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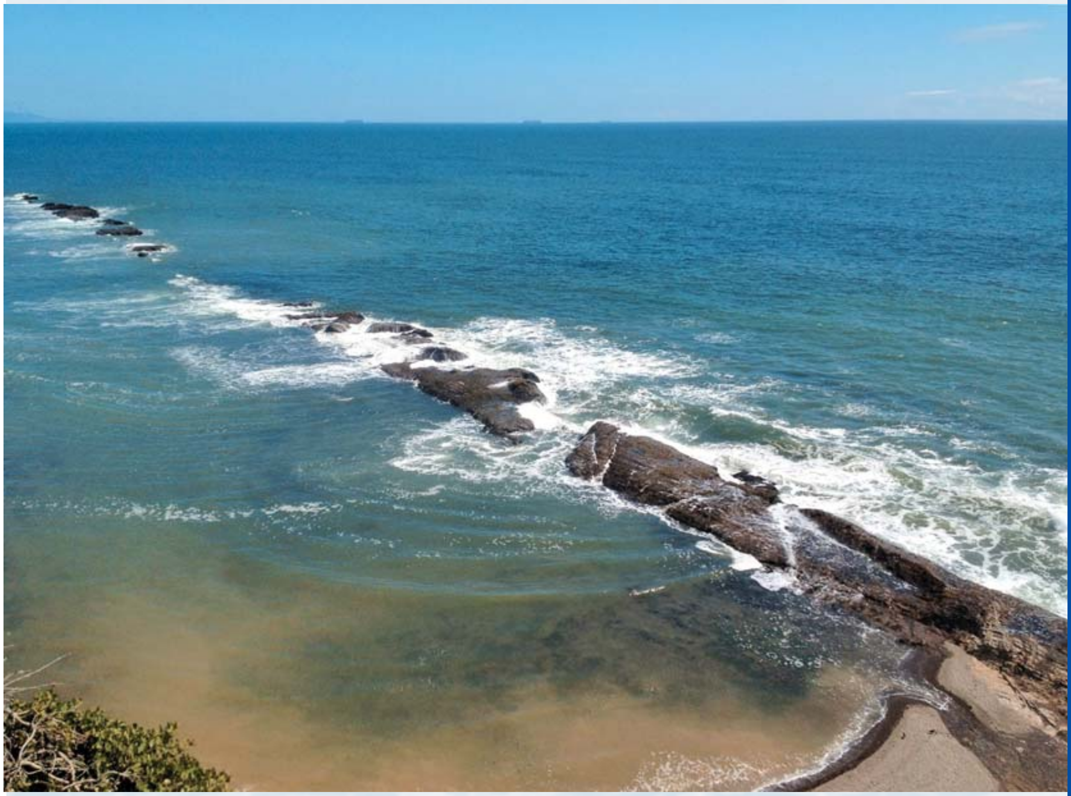

Southern California Coastal Water Research Project

Technical Report 853

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ABSTRACT

Stormwater is one of the more challenging sources of coastal pollution to abate, partly because stormwater also involves complex natural processes and differentiating these natural processes from anthropogenic excesses is difficult. The goal of this study was to identify what are the natural concentrations of stormwater constituents along the 1,377 km coastline of California, USA. Twenty-eight ocean reference sites, *a priori* defined by lack of human disturbance within its adjacent watershed, were sampled between 2008 and 2014. Samples were collected directly in front of flowing runoff following 78 site-events (combination of sampling sites and storm events), then measured for 57 constituents and toxicity to three endemic marine organisms. Results indicated a complete lack of toxicity and undetectable levels of anthropogenic constituents (i.e., current use pesticides) at ocean reference sites. The range of concentrations in ocean receiving waters adjacent to these undeveloped watersheds for naturally-occurring constituents (i.e., total suspended solids, nutrients, trace metals) typically ranged three to four orders of magnitude. With few exceptions, concentration ranges were comparable for different regions of the state, which vary in geology, rainfall, and oceanic currents. Storm characteristics (i.e., rainfall quantity, intensity, duration) did not explain these variations in concentration. The reference site information is now being used to establish targets for marine protected areas subject to runoff from developed watersheds.

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INTRODUCTION

Stormwater has been the focus of management actions, particularly in the last two decades, because of its potential for environmental impact (National Research Council 2009). Stormwater flushes contaminants deposited in coastal watersheds, transporting them to downstream waterbodies, sometimes to the detriment of coastal ecosystems. Stormwater runoff from developed watersheds with urban and agricultural land uses is known to contain pesticides, trace metals, nutrients, and eroded sediment (Tiefenthaler et al 2008, Stein et al 2006, Schiff et al 2004). Watershed development often exacerbates potential environmental risk by increasing peak flow, reducing time to peak flow, and changing total runoff volume associated with increased imperviousness (Leopold 1968, Hawley et al 2012). Ultimately, impacts to downstream receiving waters can occur, including aquatic toxicity and alterations to resident biological communities (Walsh et al 2005, Bay et al 2003).

Despite the increased regulatory focus on stormwater, making progress to reduce these pollutants can sometimes be slow. Part of the challenge associated with remediating stormwater inputs has been establishing appropriate clean-up targets. Some constituents in stormwater are clearly anthropogenic in origin, such as man-made pesticides. However, some of the constituents in stormwater are naturally-occurring, and would be present regardless of human intervention. Examples include suspended sediments, trace metals, and nutrients (Schiff and Weisberg 1999). In fact, complete absence of these constituents would result in equally detrimental impacts such as beach erosion and insufficient nutrient and organic enrichment for ocean processes (Ryther and Dunstan 1971).

The problem of identifying naturally-occurring levels of stormwater constituents in ocean receiving waters is especially problematic in areas like California, USA. California has extensive urban development along its coastline, including three of the top eight most populous cities in the USA (Los Angeles, San Francisco, and San Diego). California also has extensive agricultural development along its coastline, including the Salinas Valley, which produces the majority of the lettuce consumed within the USA. Juxtaposed against California's extensive urban and agricultural development is the promulgation of 580 km coastline miles for Areas of Special Biological Significance (ASBS), which are water quality marine protected areas where the regulatory mandate is "maintenance of natural water quality" and "no discharge of waste" (SWRCB 2012).

Little work has been targeted at determining the appropriate, naturally occurring level of stormwater constituents in coastal receiving waters. The literature is flush with measurements of runoff samples from the mouths of rivers and creeks or in adjacent estuaries (Carpenter et al 1998, Brezonik et al 2002), especially in California (Ackerman and Schiff 2003). Conversely, few studies have measured background concentrations of trace metals and nutrients along the coast of California, and these studies were all-too-often distant from shore and frequently conducted during dry weather (Sanudo-Wilhelmy and Flegal 1991, Smail et al. 2012). Rarely have very near-coastal water column samples been collected following storm events specifically to assess issues of background conditions (Schiff et al 2011), and never has there been a survey extending the length of the California coastline. As a result, most attempts to identify targets for coastal water quality rely on regulatory standards developed by state or federal agencies. These regulatory standards are most often developed using toxicity benchmarks, which identify how much pollutant is allowable before adverse effects may occur, as opposed to the "natural" level at which marine habitats (including ASBS) thrive.

The goal of this study is to define the naturally occurring levels of stormwater constituents in the near-coastal environment of the Pacific Ocean along the coast of California, USA. Relationships among geography and storm characteristics will be used to explain the variability in these naturally-occurring concentrations. Finally, the naturally occurring concentrations will be used to establish benchmarks of acceptable constituent concentrations for marine water quality protected areas for the state.

METHODS

There were three primary design elements for this study. The first design element was a focus on ocean receiving waters. All of the samples collected for this study were collected from the ocean, not from flowing rivers or creeks prior to entering the ocean. The second design element was the use of reference sites to define natural water quality. Reference sites are beaches adjacent to the mouths of rivers or creeks that drain undeveloped watersheds. Reference site selection followed five criteria: 1) the site must be an open beach with breaking waves (i.e., no enclosed bays); 2) the beach must have drainage from a watershed that produces flowing surface waters during storm events; 3) the reference watershed should be similar in size to the watersheds that discharge to ASBS; 4) the watershed must be comprised of primarily (>90%) open space; and 5) neither the shoreline nor any segment within the contributing watershed can be on the State's 2006 list of impaired waterbodies (e.g., §303d list). The third design element was a focus on wet weather. This assumes that no discharge of waste occurred during dry weather.

A total of 28 sites were sampled, split roughly evenly between the three regions of the state (Figure 1, Table 1). The North Region extended from Oregon to Bodega Head. The Central Region extended from Bodega Head to Point Conception. The South Region extended from Point Conception to Mexico. Up to 6 storm events were sampled per site. A storm was defined as any wet weather event that resulted in surface flow across the beach into the ocean receiving water. Pre-storm samples were collected prior to (<48 hours) rainfall, and post-storm samples were collected during or immediately following (<24 hours) rainfall, with most post-storm samples collected less than 2 hours after rainfall cessation. Samples were collected in the ocean at the initial mixing location of the reference watershed discharge in the receiving water. Both pre- and post-storm samples were collected by direct filling of pre-cleaned sample containers just below the water surface.

Laboratory Analysis

All water samples were analyzed for 57 constituents in five categories (Appendix 1): 1) general constituents including total suspended solids (TSS), oil and grease, and salinity; 2) nutrients including nitrate (NO_3-N), nitrite (NO_2-N), ammonia (NH_3-N), and ortho-phophate (PO_4-P); 3) total [unfiltered] trace metals (arsenic, cadmium, chromium, copper, nickel, lead, silver, zinc); 3) pyrethroid (9 pyrethroids plus fipronyl) and organophosphorus (8 OPs) pesticides; 4) total polycyclic aromatic hydrocarbons (25 PAHs); and 5) three different short-term chronic toxicity tests using endemic species (egg fertilization of the purple sea urchin *Strongylocentrotus purpuratus*, spore germination and tube growth of the giant kelp *Macrocycstis pyrifera*, and normal growth and development of the Mediterranean mussel *Mytilus galloprovincialis*). All sample analysis followed standard methods and/or EPA approved procedures (APHA 2006, US EPA 1995, SWRCB 2012). Trace metals were prepared for analysis using ammonium pyrrolidine dithiocarbamate (APDC), a chelation method that concentrates trace metals and removes matrix interferences (USEPA 1996).

The project focused on performance-based measures of quality assurance. Except for one storm analyzing reference sites in the central region, laboratory data quality was quite good: 100% sample completeness, no laboratory blank samples were greater than the method detection limit; 90% success meeting data quality objectives (DQOs) for precision using laboratory duplicates; 96% success meeting DQOs for accuracy using spiked samples. The trace metals from the central region for the first storm sampled in November 2013 suffered from significant interferences, and therefore were removed from the data set. The interferences were remedied in the subsequent two storms, meeting all DQOs, and were included in all data analyses.

Data Analysis

Data analysis followed three steps. The first step was verifying the selection of reference drainage sites. This validation was achieved by examining the reference site data for known anthropogenic contamination (i.e., synthetic pesticides), testing for the presence of toxicity, and examining the reference data set for outlier samples of naturally occurring constituents. Outliers were identified by utilizing a one-tailed Grubb's test, after logarithmic transformation, if needed. The second data analysis step tested for differences in naturally occurring concentrations among the three regions of the state using ANOVA and Tukey post hoc analysis. All constituents reported as non-detectable or detected but not quantifiable by the laboratory were treated as one-half the detection limit (Appendix 1). The third data analysis step examined potential relationships among parameters, potentially explaining differences among reference drainage sites. In this analysis, correlation coefficients were calculated between rainfall quantity, rainfall intensity, rainfall duration, TSS and salinity with each of the post-storm chemical concentrations.

RESULTS

Across the 78 site-events sampled from reference sites during this study, rainfall ranged from 0.2 to 65.5 mm. Generally, rainfall was greater to the north and decreased moving south (Table 2). Median rainfall quantity in the northern region (26.4 mm/event) was more than double the central region (10.4 mm/event) and triple the southern region (8.4 mm/event). Correspondingly, the northern region had greater median rainfall intensity and duration than either the central or southern regions.

All 28 reference sites appeared to have little to no human influence. No site had detected and quantifiable concentrations of synthetic pesticides. Moreover, no reference site exhibited toxicity to any of our three test species: mussel, purple sea urchin, and giant kelp. Two percent of all analyses for naturally occurring compounds (i.e., TSS, nutrients, trace metals) were defined as anomalously high values and removed as outliers (Table 3). The percent of outliers ranged from 1% of all analyses in the northern region to 4% in the southern region. The most commonly occurring outliers were for ammonia and total PAH (9% each of either all ammonia or all PAH analyses). No TSS, arsenic, cadmium, chromium, lead, nickel, silver or zinc analyses were determined to be outliers.

Several constituents were not quantified in any sample from reference sites along the California coast following storm events (Table 4). These constituents included organophosphorus and pyrethroid pesticides. Similarly, 100% of the samples for ammonia and oil and grease were non-detectable. In contrast, nearly every sample was detected for TSS, arsenic, cadmium, chromium, copper, nickel, and zinc. Concentrations within each of these constituents routinely ranged between three and four orders of magnitude statewide.

There were a handful of constituents that were frequently detected in some regions, but not others (Table 4). A good example is mercury. In the central region, 100% of the mercury measurements were detected, ranging from 0.0002 to 0.0007 µg/L. However, 100% of the mercury measurements in the north and south regions were not detected. This is attributed, in part, to the detection limit of mercury in these two regions (0.0012 µg/L) being greater than the central coast maximum concentration. Detection limits also played a role in PAH concentrations among regions. Approximately half of the total PAH measurements from the northern region were detected, but virtually none of the measurements had detectable total PAH concentrations in the southern region, yet these two regions had identical detection limits (0.025 µg/L). The central coast also had 100% non-detectable total PAH concentrations, but the detection limit was 0.125 µg/L, about 20% greater than the maximum total PAH concentration in the northern region (0.108 µg/L). Therefore, detection limits can play a crucial role in the interpretation of naturally occurring concentrations among regions for these constituents. The detection limits for the remaining 17 constituents were, on average, within a factor of two, presumably making sensitivity a non-issue for these pollutants (Appendix 1).

After taking into account differences in detection limits, there were some significant differences in mean concentrations among regions (Table 4, Appendix 2). Mean concentrations of copper, nickel, and nitrate were significantly greater in the northern region than the central region. Conversely, mean concentrations of selenium and silver were greater in the central region than the northern region. The southern region did not have significantly greater (or lower) concentrations than either the northern or central regions for any parameter.

There were some significant relationships between constituent concentrations and storm characteristics that could account for the range in natural variability observed at reference sites (Table 5). The highest correlation coefficients and greatest number of constituents were correlated with TSS. Several relationships with TSS were clearly spurious, including ammonia, oil and grease, ortho-phosphate, silver, and total PAH, typically from a high frequency of non-detectable values (Appendix 3). Many of the frequently detected trace metals exhibited statistically positive relationships with TSS. However, TSS and most trace metals were not significantly correlated with rainfall quantity, intensity, or duration.

Regardless of region, average concentrations were relatively similar pre-storm to post-storm (Figure 2). While individual constituents within individual storms varied, the average ratio of pre-storm:post-storm concentrations was near one. In general, the variability around one increased from north to south, with ortho-phosphate in the southern region being the constituent with the greatest deviation from one. Regardless, there was not a consistent pattern of higher post-storm concentrations among constituents within any region and no constituent was significantly greater than 1.

DISCUSSION

This study represents the first attempt at characterizing naturally occurring concentrations of stormwater constituents in the near-coastal zone of California following wet weather events. This study has produced an initially robust data set for setting natural water quality guidelines based on three inferences. First, site selection to avoid human influence was rigorous, which was then verified by lack of toxicity, non-detectable concentrations of synthetically produced chemicals, and few outlier concentrations of naturally occurring constituents that might indicate human contributions. Second, the sites were geographically distributed among the southern, central, and northern regions of the state. Capturing this spatial variability is important for quantifying the range in naturally occurring concentrations due to differences in local geology or land cover. Third, multiple storms were sampled at each site, sometimes across multiple wet seasons, helping capture temporal variability. Capturing this temporal variability is important for quantifying the range in naturally-occurring concentrations due to differences in precipitation such as rainfall quantity, intensity or duration.

Ultimately, this study found tremendous variability in naturally occurring concentrations, typically exceeding three or four orders of magnitude for most constituents that were frequently detected. Although we know that spatial and temporal variability are important components of this variability, we were unable to explain the root sources of this variability. Some differences in concentrations were observed among regions (i.e., the northern region had higher nutrient concentrations), but the majority of constituents had similar distributions among regions. Furthermore, few relationships between precipitation and concentrations were observed. Together, these results indicate that utilizing normalizing factors such as precipitation to better define naturally-occurring concentrations is not advisable at this time. Further exploration into natural variability may prove fruitful after further data collection, especially if examining within-region or within-site relationships. In particular, additional data collection during years with above average rainfall may reveal relationships not present during the below average rainfall years sampled in this study.

One limitation to using the naturally occurring concentrations derived from this study is differences in analytical sensitivity among regions. While different laboratories were used in an effort to alleviate sample shipping and holding time issues, the differences in detection limits hindered our ability to compare data across regions for two specific constituents: total PAH and mercury. In both cases, maximum concentrations in one region were below the minimum detection limit in another. Comparability in sensitivity, and quantified accuracy and precision at these low levels, should be addressed in large-scale surveys that use this distributed sampling and analytical approach (Gossett et al 2003).

A major benefit of this data set is the ability to translate narrative standards for ASBS, such as "maintenance of natural water quality," into numerical guidelines. There are a number of statistical (and social) approaches to making this translation. In the case of California, managers opted to use the 85th percentile of the naturally occurring concentrations within each region as their cutpoint (Table 6). This relatively conservative approach to estimating natural water quality guards against minor anthropogenic contributions in the reference data set (e.g., Type II error), which is important for locations like marine protected areas. In an effort to guard against overly restrictive guidelines due to local natural factors, the algorithm for applying the guideline not only includes exceeding the 85th percentile, but also requires an increase in concentrations pre- to post-storm to account for uncharacteristically high local receiving water concentrations. This is logical since we found that, on average, ocean receiving water concentrations were comparable pre- to post-storm at reference sites. Finally, state regulators have the option for ranking and prioritizing which guideline exceedences to enforce based on frequency and magnitude. For example, if only 15% of the data set near ASBS discharges exceeds the natural water quality guidelines (i.e., the reciprocal of the reference data sets' 85th percentile), managers may take different actions than if the frequency exceeds more than 15% of the data set near ASBS discharges.

The naturally occurring concentrations we observed in near coastal waters following storm events was similar to, or less than, State of California regulatory criteria (Table 6). For example, the natural water quality guidelines based on this study were universally lower than acute or instantaneous maxima criteria. Even for chronic water quality criteria, only four constituents were comparable to natural water quality guidelines (chromium, nickel, silver, zinc). The only exception was for total PAH, which has a chronic water quality criterion an order of magnitude less than the natural water quality guidelines in any of the three regions. This is due, at least in part, to the fact that the criterion was based on bioaccumulation estimates and effects on human health, as opposed to the natural water quality guideline designed to protect aquatic life.

The State of California also lists “background” seawater concentrations, measured during the 1970s at distances far from shore during dry weather (SWRCB 2012), which many regulated parties felt was an unfair comparison to nearshore, wet weather concentrations during 2014. In this case, the natural water quality guidelines were comparable to, or greater than, estimates of background seawater concentrations. While background and natural concentrations were comparable for arsenic, copper, mercury, nickel, and silver, background concentrations of zinc were lower than the naturally-occurring concentrations observed during this study in most regions. The concentrations provided herein represent the first estimates of naturally occurring concentrations, which for many constituents were previously unreported, including cadmium, copper, nickel and selenium.

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Figure 1. Map of ASBS and reference site locations.

Figure 2. Pre-storm to post-storm concentration comparisons within the: A) northern region; B) central region; C) southern region. Symbols define parameters. Trace metals in µg/L. Organics in ng/L.

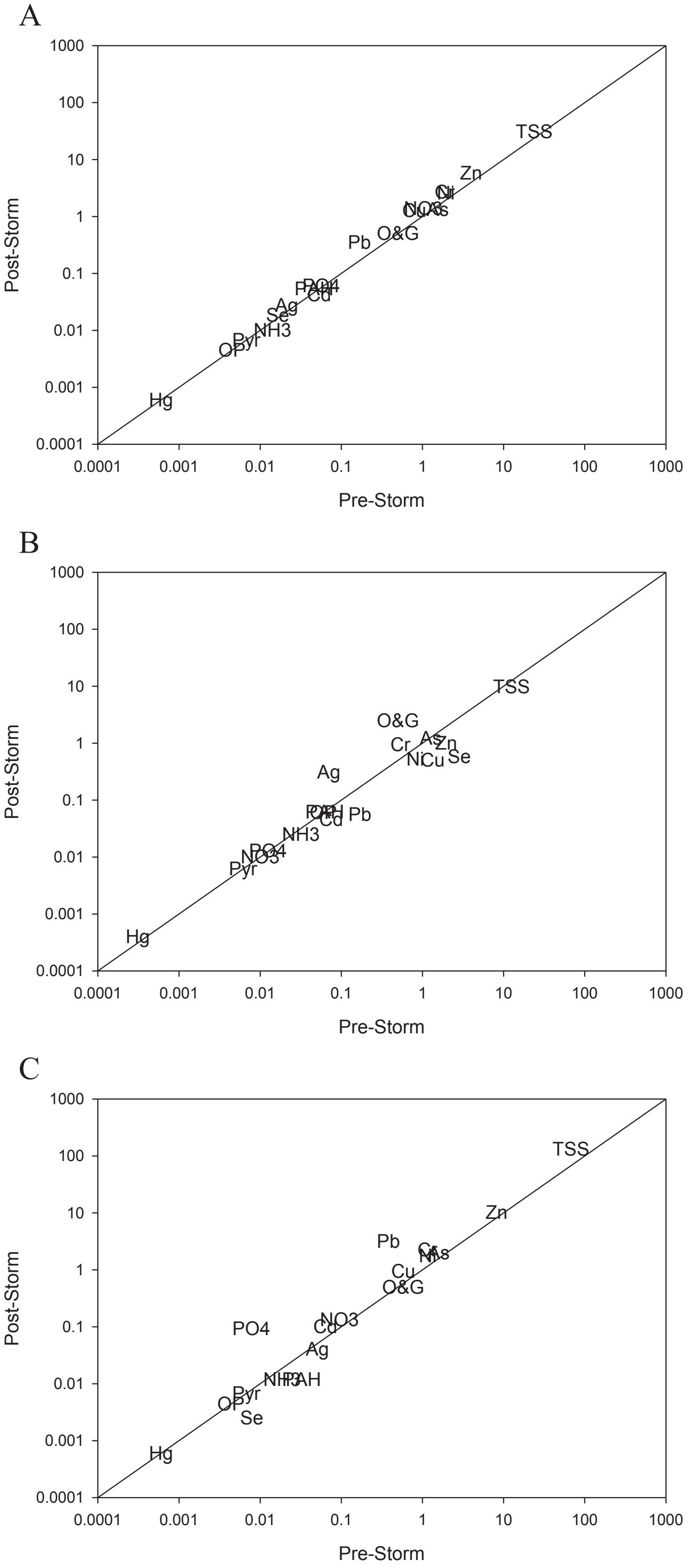


Table 1. Reference site locations and number of storm events sampled.

ASBS Number	ASBS Name	Region	Latitude	Longitude	Site Name	Number Pre-Storm Samples	Number Post-Storm Samples
2	Del Mar Landing	North	38.597	-123.351	Kruse Creek	3	3
5	Saunders Reef	North	39.126	-123.718	Greenwood Creek	3	3
6	Trinidad Head	North	41.141	-124.146	Agate Creek	3	3
6	Trinidad Head	North	41.078	-124.155	Martin Creek	3	3
7	King Range	North	39.711	-123.808	Hardy Creek	3	3
8	Redwood National Park	North	41.358	-124.077	Epsa Creek	1	1
8	Redwood National Park	North	41.700	-124.142	Nickel Creek	3	3
8	Redwood National Park	North	41.388	-124.071	Squashan Creek	2	2
-	-	Central	36.070	-121.600	Big Creek	1	3
-	-	Central	36.281	-121.858	Big Sur River	1	3
-	-	Central	36.422	-121.913	Doud Creek	1	3
-	-	Central	37.163	-122.362	Gazos Creek	1	3
-	-	Central	36.934	-121.864	La Selva Beach	1	3
-	-	Central	36.482	-121.938	Malpaso Creek	1	3
-	-	Central	36.698	-121.809	Marina State Beach	1	3
-	-	Central	37.041	-122.231	Scott Creek	1	2
-	-	Central	36.4563	-121.925	Soberanes Creek	1	3
-	-	Central	36.238	-121.816	Sycamore Creek	1	1
-	-	Central	37.358	-122.402	Tunitas Creek	1	3
21	San Nicholas Island	South	33.277	119.521	San Nicholas Island	1	1
21	San Nicholas Island	South	37.266	119.498	San Nicholas Island	4	5
23	San Clemente Island	South	32.981	118.538	San Clemente Island	2	2
24	Laguna to Latigo Point	South	34.062	-118.986	Deer Creek	2	2
24	Laguna to Latigo Point	South	34.042	-118.915	Nicholas Canyon	5	5
33	Irvine Coast	South	33.560	-117.822	El Morro Canyon	6	6
-	-	South	33.416	-118.395	Goat Harbor, Catalina Island	2	2
-	-	South	33.410	-118.382	Italian Gardens, Catalina Island	3	3
-	-	South	33.381	-117.577	San Onofre Creek	1	1
	Total	North				21	21
	Total	Central				11	30
	Total	South				26	27
	Total	**All CA**				**58**	**78**

Table 2. Summary of rainfall characteristics at reference sites sampled during this study.

Region		Intensity (mm/hr/event)	Quantity (mm/event)	Duration (hr/event)
North	Ave	6.4	37.3	23.5
	Med	5.3	26.4	19.0
	Min	4.1	12.2	6.2
	Max	16.5	115.1	53.0
Central	Ave	5.3	18.8	12.2
	Med	4.6	10.4	12.7
	Min	1.8	3.8	0.8
	Max	21.1	63.5	30.3
South	Ave	6.4	15.2	19.1
	Med	5.1	8.4	11.5
	Min	1.5	2.3	3.6
	Max	16.8	65.5	50.0

Table 3. Percent of ASBS reference site samples identified as outliers.

Analyte	Percent of Analyses			
	North (n=21)	Central (n=30)	South (n=27)	Total (N=78)
Ammonia as N	10	3	15	9
Nitrate as N	0	13	0	5
Oil & Grease	5	0	6	3
Ortho-Phosphate as P	0	3	0	1
Total Suspended Solids	0	0	0	0
Arsenic	0	0	0	0
Cadmium	0	0	0	0
Chromium	0	0	0	0
Copper	0	0	4	1
Lead	0	0	0	0
Mercury	5	0	0	1
Nickel	0	0	0	0
Selenium	0	0	24	8
Silver	0	0	0	0
Zinc	0	0	0	0
Total PAH	0	3	23	9
Any Analyte	**1**	**2**	**4**	**2**

Table 4. Summary of concentrations (percent non-detectable, minimum, maximum, median) at reference sites in the three regions of California.

Analyte Name	Northern California					Central California					Southern California				
	% ND	Min	Max	Median	Mean	% ND	Min	Max	Median	Mean	% ND	Min	Max	Median	Mean
General (mg/L)															
Ammonia as N	100	0.01	0.01	0.01	0.01	100	0.025	0.025	0.025	0.025	100	0.01	0.015	0.01	0.01
Nitrate as N	5	0.005	3.14	0.96	1.4	100	0.01	0.01	0.01	0.01	59	0.005	0.84	0.005	0.13
Oil & Grease	100	0.5	0.5	0.5	0.5	100	2.5	2.5	2.5	2.5	100	0.5	0.5	0.5	0.5
Ortho-Phosphate as P	14	0.005	0.12	0.06	0.06	100	0.013	0.015	0.013	0.013	53	0.005	1.0	0.005	0.09
Total Suspended Solids	0	9.3	59.4	28.6	31.1	3	2.0	29.0	9.0	9.9	11	0.25	1692	7.7	132.7
Metals (µg/L)															
Arsenic	0	0.38	2.16	1.29	1.33	0	0.49	1.80	1.53	1.40	4	0.003	14.1	1.5	2.0
Cadmium	0	0.02	0.07	0.04	0.04	0	0.01	0.07	0.04	0.04	4	0.001	0.95	0.03	0.10
Chromium	0	0.73	5.41	1.98	2.68	0	0.12	7.55	0.57	1.20	7	0.006	30.6	0.37	2.25
Copper	0	0.51	3.62	1.12	1.28	13	0.0025	1.61	0.27	0.35	4	0.003	5.9	0.40	0.94
Lead	0	0.07	1.09	0.28	0.35	26	0.001	0.20	0.03	0.05	11	0.001	71.3	0.08	3.1
Mercury	100	0.0006	0.0006	0.0006	0.0006	0	0.0002	0.0007	0.0004	0.0004	100	0.0006	0.0006	0.0006	0.0006
Nickel	0	0.78	5.4	2.4	2.6	0	0.16	1.37	0.50	0.61	4	0.001	15.8	0.44	1.8
Selenium	29	0.00	0.04	0.02	0.02	0	0.03	0.14	0.05	0.06	100	0.0025	0.0025	0.0025	0.0025
Silver	67	0.01	0.13	0.01	0.03	0	0.11	0.75	0.22	0.39	52	0.005	0.13	0.01	0.04
Zinc	0	1.41	13.28	5.68	5.81	4	0.00	1.73	0.50	0.63	7	0.001	129	1.9	10.3
Organics (µg/L)															
∑ Organophosph-orus Pesticides	100	0.003	0.006	0.006	0.005	100	0.060	0.060	0.060	0.060	100	0.002	0.006	0.006	0.004
∑ PAH	52	0.007	0.402	0.013	0.054	100	0.063	0.063	0.063	0.063	100	0.011	0.013	0.013	0.012
∑ Pyrethroid Pesticides	100	0.0068	0.0068	0.0068	0.0068	100	0.0062	0.0062	0.0062	0.0062	100	0.0065	0.0068	0.0068	0.0067

Table 5. Correlation coefficients among chemical concentrations and rainfall characteristics and total suspended solids (TSS) at reference sites in each of the three regions of California. Values in BOLD are statistically significant ($p < 0.05$).

