Investigating trace metal transport mechanisms in an intensive horticultural catchment

Final Report - Coffs Harbour City Council Environmental Levy Program

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Executive Summary

We performed dissolved trace metal investigations in Double Crossing Creek, a tributary of Hearnes Lake estuary and part of the Solitary Islands Marine Park (SIMP), to assess the potential influence of horticultural activity and rain events on water quality.

Time series measurements of dissolved trace metals was undertaken from 27 January to 3 April 2018 over multiple hydrological regimes. After a 109 mm rain event on 25 February, Hearnes Lake began to drain to the ocean. After the estuary drained, streamflow past our sample site was exclusively from the upstream catchment.

The concentrations and export rates of dissolved trace metals in Double Crossing Creek increase after rainfall events of various magnitudes. Rain events of 30 mm were sufficient to increase dissolved contaminant concentrations above the Australia and New Zealand Environment and Conservation Council (ANZECC) water quality guideline (WQG) values for both fresh and marine water.

Generally, export rates of dissolved contaminants were greatest when rainfall exceeded 50 mm. The elements mercury (Hg), copper (Cu), and zinc (Zn) exceeded either the ANZECC freshwater or marine WQG for more than 20 % of sampling events, in both wet and dry conditions. During and within 24 hours after rain events, Hg and Zn exceeded ANZECC WQG by more than 10 fold during our sampling. Flushing of agricultural soils containing these trace metals is believed to be the source of dissolved Hg, Cu, and Zn to Double Crossing Creek.

Estimated export rates of dissolved trace metals were high compared to examples from the literature on a per area basis.

Comparisons of trace metal export from Double Crossing Creek to subsequent sediment burial rates of trace metals in Hearnes Lake revealed the estuary may be a source of dissolved Hg, Cd, and Mn to a sanctuary zone of the SIMP at times when the estuary is hydrologically connected to the ocean. At times when Hearnes Lake is closed, the estuary is believed to retain upstream inputs.

No data on the ecological effect of trace metal export was collected. We suggest analyses of the chemical speciation and biological accumulation of trace metals (especially Hg) is undertaken to better understand the ecological implications of trace metal export from this horticultural catchment to the SIMP.

To prevent dissolved contaminant exposure in areas downstream of intensive horticulture we recommend actions to reduce use of products which may contain Hg, Zn, and Cu and to minimize and capture runoff during rain events.

1. Introduction

Intensive horticultural land use often requires the addition of fertilizer nutrients and other environmental contaminants (fungicides, herbicides, pesticides, etc.). The repeated, industrial-scale application of horticultural treatment products can lead to eutrophication, acute toxicity and mortality events as well as biomagnification through the food chain occurring in nearby terrestrial and aquatic environments (Neumann and Dudgeon 2002, Beman et al. 2005, Arias-Estévez et al. 2008).

Elemental constituents of industrial horticulture products, such as fertilizers, pesticides, fungicides, and herbicides, can include trace metals, such as lead (Pb), zinc (Zn), copper (Cu), mercury (Hg), and others. These elements can have adverse health effects on biota and human health, affecting processes such as neural and embryonic development, reproductive success, hormone cycling, behaviour, and overall organism fitness (Depledge et al. 1995, Duruibe et al. 2007). Trace metals can also bioaccumulate and biomagnify in the food web affecting all trophic levels from producers to top predators (Snodgrass et al. 2000, Rainbow 2007), and even human consumers (Authman et al. 2013).

Water can transport contaminants away from horticultural lands. While many trace metals (e.g. Pb, Zn, Cu) can be preferentially bound to suspended sediment or organic material particles, they can also be exported in a more bioavailable dissolved form (Collins and Jenkins 1996, Roussiez et al. 2011, Bergamaschi et al. 2012). Chemical and biological parameters such as pH, dissolved oxygen, organic material content, salinity, and microbial activity can affect the portioning between dissolved and particulate trace metals as they are transported downstream (Olsen et al. 1982, De Lacerda and Abrao 1984).

Different hydrological regimes (i.e. dry, rain, flooding, inundation) can influence trace metal transport. For example, during a 'first flush' event (a soil-saturating rain event after a sustained dry period), overland surface water runoff is often the dominant transport pathway for horticultural trace metals (Tong and Chen 2002, Delpla et al. 2011). Roussiez et al. (2013) reported greater fractions of dissolved trace metal concentrations during flooding events from a river in France. Additionally, the inputs of groundwater following flooding events can constitute a considerable portion of contaminant loading to downstream waterways (Berka et al. 2001, Santos et al. 2011).

Identifying the drivers and export rates of dissolved trace metals can be useful for land managers to mitigate adverse ecological effects in estuaries draining intensive horticultural land use. Data pertaining to the chemical composition of horticultural runoff, especially during episodic hydrologic events, such as floods, may prove important in reducing runoff risk and identifying contaminants of concern.

The objective of this work was to identify and quantify dissolved contaminant exports into a habitat protected estuary over varying hydrological regimes in a recently established horticultural industry (blueberry cultivation) on the east coast of Australia, where episodic hydrology is believed to drive estuarine discharge into the Pacific ocean (Eyre 1998). To identify specific contaminants of concern, we compared empirical concentrations to water quality guidelines (WQG). A secondary objective was to identify hydrological processes which increase dissolved trace metal concentrations and exports to the Solitary Islands Marine Park (SIMP). Our hypothesis is that rainfall events drive increased dissolved trace

metal contaminant loading into the estuary. To evaluate the effect of hydrology on trace metal loading in the horticulturally impacted estuary, we conducted time series measurements of dissolved trace metal and ion concentrations, groundwater tracers, and other water quality parameters during dry and flood conditions, using an increasingly intense sampling method during rain events.

This report builds on the work of White et al. (2018a) which focused on nutrient observations from the same water samples and Conrad et al. (2019) who revealed the history of trace metal pollution in sediments of Hearnes Lake. Here, we focus on dissolved trace metals using the same samples as White et al. (2018a).

2. Methods

2.1 Study area

Time series measurements were taken in Double Crossing Creek, the primary input into Hearnes Lake estuary on the subtropical east coast of Australia (Figure 1). Hearnes Lake estuary is within a habitat protected zone of the Solitary Islands Marine Park (SIMP). Average annual rainfall in this region is 1685 mm per year, with > 60 % occurring between January and May (Department of Land and Water Conservation 2001). Hearnes Lake estuary is an intermittently closed and open lake or lagoon (ICOLL) meaning during times of low hydrological input from the upstream catchment there is a sandbank preventing the estuary mouth from connecting with the ocean. During high rainfall events the estuary area (~ 10 ha^2, Haines 2006a) fills, overtopping and scouring the sandbank, allowing tidal connectivity and discharge into the SIMP.

Total catchment area of Hearnes Lake is 6.8 km^2. Land use within the catchment is 36 % forest, 25 % cleared land, and 23 % horticultural (16 % of which is blueberry horticulture) with an additional 13 % being abandoned agricultural land. A small quarry operates in the catchment (0.05 km^2, 1.1 % of land use). Considerable amounts of dissolved nitrates and nitrites (NO$_x$) have been observed during high rainfall events in other nearby waterways draining similar intensive horticulture (White et al. 2018a, White et al. 2018b). Conrad et al. (2019) reported moderate to severe sediment enrichment in Hearnes Lake with phosphorus (P), cadmium (Cd), arsenic (As), and zinc (Zn), associated with upstream horticultural activities.

