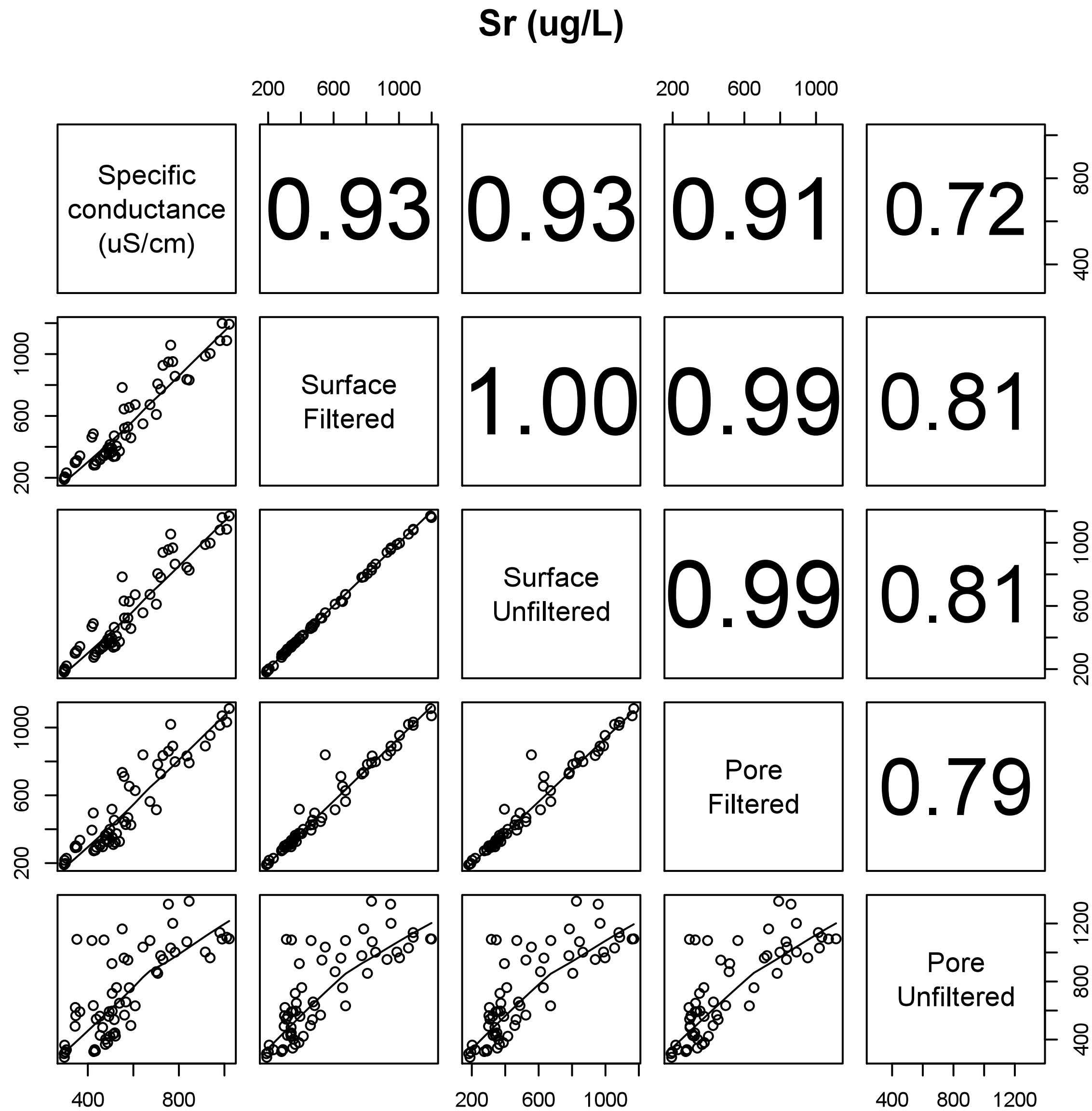


Specific conductance (uS/cm)
-0.14
-0.03
0.07
-0.10
Surface Filtered
0.34
0.04
0.28
Surface Unfiltered
-0.06
0.30
Pore Filtered
0.32
Pore Unfiltered