	Maximum Intensity	Storm Rainfall	Storm Duration	TSS
Ammonia as N	*-0.23*	*-0.18*	*0.04*	**-0.48**
Nitrate as N	*-0.06*	*0.11*	*-0.06*	**0.58**
Oil & Grease	*-0.21*	**-0.25**	*-0.01*	**-0.38**
Ortho-Phosphate as P	*0.07*	**0.34**	*0.17*	**0.51**
Total Suspended Solids	*0.20*	*0.16*	*0.22*	-
Arsenic	*-0.08*	**-0.42**	*-0.08*	*0.14*
Cadmium	*0.02*	*-0.19*	*-0.02*	**0.47**
Chromium	*0.14*	**0.33**	**0.26**	**0.66**
Copper	**0.25**	**0.36**	**0.38**	**0.70**
Lead	*0.18*	*0.23*	**0.30**	**0.81**
Mercury	**0.27**	*0.19*	*0.22*	**0.42**
Nickel	*0.15*	**0.35**	*0.24*	**0.82**
Selenium	*-0.08*	**0.28**	*-0.04*	*-0.02*
Silver	*-0.01*	*0.03*	**-0.35**	**-0.45**
Zinc	**0.25**	*0.17*	**0.35**	**0.53**
Total PAH	*-0.18*	*-0.03*	*0.05*	**-0.27**

Table 6. Natural water quality guidelines used by the State of California for Areas of Special Biological Significance. For comparison, water quality criteria and open ocean concentrations are also presented.

Analyte	85th percentile			Water Quality Objectives			Background Seawater Concentrations
	North	Central	South	Chronic[a]	Acute[b]	Instantaneous Max[c]	
General (mg/L)							
Ammonia as N	0.010	0.025	0.015	0.6	2.4	6.0	--[e]
Nitrate as N	2.84	0.01	0.34	-[d]	-[d]	-[d]	--
Oil & Grease	0.5	2.5	0.5	-	-	-	--
Ortho-phosphate as P	0.090	0.013	0.100	-	-	-	--
Total Suspended Solids	42	16	48	-	-	-	--
Metals (µg/L)							
Arsenic	1.7	1.6	1.8	8	32	80	3
Cadmium	0.06	0.05	0.15	1	4	10	--
Chromium	4.2	1.6	1.9	2	8	20	--
Copper	1.8	0.6	1.5	3	12	30	2
Lead	0.5	0.1	0.5	2	8	20	--
Mercury	0.0006	0.0007	0.0006	0.04	0.16	0.4	0.0005
Nickel	4.5	1.1	1.3	5	20	50	--
Selenium	0.03	0.07	0.003	15	60	150	--
Silver	0.06	0.64	0.08	0.7	2.8	7	0.16
Zinc	9.7	1.0	18.6	20	80	200	8
Organics (µg/L)							
Total PAHs	0.0474	0.0625[f]	0.0125	0.0088	-	-	-
Total Organophosphorus pesticides	0.006	0.06	0.006	-	-	-	-
Total Pyrethroid pesticides	0.00675	0.00615	0.00675	-	-	-	-

[a] Chronic is defined as 6-month median, [b] Acute is defined as daily maximum, [c] Instantaneous maximum is a single sample, [d] - indicates no water quality objective for these analytes, [e] -- indicates background concentrations set to zero , [f] 0.0325 µg/L if only 13 PAH listed California Ocean Plan (SWRCB 2012) are used.

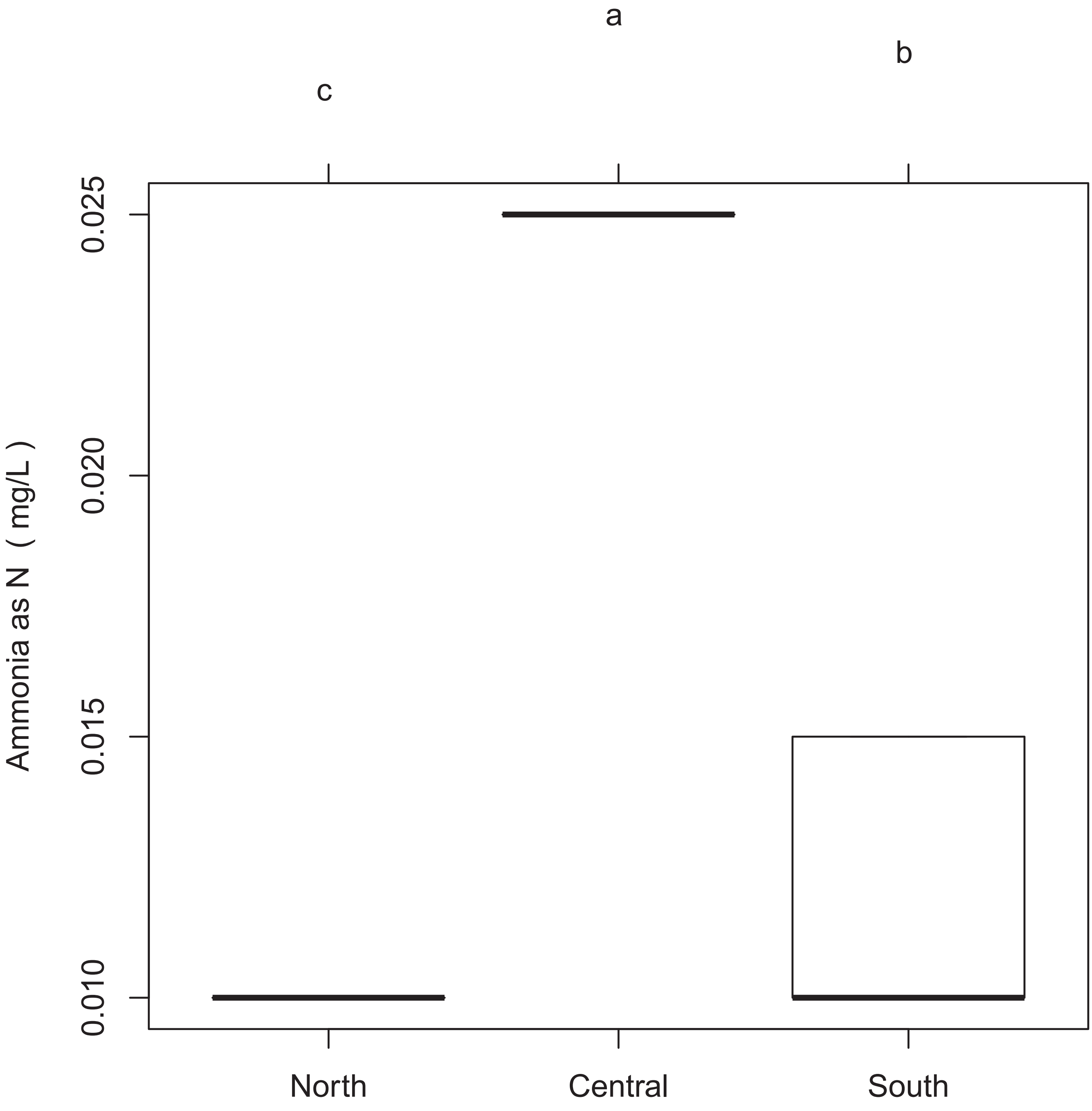
APPENDIX

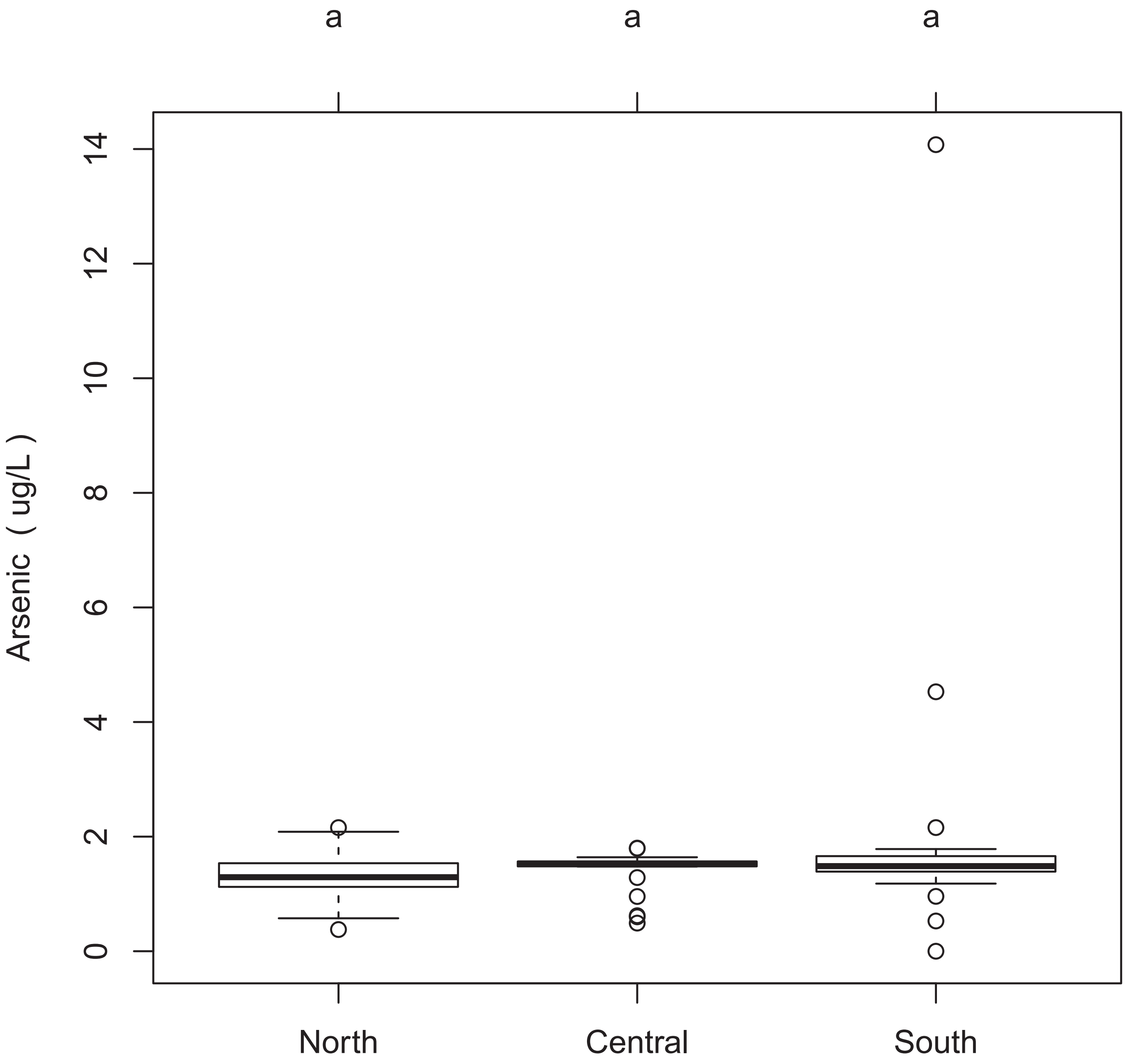
Appendix 1. Range of method detection limits by region.

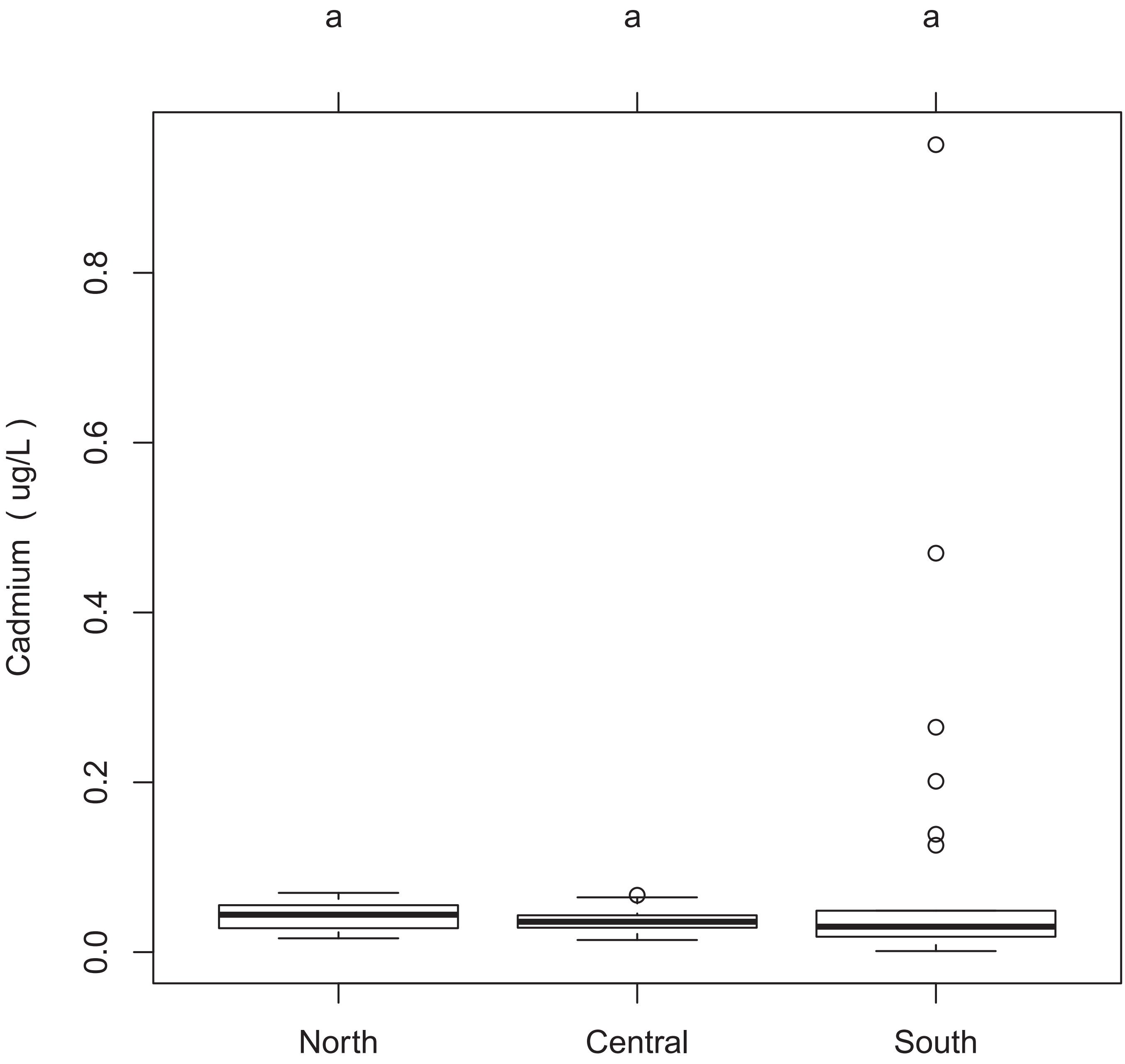
Analyte	North	Central	South
Ammonia as N (mg/L)	0.02	0.05	0.02, 0.03
Nitrate as N (mg/L)	0.01	0.02	0.01
Oil and Grease (mg/L)	1	5	1
Orthophosphate as P (mg/L)	0.01	0.025	0.01
Total Suspended Solids (mg/L)	0.5	2	0.5
Arsenic (µg/L)	0.005	0.005	0.005, 0.01
Cadmium (µg/L)	0.0025	0.0025,	0.0025, 0.005
Chromium (µg/L)	0.0125	0.0125	0.0125, 0.025
Copper (µg/L)	0.005	0.005	0.005, 0.01
Lead (µg/L)	0.0025	0.0025	0.0025, 0.005
Mercury (µg/L)	0.0012	0.0002	0.0012
Nickel (µg/L)	0.0025	0.0025	0.0025, 0.005
Selenium (µg/L)	0.005	0.005	0.005
Silver (µg/L)	0.01	0.01	0.01, 0.02
Zinc (µg/L)	0.0025	0.0025	0.0025, 0.005
Total PAHs (µg/L)	0.013, 0.025	0.125	0.021, 0.025
Acenaphthene	0.001	0.005	0.001
Acenaphthylene	0.001	0.005	0.001
Anthracene	0.001	0.005	0.001
Benz(a)anthracene	0.001	0.005	0.001
Benzo(a)pyrene	0.001	0.005	0.001
Benzo(b)fluoranthene	0.001	0.005	0.001
Benzo(e)pyrene	0.001	0.005	0.001
Benzo(g,h,i)perylene	0.001	0.005	0.001
Benzo(k)fluoranthene	0.001	0.005	0.001
Biphenyl	0.001	0.005	0.001
Chrysene	0.001	0.005	0.001
Dibenz(a,h)anthracene	0.001	0.005	0.001
Dibenzothiophene	0.001	0.005	0.001
Dimethylnaphthalene, 2,6-	0.001	0.005	0.001
Fluoranthene	0.001	0.005	0.001
Fluorene	0.001	0.005	0.001
Indeno(1,2,3-c,d)pyrene	0.001	0.005	0.001
Methylnaphthalene, 1-	0.001	0.005	0.001
Methylnaphthalene, 2-	0.001	0.005	0.001
Methylphenanthrene, 1-	0.001	0.005	0.001
Naphthalene	0.001	0.005	0.001
Perylene	0.001	0.005	0.001
Phenanthrene	0.001	0.005	0.001
Pyrene	0.001	0.005	0.001
Trimethylnaphthalene, 2,3,5-	0.001	0.005	0.001
Total Organophosphorus pesticides (µg/L)	0.005, 0.012	0.06	0.006, 0.024
Chlorpyrifos	0.0005	0.018-0.019	0.0005
Diazinon	0.0005	0.014-0.015	0.0005
Ethoprop	0.001	0.012-0.013	0.001
Fenchlorphos	0.002	0.013-0.014	0.002
Malathion	0.003	0.018-0.019	0.003
Parathion, methyl	0.001	0.014-0.015	0.001
Tokuthion	0.003	0.027-0.029	0.003
Trichloronate	0.001	0.004, 0.0042	0.001

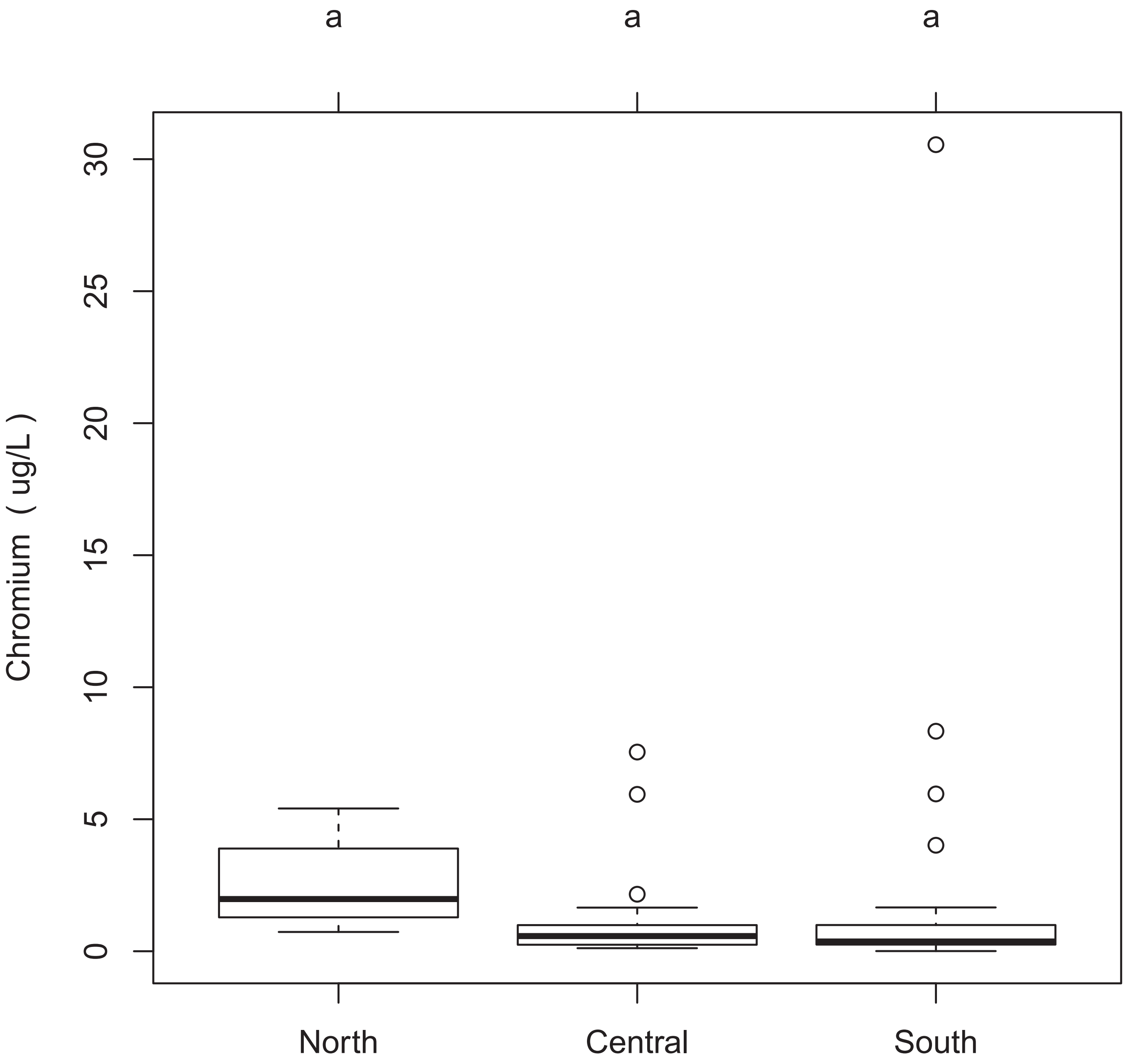
Analyte	**North**	**Central**	**South**
Total Pyrethroid pesticides (µg/L)	0.0135	0.00615	0.013, 0.0135
Bifenthrin	0.0005	0.0017, 0.0018	0.0005
Cyfluthrin, total	0.0005	0.0011, 0.0012	0.0005
Cyhalothrin, Total lambda-	0.0005	0.0005	0.0005
Cypermethrin, total	0.0005	0.0029 – 0.0031	0.0005
Deltamethrin/Tralomethrin	0.0005	0.0016, 0.0017	0.0005
Esfenvalerate/Fenvalerate, total	0.0005	0.0007, 0.0008	0.0005
Fenpropathrin	0.0005	0.0003	0.0005
Permethrin, cis-	0.005	0.0012, 0.0013	0.005
Permethrin, trans-	0.005	0.0023, 0.0025	0.005

Appendix 2. Comparison of parameter concentrations across regions.