Our sample site was ~ 2 km upstream of the estuary mouth, at the upper reaches of the tidal range (Haines 2006a, Figure 1B). Total catchment area upstream of our sample site was 4.7 km^2. Our sample site was selected here because catchment runoff entering narrow upstream extremities of ICOLLs can be reflective of the inflowing water quality (Haines 2006b) and this location has limited the influence of the residential development downstream near the estuary body.
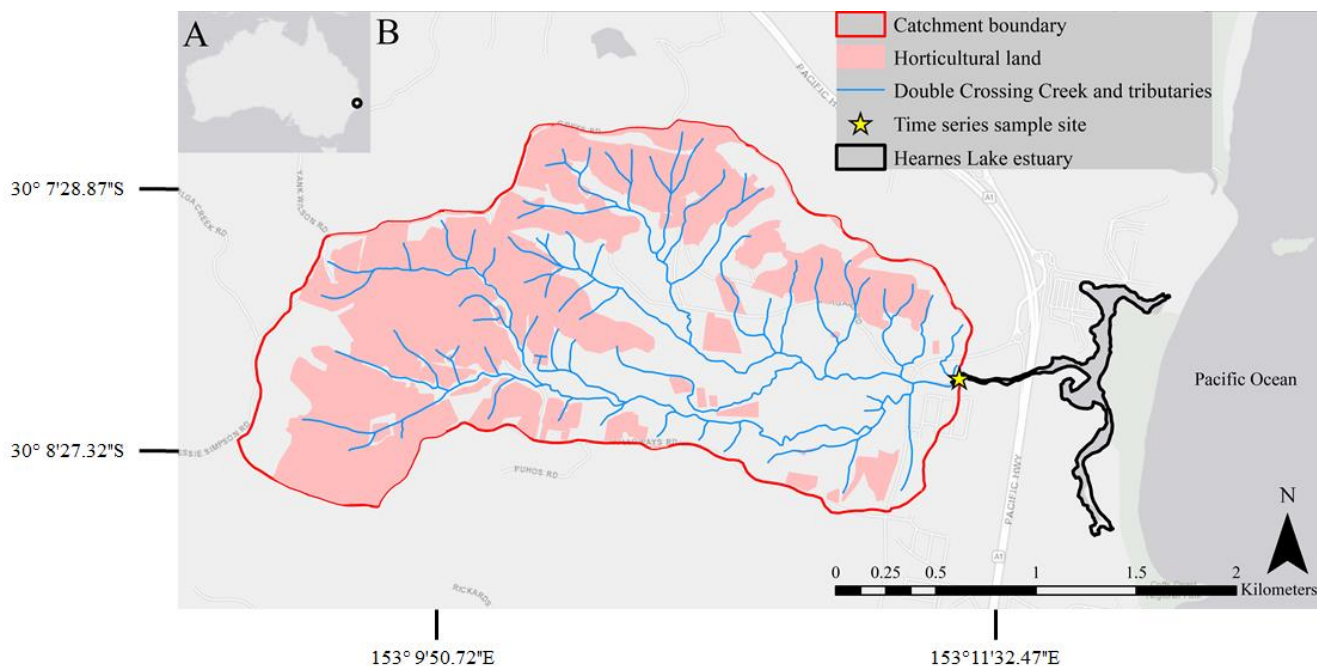
Figure 1. A) Study area on the east coast of Australia (black circle). B) Our Hearnes Lake estuary (black outline) time series station (star) and catchment (4.7 km^2, red outline). Horticultural land (pink) comprises 23 % of the catchment. A total of 107 time series measurements of dissolved ion concentrations, groundwater tracers, and other water quality parameters were conducted here over dry and flood periods between 27 Jan and 4 Apr 2018.

2.2 Sample collection

Time series sampling was conducted in a 2 m^2 shed downstream of intensive horticulture in Double Crossing Creek from 27 January to 4 April, 2018 (Figure 1B). Three 12 V deep cycle batteries connected in parallel, solar panels, and a petroleum fuel generator were used to power pumps and analytical instruments. Creek water was pumped continuously from approximately 30 cm below the surface using a submersible bilge pump. Water quality parameters (dissolved oxygen, pH, conductivity, salinity) were measured every 10 minutes using a calibrated Hydrolab MS5. The decay activity of the natural radioisotope groundwater tracer ^{222}Rn ($T_{1/2} = 3.83$ days) was monitored with a Durridge Rad7 radon detector using the setup described in Burnett et al. (2010). ^{222}Rn observations (dpm L^{-1}) were logged every 10 minutes throughout the time series. On site rainfall rate was recorded at each sampling event using a 100 mL graduated cylinder attached to the shed.

Discrete sampling was performed by triple rinsing a 60 mL polystyrene syringe with water from the pump. For dissolved ions, sample water was passed through a 0.7 μm microfibre filter then syringed into triple rinsed 10 mL polyethylene. Samples were kept cool for transport back to the lab and then frozen until time of analysis.

Throughout the time series, discrete samples were taken once daily when rainfall was less than 50 mm in 24 h. When rainfall events above 50 mm 24 hr^{-1} occurred, sampling was conducted in 2 to 4 hour increments. A total of 107 discrete sampling events took place throughout the time series.

2.3 Dissolved trace metal and ion analysis

For dissolved ion analysis, samples were acidified by injecting 0.1 mL of 70 % (15.8 mol L^{-1}) nitric acid (HNO_3) (Santos et al. 2011). Trace metals and other ion concentrations were determined using a Perkin-Elmer Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The ICP-MS was calibrated before and after running samples. To account for background drift, standards were routinely run between samples.

Dissolved organic carbon (DOC) concentrations were analysed using an Aurora 1030W total organic C analyser coupled with an isotope mass spectrometer and continuous flow system as outlined in Looman et al. (2019).

2.4 Calculations and water quality guidelines

Creek discharge was calculated from *in situ* depth logging data from a Unidata Starflow Ultrasonic Doppler deployed on the bottom of the creek, catchment runoff (mm) data retrieved from the Australian Landscape Water Balance database (Frost et al. 2018), and catchment area. Daily trace metal and ion exports were calculated as concentration (ex: g L^{-1}) multiplied by the creek discharge, and total catchment area to yield total amount of contaminant exported each day (ex: g contaminant per day).

We compared our measured dissolved trace metal and ion concentrations to the Australia New Zealand Environment and Conservation Council (ANZECC) water quality guidelines (WQG) retrieved from the online database. If no WQG was available from the online database, we used the values from the ANZECC and ARMCANZ Australian and New Zealand guidelines for fresh and marine water quality (Anzecc 2000). Due to the tendency of some trace metals to bioaccumulate, and existing anthropogenic alterations to catchment land, we used WQG values at the 95 % species protection level (appropriate for 'slightly to moderately disturbed systems'). Due to shifts in the water chemistry (discussed later) we used both the freshwater (FW) and marine WQG for comparison.

2.5 Principal component analysis

Principal component analysis (PCA) was performed on IBM SPSS Statistics software (version 24) to interpret associations in the variance of data. After eigenvalue and scree plot inspection, we extracted components with 2 fixed factors. Varimax rotation was selected to extract components orthogonally (Helena et al. 2000, Li and Zhang 2010). Nutrient data from White et al. (2018a) was included in the PCA.

3. Results

3.1 Dissolved concentrations and exports

There were 44 of 66 days with no rainfall. Three rainfall events > 50 mm occurred during the time series. The first, on 25 Feb, totalled 109 mm. During this time, the ICOLL overtopped the sand barrier and began to drain into the Pacific Ocean for the remainder of the time series. The greatest rainfall (161 mm) occurred on 25 Mar. Catchment runoff (measured as mm m^{-2} of catchment; obtained from Australian Bureau of Meteorology) trends increased with each

subsequent rain event (Figure 2). Runoff increased from 0.1 to 0.8 mm m^{-2} on 5 Feb after a 31 mm rain event. On 25 Feb catchment runoff increased from 0.2 to 1.2 mm m^{-2}. On 7 Mar a 78 mm rain event cause catchment runoff to increase from 0.4 to 3.2 mm m^{-2}. Catchment runoff reached a maximum with the greatest rainfall on 25 Mar at 3.7 mm m^{-2}.

After the estuary opened to the ocean on 25 Feb, salinity rapidly decreased from ~ 20 to ~ 2.5 (Figure 2). pH displayed a similar trend, averaging 7.1 before the initial major rain event and 6.6 afterwards. Additionally, pH briefly decreased with each subsequent rain event > 50 mm. The natural groundwater tracer ^{222}Rn had an opposite trend to salinity and pH, averaging 1.06 dpm L^{-1} before the initial rain event, and was consistently elevated (mean 1.91 dpm L^{-1}) after the initial rain event. Dissolved oxygen (DO, % saturation) steadily decreased after a 30 mm rain event on 5 Feb, reaching a minimum of 0.1 %. DO also fell after the initial major rain event on 25 Feb, but increased rapidly on 26 Feb, and remained relatively elevated for the remainder of the time series.

Data on all dissolved ion concentration and catchment export appears in Table 1. Our discussion centres on the elements that were above the ANZECC FW or marine WQG. In general, patterns of dissolved trace metal concentrations and catchment exports increased within 1 to 2 days following rainfall, even in some instances when rain was less than 50 mm (i.e. chromium, Cr and cobalt, Co; Figure 2).

Dissolved mercury (Hg) concentration was greatest during and immediately after the first flush event (25 to 27 Feb). Both dry and flooding conditions saw dissolved Hg concentrations which exceeded both FW and marine ANZECC WQG (2.99 nmol L^{-1} FW, n = 14; 1.99 nmol L^{-1} marine, n = 24, Figure 3). Patterns of Hg export closely followed dissolved Hg concentrations, with majority of export occurring during the first flush event (84 g exported from 25-28 Feb, 31 g export for the remainder of the time series).

Cadmium (Cd) concentration reached maximum of 21.35 nmol L^{-1} on 28 Feb, 3 days after the first flush event, and one day after a 26 mm rain event on 27 Feb. Cd concentrations exceeded the ANZECC FW WQG value (1.78 nmol L^{-1}) a total of four times, twice after the first flush event on 28 Feb, and twice during a > 50 mm rain event on 7 Mar. Export of Cd was ~ 5 times greater during the first flush event than the next rain event on 7 Mar. Cd concentrations did not exceed the ANZECC marine WQG (48.93 nmol L^{-1}).