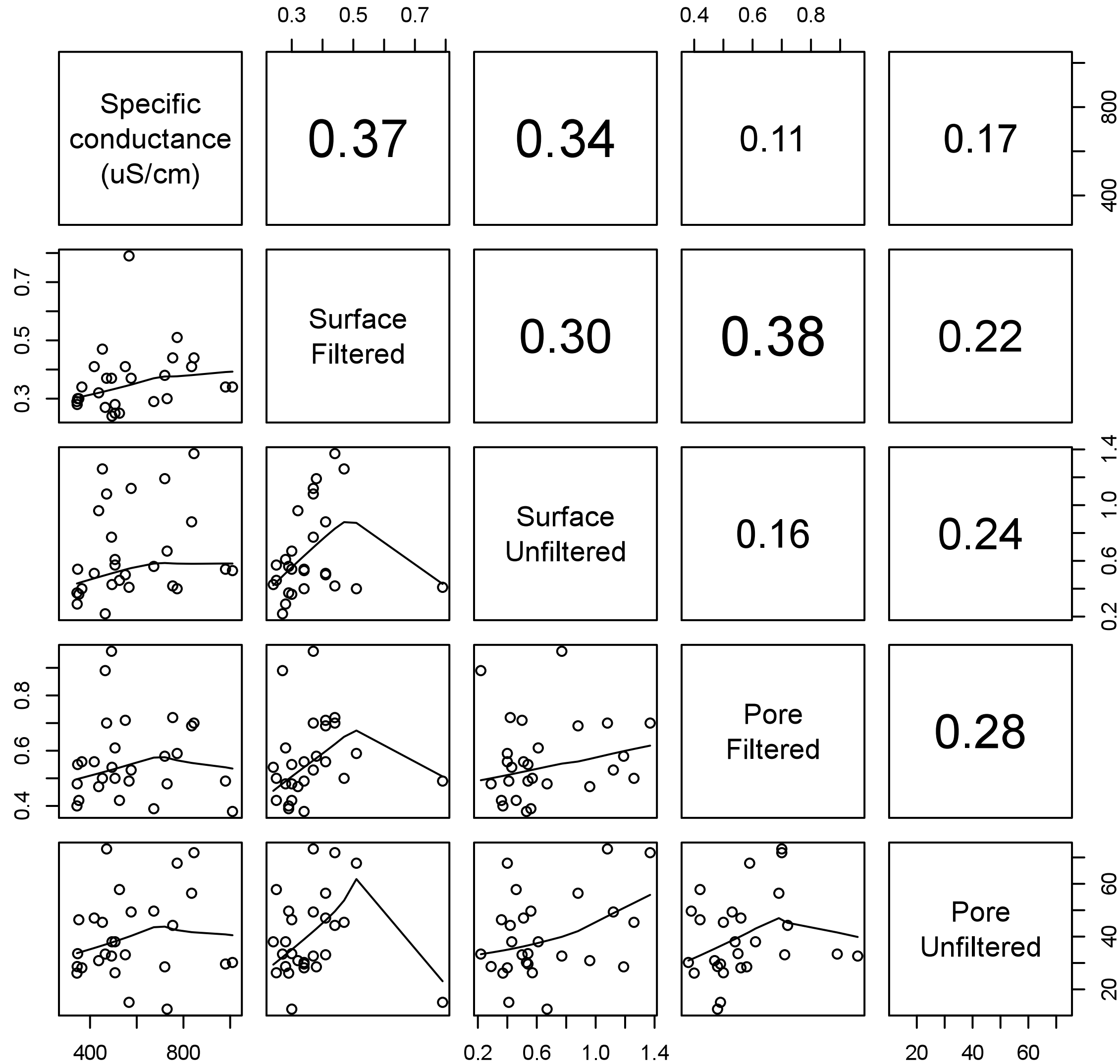

Se (ug/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.64
0.59
0.59
0.19
0.95
0.92
0.50
0.88
0.54
0.43


Sn (ug/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
-0.21
-0.01
-0.08
0.34
0.42
0.61
0.33
0.54
0.52
0.47