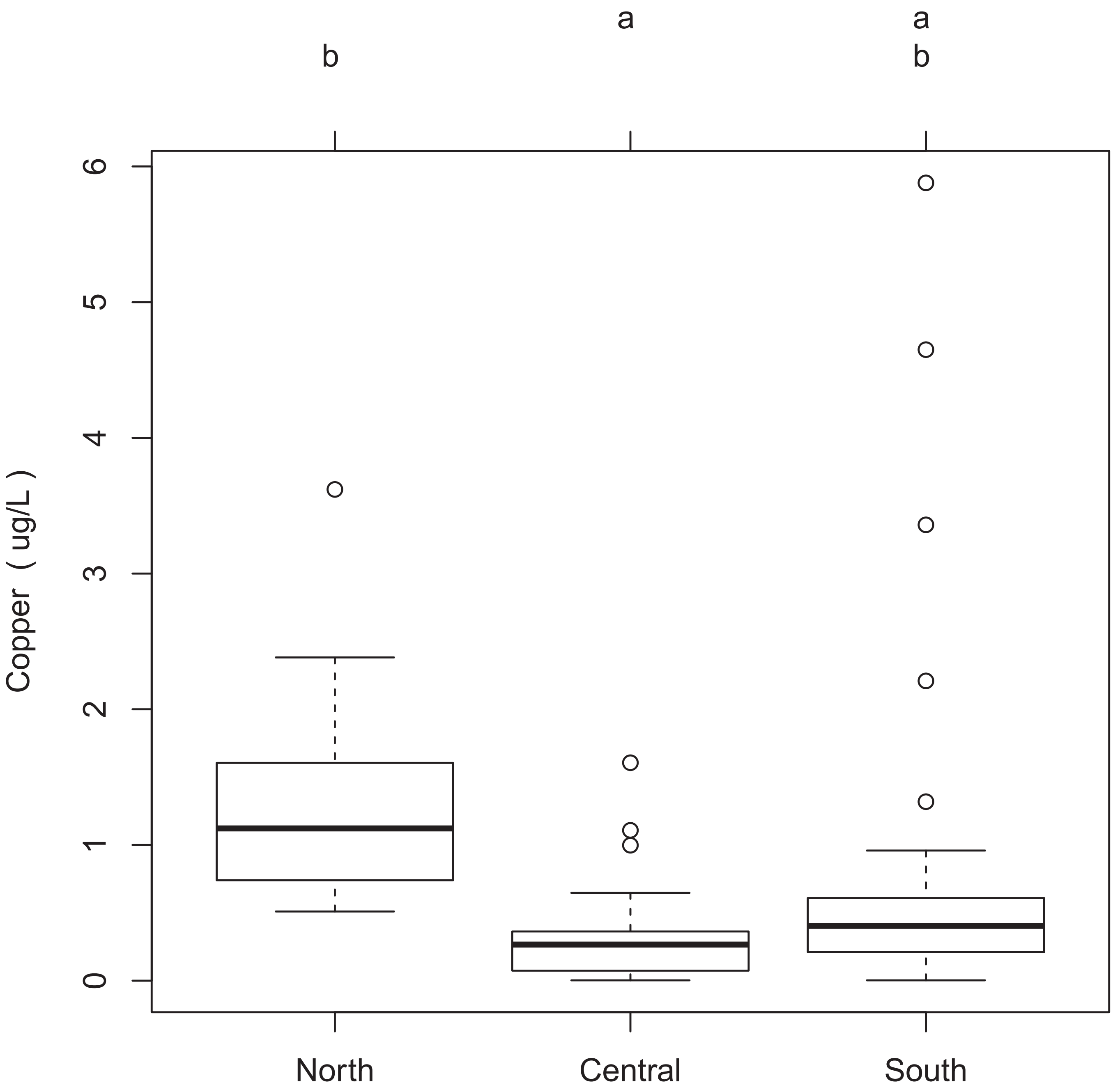


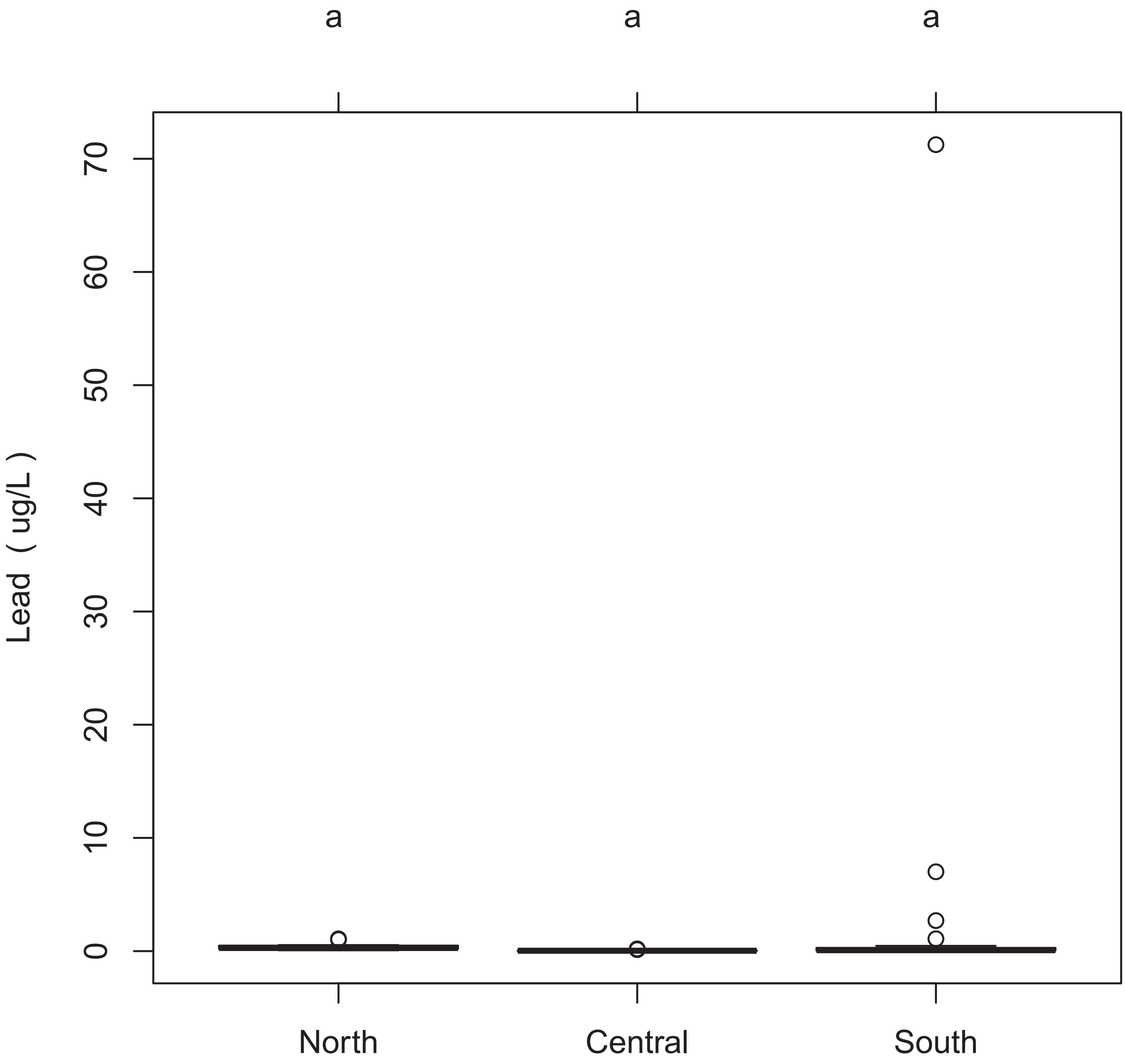

a
a
a
Arsenic (ug/L)
0
2
4
6
8
10
12
14
North
Central
South

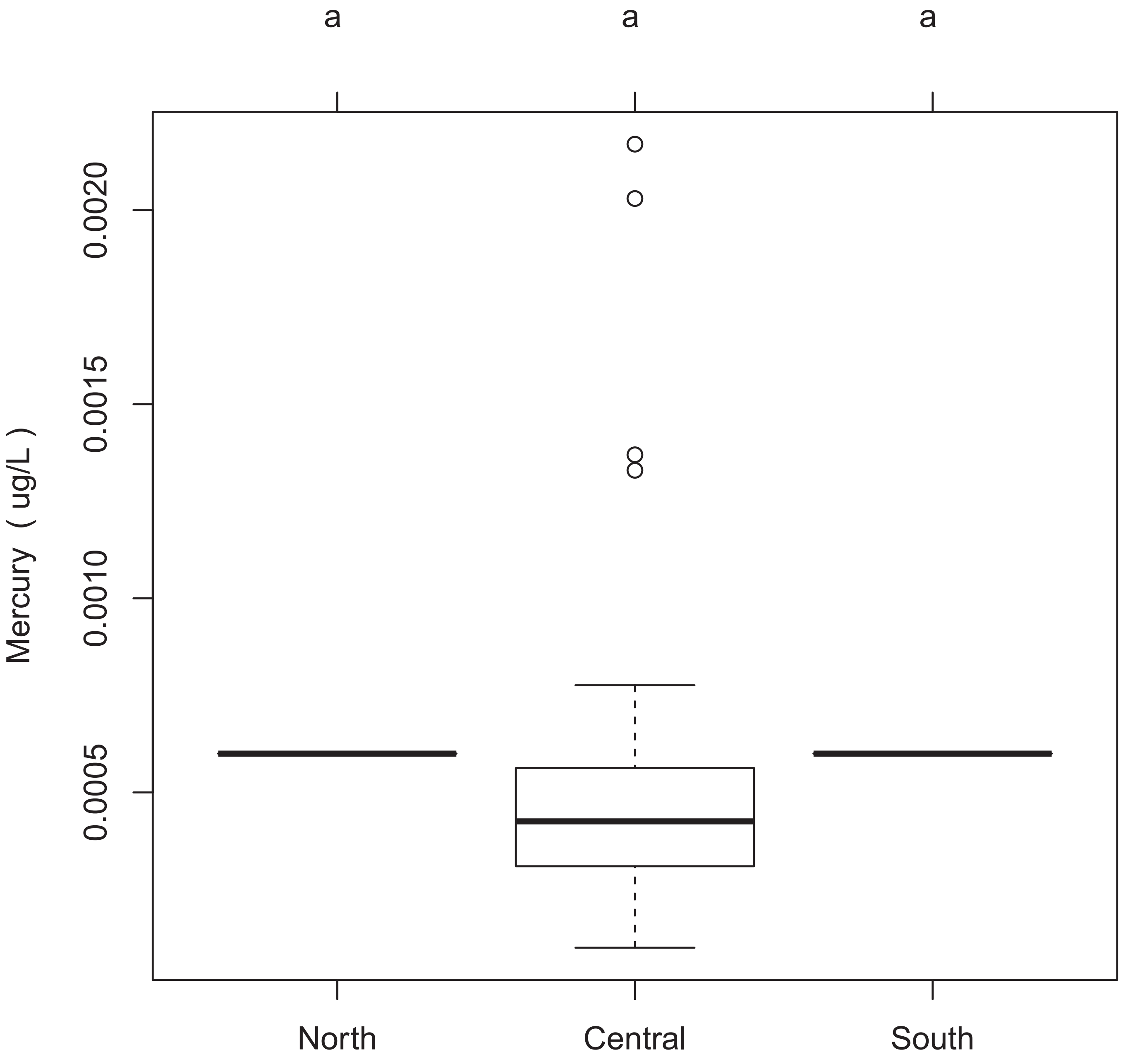

a
a
a
Cadmium (ug/L)
0.0
0.2
0.4
0.6
0.8
North
Central
South

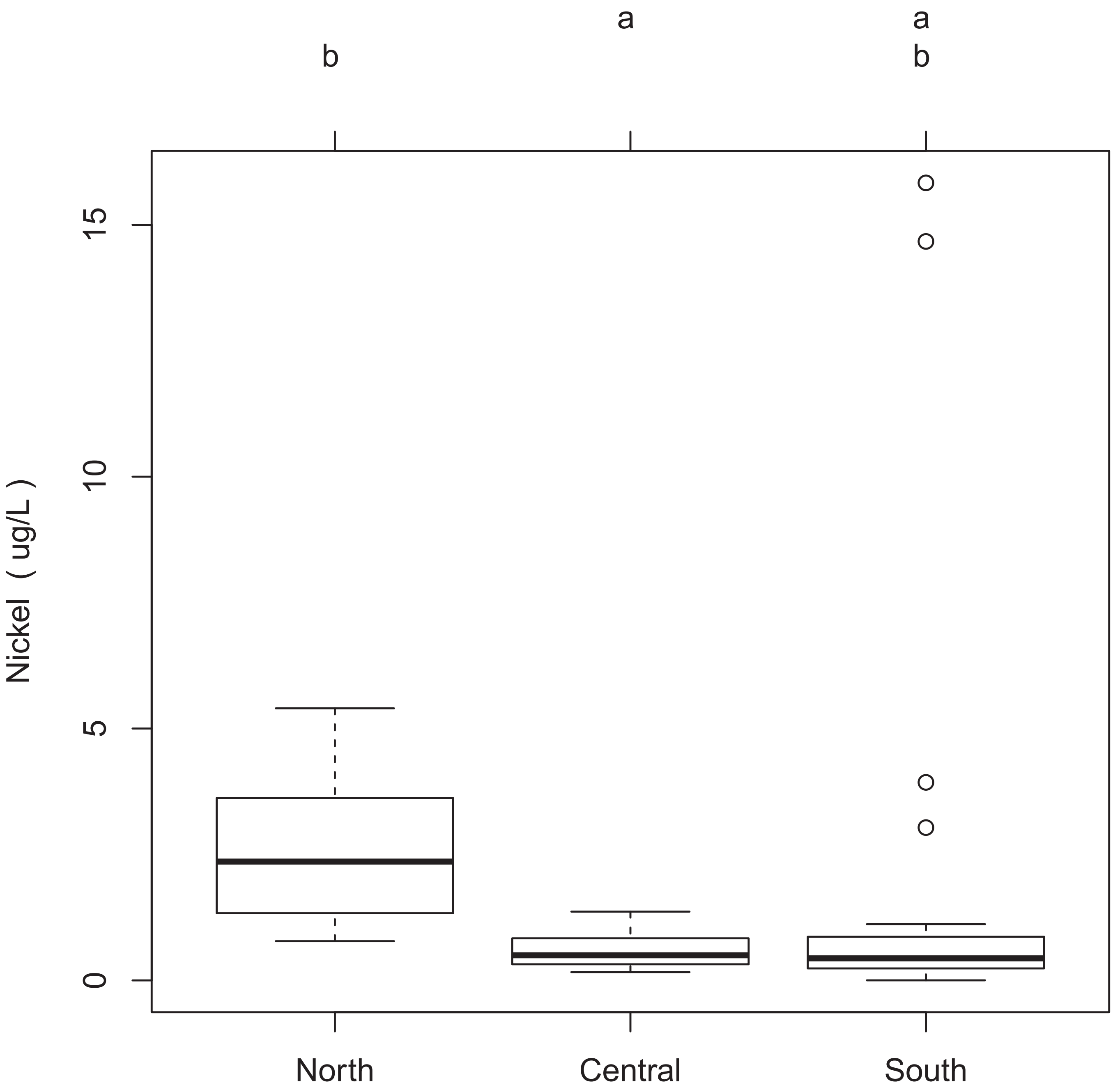


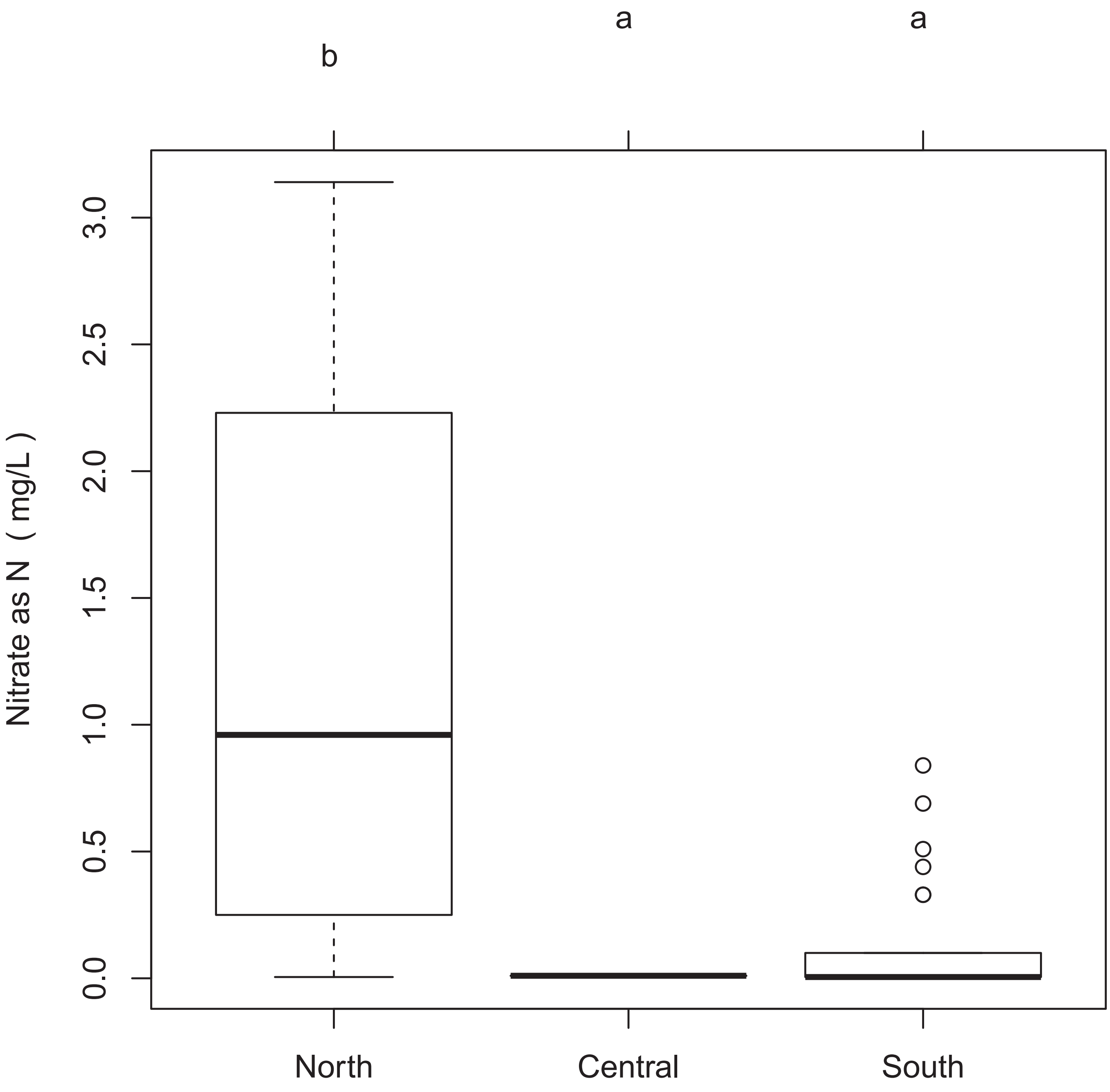
a
a
a
Chromium (ug/L)
0
5
10
15
20
25
30
North
Central
South

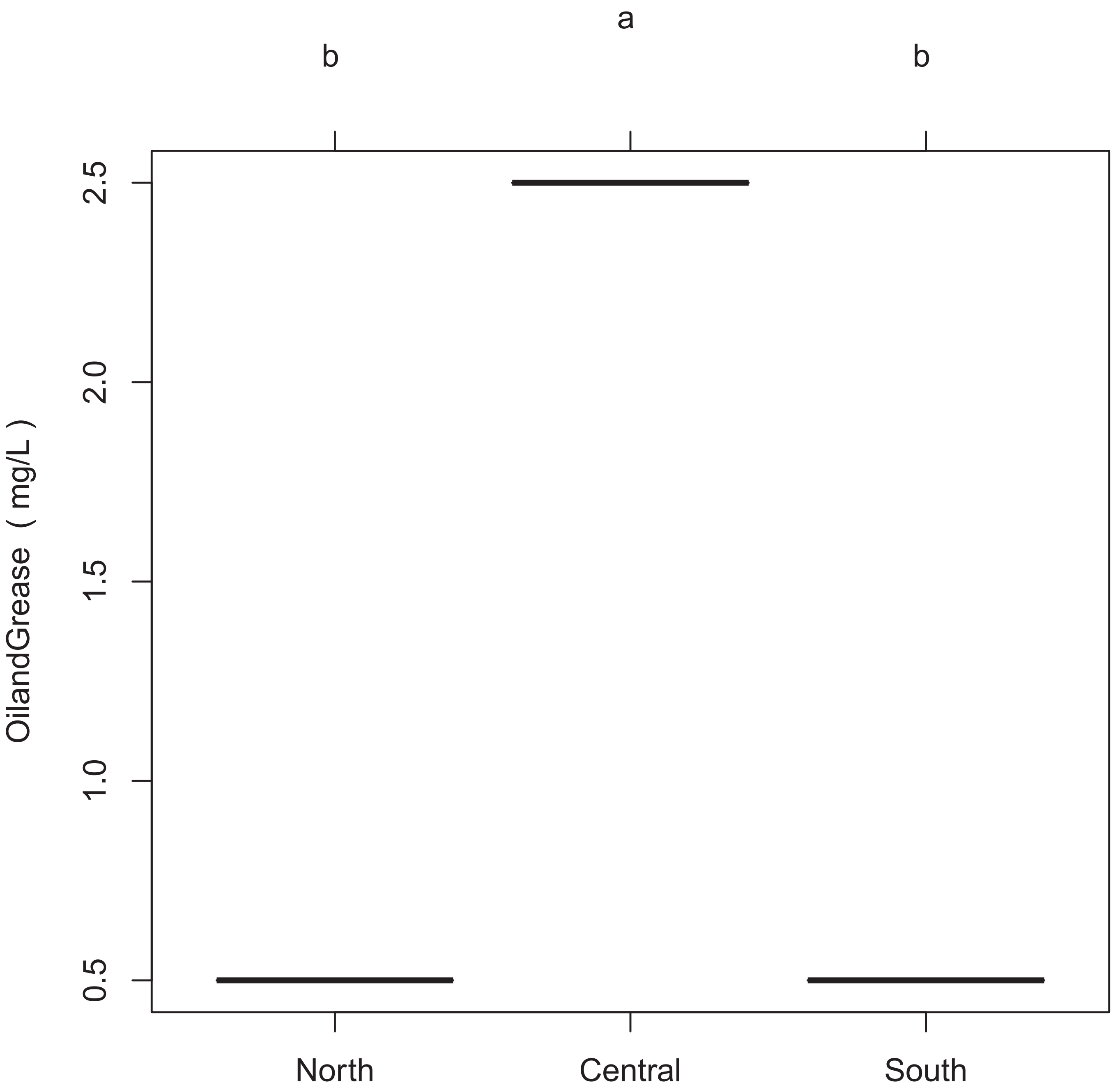

b
a
a
b
Copper (ug/L)
0
1
2
3
4
5
6
North
Central
South

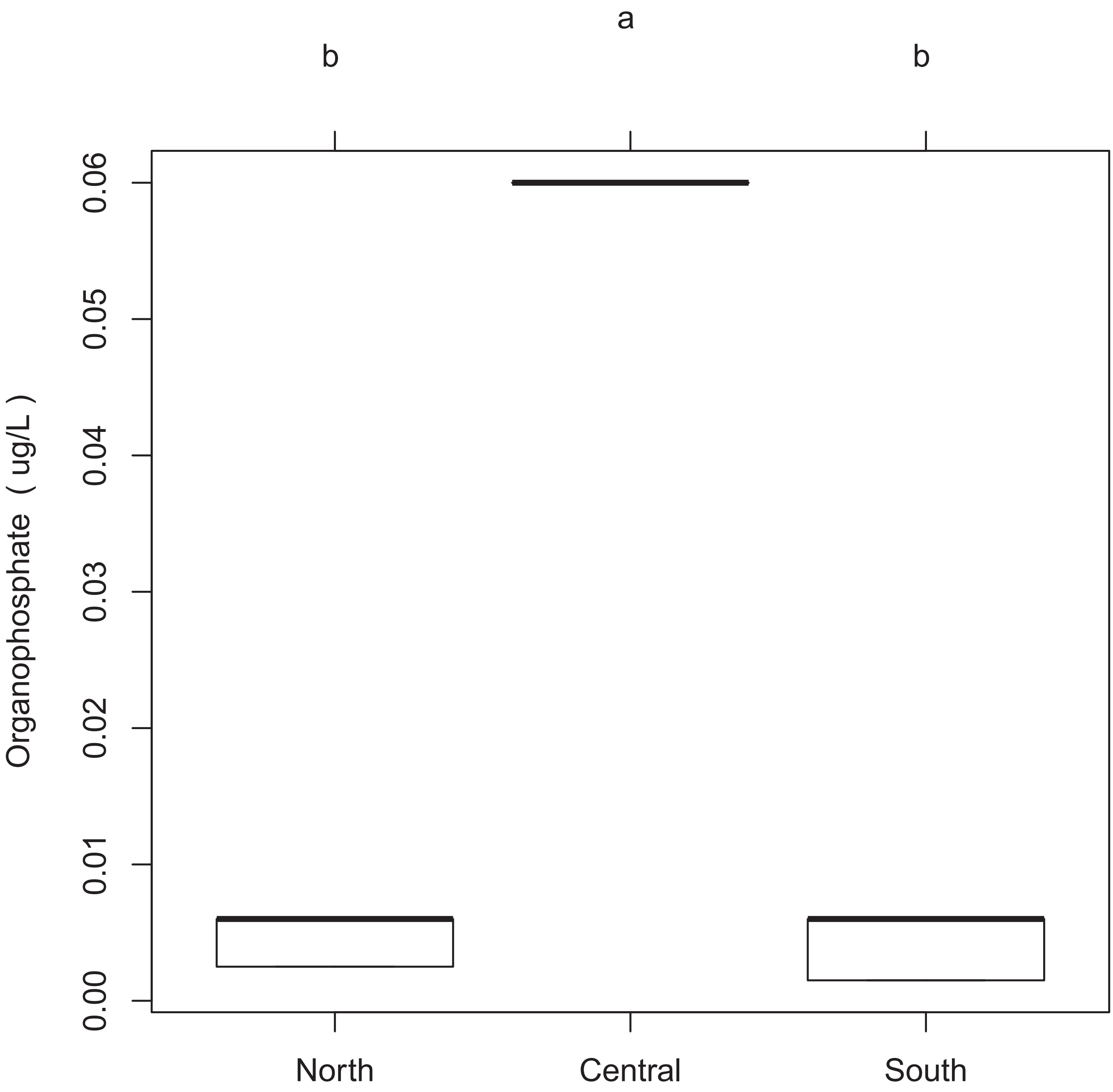

a
a
a
Lead (ug/L)
0
10
20
30
40
50
60
70
North
Central
South

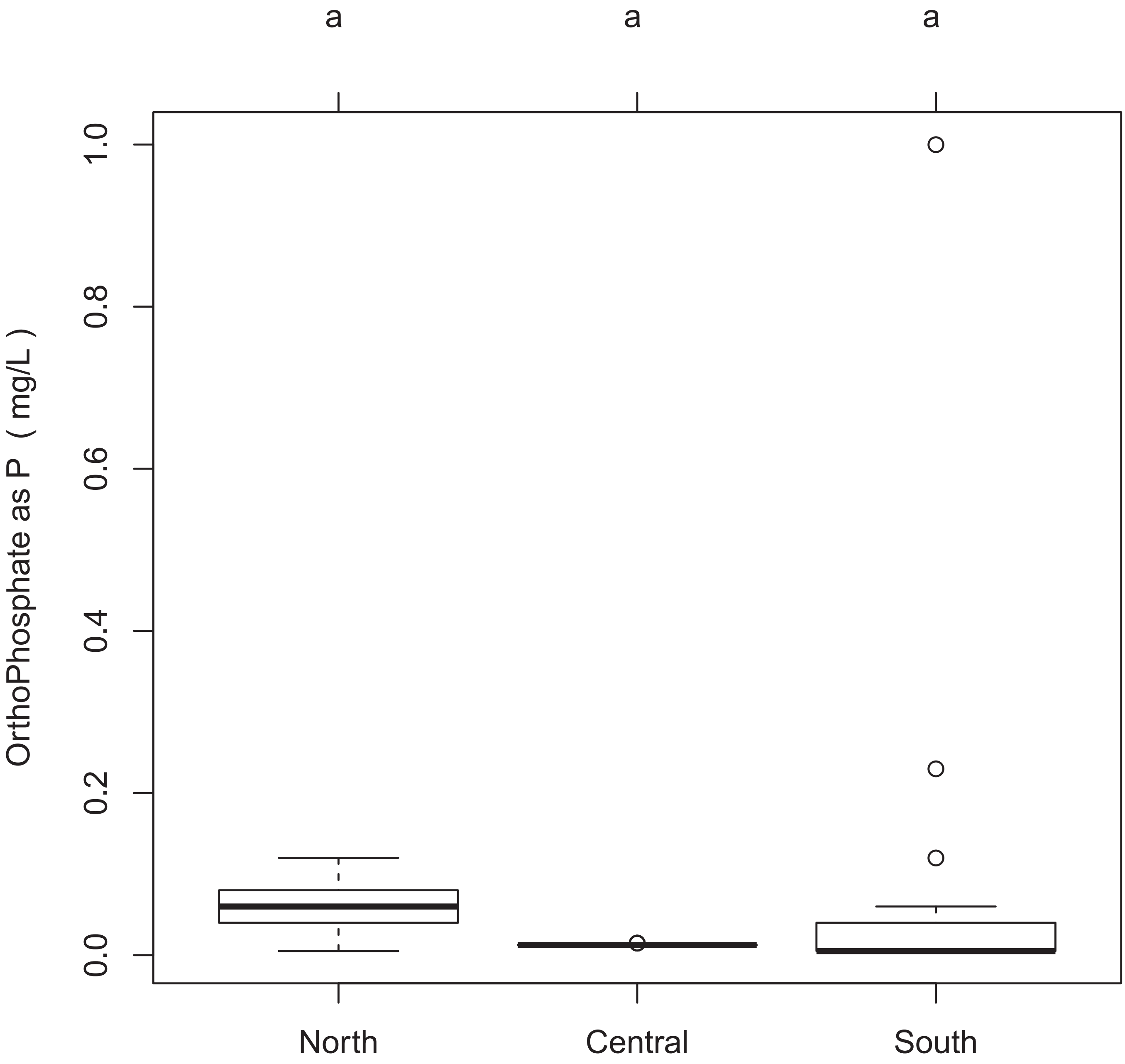

a
a
a
Mercury (ug/L)
0.0020
0.0015
0.0010
0.0005
North
Central
South


b
a
a
b
15
10
5
0
Nickel (ug/L)
North
Central
South

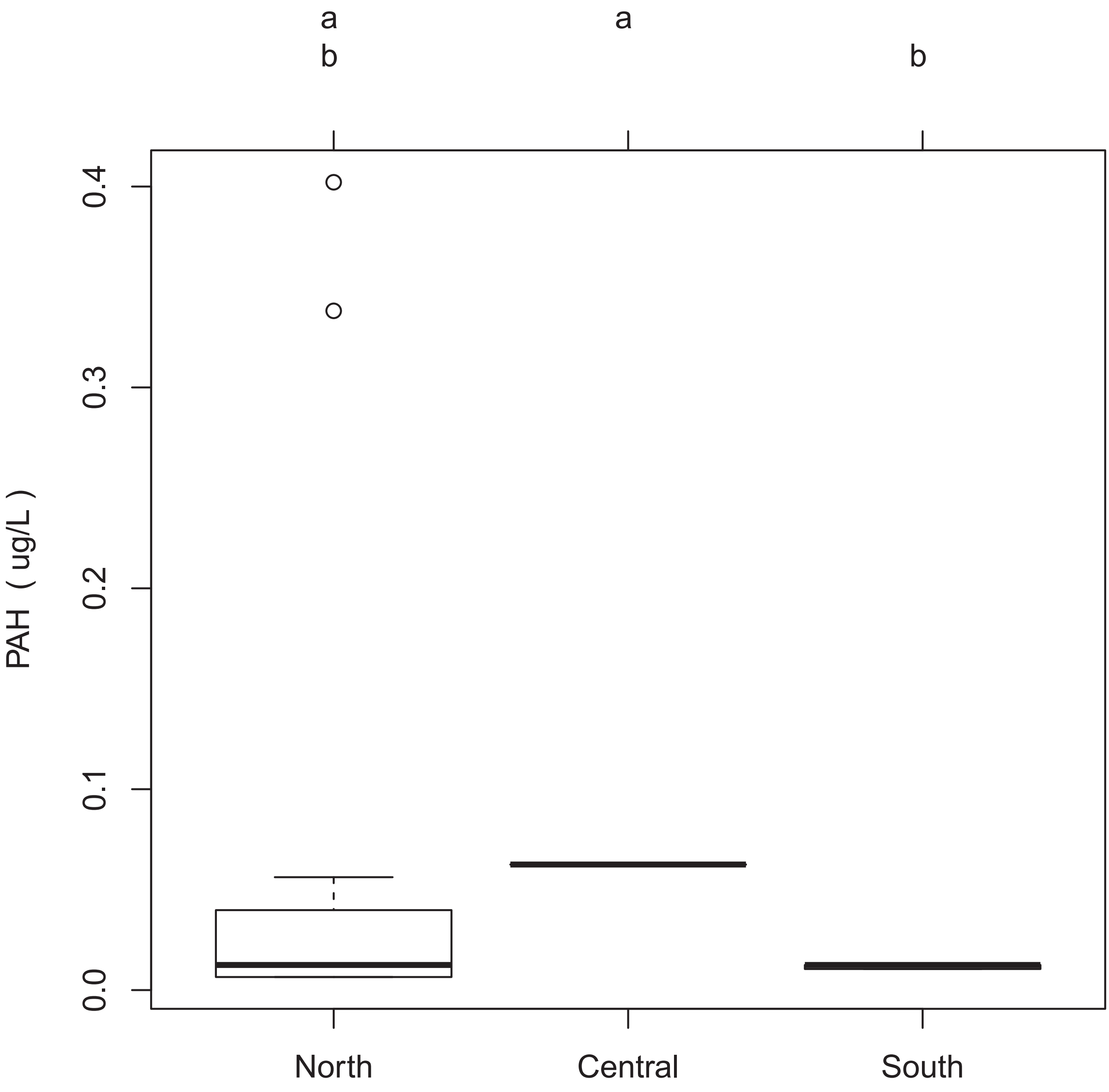

b
a
a
Nitrate as N (mg/L)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
North
Central
South