Our analysis measured total chromium (Cr), and did not distinguish between trivalent (CrIII) and the more toxic hexavalent (CrVI) forms. ANZECC WQG values for CrIII and CrVI were used for comparison. Total Cr concentrations exceeded the FW WQG for Cr(III) once during dry conditions on 15 Feb. Total Cr exceeded FW WQG value for Cr(VI) for 18 of 107 samples (17 %) during both dry and rain conditions. Total Cr exceeded the marine WQG for CrVI for 14 of 107 samples (13 %). No total Cr concentrations exceeded marine WQG for CrIII. Low creek flow during dry conditions signified the increased concentration of Cr on 15 and 16 Feb was not accompanied with an increased export (1.63 and 0.81 g day^{-1}). Catchment export of Cr was greatest during the 26 Mar rain event (12.5 g day^{-1}).

Copper (Cu) concentration and export was greatest during the Mar 7 rain event. Export of Cu was also elevated after the large 25 March rain event. Dissolved Cu concentrations exceeded

both ANZECC WQG guidelines over 30 % of samples (FW 22.03 nmol L^{-1}, n = 34; marine 20.46 nmol L^{-1}, n = 42).

Zinc (Zn) concentration was greatest following the first flush event, however patterns of Zn export were not congruent with the highest concentrations. The two major rain events after the first flush (7 and 25 Mar) caused catchment export to exceed 300 g day^{-1}. Zn export after the 25 Mar rain event was more than double the first flush export (332.8 vs 709.1 g day^{-1}). Zn concentrations exceeded the FW WQG (0.12 μmol L^{-1}) on 63 % of samples (n = 67) and the marine WQG (0.23 μmol L^{-1}) on 39 % of samples (n = 42).

Cobalt (Co) concentration reached maxima before the first flush event (139 nmol L^{-1}). The greatest concentration of Co occurred on 21 Feb in dry conditions. Largest export was during the first flush event (20 g day^{-1}), however all rain events, including the < 50 mm event on 5 Feb, caused elevated Co export. Co concentrations exceeded marine WQG for 11 out of 107 samples (10 %). The FW WQG for Co is undetermined at this time.

Manganese (Mn) concentrations were elevated in the dry period before the first rain event (9.94 μmol L^{-1}), however, Mn export was greatest during the first flush event (1.5 kg day^{-1}). Additionally, the first small rain event and two subsequent > 50 mm rain events after the first flush caused a relatively low increase in Mn export. Mn concentrations never exceeded the FW WQG, however 53 % of samples exceeded the marine WQG for Mn (n = 57) in both dry and wet conditions.

Concentration and export of aluminium (Al) was greater during the two rain events following the first flush event, perhaps driven by lithogenic inputs from increased catchment runoff (supported by BOM data). Al WQG values are different depending on pH. When pH was > 6.5, Al concentrations exceeded FW WQG for 24 of 97 samples (25 % of samples with pH > 6.5). For all samples when pH was < 6.5 (n = 10), Al concentrations exceeded FW WQG Al pH > 6.5. There is no high reliability marine WQG for Al, therefore no comparisons were made.

3.2 Principal component analysis

The two extracted components accounted for 55 % of the variability within the data (appendix Table A2). Component 1 accounted for 45 % of variance, while component 2 accounted for 10 % with no correlations between these two components (Table A3). Conductivity, pH, and seawater ions (S, Mg, Cl, Na, K, Ca, Br) were positively correlated with component 1, while nitrogen species (NO_x and NH_4), ^{222}Rn, Zn, and Fe were negatively correlated (Figure 4, Table A4). Trace elements including Ni, Cr, Cd, Cu, Co, As, P were slightly positively correlated with components 1 and 2. Runoff, rainfall, and creek discharge (flow) were negatively correlated with component 2.

Table 1. Range, mean, and standard errors of concentration and daily catchment export of water quality parameters and dissolved ions from our Double Crossing Creek time series.

Parameter	Unit	Concentrations Min - Max	Concentrations Mean ± StE	ANZECC WQG FW	ANZECC WQG Marine	% of samples over WQG FW	% of samples over WQG Marine	Times over WQG FW	Times over WQG Marine	Export mass day⁻¹	Export Min - Max	Export Mean ± StE
pH	-	6.3 - 7.22	6.78 ± 0.02	6.5-8.0	8.0-8.4	9	100	-	-	-	-	-
DO	%	0.1 - 121.6	56.6 ± 3.33	85-110	90-110	76	81	-	-	-	-	-
Salinity	ppt	0.05 - 20.52	7.01 ± 0.77	-	-	-	-	-	-	-	-	-
Rainfall	mm	0 - 149	5.55 ± 1.66	-	-	-	-	-	-	-	-	-
Runoff	mm	0.02 - 3.72	0.68 ± 0.07	-	-	-	-	-	-	-	-	-
Discharge	$m^{-3}\ day^{-1}$	93.5 - 17382	3174 ± 349.6	-	-	-	-	-	-	-	-	-
^{222}Rn	$dpm\ L^{-1}$	0.52 - 2.37	6.78 ± 0.04	-	-	-	-	-	-	-	-	-
Al	$\mu mol\ L^{-1}$	0.23 - 8.72	1.94 ± 0.17	2.0384	-	31	-	4.28	-	kg	0.001 - 3.39	0.25 ± 0.05
DOC	$\mu mol\ L^{-1}$	BDL - 695	432 ± 13.3	-	-	-	-	-	-	kg	BDL - 80.22	15.6 ± 1.6
As	$nmol\ L^{-1}$	BDL - 89.8	23.2 ± 1.79	493.85	-	0	-	0	-	g	BDL - 31.72	4.52 ± 0.55
Cd	$nmol\ L^{-1}$	BDL - 21.35	0.67 ± 0.24	1.7792	48.93	4	0	12	0	g	BDL - 10.65	0.22 ± 0.1
Cr	$nmol\ L^{-1}$	BDL - 42.12	4.99 ± 0.56	7.69*	8.46*	17	13	5.475	4.98	g	BDL - 12.37	0.84 ± 0.14
Cu	$nmol\ L^{-1}$	7.73 - 127.3	20 ± 1.27	22.03	20.46	32	39	5.78	6.22	g	0.074 - 120.59	4.98 ± 1.18
Fe	$\mu mol\ L^{-1}$	0.43 - 7.62	2.78 ± 0.16	-	-	-	-	0	-	kg	0.006 - 2.89	0.58 ± 0.06
Mn	$\mu mol\ L^{-1}$	0.17 - 9.94	2.13 ± 0.18	34.58	1.36	0	53	0	7.29	kg	0.003 - 1.52	0.31 ± 0.03
Ni	$nmol\ L^{-1}$	BDL - 49.58	3.98 ± 0.65	187.41	1192.6	0	0	0	0	g	BDL - 10.51	0.86 ± 0.17
Pb	$nmol\ L^{-1}$	0.69 - 20.85	3.69 ± 0.3	16.41	21.24	< 1	0	1.27	0	g	0.028 - 49.67	2.54 ± 0.51
Zn	$nmol\ L^{-1}$	20.2 - 1542	266 ± 26.01	122.36	229.43	63	39	12.6	6.72	g	0.765 - 709.10	73.35 ± 12.6
Hg	$nmol\ L^{-1}$	BDL - 23.08	1.8 ± 0.31	2.99	1.99	13	22	7.72	11.57	g	BDL - 15.77	1.08 ± 0.24
B	$\mu mol\ L^{-1}$	3.93 - 239.9	81.7 ± 8.62	-	-	-	-	-	-	kg	0.009 - 9.37	1.49 ± 0.19
Si	$\mu mol\ L^{-1}$	69.4 - 239.1	165 ± 3.36	-	-	-	-	-	-	kg	0.430 - 73.29	14.33 ± 1.49
V	$nmol\ L^{-1}$	3.24 - 98.59	27.2 ± 2.09	117.78	1963	0	0	0	0	g	0.046 - 19.24	3.12 ± 0.3
Co	$nmol\ L^{-1}$	2.14 - 139.5	11.1 ± 1.54	-	16.97	0	10	-	8.22	g	0.019 - 20.42	2.06 ± 0.3
Mo	$nmol\ L^{-1}$	0.73 - 42.5	11.5 ± 0.83	1.56	1563.5	0	0	0	0	g	0.066 - 15.62	2.24 ± 0.21
Ba	$nmol\ L^{-1}$	392 - 7098	856 ± 66.87	7.28	7281.9	0	0	0	0	kg	0.011 - 5.51	0.38 ± 0.06
Ca	$mmol\ L^{-1}$	0.16 - 7.39	2.6 ± 0.26	-	-	-	-	-	-	kg	2.097 - 1100.05	182.4 ± 21
Mg	$mmol\ L^{-1}$	0.25 - 33.22	111 ± 1.2	-	-	-	-	-	-	kg	2.284 - 3093.19	440.4 ± 58.5
K	$mmol\ L^{-1}$	0.19 - 6.69	2.39 ± 0.24	-	-	-	-	-	-	kg	1.576 - 957.73	162.4 ± 19
Na	$mmol\ L^{-1}$	1.49 - 301.5	102 ± 11.35	-	-	-	-	-	-	Mg	0.014 - 25.93	3.79 ± 0.52
Cl^{-}	$mmol\ L^{-1}$	1.65 - 367.3	121 ± 13.63	-	-	-	-	-	-	Mg	0.023 - 48.92	6.96 ± 0.96
S	$mmol\ L^{-1}$	0.26 - 18.06	6.1 ± 0.64	-	-	-	-	-	-	Mg	0.003 - 2.22	0.33 ± 0.04
Br	$\mu mol\ L^{-1}$	2.24 - 580.2	190 ± 21.76	-	-	-	-	-	-	kg	0.071 - 170.15	24.17 ± 3.38