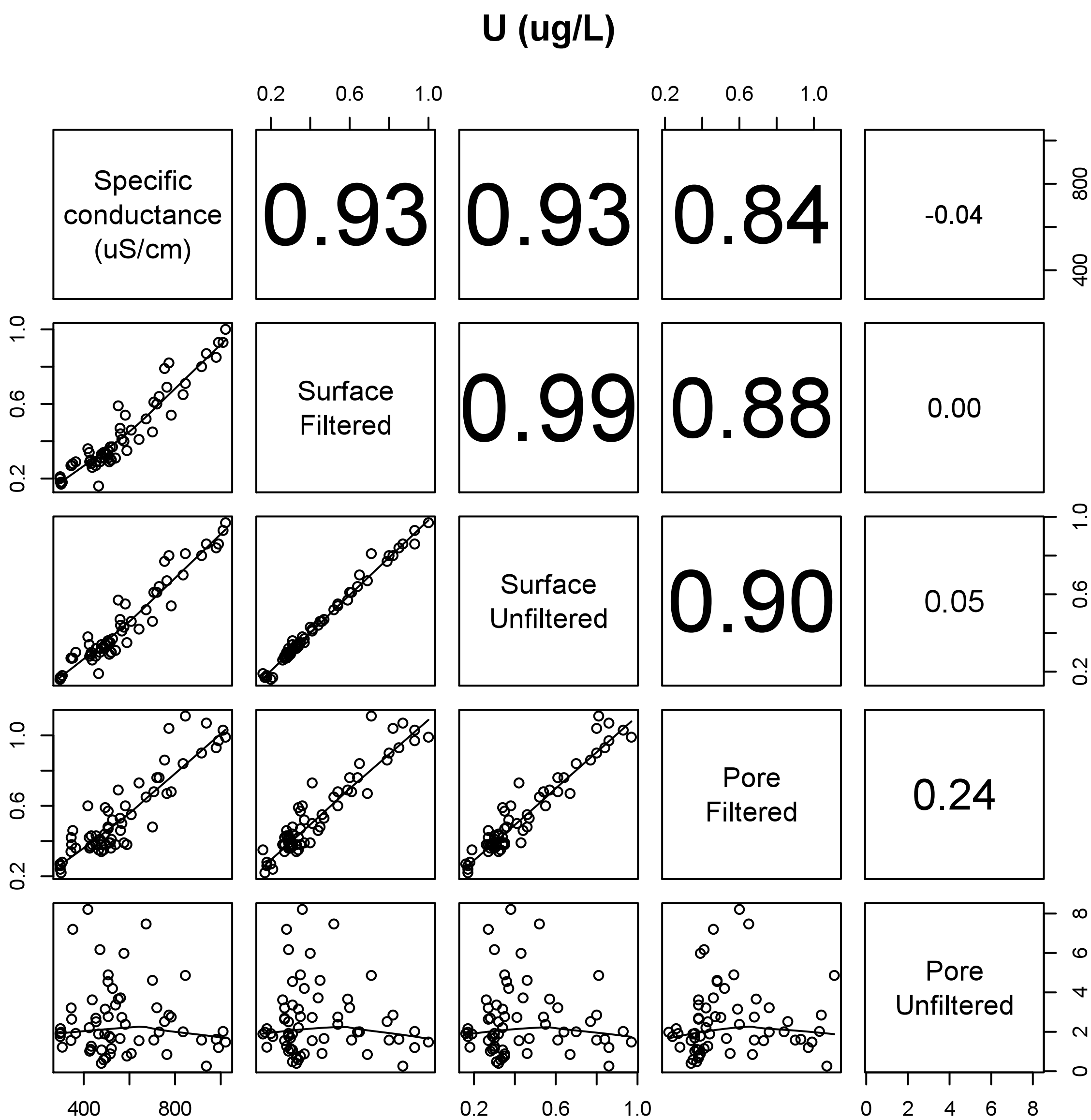

SO4 (mg/L)
Specific conductance (uS/cm)
0.91
0.90
Surface Filtered
0.99
Pore Filtered
50
100
200
300
400
600
800
1000
150
250


Sr (ug/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.93
0.93
0.91
0.72
1.00
0.99
0.81
0.99
0.81
0.79
200
600
1000
400
800
1200