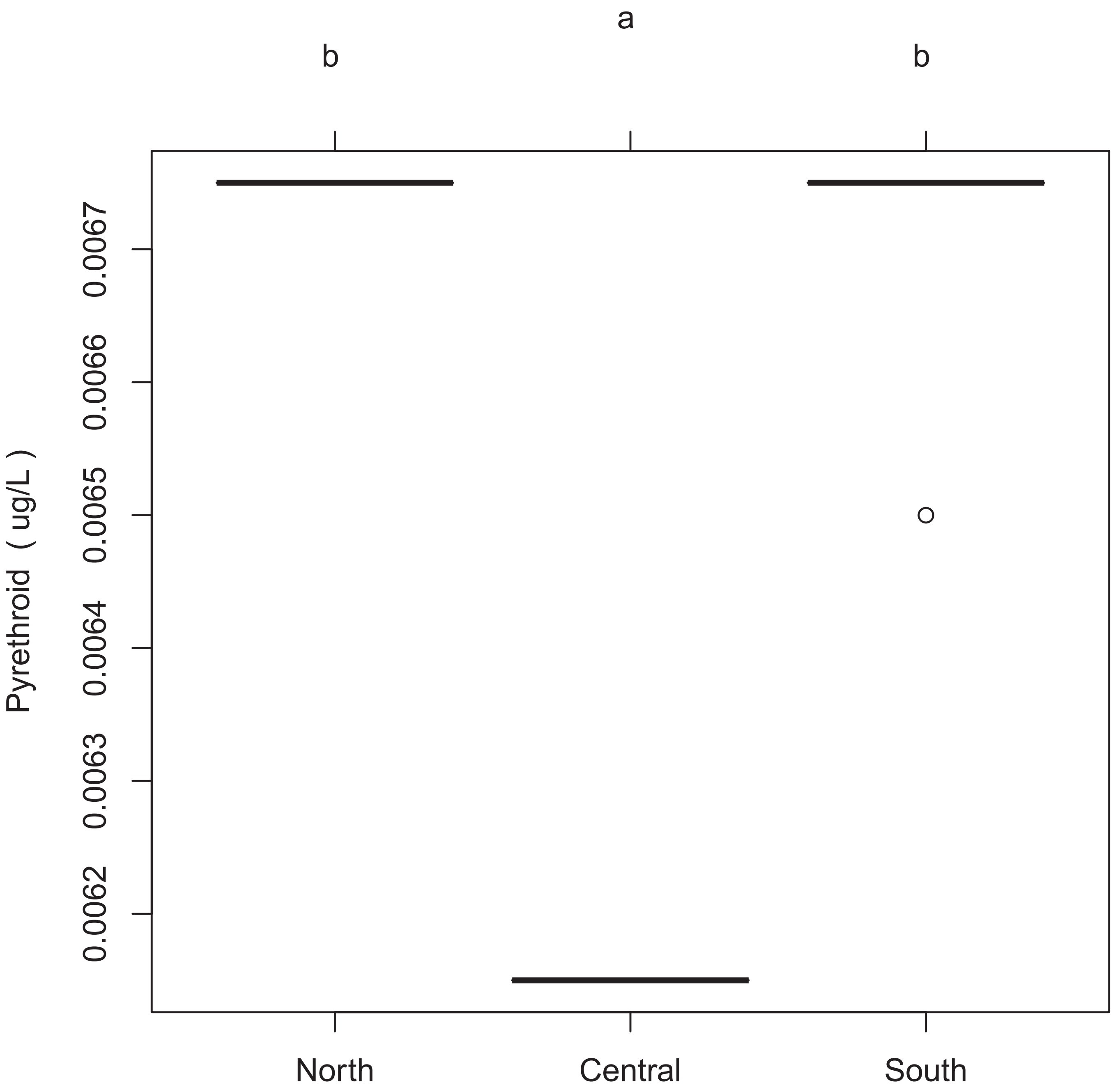

b
a
b
OilandGrease (mg/L)
0.5
1.0
1.5
2.0
2.5
North
Central
South

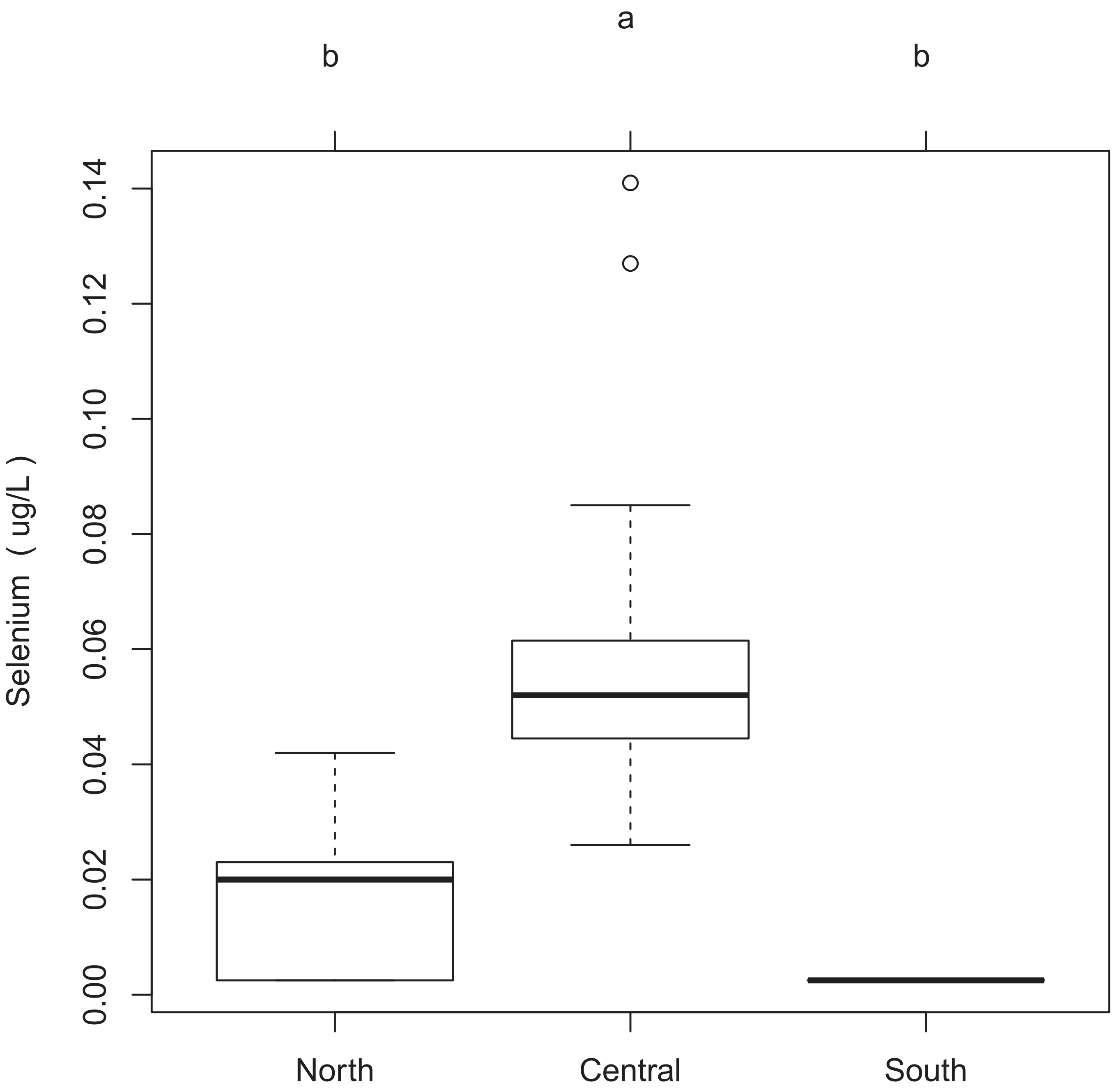

b
a
b
Organophosphate (ug/L)
0.06
0.05
0.04
0.03
0.02
0.01
0.00
North
Central
South

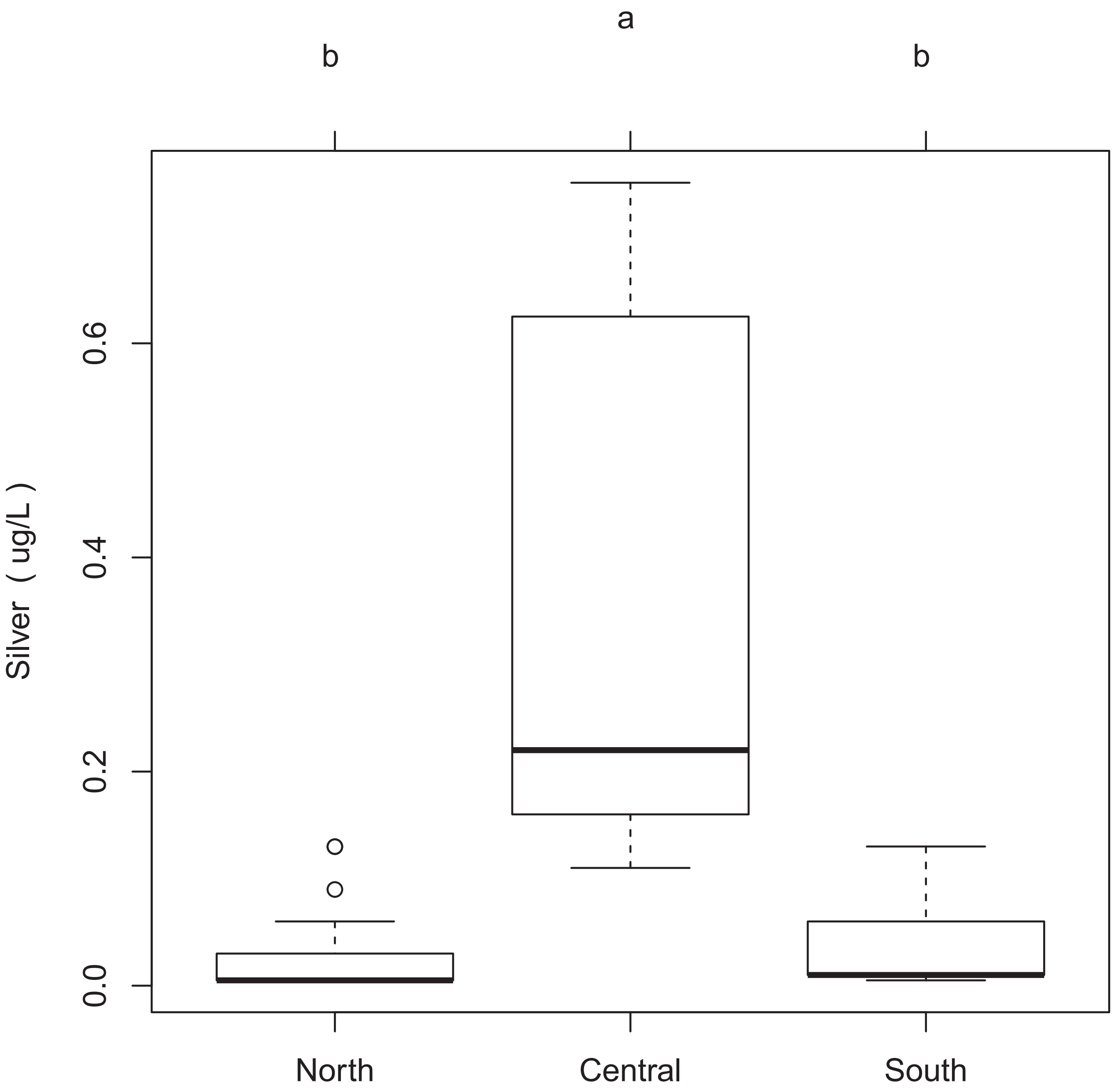


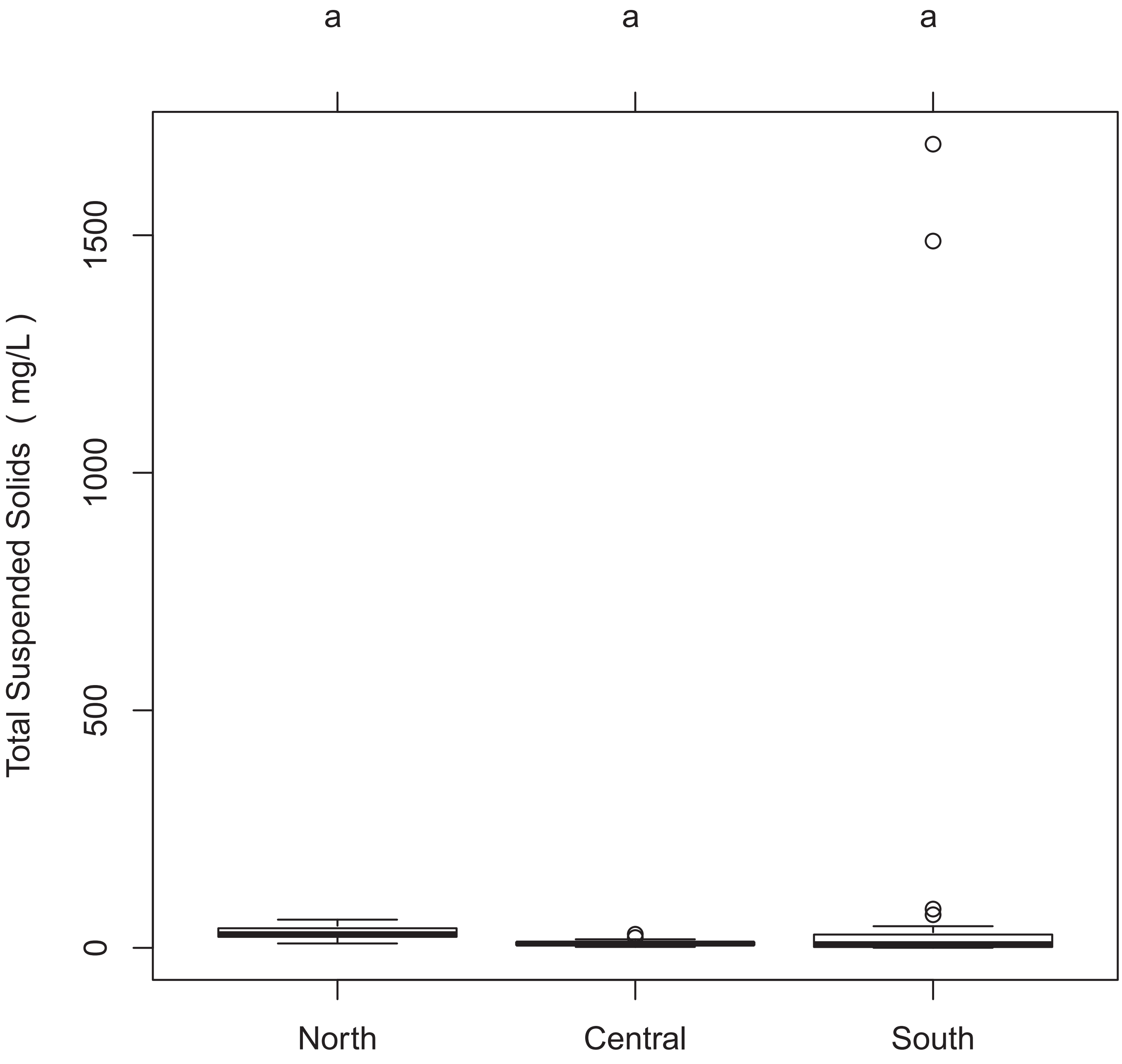
a
a
a
OrthoPhosphate as P (mg/L)
0.0
0.2
0.4
0.6
0.8
1.0
North
Central
South

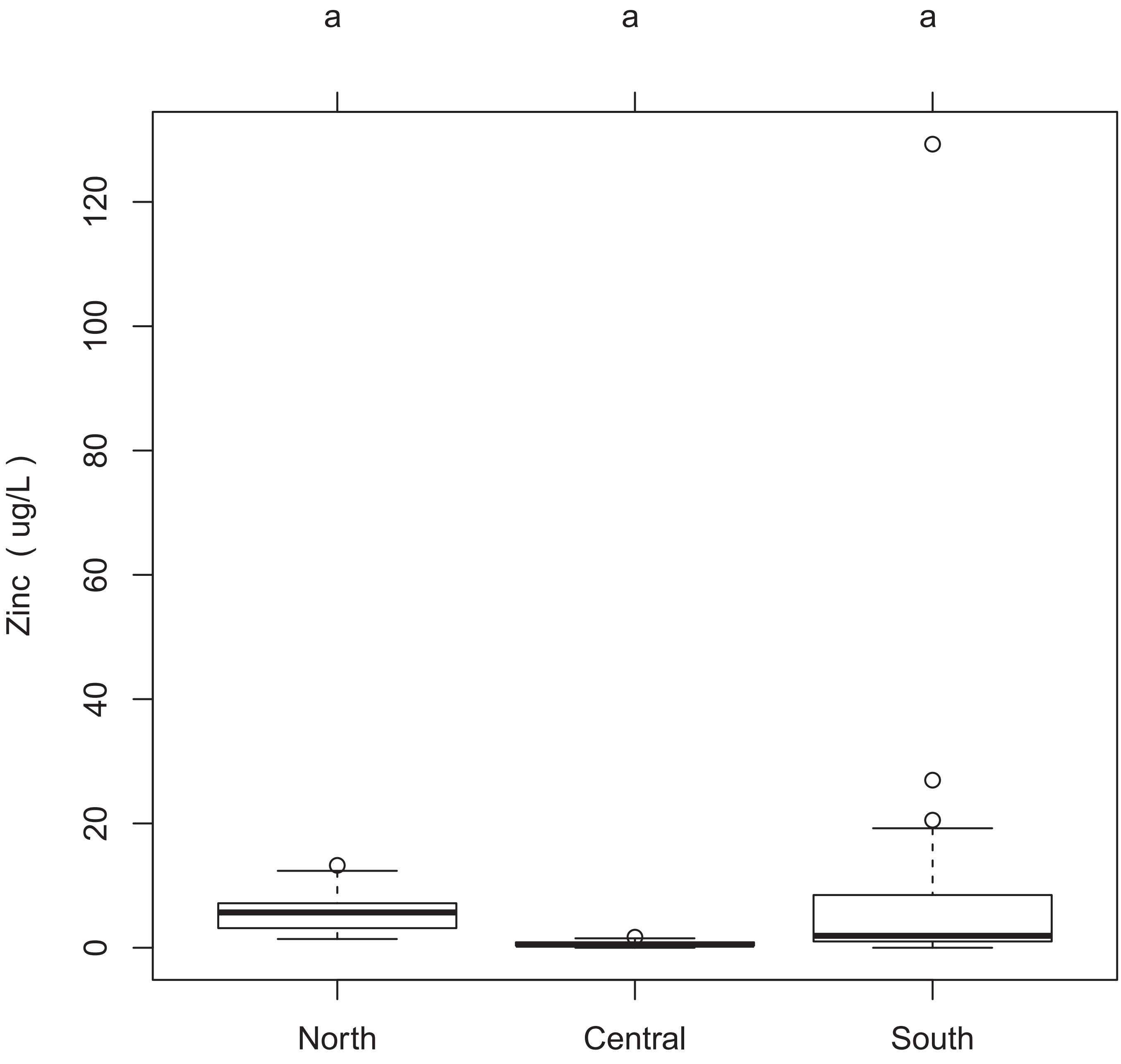

a
b
a
b
0.0
0.1
0.2
0.3
0.4
PAH (ug/L)
North
Central
South


a
b
b
Pyrethroid (ug/L)
0.0062
0.0063
0.0064
0.0065
0.0066
0.0067
North
Central
South

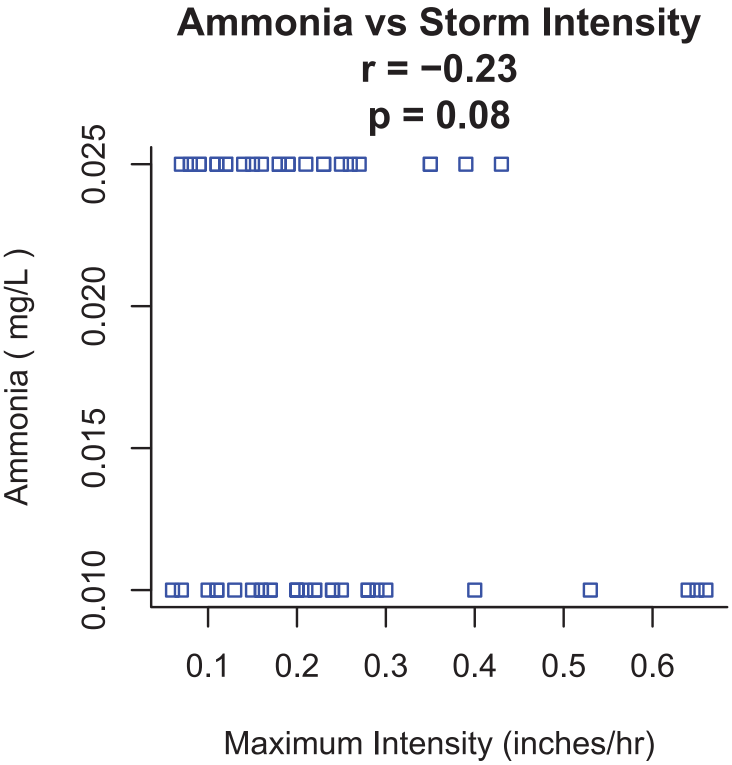

b
a
b
Selenium (ug/L)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
North
Central
South

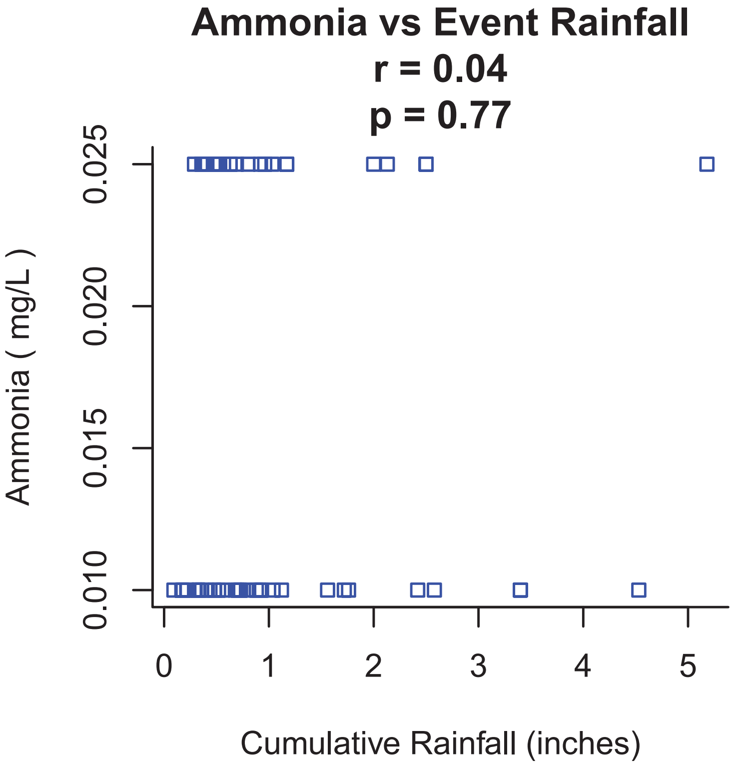

b
a
b
Silver (ug/L)
0.0
0.2
0.4
0.6
North
Central
South

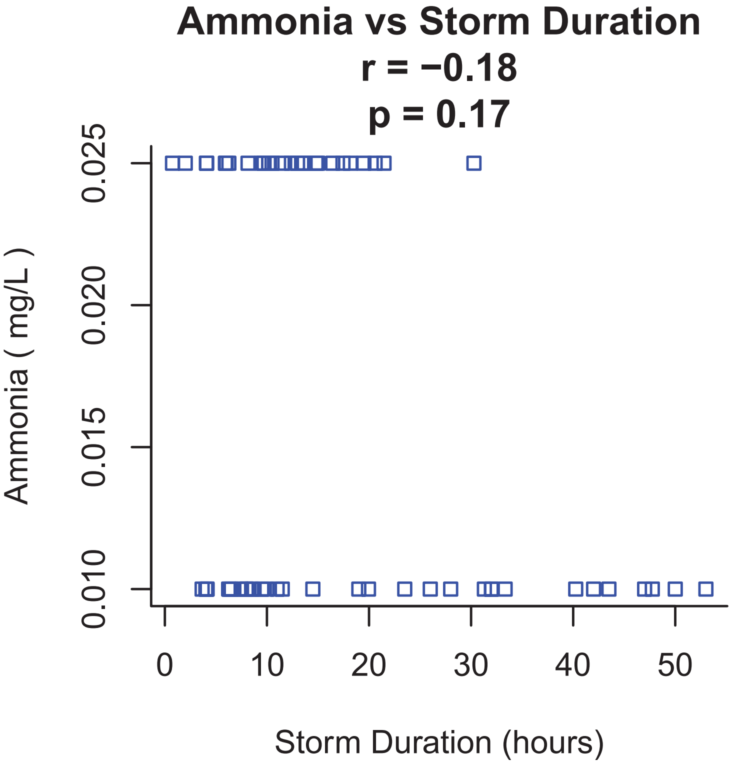

a
a
a
Total Suspended Solids (mg/L)
0
500
1000
1500
North
Central
South

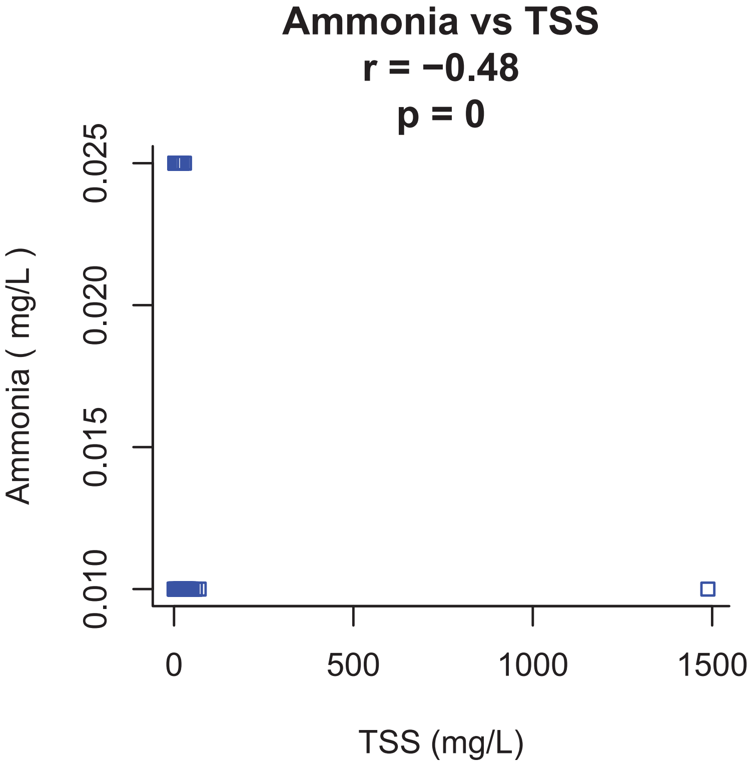

a
a
a
Zinc (ug/L)
0
20
40
60
80
100
120
North
Central
South

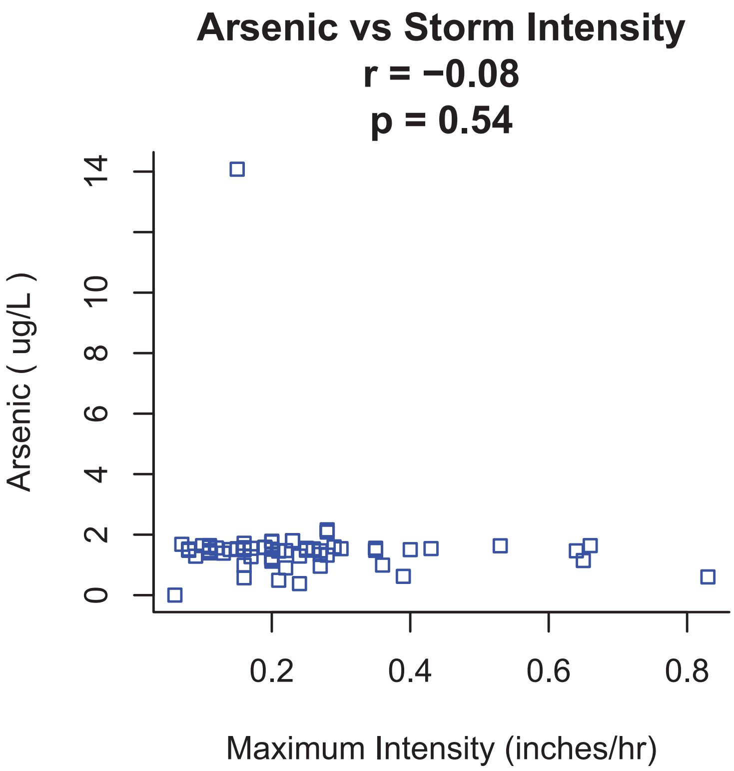
Appendix 3. Rainfall and TSS correlations with parameter concentrations

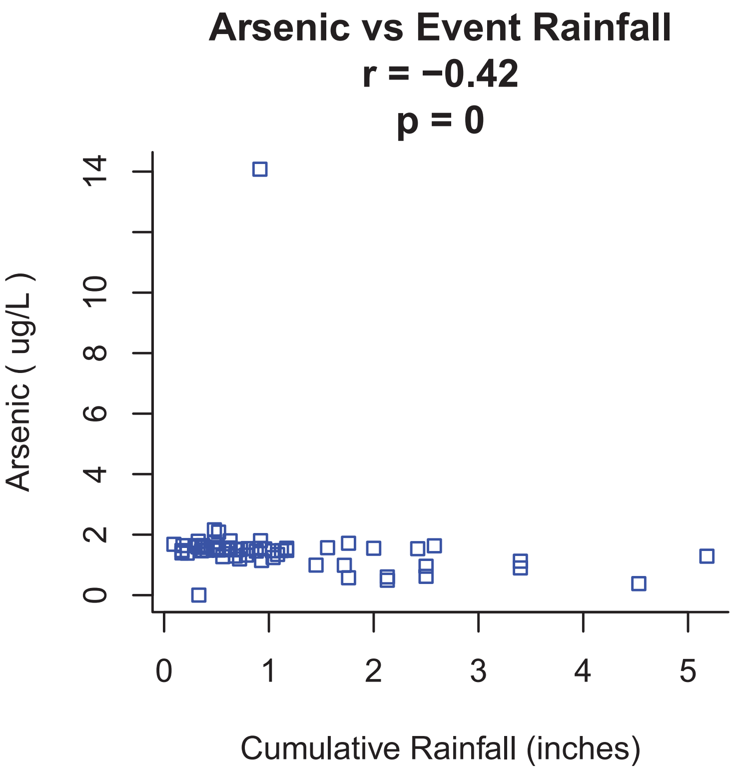

Ammonia vs Storm Intensity
r = −0.23
p = 0.08
Ammonia (mg/L)
0.010
0.015
0.020
0.025
0.1
0.2
0.3
0.4
0.5
0.6
Maximum Intensity (inches/hr)