* Cr(VI) ANZECC guideline
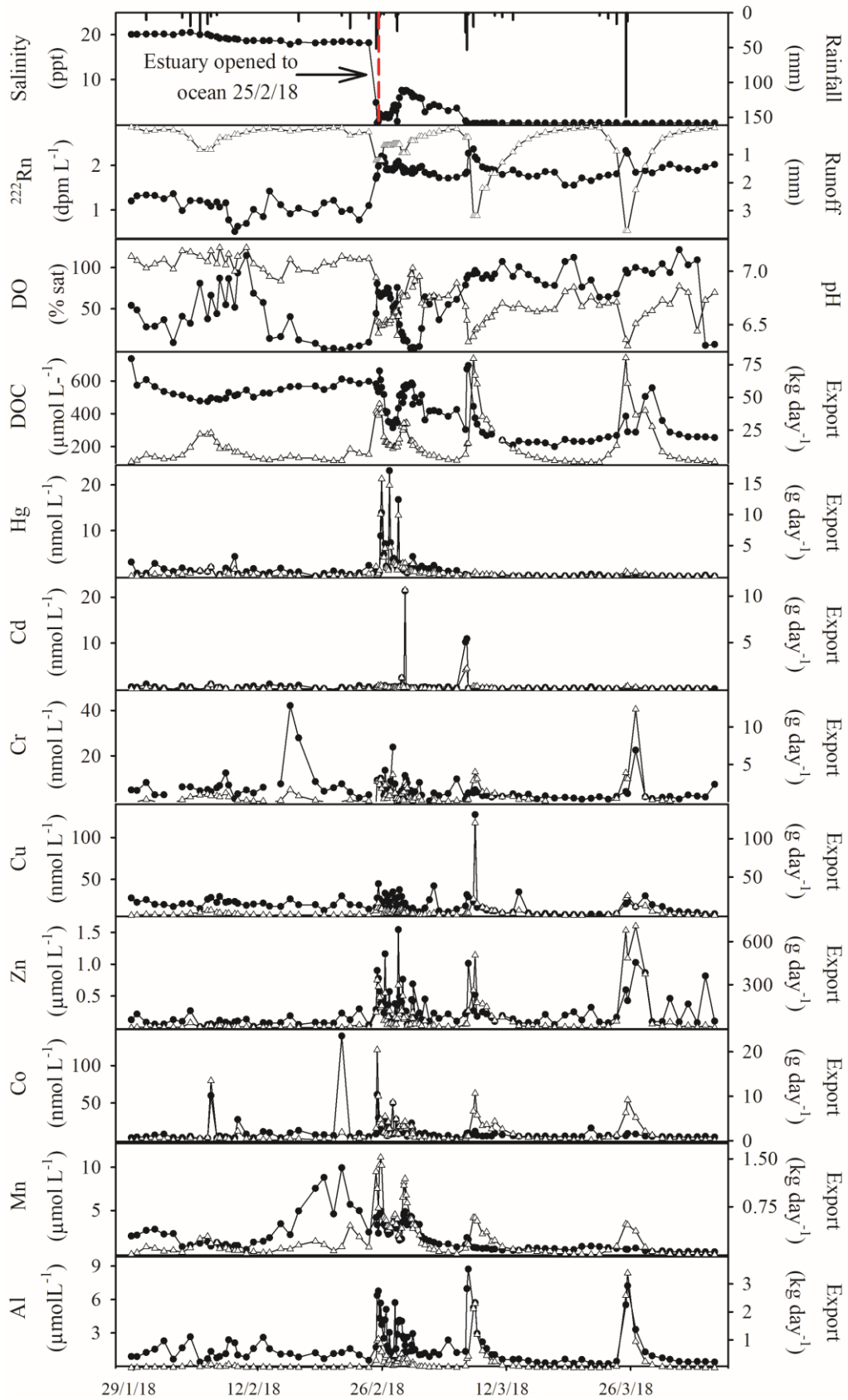
Figure 2. Time series observations of key parameters from 27 Jan to 4 Apr 2018. The left axes (dark circles) represent salinity, ^{222}Rn, dissolved oxygen (DO % saturation), or trace metal concentrations, while the right axes (open triangles) represent rainfall, catchment runoff, pH, or export loads.
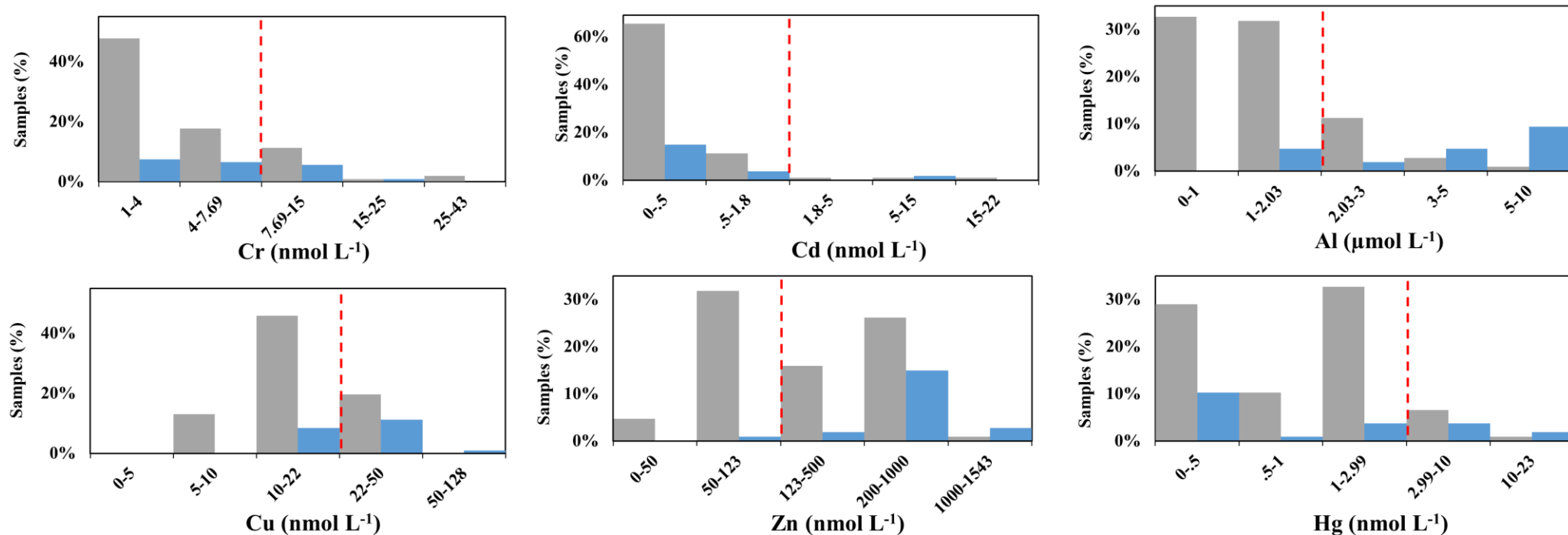
Figure 3. Histograms of dissolved trace metals which frequently exceeded the ANZECC freshwater (FW) or marine water quality guidelines (WQG) during dry (grey) and rain (blue) events from our Double Crossing Creek time series. Observations to the right of the red dotted line are above the ANZECC trigger value. Note the different scale of each y-axis.
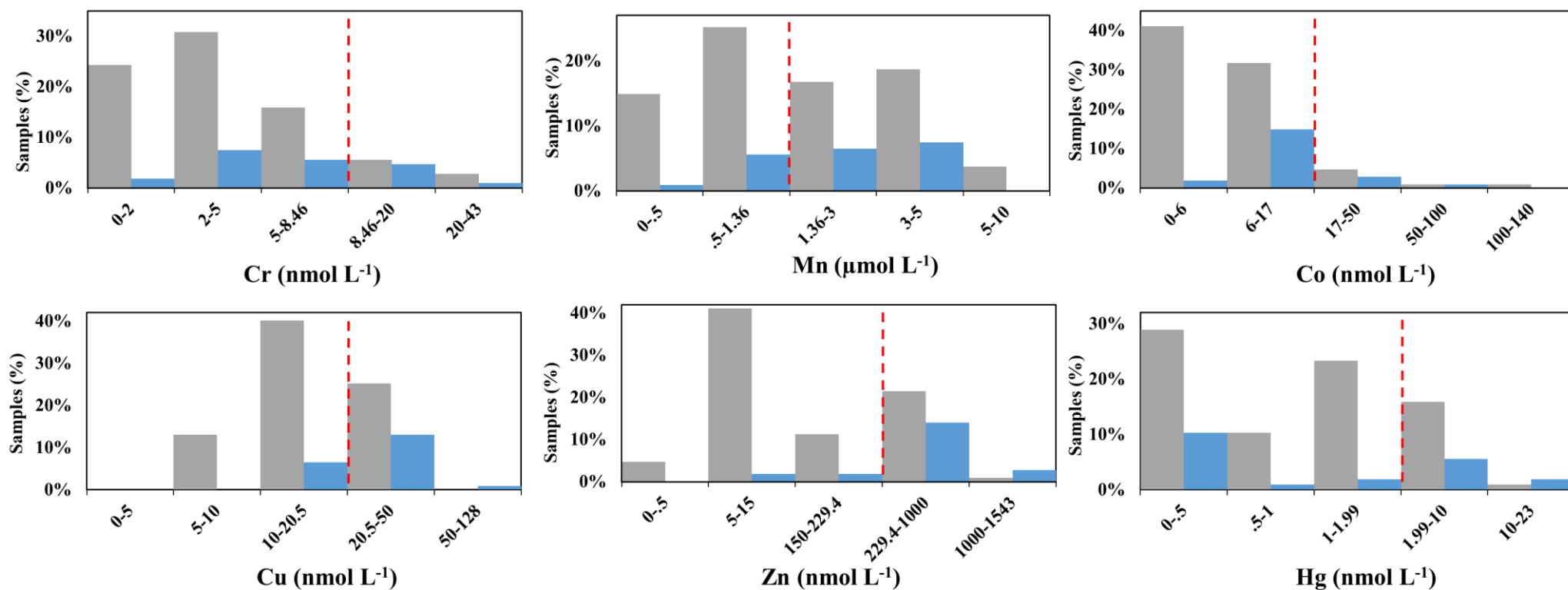
Figure 3 (cont.). Histograms of dissolved trace metals which frequently exceeded the ANZECC freshwater (FW) or marine water quality guidelines (WQG) during dry (grey) and rain (blue) events from our Double Crossing Creek time series. Observations to the right of the red dotted line are above the ANZECC trigger value. Note the different scale of each y-axis.
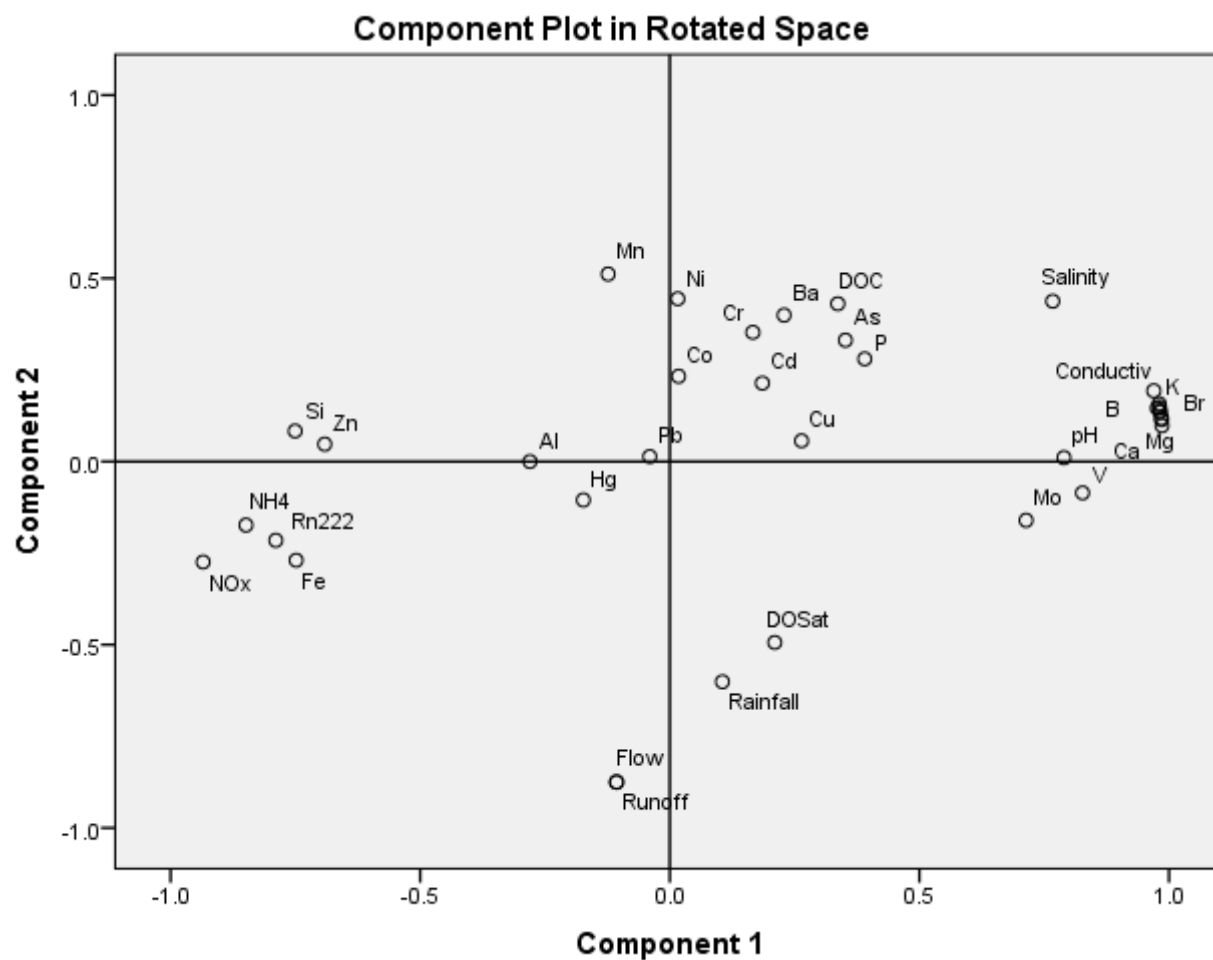
Figure 4. Contribution of each variable to principal component loadings from principal component analysis (PCA). Nutrient data from White et al. (2018a).