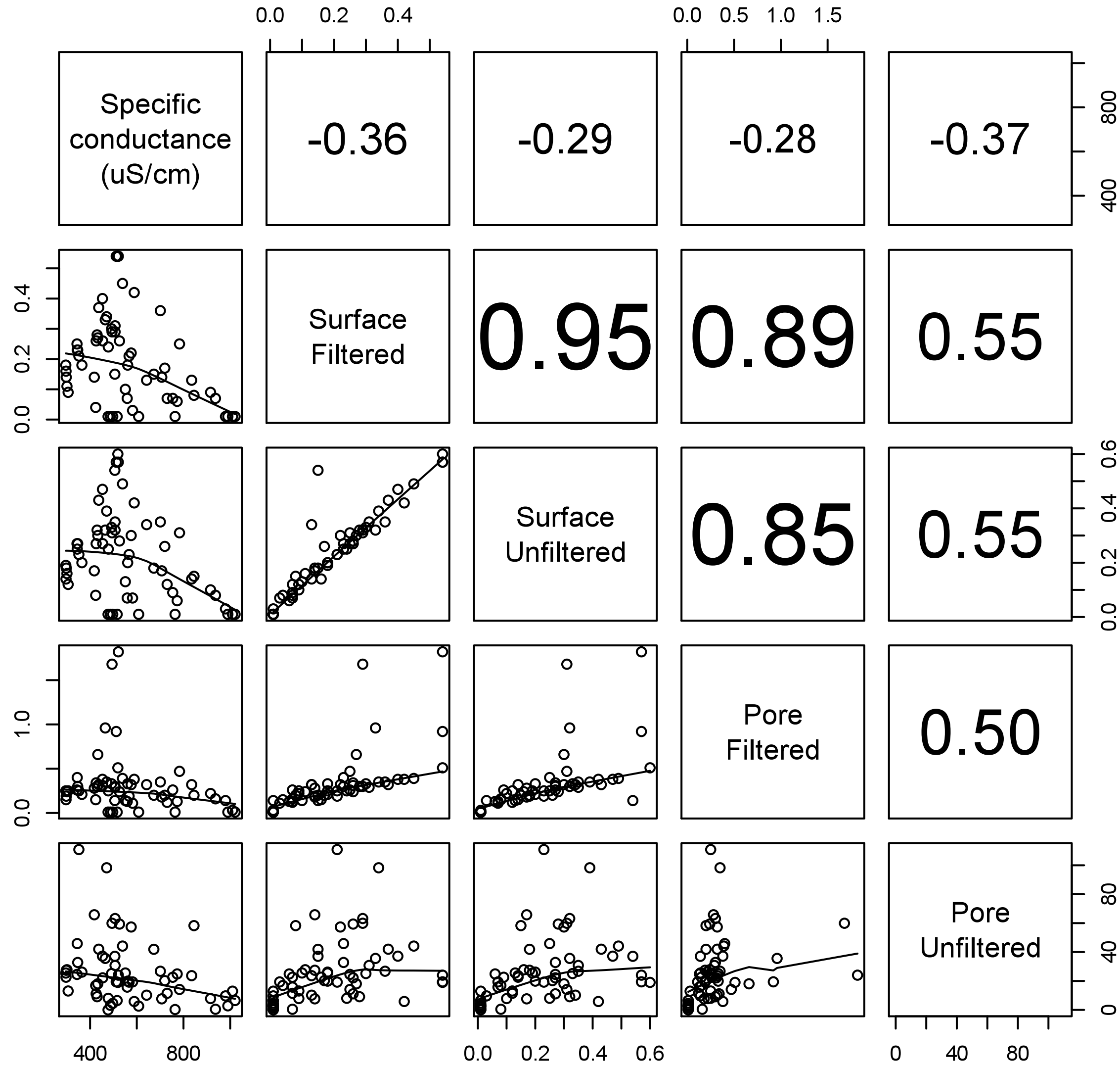
Ti (ug/L)



Specific conductance (uS/cm)
0.37
0.34
0.11
0.17
Surface Filtered
0.30
0.38
0.22
Surface Unfiltered
0.16
0.24
Pore Filtered
0.28
Pore Unfiltered