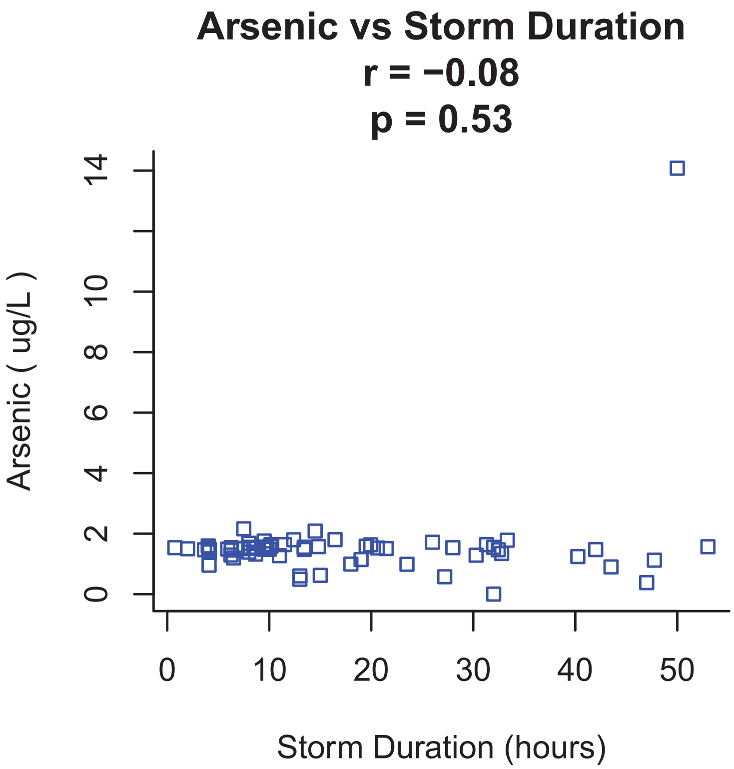

Ammonia vs Event Rainfall
r = 0.04
p = 0.77
Ammonia (mg/L)
0.010
0.015
0.020
0.025
0
1
2
3
4
5
Cumulative Rainfall (inches)

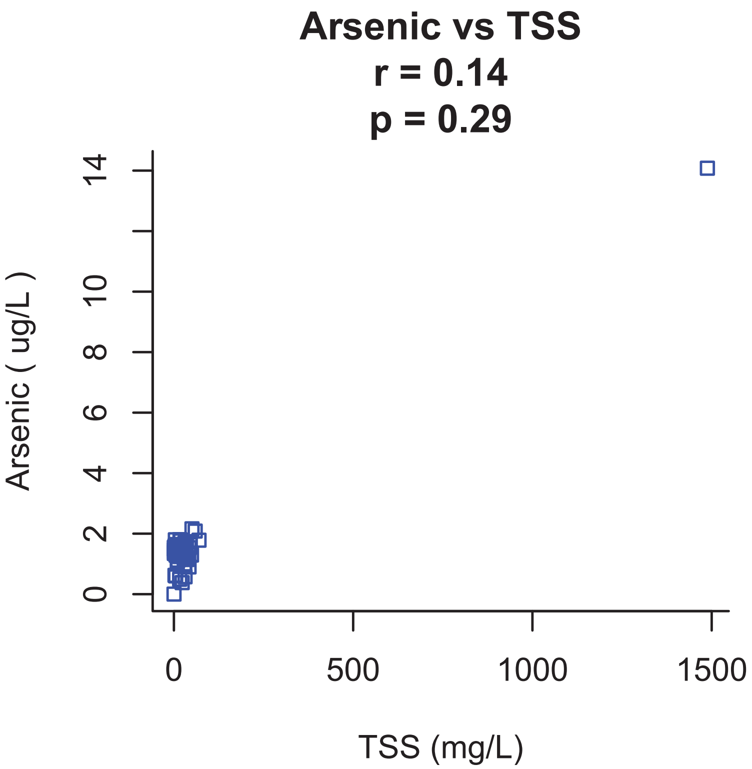

Ammonia vs Storm Duration
r = −0.18
p = 0.17
Ammonia (mg/L)
0.010
0.015
0.020
0.025
0
10
20
30
40
50
Storm Duration (hours)

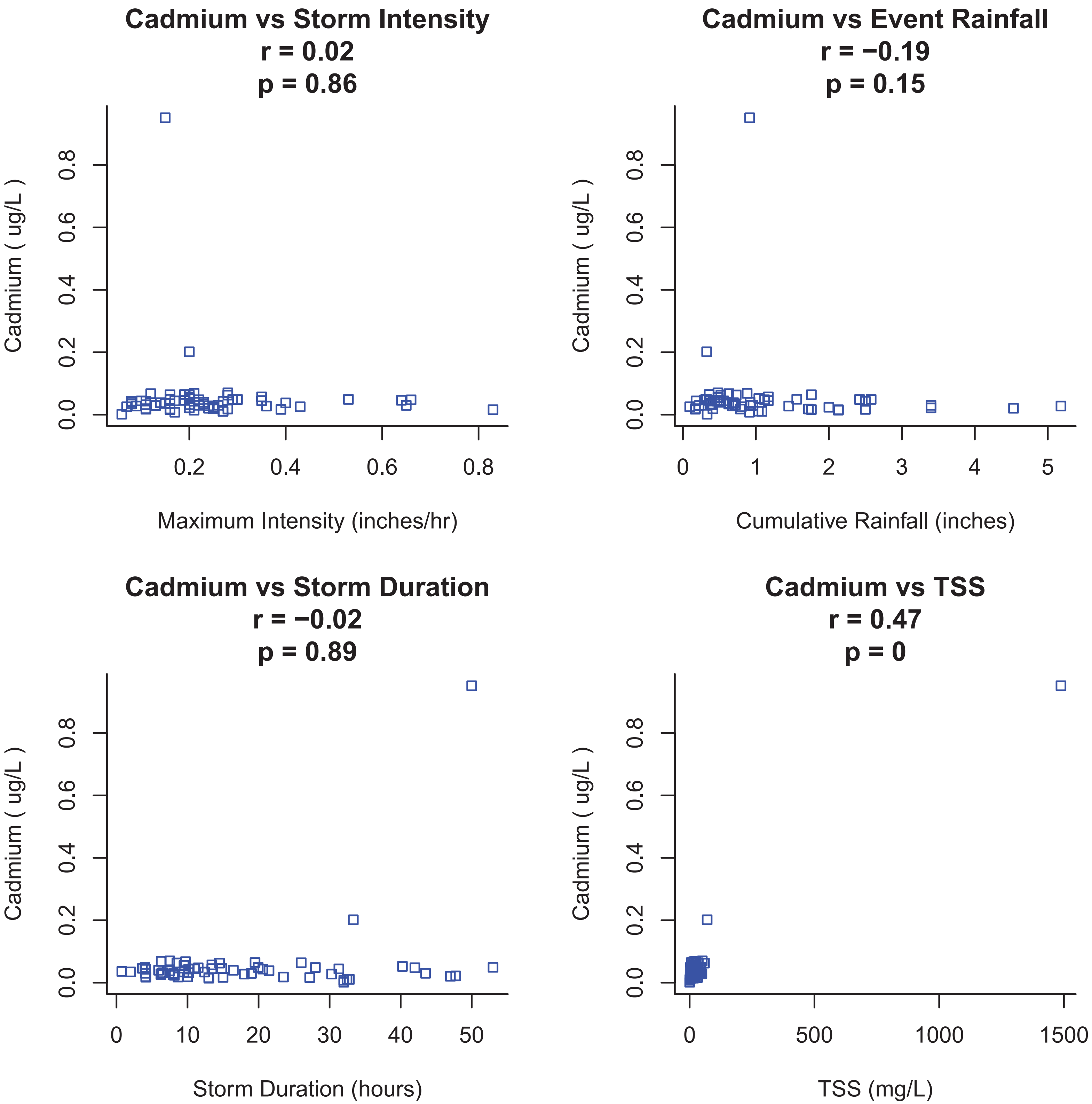

Ammonia vs TSS
r = −0.48
p = 0
Ammonia (mg/L)
0.010
0.015
0.020
0.025
0
500
1000
1500
TSS (mg/L)

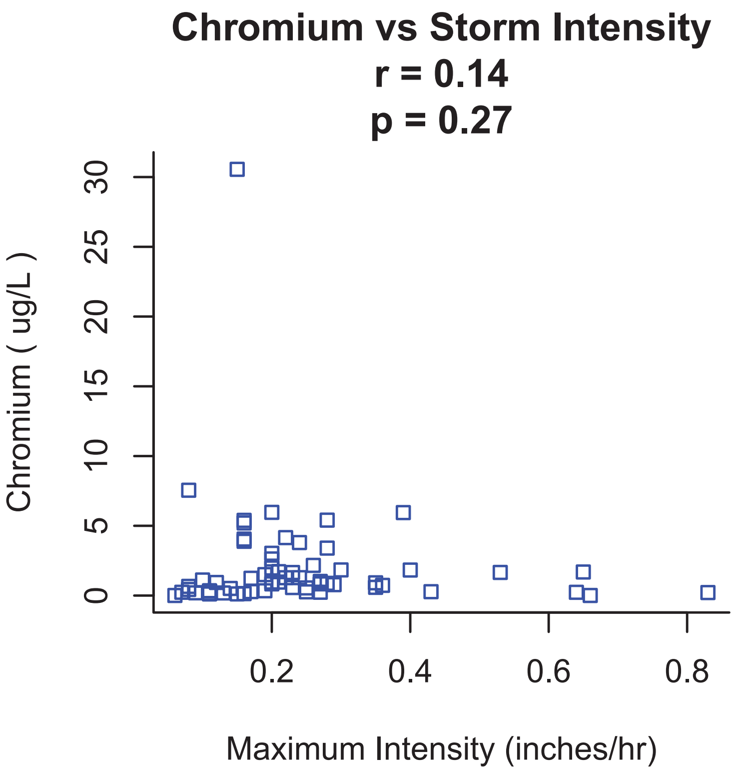

Arsenic vs Storm Intensity
r = −0.08
p = 0.54


Arsenic vs Event Rainfall
r = −0.42
p = 0

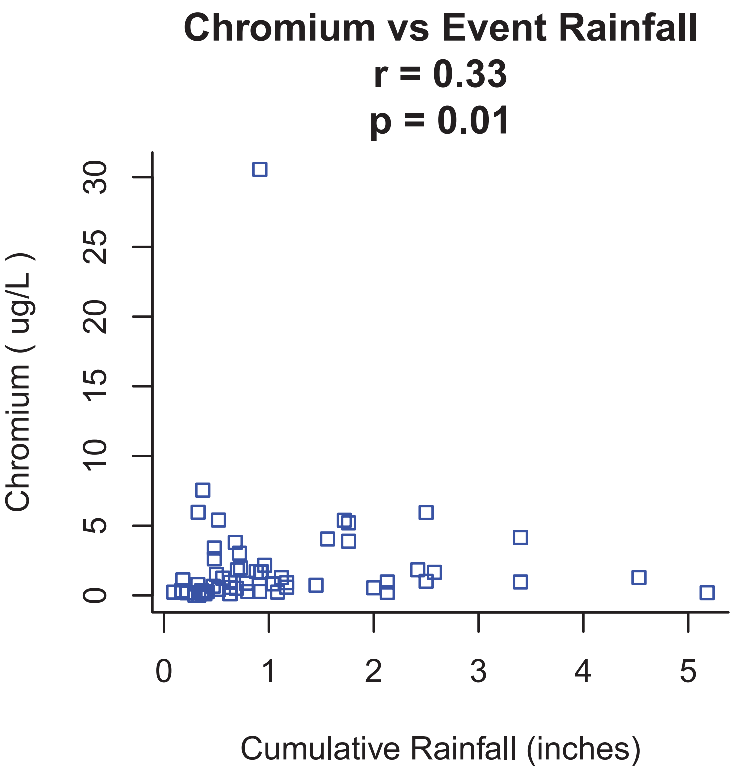

Arsenic vs Storm Duration
r = −0.08
p = 0.53


Arsenic vs TSS
r = 0.14
p = 0.29

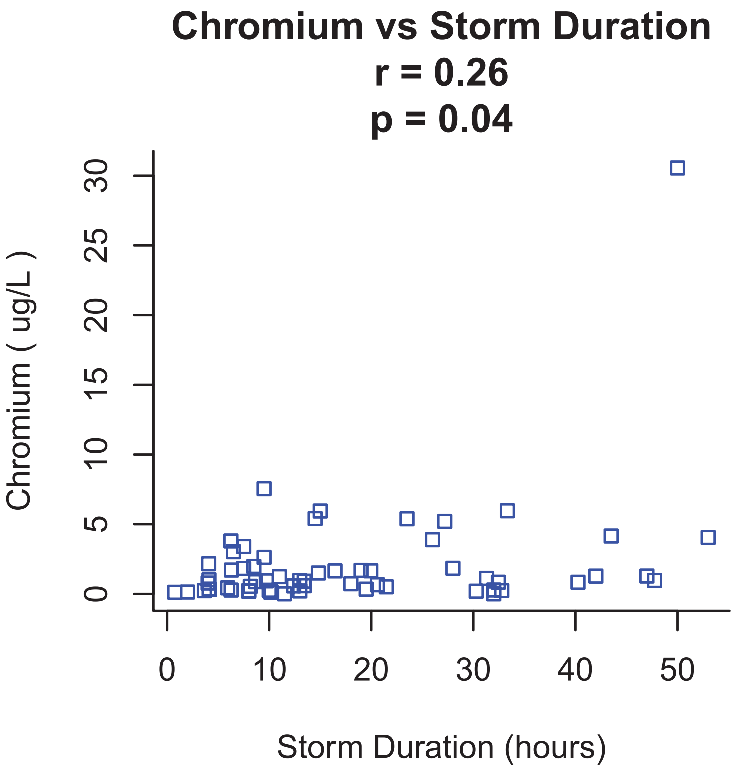

Cadmium vs Storm Intensity
r = 0.02
p = 0.86
Cadmium (ug/L)
0.0
0.2
0.4
0.6
0.8
0.2
0.4
0.6
0.8
Maximum Intensity (inches/hr)
Cadmium vs Event Rainfall
r = −0.19
p = 0.15
Cadmium (ug/L)
0.0
0.2
0.4
0.6
0.8
0
1
2
3
4
5
Cumulative Rainfall (inches)
Cadmium vs Storm Duration
r = −0.02
p = 0.89
Cadmium (ug/L)
0.0
0.2
0.4
0.6
0.8
0
10
20
30
40
50
Storm Duration (hours)
Cadmium vs TSS
r = 0.47
p = 0
Cadmium (ug/L)
0.0
0.2
0.4
0.6
0.8
0
500
1000
1500
TSS (mg/L)



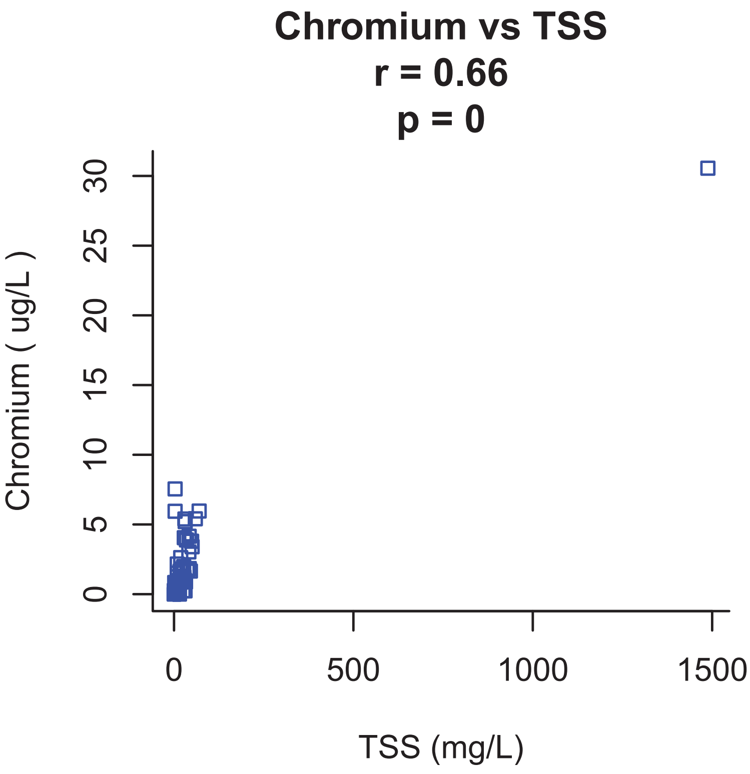
Chromium vs Storm Intensity
r = 0.14
p = 0.27



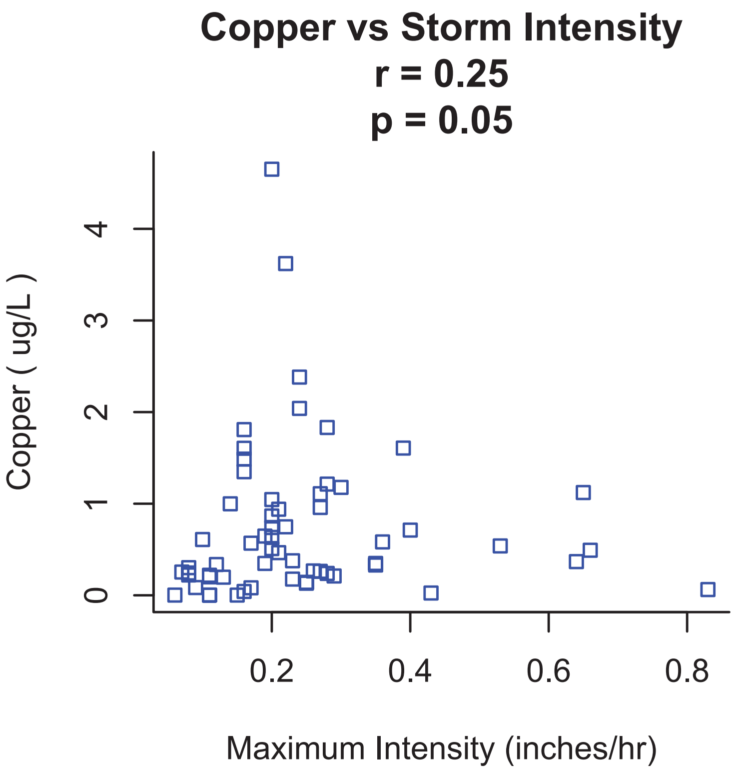
Chromium vs Event Rainfall
r = 0.33
p = 0.01



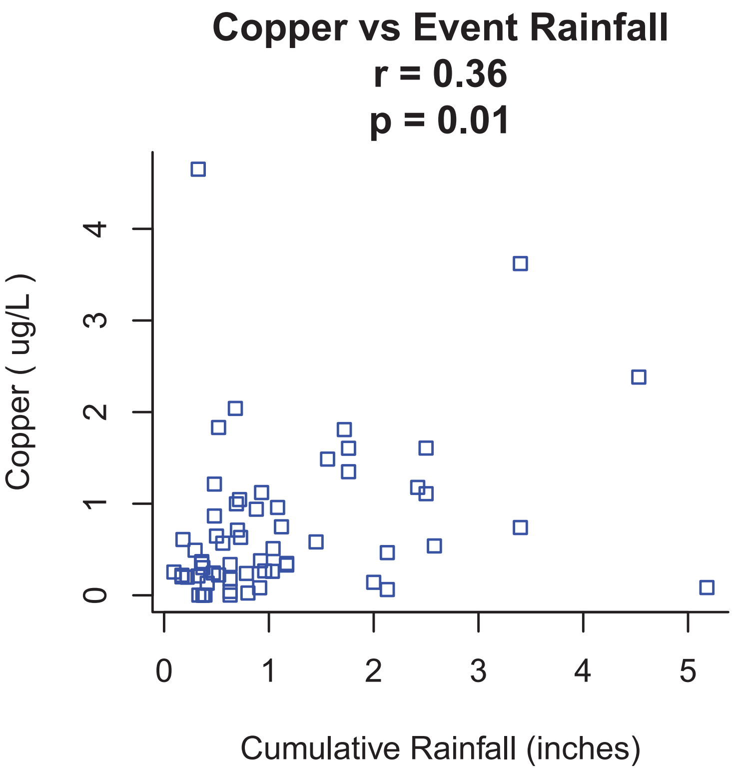
Chromium vs Storm Duration
r = 0.26
p = 0.04



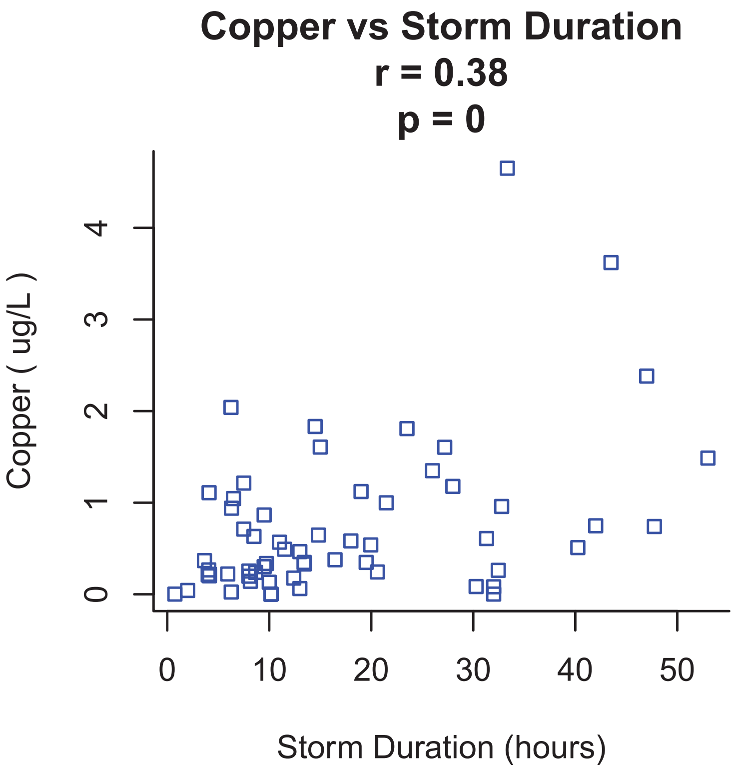
Chromium vs TSS
r = 0.66
p = 0



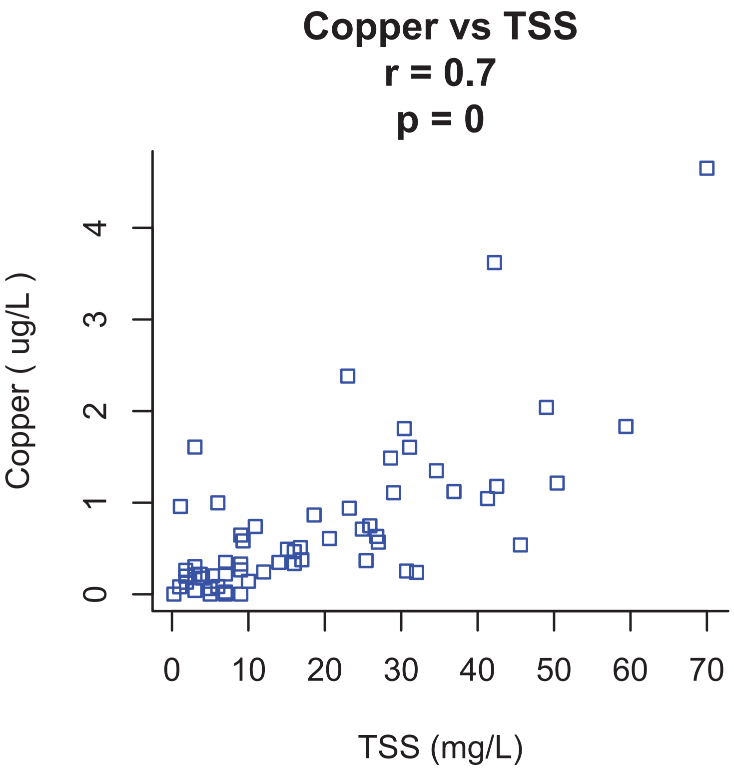
Copper vs Storm Intensity
r = 0.25
p = 0.05



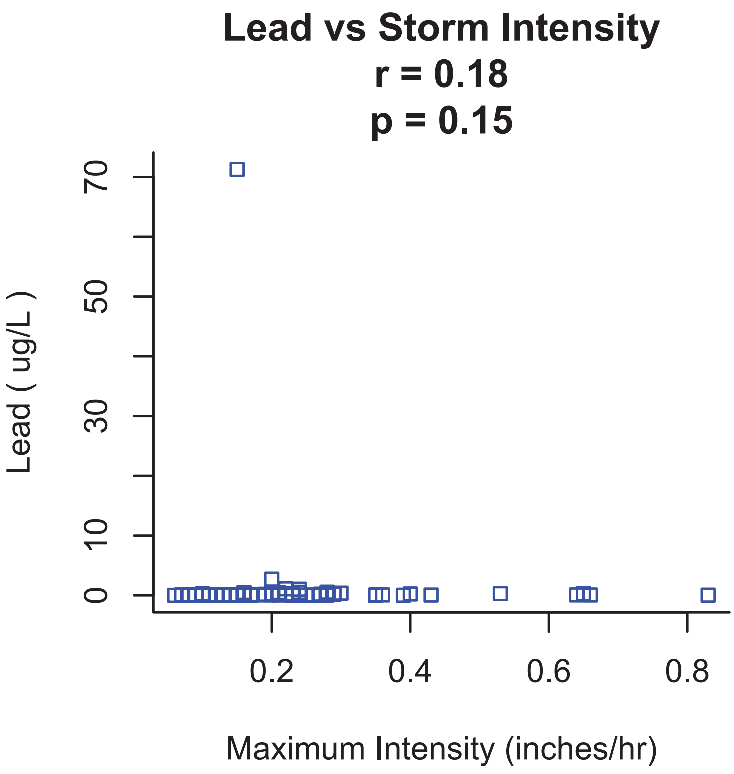
Copper vs Event Rainfall
r = 0.36
p = 0.01