4. Discussion

4.1 Effect of rainfall on trace metal transport

The first rain event > 50 mm was directly related to an elevated groundwater flow (as traced by ^{222}Rn). After this first flush, ^{222}Rn increased only slightly after each subsequent rain event (Figure 2). Santos et al. (2011) reported some trace metal concentrations reached maximum 8 to 10 days after flood events due to delayed groundwater inputs in the Tuckean swamp on the northern coast of NSW. The short sustained durations of increased dissolved contaminants after rainfall (with the exception of Al) likely reflects the effect of surface runoff and not groundwater inputs on dissolved contaminant concentrations in Double Crossing Creek as indicated by our groundwater tracer (^{222}Rn). Therefore, overland surface runoff is most likely driving the short term increased contaminant loading observed during the rain events.

These results are supported by other studies which highlight the role of rainfall events in increasing dissolved contaminant export (Grimshaw et al. 1976, Xue et al. 2000, Lyons et al. 2006, Suescún et al. 2017). During our time series measurements, concentrations of many of the trace elements were elevated during and shortly after rainfall events, then generally returned to baseline levels within ~ 2 days (Figure 2). Elements which exceeded WQGs during dry periods were zinc (Zn) and copper (Cu), and occasionally mercury (Hg) and chromium (Cr). Although the exact source of these contaminants during dry periods is unknown, anthropogenic activities upstream in the catchment are likely to be the source of these elevated concentrations. The changes in concentrations and turbidity we observed were on similar timescales. Short term fluctuations of our contaminant concentrations are likely demonstrative of the affinity of dissolved trace metals to bind to suspended particles which then deposit when the discharge returns to baseline levels (Hart 1982, Soto et al. 1994).

Export rates of our dissolved metals during rain events ranged from 31 % (Cd) to 70 % (Al), despite only 21 % of our sampling efforts occurring during these rain events. Our range of percentages are relatively high when compared to the literature. For instance, Palleiro et al. (2014) reported rain events to account for between 27-49 % of the dissolved contaminant export from a three year monitoring of an agricultural use catchment in Spain. Roussiez et al. (2013) reported a 16 h flood event which contributed 91 % of annual metal export was responsible for only 0-20% of annual dissolved metal exports. Both of these studies were conducted for at least 1 year. While baseline sampling was more frequent (daily) in our study, it is possible that our shorter time scale (~3 months) may have missed or overestimated the largest annual flood events. Despite uncertainties, our results suggest dissolved contaminant loading in Double Crossing Creek is highly dependent on episodic rainfall and runoff events.