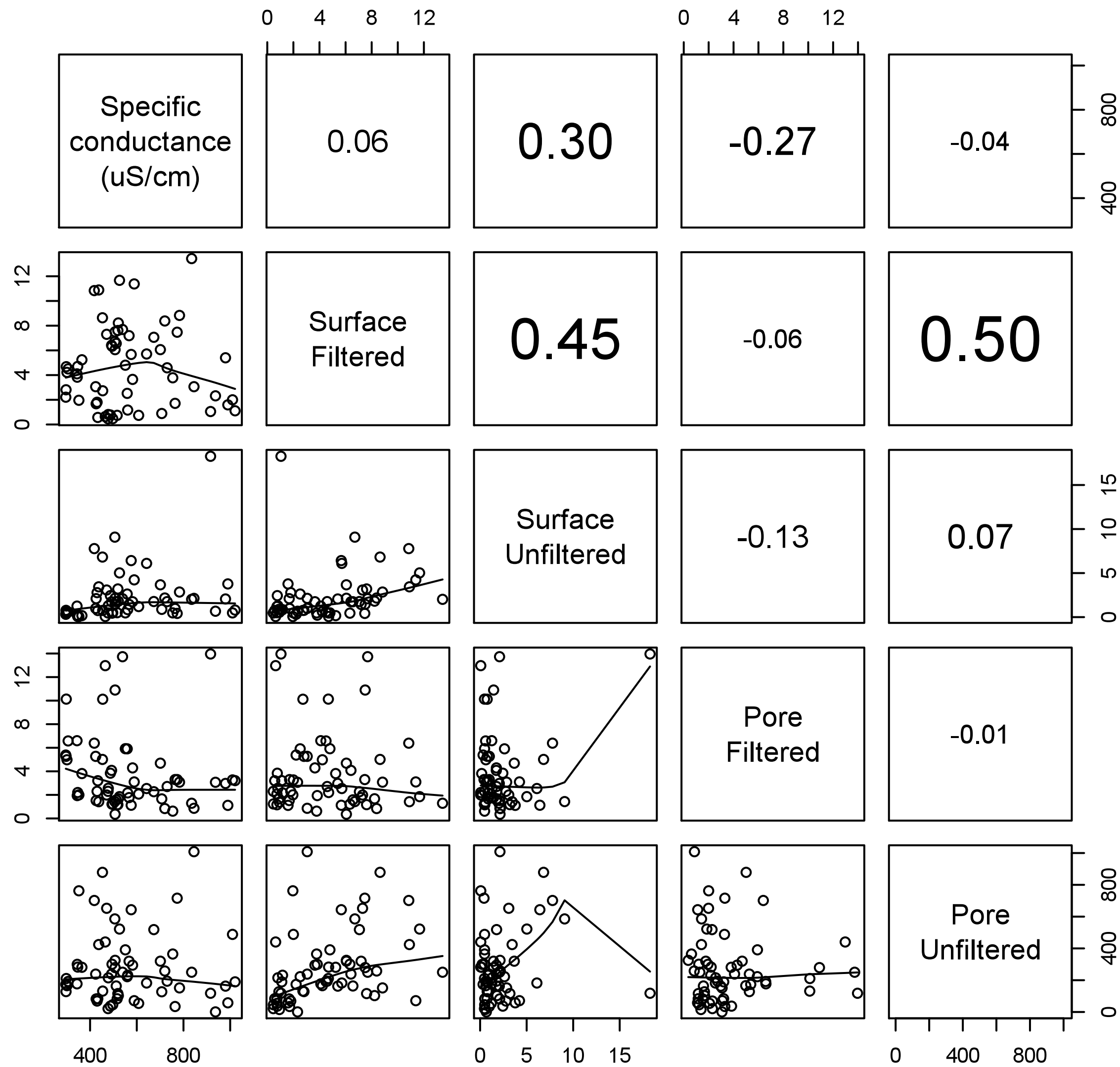

U (ug/L)
Specific conductance (uS/cm)
Surface Filtered
Surface Unfiltered
Pore Filtered
Pore Unfiltered
0.93
0.93
0.84
-0.04
0.99
0.88
0.00
0.90
0.05
0.24
0.2
0.6
1.0
400
800
0
2
4
6
8

V (ug/L)



Specific conductance (uS/cm)
-0.36
-0.29
-0.28
-0.37
Surface Filtered
0.95
0.89
0.55
Surface Unfiltered
0.85
0.55
Pore Filtered
0.50
Pore Unfiltered
0.0 0.2 0.4
0.0 0.5 1.0 1.5
400 800
0.0 0.2 0.4
0.0 0.2 0.4 0.6
0.0 1.0
0 40 80

Zn (ug/L)



Specific conductance (uS/cm)
0.06
0.30
-0.27
-0.04
Surface Filtered
0.45
-0.06
0.50
Surface Unfiltered
-0.13
0.07
Pore Filtered
-0.01
Pore Unfiltered