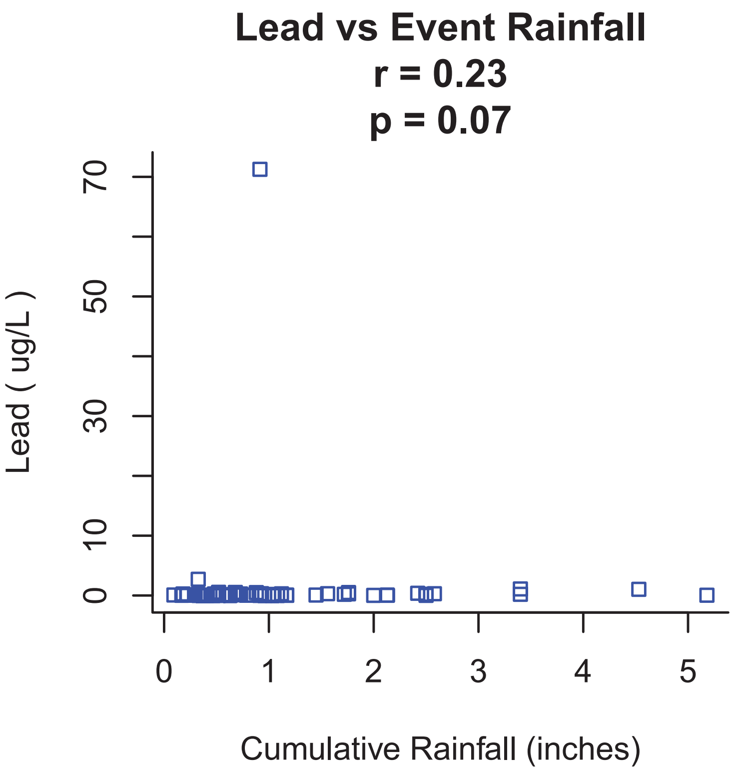


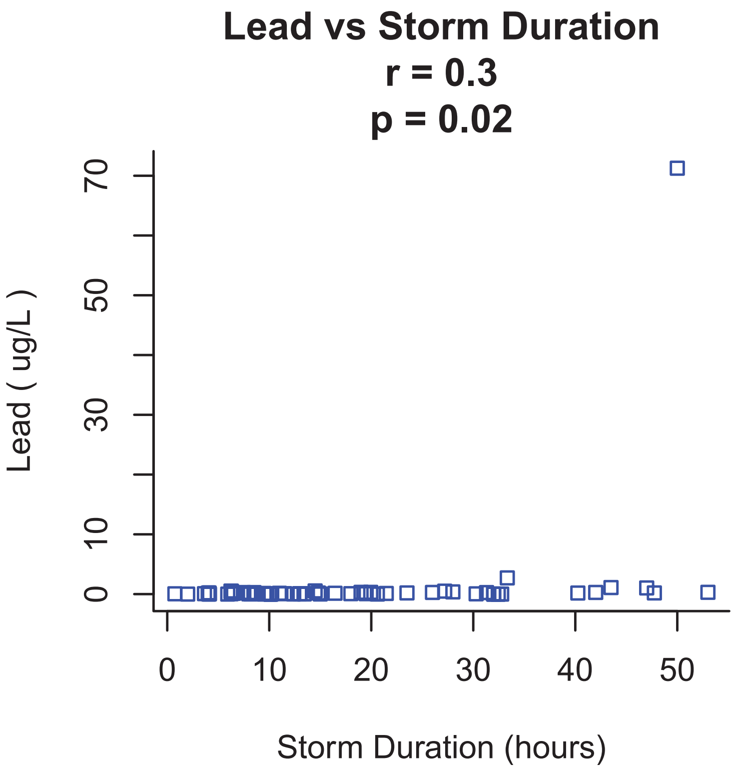
Copper vs Storm Duration
r = 0.38
p = 0

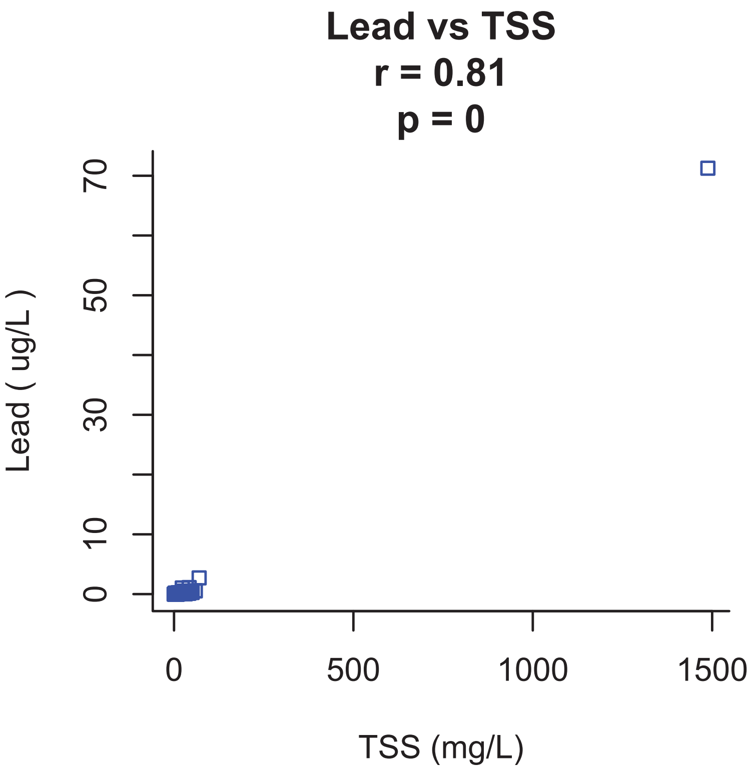


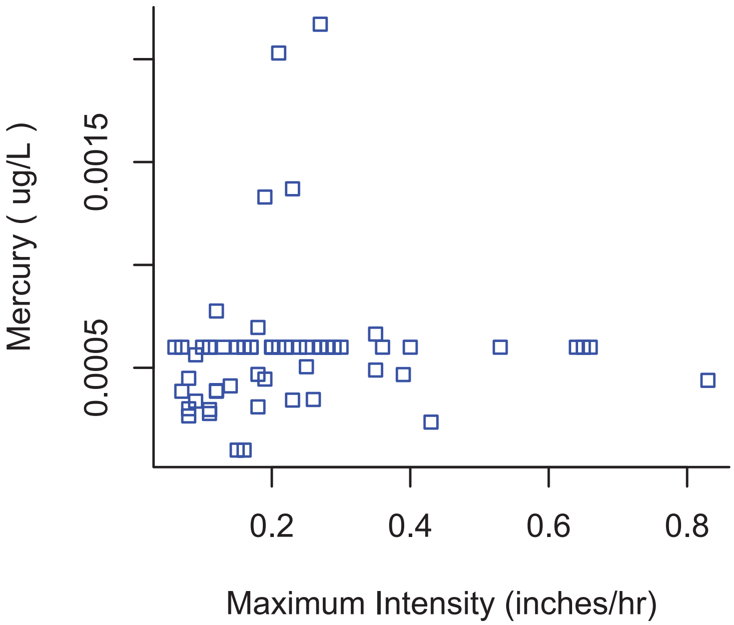
Copper vs TSS
r = 0.7
p = 0


Lead vs Storm Intensity
r = 0.18
p = 0.15
Lead (ug/L)
0
10
30
50
70
0.2
0.4
0.6
0.8
Maximum Intensity (inches/hr)

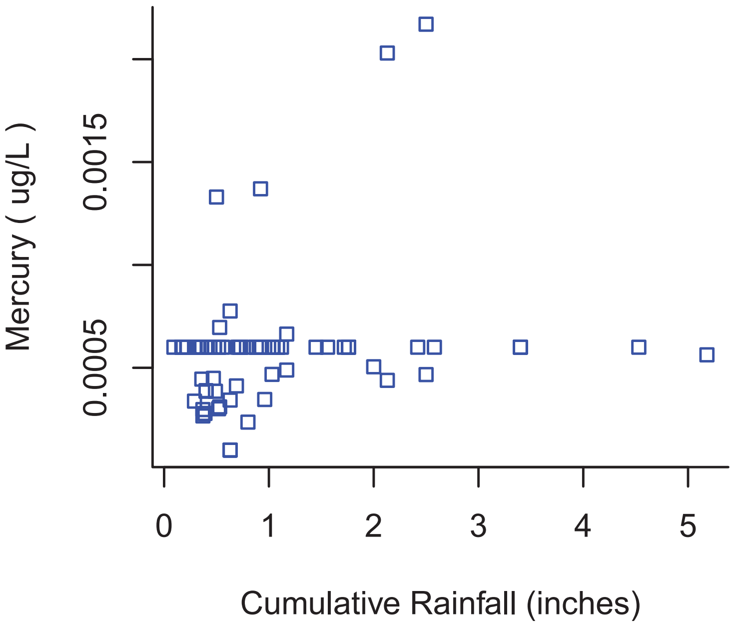

Lead vs Event Rainfall
r = 0.23
p = 0.07
Lead (ug/L)
0
10
30
50
70
0
1
2
3
4
5
Cumulative Rainfall (inches)


Lead vs Storm Duration
r = 0.3
p = 0.02
Lead (ug/L)
0
10
30
50
70
0
10
20
30
40
50
Storm Duration (hours)

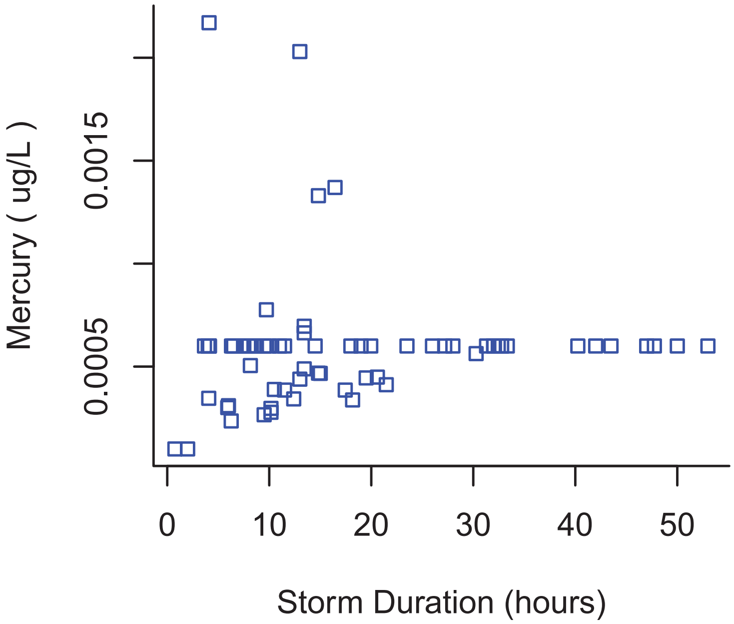

Lead vs TSS
r = 0.81
p = 0
Lead (ug/L)
0
10
30
50
70
0
500
1000
1500
TSS (mg/L)



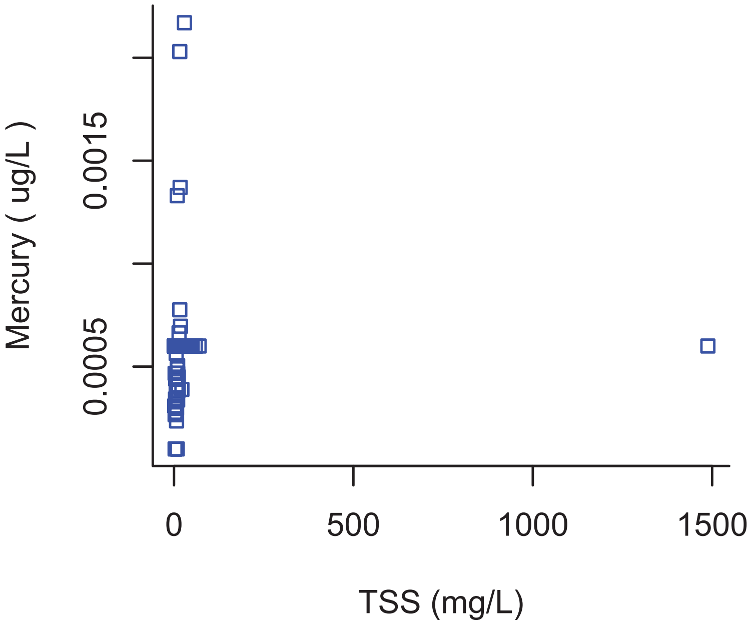
Mercury vs Storm Intensity
r = 0.27
p = 0.02



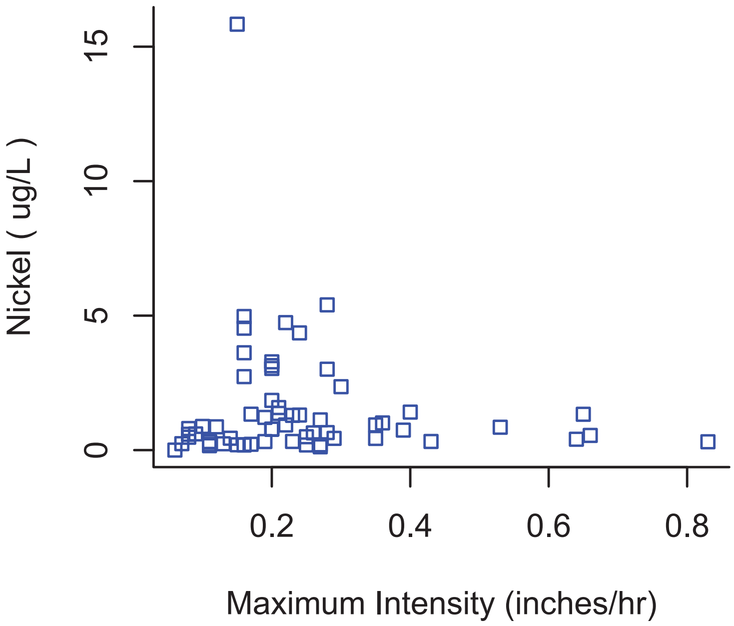
Mercury vs Event Rainfall
r = 0.19
p = 0.13



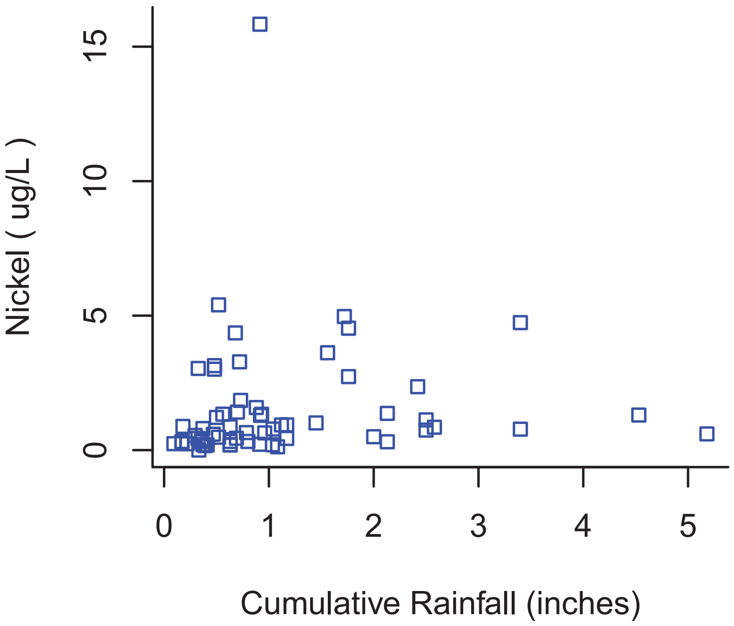
Mercury vs Storm Duration
r = 0.22
p = 0.07



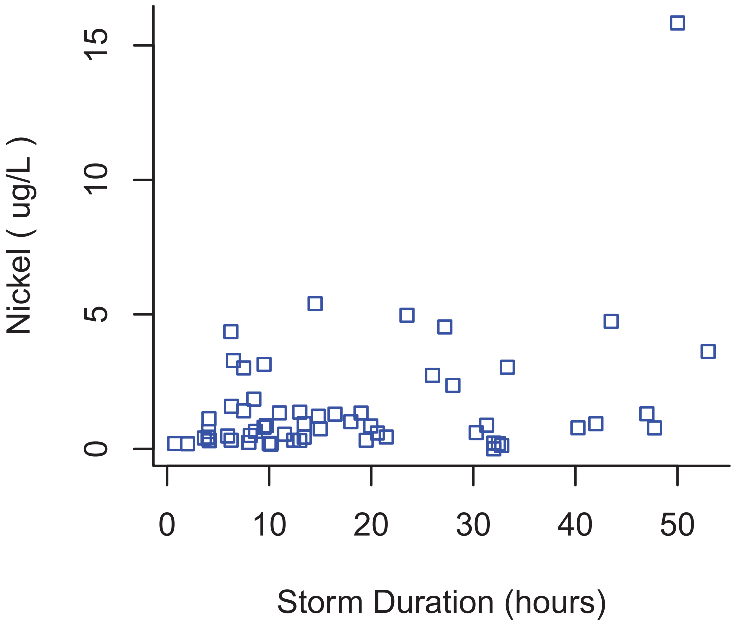
Mercury vs TSS
r = 0.42
p = 0



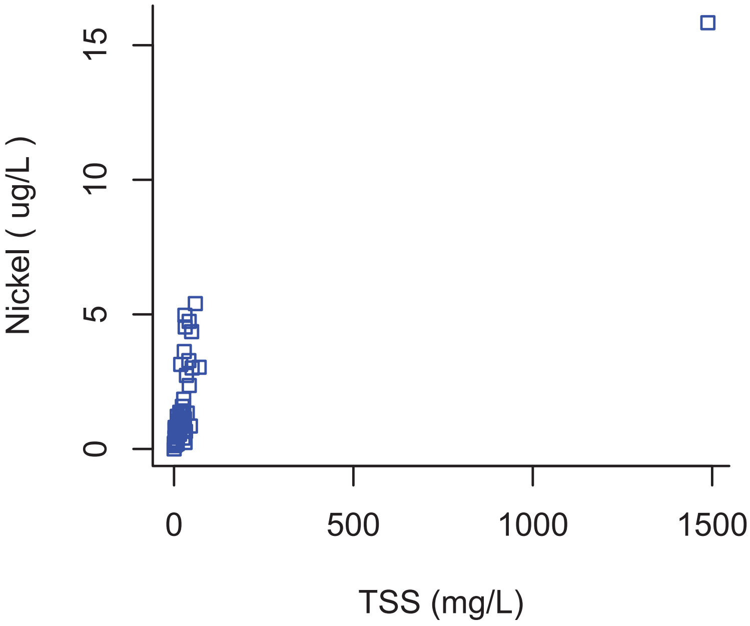
Nickel vs Storm Intensity
r = 0.15
p = 0.25



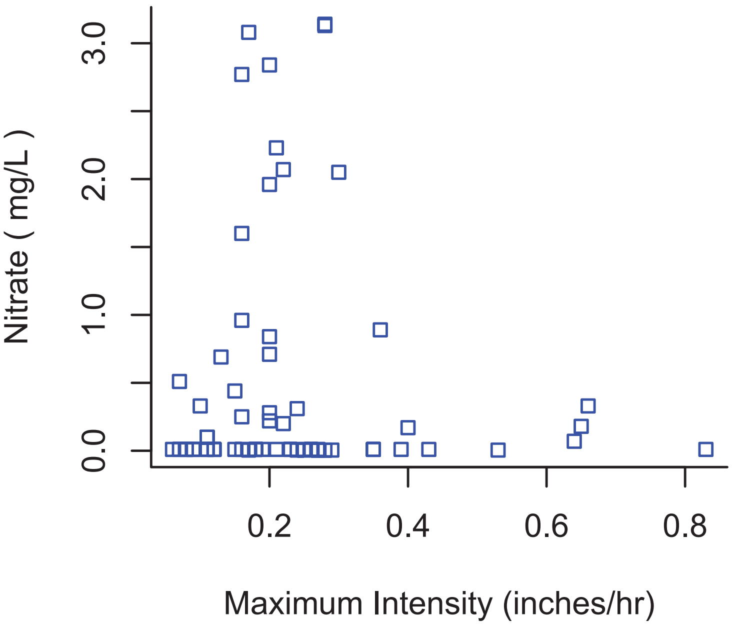
Nickel vs Event Rainfall
r = 0.35
p = 0.01



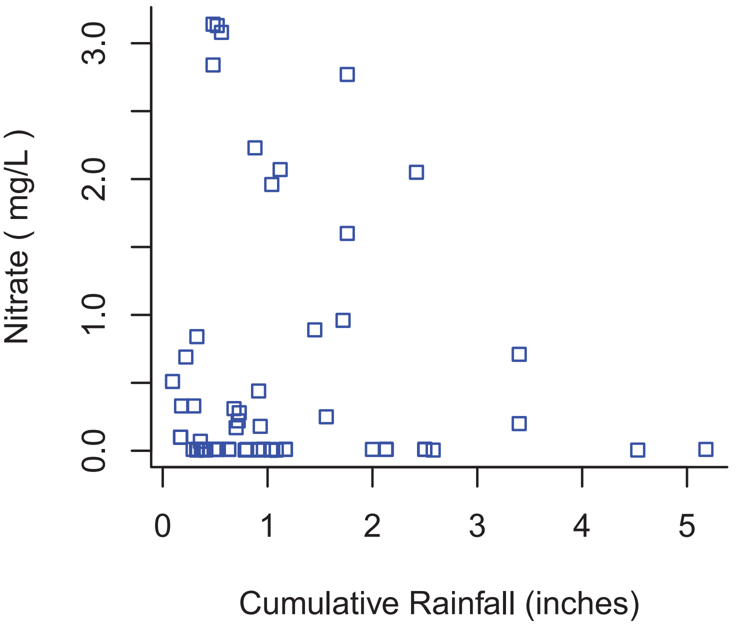
Nickel vs Storm Duration
r = 0.24
p = 0.06



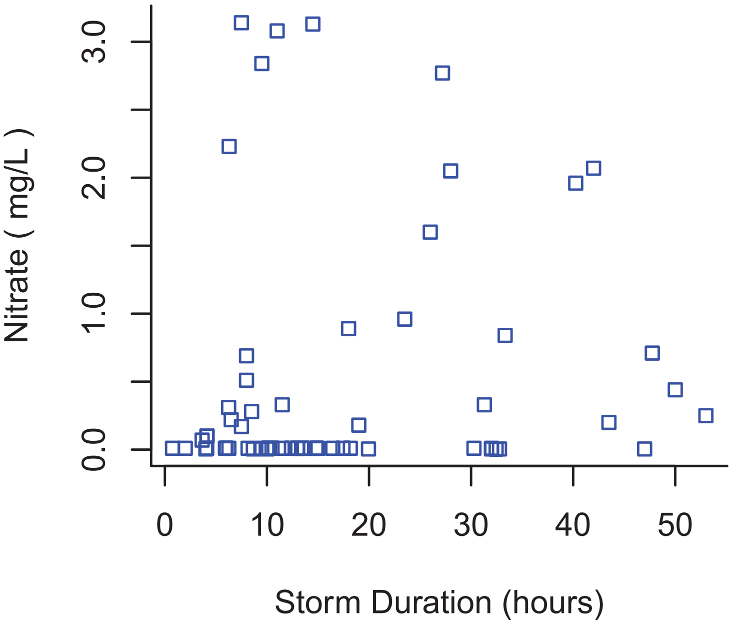
Nickel vs TSS
r = 0.82
p = 0



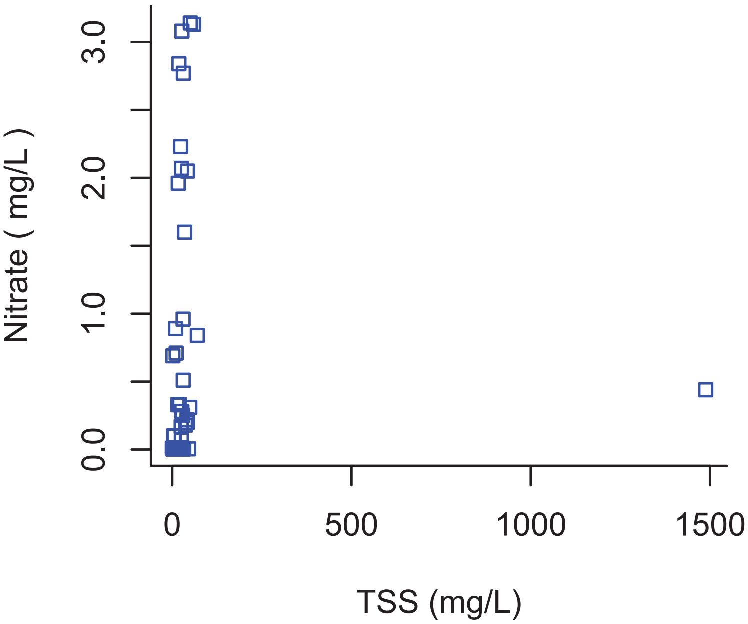
Nitrate vs Storm Intensity
r = −0.06
p = 0.62



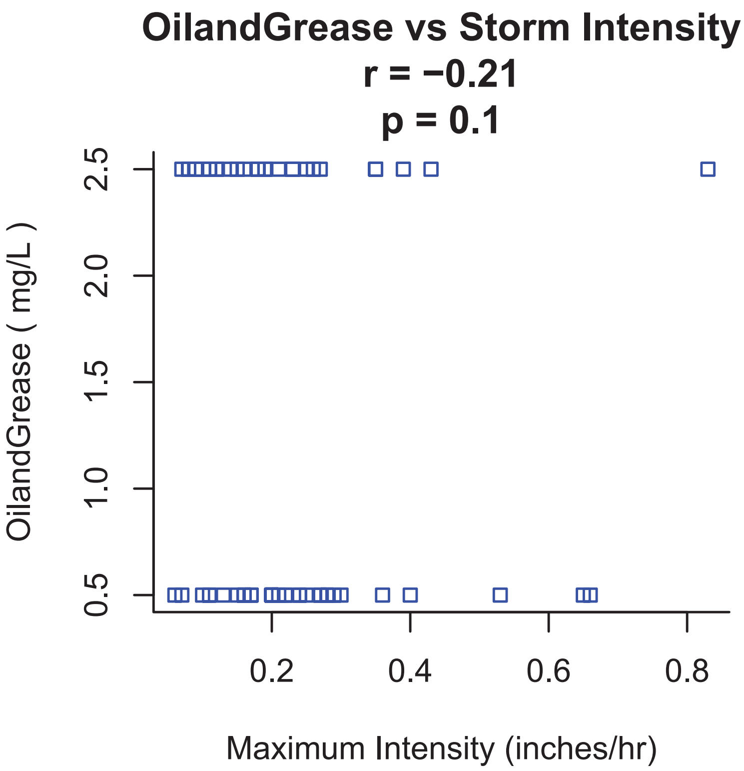
Nitrate vs Event Rainfall
r = −0.06
p = 0.66

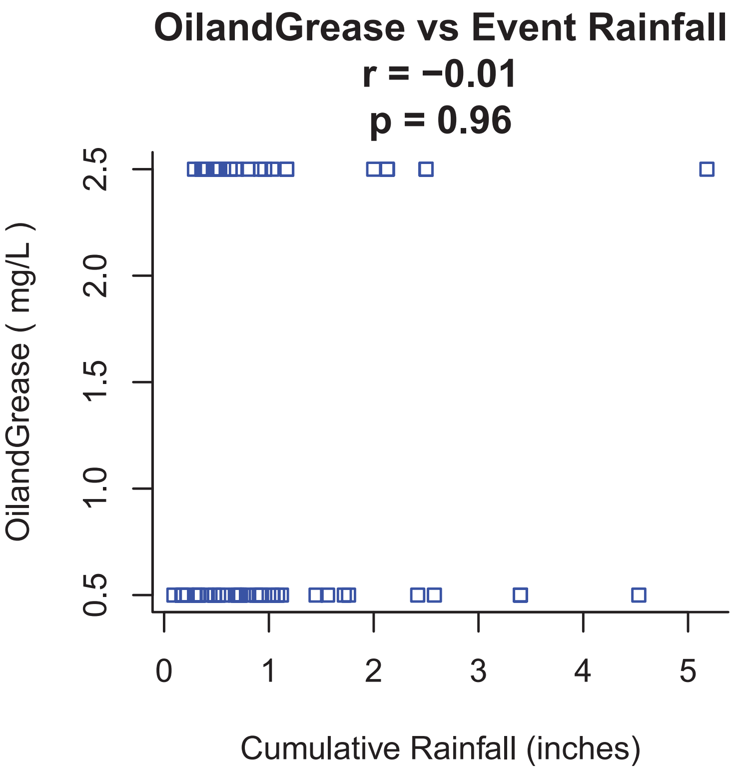


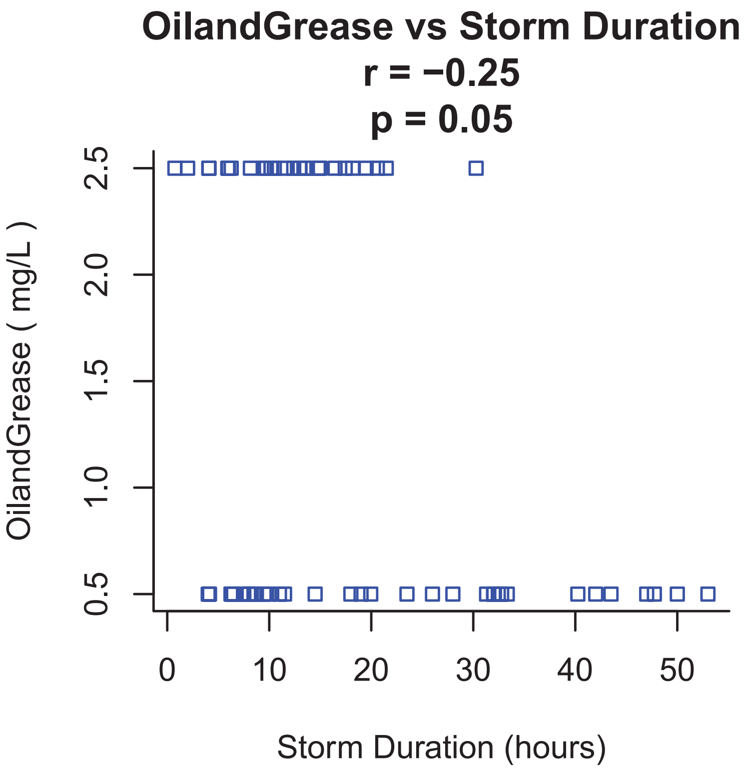
Nitrate vs Storm Duration
r = 0.11
p = 0.4