4.2 Context of contaminant loads

Copper (Cu), zinc (Zn), mercury (Hg), manganese (Mn), and aluminium (Al) exceeded ANZECC FW or marine WQG for more than 20 % of sampling events (Table 1). In addition to frequent exceedances of the ANZECC WQG, these elements ranged from 4.28 (Al) to 12.6 (Zn) fold greater than their ANZECC trigger values (Figure 5). The relatively high frequency and magnitude of exceedances of both FW and marine WQG mean these aforementioned trace metals are of concern, especially given the connectivity of the catchment to the SIMP.
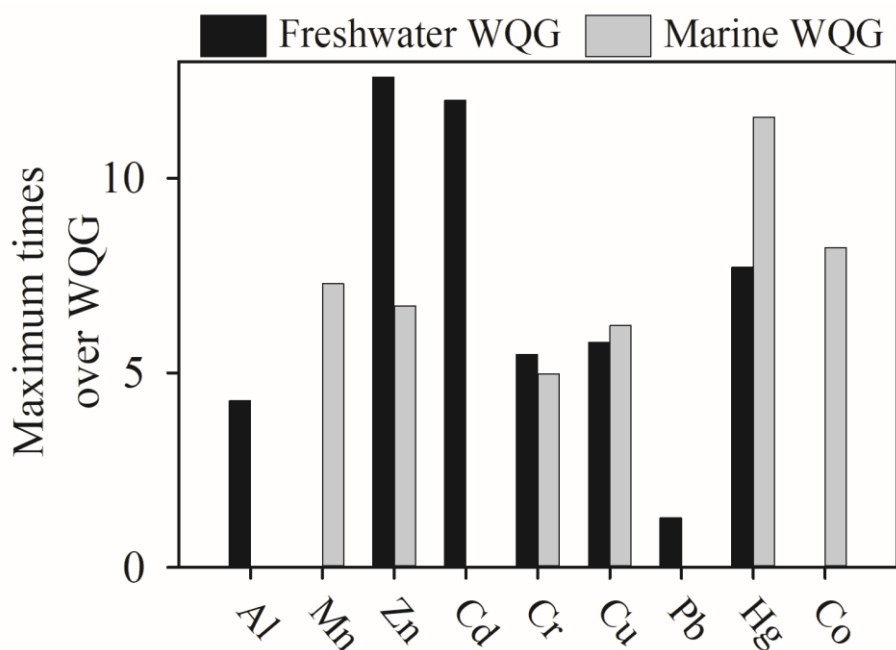
Figure 5. Bar graph of the maximum times over freshwater (black) and marine (grey) WQG for dissolved contaminants from our Double Crossing Creek time series observations.

Dissolved concentrations and exports of Hg from our catchment are greater than other reports from the literature. In a review of Hg export from freshwater streams Shanley and Bishop (2012) reported base flow concentrations of Hg to be between 0.5 to 2 ng L^{-1}. Concentrations of Hg from our catchment were on the order of μg before the first flush event. Our observed dissolved Hg concentrations were orders of magnitude greater than dissolved Hg concentrations during a high flow event from an agricultural catchments of the Corn Belt in the United States (4.63 μg L^{-1} vs. 0.76 ng L^{-1}, Lyons et al. 2006). However the filter size was larger in our study (.7 vs .4 μm filters), allowing for the possibility of Hg bound to small organic particles to pass through our relatively larger filter size (Alpers et al. 2014). Balogh et al. (2005) reported unfiltered total Hg (THg) concentrations on the scale of ng L^{-1} during flooding and snowmelt events of agricultural areas of Minnesota, USA, orders of magnitude lower than our concentrations, despite the sampling being for sediment bound Hg in addition to dissolved. Hg exports were far less for our study (3.94 g yr^{-1} vs 28 kg yr^{-1} THg), due to much larger catchment areas in Balogh et al. (2005) allowing for dilution. However, the connectivity of our catchment to an environmental protected area of the SIMP should be considered when interpreting the implications of Hg export. Additionally, our study did not sample for unfiltered Hg, meaning the export of THg exported from this catchment may be underestimated.

Other studies from agricultural catchments report various dissolved contaminant loadings. In a yearlong monitoring of a smaller (3.28 km^2), but more intensively cultivated (86 % horticulture) wheat and sunflower catchment in SE France, Roussiez et al. (2013) reported mean concentrations of dissolved chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), arsenic (As), and cadmium (Cd) which were orders of magnitude greater than our mean concentrations for these elements, while their mean dissolved aluminium (Al) concentration was only 33 % greater than what was found in Double Crossing Creek (Table 3 of Roussiez et al. 2013). Despite higher agricultural land use in the French catchment, and greater

dissolved concentrations, area normalised annual exports (ex: g km^{-2} yr^{-1}) from Roussiez et al. (2013) were lower than what was found in this catchment for Cr, Cu, Zn, Pb, As, Cd, and Al.

4.3 Dissolved export versus sediment burial

Dissolved contaminants undergo many chemical changes in estuaries, due to changes in pH, salinity, conductivity, dissolved oxygen, and other environmental factors (Mendiguchía et al. 2007, Thanh-Nho et al. 2018). Fate of dissolved contaminants in estuaries may be uptake by biota (de Souza Machado et al. 2016, Kulkarni et al. 2018) or binding to sediment particles, decreasing bioavailability (Tessier and Campbell 1987). Sediment bound contaminants are often deposited in estuaries, as they are natural sites of increased sedimentation (Benninger et al. 1975, Conrad et al. 2017). Alternatively, dissolved contaminants could be exported to the coastal ocean, where similar processes may occur under different physical and geochemical conditions (Hydes and Kremling 1993, Haynes and Johnson 2000, Sanders et al. 2015).

Our study did not measure the particle adsorption, biological uptake, or export to the ocean, but comparisons to literature may prove useful. Conrad et al. (2019) recently identified sediment pollution and contaminant flux rates within our receiving estuary (Hearnes Lake). We have compared our dissolved contaminant export rates (mean of daily export rates from our 66 day time series multiplied by 365 to give kg yr^{-1} exports) with the most recent mean sediment burial rates from sediment cores taken within the Hearnes Lake estuary body (from Conrad et al. 2019, published and unpublished data, Figure 6).
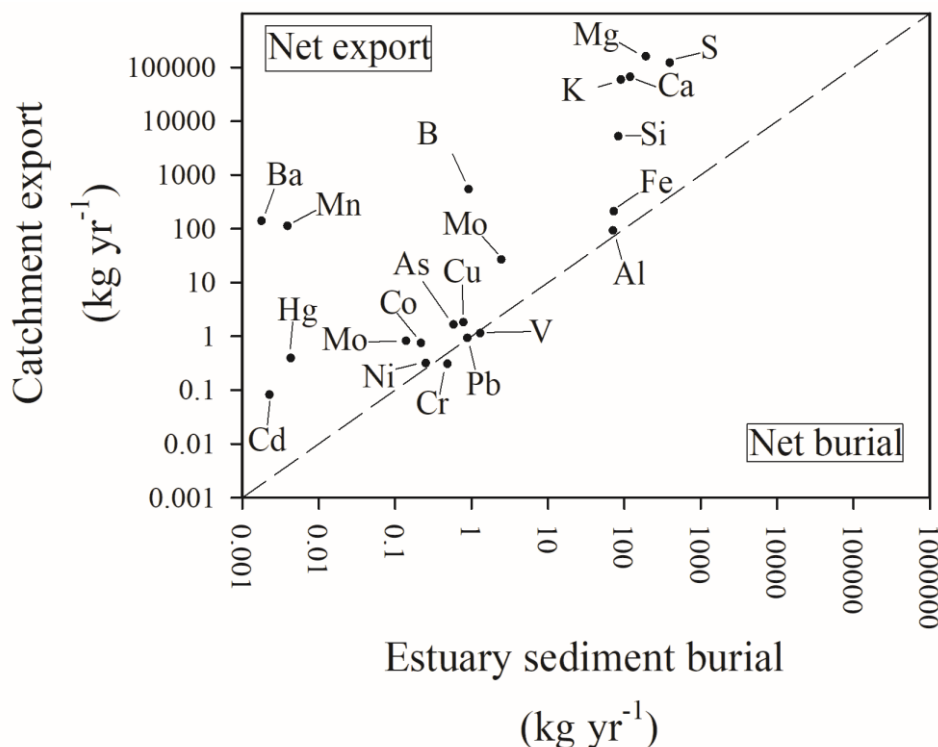
Figure 6. Catchment export of dissolved elements plotted against total estuary sediment burial (both in kg yr^{-1}) from Conrad et al. (2019). Note the logarithmic scale of each axis. Dotted line represents 1:1 ratio of export and burial (as much exported to the estuary as is

buried). To the left of the line signifies net export from the estuary, while to the right signifies net burial within estuary sediments.