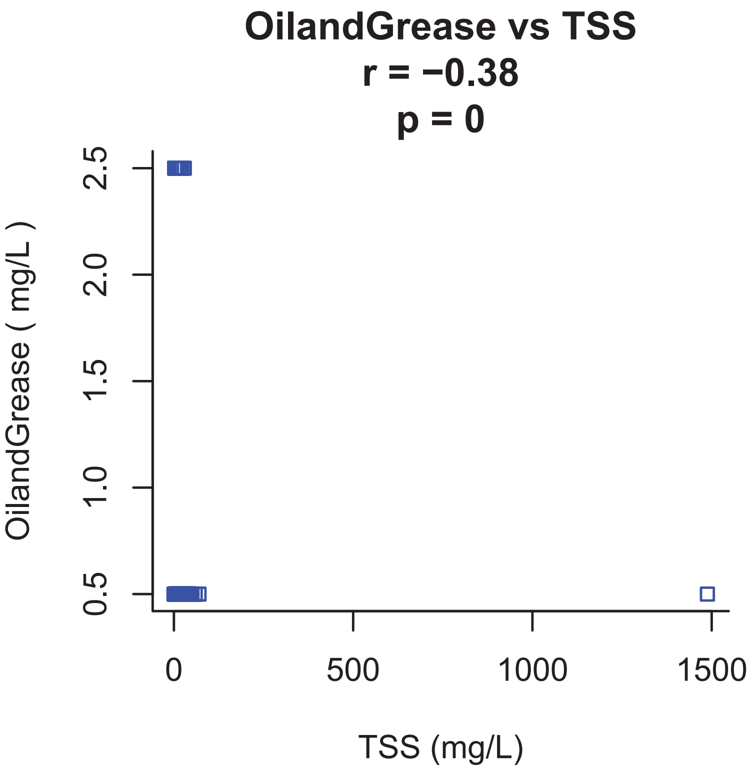


Nitrate vs TSS
r = 0.58
p = 0

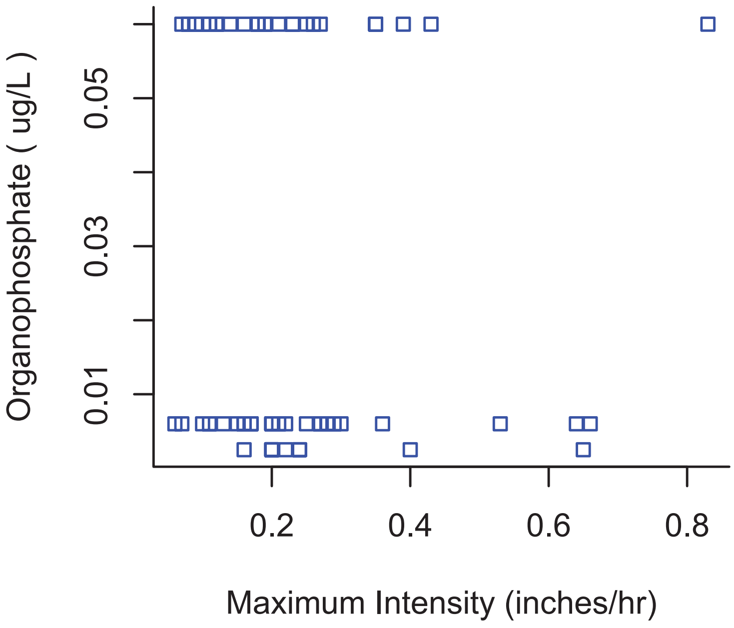

OilandGrease vs Storm Intensity
r = −0.21
p = 0.1
OilandGrease (mg/L)
0.5
1.0
1.5
2.0
2.5
0.2
0.4
0.6
0.8
Maximum Intensity (inches/hr)


OilandGrease vs Event Rainfall
r = −0.01
p = 0.96
OilandGrease (mg/L)
0.5
1.0
1.5
2.0
2.5
0
1
2
3
4
5
Cumulative Rainfall (inches)

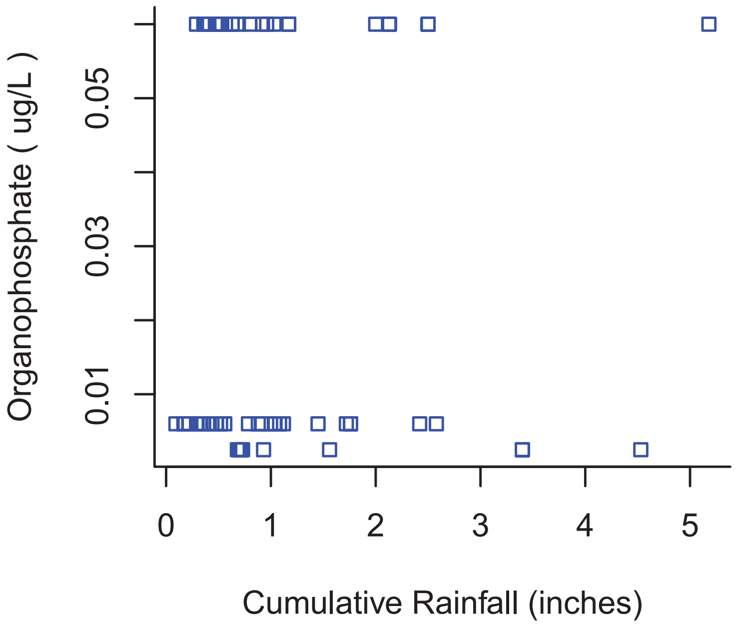

OilandGrease vs Storm Duration
r = −0.25
p = 0.05
OilandGrease (mg/L)
0.5
1.0
1.5
2.0
2.5
0
10
20
30
40
50
Storm Duration (hours)


OilandGrease vs TSS
r = −0.38
p = 0
OilandGrease (mg/L)
0.5
1.0
1.5
2.0
2.5
0
500
1000
1500
TSS (mg/L)

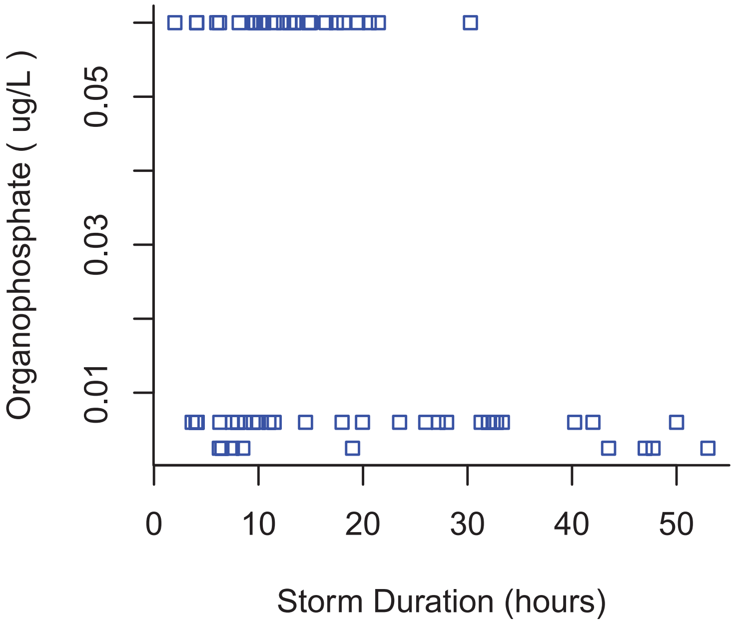
Organophosphate vs Storm Intensity
r = −0.21
p = 0.1



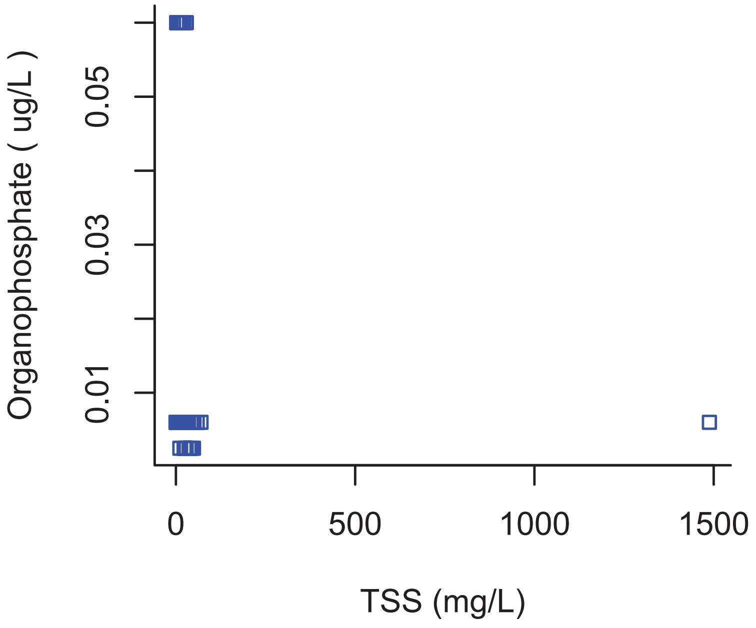
Organophosphate vs Event Rainfall
r = −0.09
p = 0.48

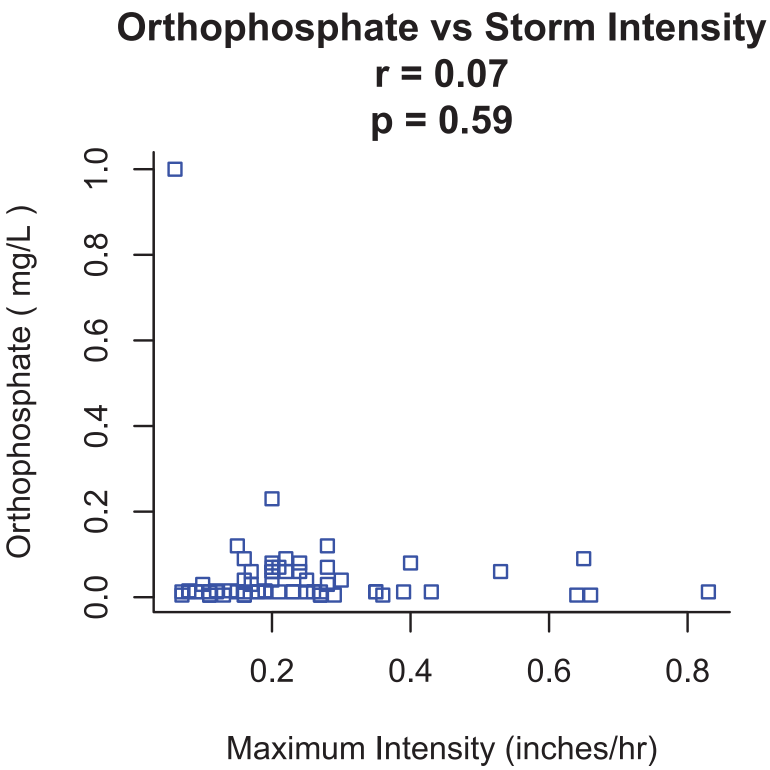


Organophosphate vs Storm Duration
r = −0.2
p = 0.11

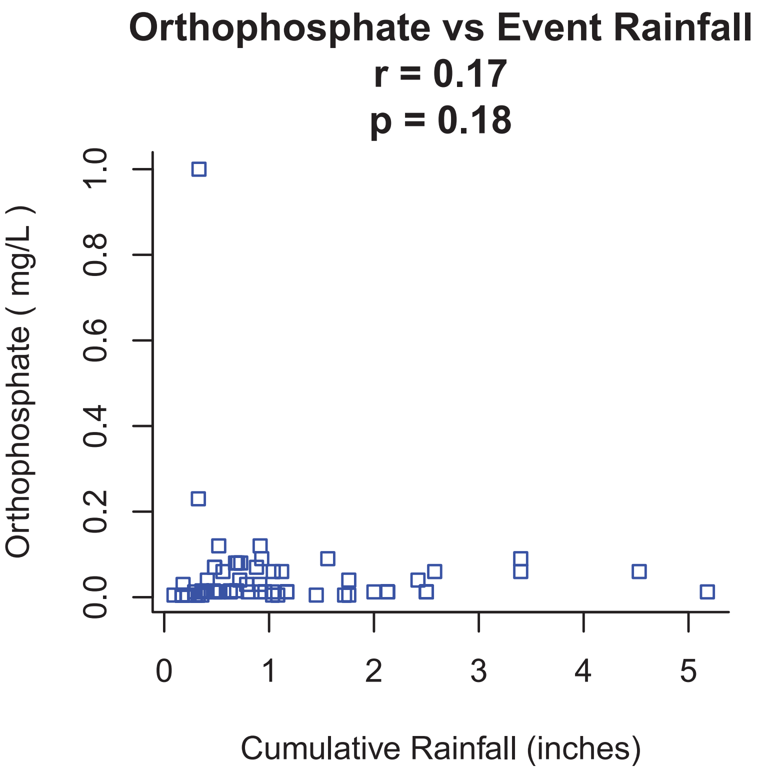


Organophosphate vs TSS
r = −0.46
p = 0

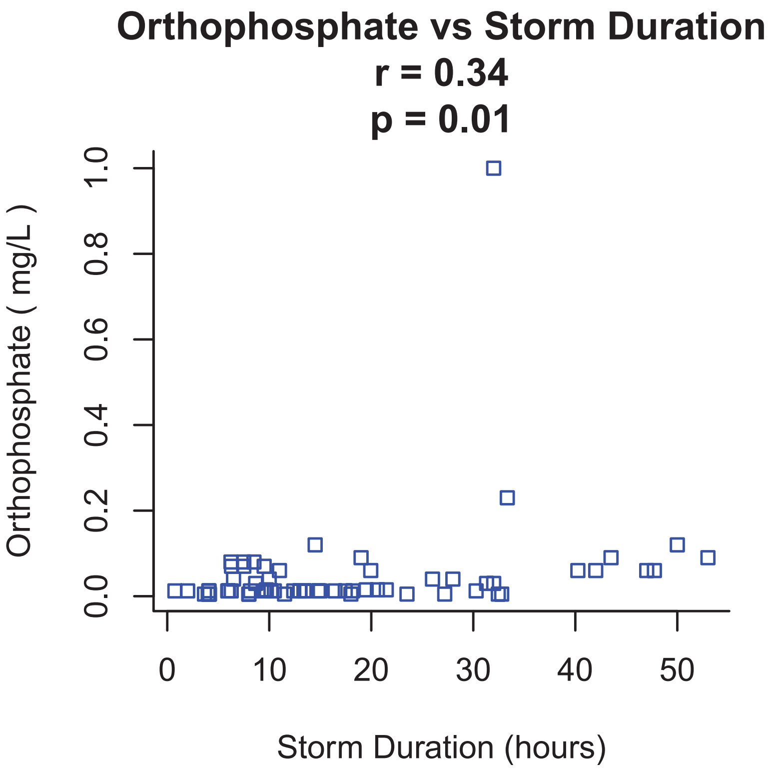




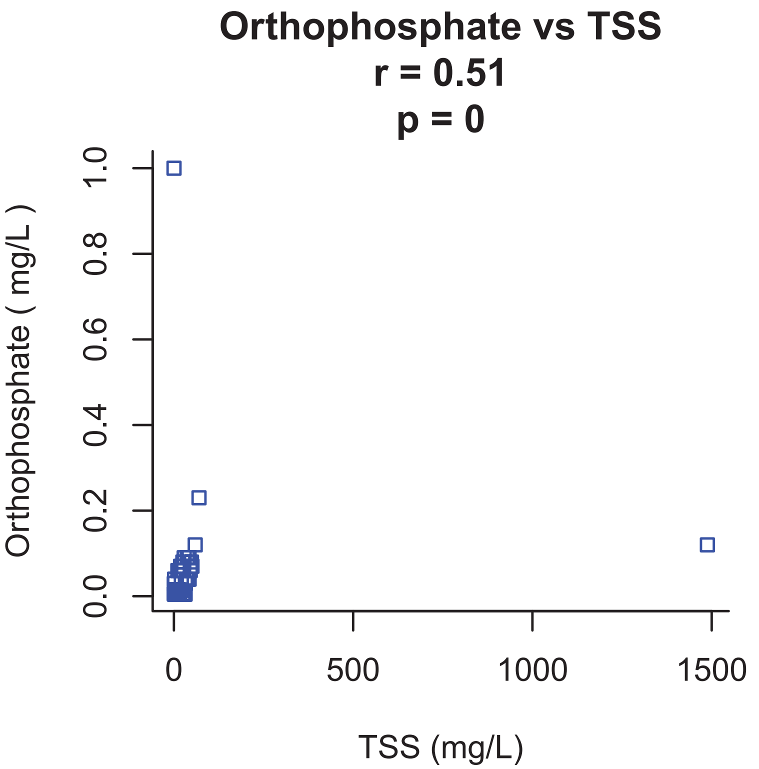
Orthophosphate vs Storm Intensity
r = 0.07
p = 0.59



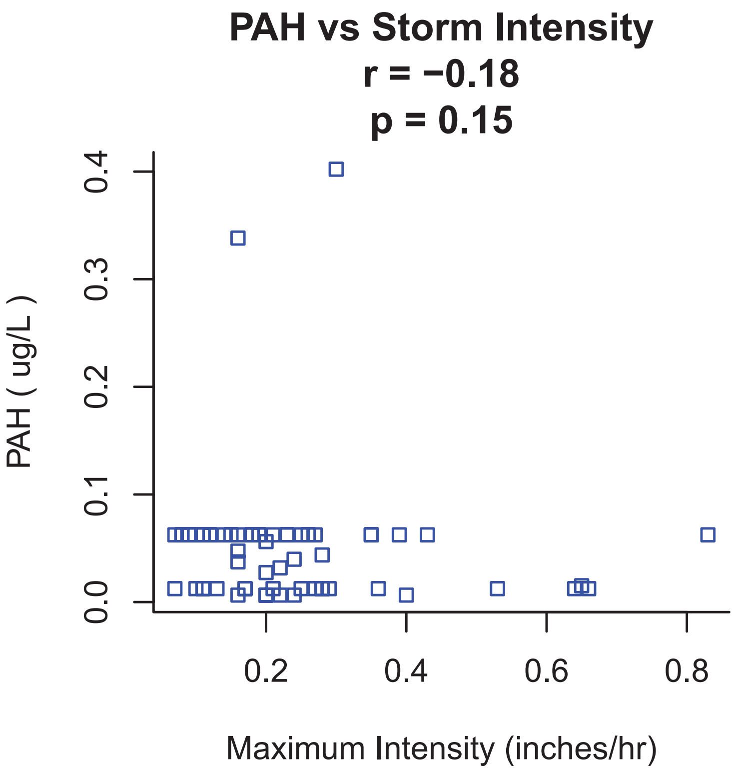
Orthophosphate vs Event Rainfall
r = 0.17
p = 0.18



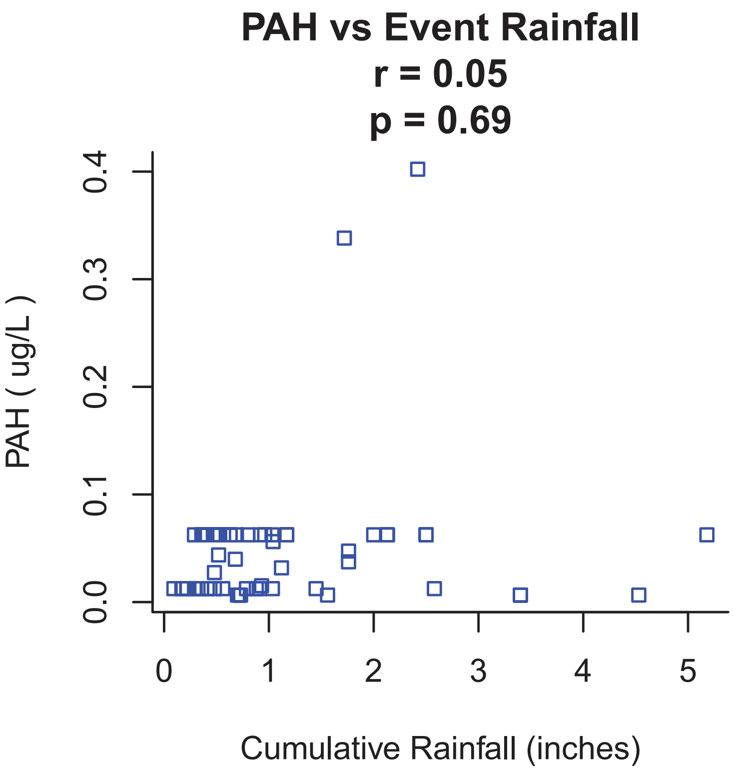
Orthophosphate vs Storm Duration
r = 0.34
p = 0.01



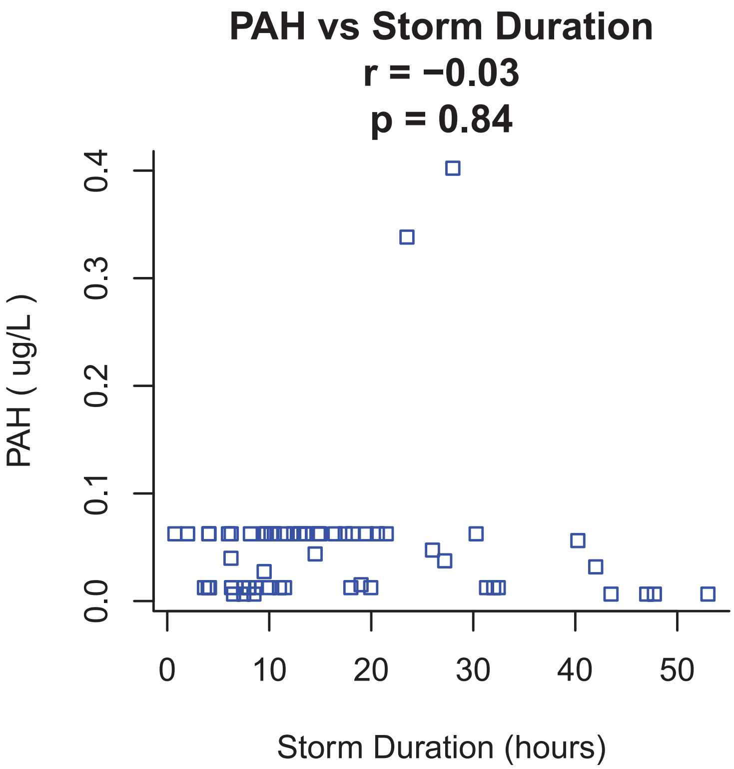
Orthophosphate vs TSS
r = 0.51
p = 0



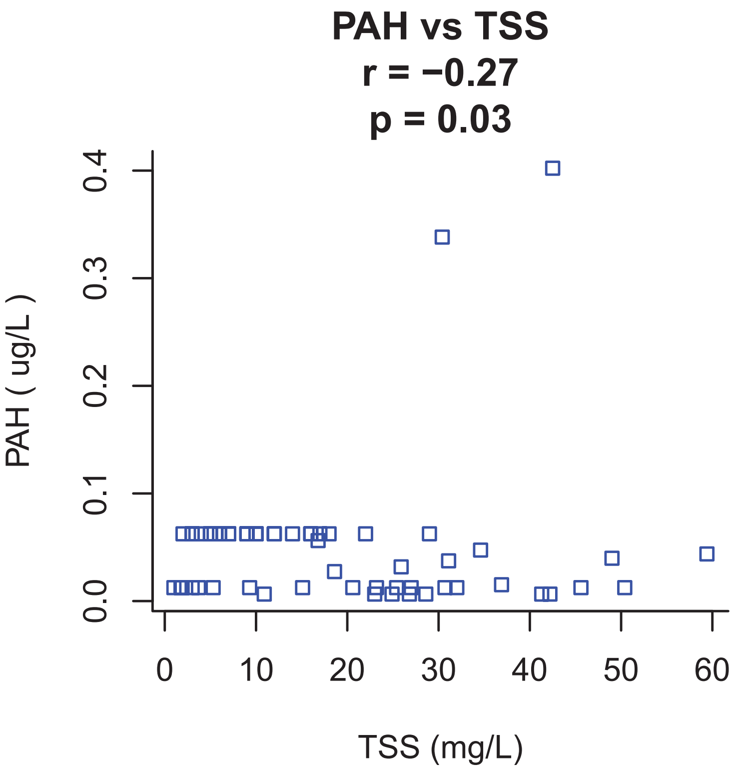
PAH vs Storm Intensity
r = −0.18
p = 0.15



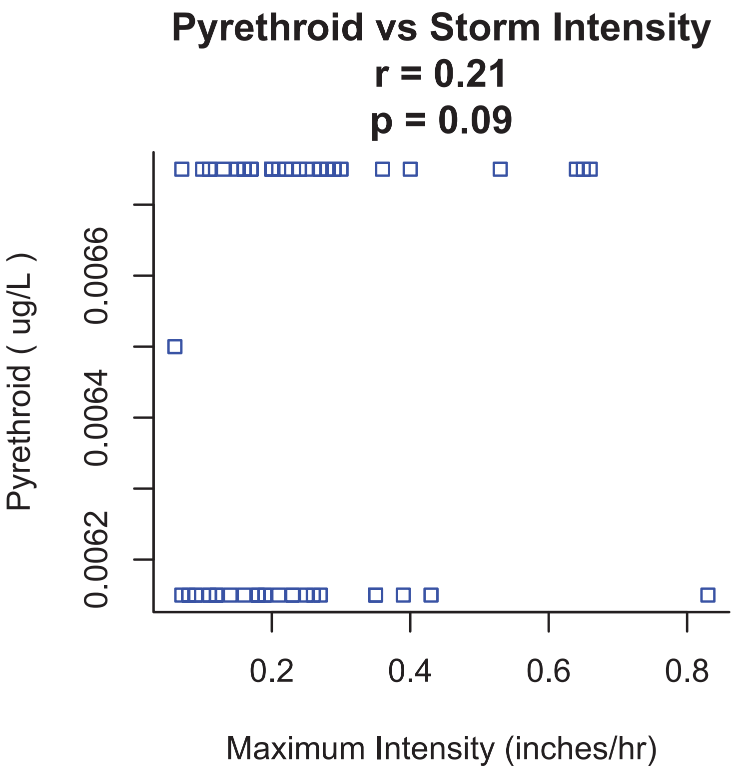
PAH vs Event Rainfall
r = 0.05
p = 0.69



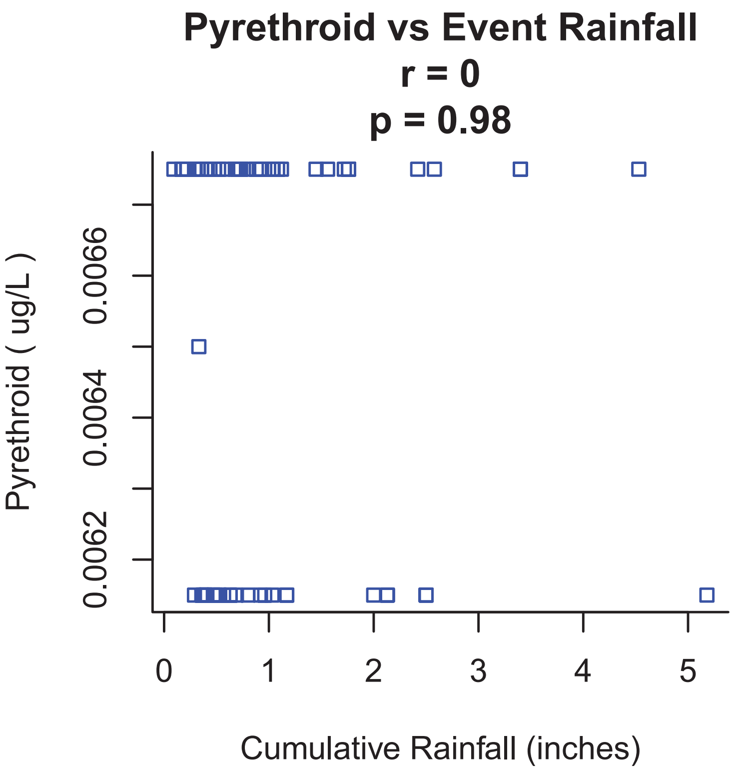
PAH vs Storm Duration
r = −0.03
p = 0.84



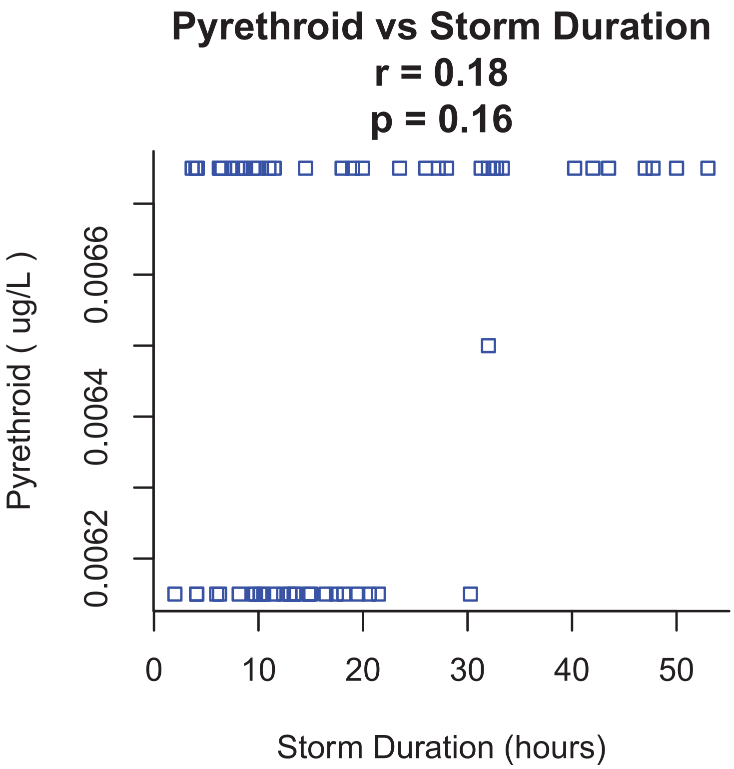
PAH vs TSS
r = −0.27
p = 0.03



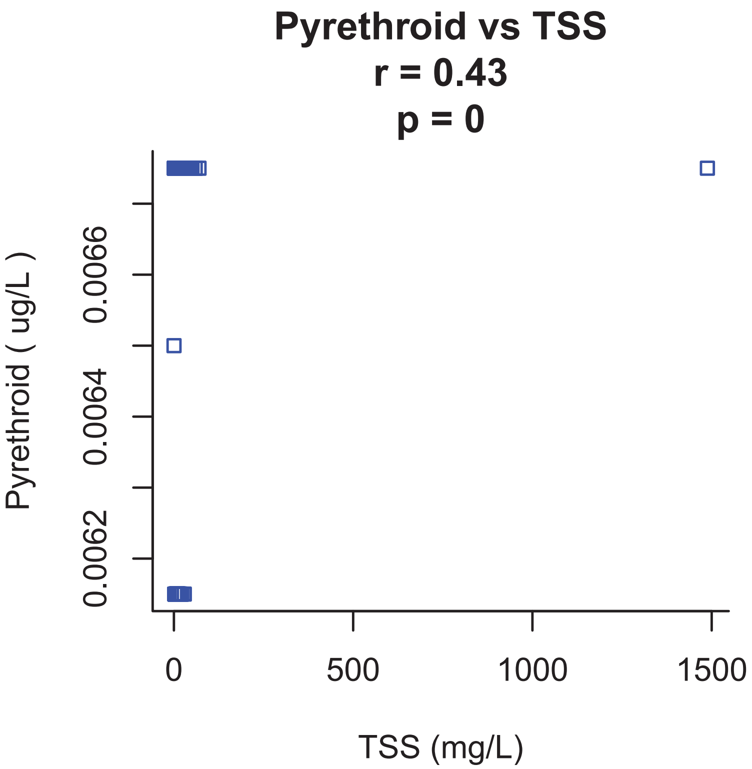
Pyrethroid vs Storm Intensity
r = 0.21
p = 0.09