Figure 6 shows the relationships between our yearly dissolved contaminant export estimations and total sediment burial rates (kg yr^{-1}) of these elements within Hearnes Lake. The dotted line represents a 1:1 ratio of export to burial, signifying the closer an element is to this line, the more similar dissolved export rates and burial rates are. Many of the particle reactive dissolved contaminants (As, Cu, Co, Mo, Ni, Cr, Pb, V, Al, Fe) plot near to this line. These elements are likely to undergo adsorption to particles when they encounter changes in pH, salinity, and organic material content that are typical along an estuarine gradient (Luoma 2017, Kulkarni et al. 2018). While our study did not measure the particle adsorption rates of these metals, other studies demonstrate the affinity of the dissolved phase of these elements to bind to suspended particles in estuarine conditions (Lion et al. 1982, Bourg 1987, Turner 1996, Mendiguchía et al. 2007). The contaminants that become adsorbed to particles may then settle out into the sediment of the estuary body (Salomons 1980, Tessier and Campbell 1987) or be exported from the estuary into the ocean. However, Conrad et al. (2019) reported enrichments of Zn in Hearnes Lake sediment cores, along with increasing sediment fluxes of Al, indicating that even though many of these metals are exported to the coastal ocean, the estuarine wetlands are efficient in sequestering a large portion of these metals.

One caveat of our study is that we did not sample particulate bound metals, which can account for a greater percentage of the total metal export than dissolved metals (Xue et al. 2000, Roussiez et al. 2013, Soto- Varela et al. 2015). It is possible that the particulate bound metals dominate burial within the estuary, as has been demonstrated in other studies (Benninger et al. 1975, Vidal-Durà et al. 2018). Alternatively, dissolved contaminants may be exported to the ocean, atmosphere, or taken up by biota. While the exact mechanism of contaminant sediment burial is unclear, our data demonstrates that sediment burial within Hearnes Lake estuary is offsetting a significant portion of the export of dissolved As, Cu, Co, Mo, Ni, Cr, Pb, V, Al, and Fe, potentially keeping these dissolved contaminants from entering the coastal ocean.

This study shows that while some contaminants may be being efficiently scoured by suspended particles, other contaminants, such as Hg, Cd, Mn, are being exported at greater proportions than they are being buried (Figure 6). The majority of the export of Hg, Cd, and Mn happened during rain events > 50 mm after the ICOLL opening (92, 94, and 89 % of exports occurring after ICOLL opening for Hg, Cd, Mn, respectively). Conrad et al. (2019) reported the accumulation of anthropogenic Cd within Hearnes Lake, however, since the ratio of catchment export to sediment burial was greater in favour of catchment export for these elements, we hypothesize that the Double Crossing Creek to Hearnes Lake estuary continuum is a source of dissolved Hg, Cd, and Mn to the coastal ocean, atmosphere, or biota.

4.4 Environmental implications

What are some biological implications of the relatively high contaminant concentrations we observed? Bioaccumulation of contaminants is highly variable between elements and taxa, and many pathways of harmful and detoxifying accumulation can occur (Hare 1992, Rainbow 2002, George 2018), making speculation of effects based purely upon waterborne

concentrations difficult. Invertebrate species are often suggested as a starting point for contaminant bioaccumulation studies (Patwardhan and Ghaskadbi 2013). Other literature suggests that while our concentrations of trace metals exceeded the ANZECC WQGs for both marine and FW, concentrations of Cu, Cd, Zn we observed are unlikely to be affecting reproductive success in urchin or coral species (Au et al. 2000, Fitzpatrick et al. 2008), but may be affecting sperm mobility in certain crustacean species (Zhang et al. 2010).

Due to complexation with Cl$^-$ ions, Cd toxicity to aquatic organisms is lesser in saltwater (Hudspith et al. 2017), however the effect of freshwater discharge with high concentrations of dissolved Cd into the estuary remain unknown at this time. Additionally, more information regarding the chemical speciation of Hg along the estuarine gradient is needed to determine the potential for biological uptake of methylmercury (Stumm and Morgan 2012, Gworek et al. 2016).

5. Conclusions

1. Both large (> 50 mm) and smaller rainfall events drove short term increases in concentrations and exports of trace metals in Double Crossing Creek.

2. Mercury (Hg), copper (Cu), and zinc (Zn) frequently (> 20 % of our 107 sampling events) exceeded the ANZECC freshwater or marine WQG.

3. Some contaminants, for example Hg, Zn, and manganese (Mn), exceeded WQG even during dry conditions.

4. Increased concentrations of these elements may be from anthropogenic inputs upstream of our sampling location.

5. Rain events transported relatively large proportions of our estimated Hg and cadmium (Cd) export rates to a sanctuary zone within the SIMP.

Because our observations integrate all sources within the catchment, it is not possible to assign a specific source to the high dissolved trace metal concentrations and loads observed. However, since intensive horticulture activities dominate the catchment land use, they are the most likely source.

Since a large proportion of samples exceeded ANZECC guidelines, we recommend management actions to minimize pollution and further studies into the chemical speciation of these contaminants and bioaccumulation in organisms in regional creeks and in the downstream areas including Hearnes Lake and other coastal habitats.