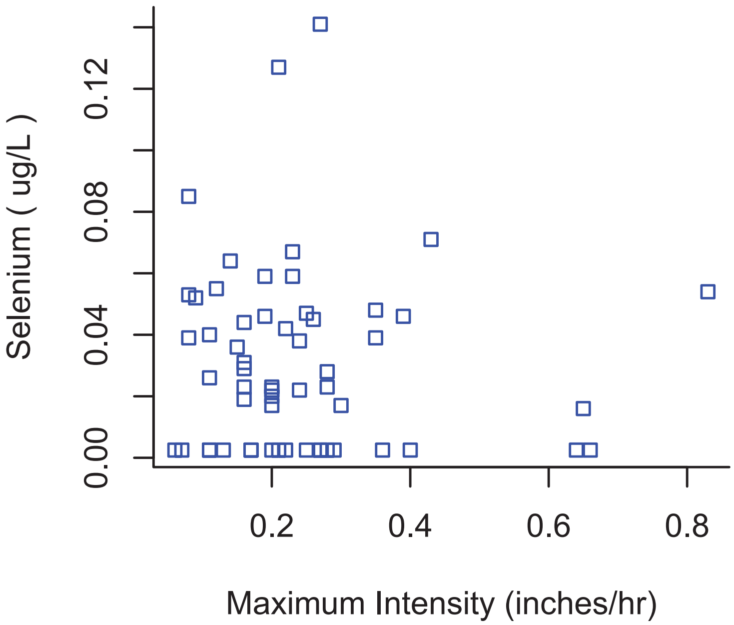
Pyrethroid vs Event Rainfall
r = 0
p = 0.98



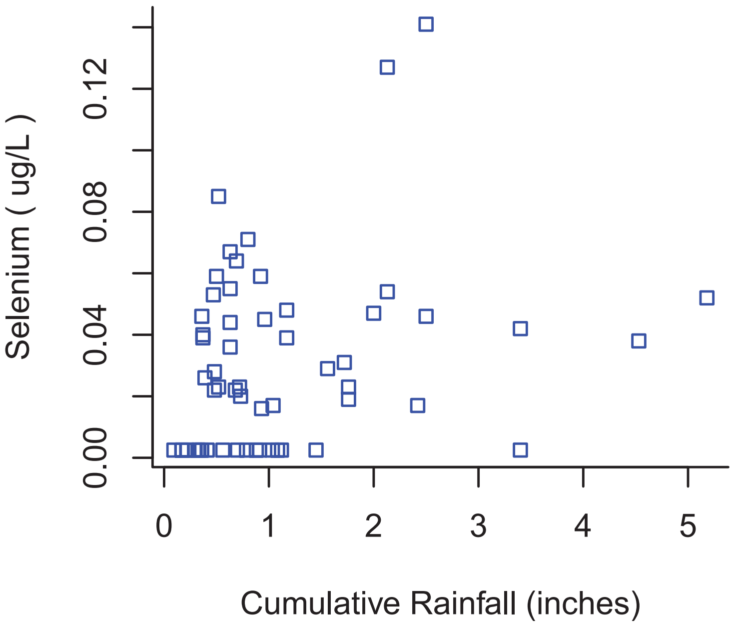
Pyrethroid vs Storm Duration
r = 0.18
p = 0.16



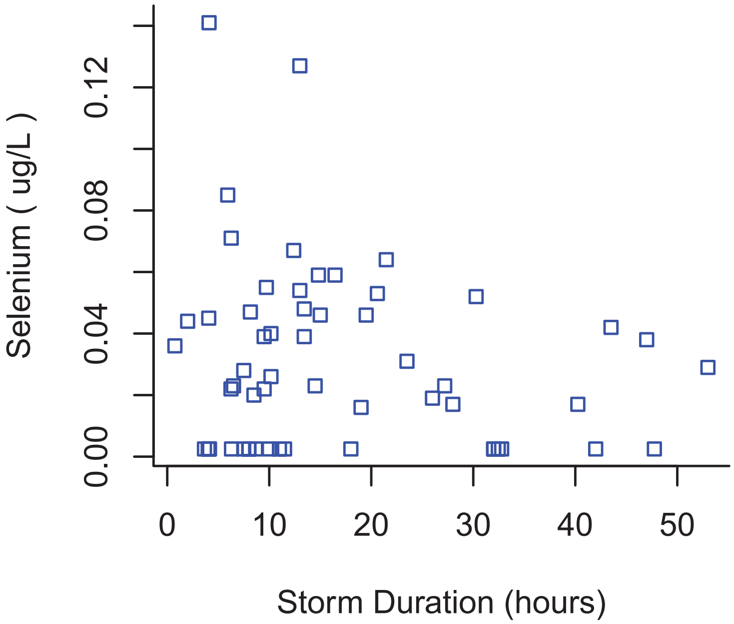
Pyrethroid vs TSS
r = 0.43
p = 0



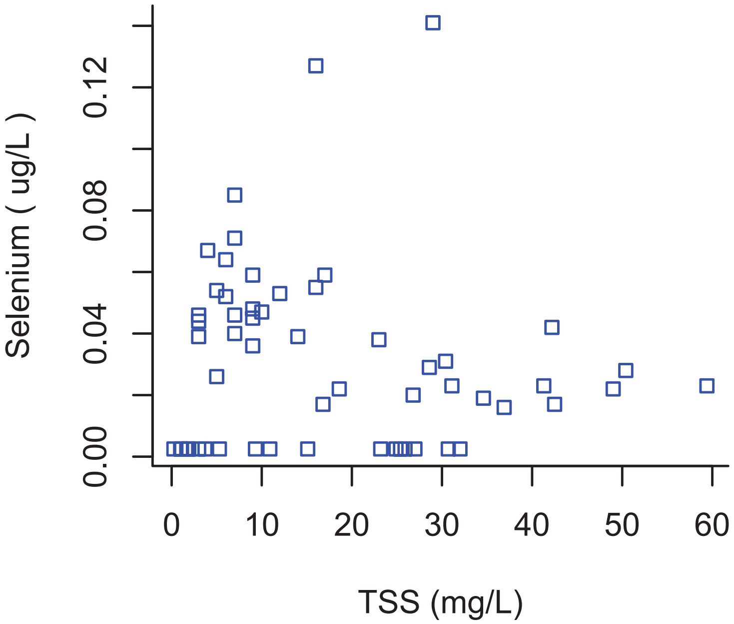
Selenium vs Storm Intensity
r = −0.08
p = 0.56



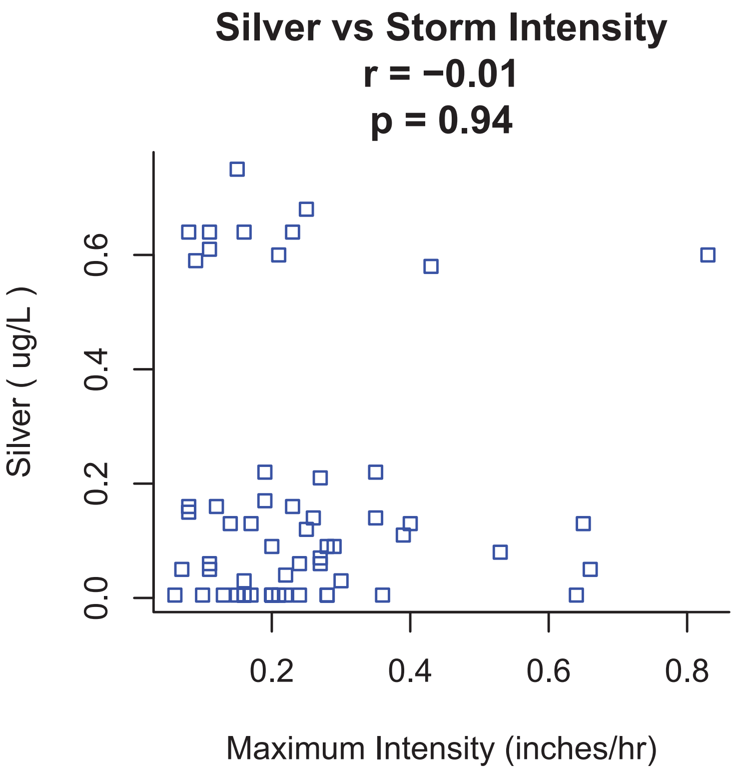
Selenium vs Event Rainfall
r = 0.28
p = 0.03



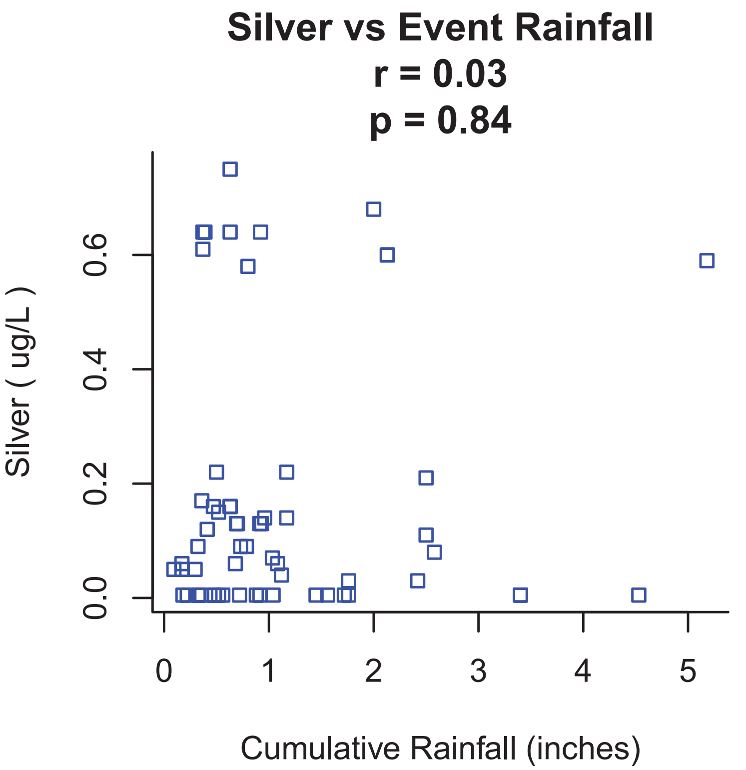
Selenium vs Storm Duration
r = −0.04
p = 0.79



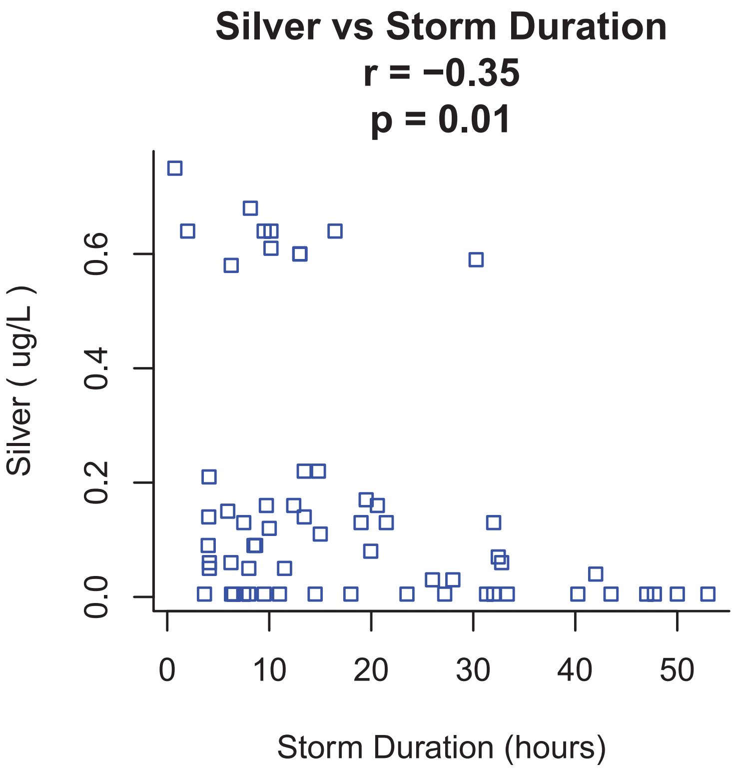
Selenium vs TSS
r = −0.02
p = 0.87



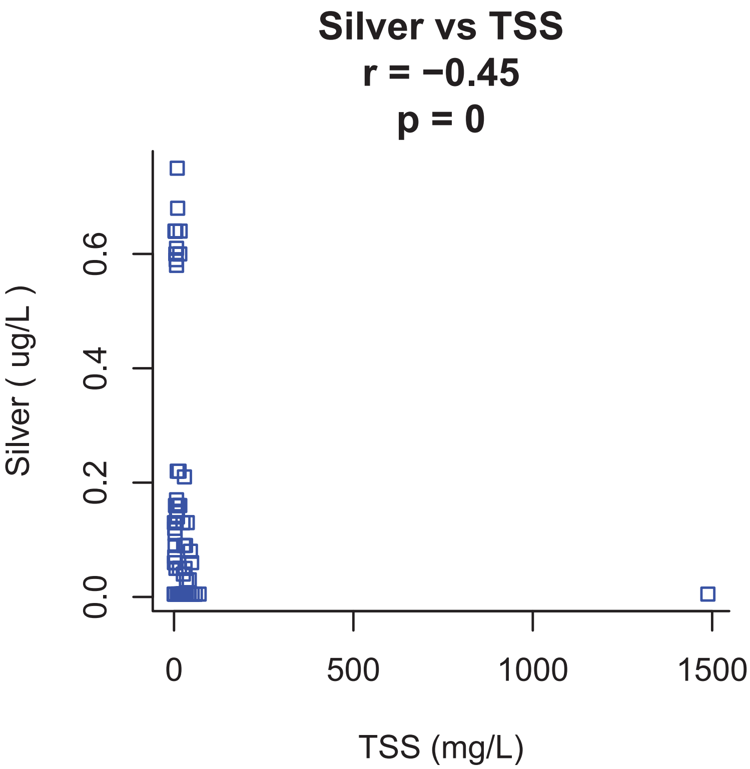
Silver vs Storm Intensity
r = −0.01
p = 0.94



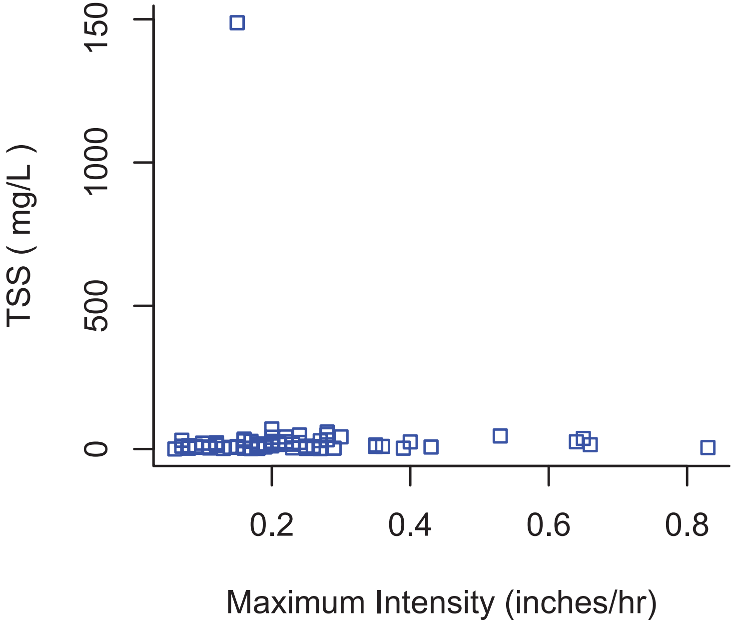
Silver vs Event Rainfall
r = 0.03
p = 0.84



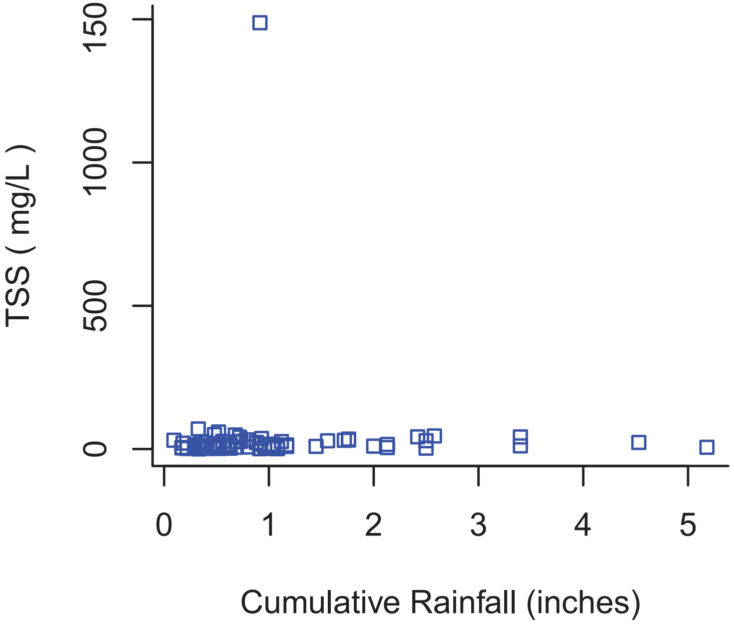
Silver vs Storm Duration
r = −0.35
p = 0.01



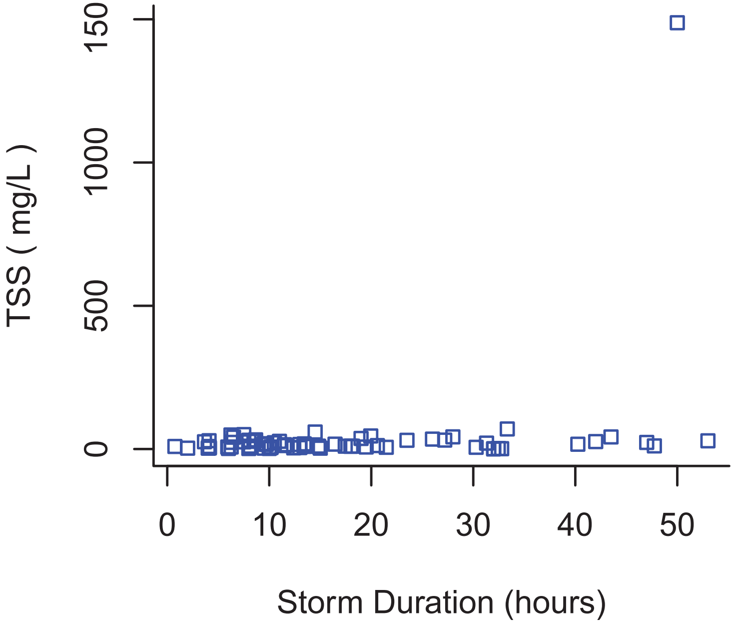
Silver vs TSS
r = −0.45
p = 0



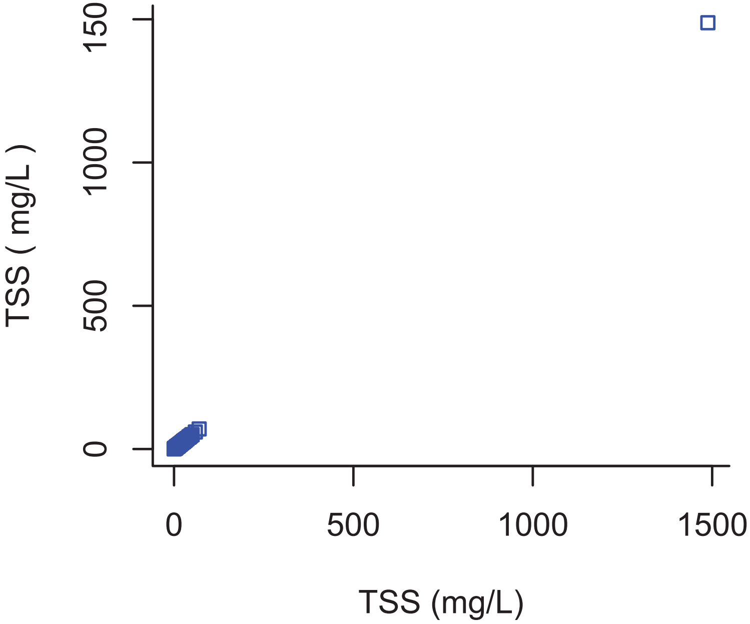
TSS vs Storm Intensity
r = 0.2
p = 0.1



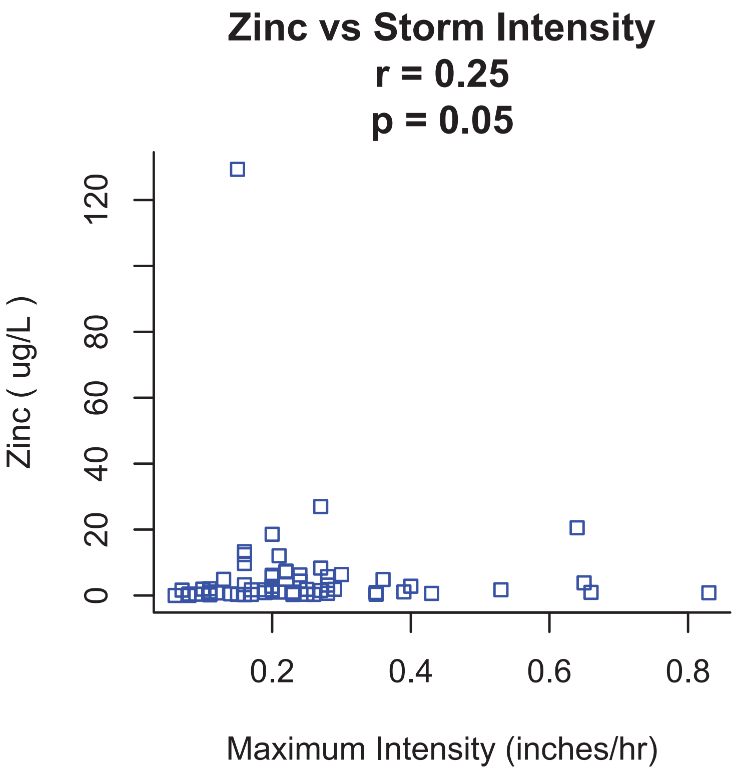
TSS vs Event Rainfall
r = 0.22
p = 0.07

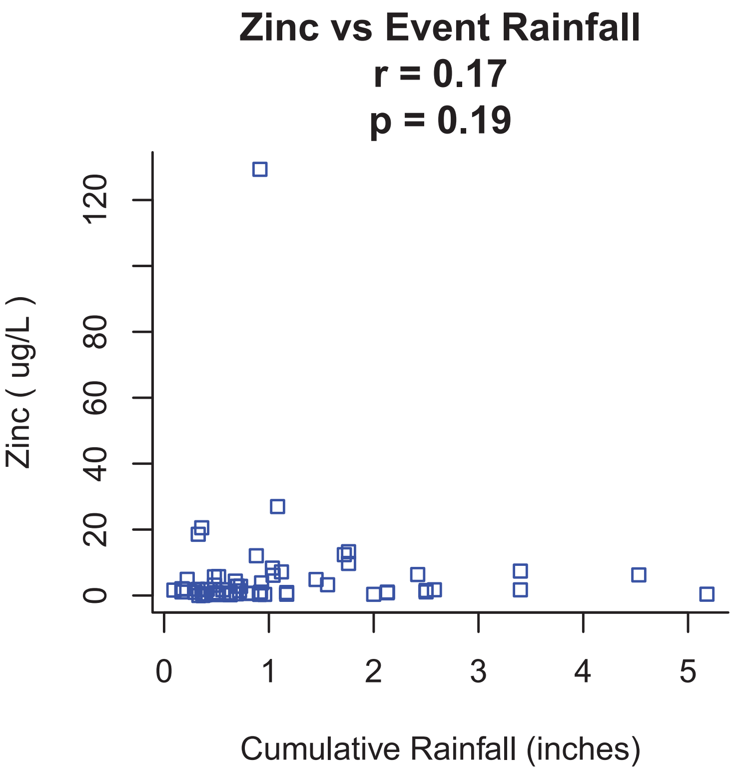


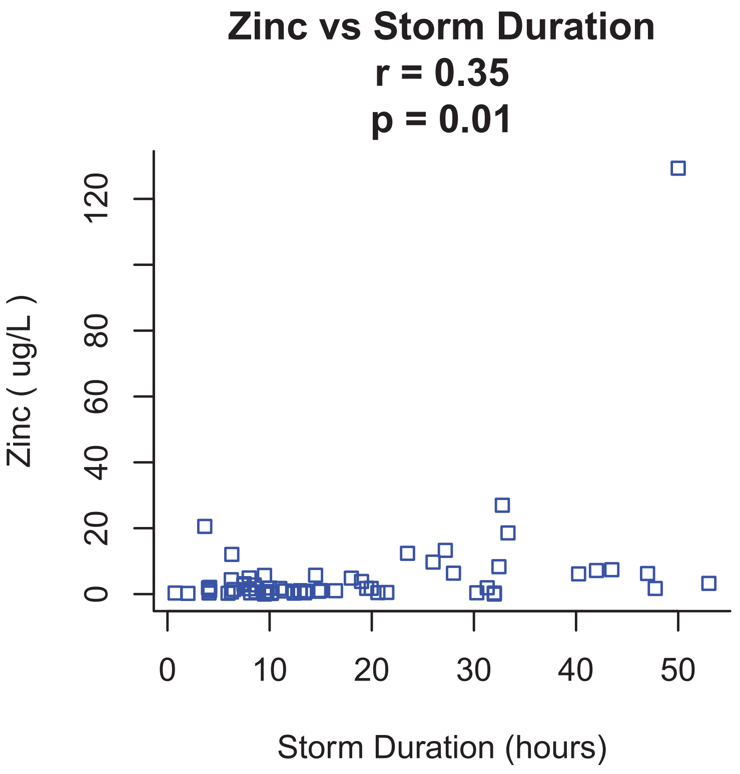
TSS vs Storm Duration
r = 0.16
p = 0.18

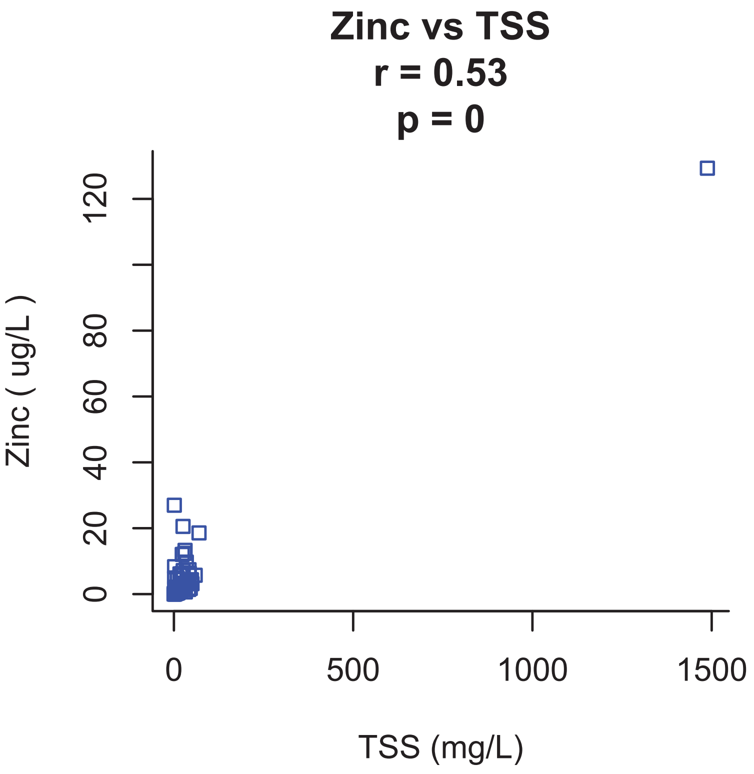


TSS vs TSS
r = 1
p = 0


Zinc vs Storm Intensity
r = 0.25
p = 0.05
Zinc (ug/L)
0
20
40
60
80
120
0.2
0.4
0.6
0.8
Maximum Intensity (inches/hr)


Zinc vs Event Rainfall
r = 0.17
p = 0.19
Zinc (ug/L)
0
20
40
60
80
120
0
1
2
3
4
5
Cumulative Rainfall (inches)


Zinc vs Storm Duration
r = 0.35
p = 0.01
Zinc (ug/L)
0
20
40
60
80
120
0
10
20
30
40
50
Storm Duration (hours)


Zinc vs TSS
r = 0.53
p = 0
Zinc (ug/L)
0
20
40
60
80
120
0
500
1000
1500
TSS (mg/L)