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Appendix

Table A1. Raw data

Sample #	Date and time	Rain (mm)	Salinity (ppt)	^{222}Rn (dpm L^{-1})	pH	DO (% sat)	Discharge (m^3 day^{-1})	Runoff (mm)	DOC (µmol L^{-1})	Al (µmol L^{-1})	As (nmol L^{-1})	Cd (nmol L^{-1})	Cr (nmol L^{-1})	Cu (nmol L^{-1})	Fe (µmol L^{-1})	Mn (µmol L^{-1})	Ni (nmol L^{-1})	Pb (nmol L^{-1})	Zn (nmol L^{-1})	Hg (nmol L^{-1})	B (µmol L^{-1})	Si (µmol L^{-1})	V (nmol L^{-1})	Co (nmol L^{-1})	Mo (nmol L^{-1})	Ba (nmol L^{-1})	Ca (mmol L^{-1})	Mg (mmol L^{-1})	K (mmol L^{-1})	Na (mmol L^{-1})	Cl (mmol L^{-1})	S (mmol L^{-1})	Br (µmol L^{-1})
1	27/01/2018 18:19	0	20.06	1.20	7.14	53.8	93.45	0.02	736.24	0.88	49.38	0.44	5.00	27.70	1.11	2.03	1.36	3.81	125.27	3.14	211.93	163.89	59.09	3.39	25.02	872.81	6.77	29.82	6.23	277.63	327.82	15.96	514.83
2	28/01/2018 9:40	0	20.08	1.32	7.1	48.3	280.35	0.06	573.41	0.87	52.86	0.36	4.81	22.50	0.99	2.13	17.38	4.49	217.04	0.70	219.54	159.59	56.73	4.41	28.04	805.96	6.93	30.17	6.43	284.77	339.64	16.15	532.67
3	29/01/2018 10:40	10	20.14	1.34	7.03	27.8	841.06	0.18	607.73	1.25	37.51	1.07	8.27	25.65	0.88	2.69	0.00	3.86	87.95	0.70	217.43	146.62	63.21	4.92	30.54	949.27	6.99	30.92	6.58	291.71	344.49	17.13	566.66
4	30/01/2018 9:55	0	20.16	1.32	7.07	28.6	654.16	0.14	565.69	1.53	39.91	0.44	2.88	20.14	0.79	2.81	0.68	4.73	60.26	2.84	224.97	149.69	56.14	6.96	32.62	838.95	7.07	31.10	6.42	286.83	341.89	17.29	558.67
5	31/01/2018 10:35	0	20.15	1.25	7.11	36.4	467.26	0.1	535.82	2.28	56.06	0.18	2.88	19.83	0.75	2.25	4.26	3.86	60.11	1.65	233.27	169.45	66.55	8.14	28.87	1029.08	7.05	32.40	6.59	294.14	350.95	16.82	560.39
6	1/02/2018 11:48	0	19.97	1.36	7.02	8.8	560.71	0.12	520.42	0.65	4.40	0.00	-1.92	17.47	2.40	2.31	2.90	3.57	128.33	1.10	226.55	158.11	75.97	3.90	24.18	1278.85	7.16	31.35	6.44	290.28	347.53	17.38	561.32
7	2/02/2018 12:01	7	20.44	0.99	7.19	40.6	934.51	0.2	512.43	1.65	30.30	0.62	6.35	20.77	0.80	0.79	5.62	15.69	100.03	1.84	238.56	152.10	38.48	3.56	26.16	860.36	7.29	32.27	6.56	298.42	363.86	17.11	577.69
8	3/02/2018 10:01	19	20.52	1.21	7.18	32.1	2009.20	0.43	494.09	2.65	31.50	0.36	6.35	21.09	0.93	0.98	4.09	4.25	268.12	1.30	246.93	144.03	59.68	5.26	22.72	1003.23	7.39	31.83	6.69	301.45	367.32	17.37	580.16
9	4/02/2018 11:55	31	0.05	1.21	7.14	80.8	3831.51	0.82	477.83	0.38	52.99	0.00	4.64	15.07	2.45	1.19	0.00	2.52	20.19	1.20	226.12	69.40	98.59	2.14	42.50	806.75	7.16	33.22	6.33	294.36	360.10	18.06	547.05
10	5/02/2018 8:24	16	20.08	1.16	7.09	37.6	3831.51	0.82	474.42	0.69	44.45	0.27	5.19	26.12	0.92	1.36	0.00	3.43	49.71	1.05	222.75	129.79	54.38	2.88	25.85	802.61	7.09	31.47	6.39	291.23	359.27	16.86	555.76
11	5/02/2018 17:29	5	19.73	1.08	7.19	66.2	3831.51	0.82	496.34	1.34	13.88	1.07	4.23	28.33	1.32	0.85	0.00	3.76	61.79	1.99	206.39	113.42	53.00	59.73	22.51	721.85	6.28	27.92	6.12	275.78	327.81	15.08	527.38
12	6/02/2018 9:40	3	19.53	1.18	7.07	43.9	2663.36	0.57	490.74	0.76	44.98	0.27	5.96	22.35	0.60	1.28	0.00	3.14	46.04	-0.30	213.06	122.29	55.36	3.05	19.80	757.53	6.38	29.23	6.12	274.15	329.18	15.56	518.67
13	6/02/2018 17:06	0	19.19	1.07	7.22	86.9	1869.03	0.4	486.60	0.88	51.92	0.36	6.92	29.43	1.54	0.92	4.77	2.94	119.91	0.45	219.98	127.10	58.11	5.77	24.70	787.68	6.67	30.69	6.29	280.08	340.96	16.51	538.74
14	7/02/2018 9:40	0	19.18	1.16	7.06	54.7	1869.03	0.4	494.01	1.14	44.31	0.09	12.50	22.50	1.03	1.07	0.00	4.30	87.64	1.79	212.59	143.63	53.59	4.75	23.35	879.43	6.77	29.96	6.11	279.68	336.65	15.82	521.69
15	7/02/2018 17:23	0	19.01	0.78	7.16	86.5	1869.03	0.4	529.43	2.38	44.18	0.00	7.12	23.45	1.10	0.76	0.00	3.57	60.11	1.25	216.41	136.48	53.59	2.88	24.29	760.81	6.78	30.13	6.33	279.00	331.73	16.40	523.62
16	8/02/2018 10:10	0	19.09	0.52	7	51.6	1308.32	0.28	509.99	2.11	48.05	0.00	1.15	23.45	0.43	0.92	0.00	3.14	92.99	4.34	217.55	131.43	53.59	3.39	18.45	894.43	6.78	29.89	6.09	277.87	333.56	16.12	518.50
17	8/02/2018 17:55	0	18.96	0.63	7.14	93.2	1308.32	0.28	517.21	1.01	40.04	0.27	3.27	21.24	0.69	0.93	0.34	3.47	107.68	0.65	216.36	131.91	45.15	27.83	14.70	805.67	6.77	30.13	6.43	287.89	344.16	16.85	528.08
18	9/02/2018 17:26	0	18.62	0.70	7.22	114.5	887.79	0.19	544.33	0.83	36.17	0.44	5.00	18.88	0.56	0.47	3.58	5.65	133.99	1.05	200.64	129.87	58.69	8.14	20.95	936.67	6.51	28.26	6.04	264.07	322.69	15.75	523.47
19	10/02/2018 12:35	0	18.68	1.01	7.07	68.5	654.16	0.14	500.94	1.59	27.76	0.62	3.65	20.30	0.44	1.31	0.00	2.61	23.25	1.69	209.55	114.05	49.86	3.39	16.16	796.49	6.71	30.29	6.10	272.58	338.40	16.11	529.27
20	11/02/2018 14:40	0	18.66	0.85	7.02	57.4	420.53	0.09	526.35	2.60	35.10	0.27	6.15	21.56	0.52	1.43	0.00	3.33	80.15	0.50	210.15	127.69	63.99	11.71	22.31	1101.09	6.51	28.88	6.01	272.78	325.44	15.18	531.69
21	12/02/2018 8:01	0	18.68	1.42	6.95	13.8	327.08	0.07	525.14	1.57	16.15	1.07	-1.35	17.78	0.73	1.83	0.00	5.79	73.72	0.85	211.91	119.47	54.18	10.18	21.16	793.00	6.63	28.88	6.18	272.10	329.39	15.58	513.65
22	13/02/2018 14:02	0	18.67	1.12	6.91	16.1	513.98	0.11	548.10	1.09	37.11	0.62	7.69	17.63	0.49	3.45	0.00	3.81	82.44	1.79	213.93	121.21	54.97	3.39	19.80	793.80	6.44	29.32	5.98	276.38	325.49	15.61	530.38
23	14/02/2018 15:36	0	17.84	0.91	7.11	40.3	747.61	0.16	564.50	1.14	52.99	0.53	42.12	26.44	0.71	2.18	49.58	3.19	188.90	0.85	198.00	112.63	56.93	9.84	18.03	868.66	6.05	26.80	5.65	252.21	298.70	14.35	485.03
24	15/02/2018 11:06	12	18.4	1.04	7.01	12.1	560.71	0.12	567.67	0.84	38.57	0.80	27.89	19.51	0.85	4.93	25.90	2.36	52.62	1.00	205.37	131.73	52.22	13.07	19.49	783.03	6.29	27.46	5.89	267.50	320.78	15.09	510.74
25	17/02/2018 11:40	0	18.15	0.92	7	7.8	513.98	0.11	568.98	1.21	56.59	0.18	8.65	19.67	1.40	7.55	4.94	3.04	85.35	0.10	211.39	131.27	49.47	7.30	19.70	874.99	6.61	29.08	6.09	270.59	326.80	15.61	517.97
26	18/02/2018 11:05	0	18.35	1.16	7.08	1.5	327.08	0.07	547.25	0.68	57.79	0.09	4.42	12.90	1.00	8.82	0.00	2.61	78.62	0.65	206.81	127.55	41.22	7.47	20.33	811.20	6.49	27.88	5.78	264.46	312.20	15.05	510.40
27	19/02/2018 13:05	0	18.37	1.21	7.06	1.9	233.63	0.05	565.63	1.15	76.75	0.00	5.96	19.20	1.29	4.59	0.00	3.57	73.88	1.20	207.05	127.67	44.36	6.45	18.97	853.73	6.52	28.91	6.04	265.11	321.64	15.33	517.82
28	20/02/2018 11:10	4	18.49	0.96	7.14	0.1	233.63	0.05	612.00	1.23	29.76	0.36	7.69	30.21	1.65	9.94	10.39	5.36	231.72	0.85	212.40	125.66	54.77	139.48	20.12	1053.18	6.57	28.84	6.07	277.07	326.05	15.44	521.70
29	21/02/2018 9:35	22	18.38	1.00	7.12	3.4	1448.50	0.31	601.76	1.58	52.86	0.18	4.04	19.67	1.11	5.70	0.00	3.62	126.49	0.45	205.85	112.54	59.09	4.58	20.64	842.66	6.47	27.76	6.05	265.50	319.23	15.24	508.86
30	22/02/2018 10:20	0	18.17	0.78	7.11	4.9	1027.97	0.22	583.55	1.02	89.83	0.71	1.54	19.20	1.16	4.97	6.47	3.57	296.73	0.80	211.99	138.20	63.99	9.16	17.41	1043.20	6.44	27.90	5.80	264.28	320.33	15.49	515.79
31	23/02/2018 12:21	8	18.19	1.10	7.12	9.2	887.79	0.19	597.51	0.54	62.20	0.44	2.88	14.32	0.94	2.48	0.00	4.49	44.81	2.39	190.42	114.71	46.52	4.92	19.39	745.67	6.00	25.88	5.84	252.71	298.87	13.49	482.28
32	24/02/2018 7:40	51	4.82	1.71	6.94	44.2	5653.81	1.21	581.84	1.73	17.48	0.18	0.00	16.68	2.57	4.17	0.00	5.65	288.31	1.40	121.84	169.18	32.98	8.31	11.47	790.16	3.79	16.19	3.47	154.96	181.71	9.46	272.21
33	24/02/2018 10:55	42	0.26	1.77	6.53	80.4	5653.81	1.21	559.24	6.36	22.90	0.24	9.31	27.62	5.42	3.33	19.56	14.80	900.29	0.24	11.15	130.23	14.84	61.27	5.93	7097.50	0.33	0.66	0.29	4.52	5.40	0.55	7.45
34	24/02/2018 14:04	8	0.6	1.98	6.42	69.7	5653.81	1.21	533.34	6.75	23.42	0.55	9.25	44.69	4.42	2.35	11.64	10.83	774.35	0.43	9.65	108.07	10.60	30.00	3.90	1257.28	0.43	1.12	0.38	8.54	10.18	0.77	14.62
35	24/02/2018 17:15	6	2.35	2.09	6.52	67	5653.81	1.21	661.29	4.31	19.09	0.18	7.89	26.59	4.57	4.50	14.14	5.26	574.49	0.85	32.82	162.16	35.92	12.39	3.86	866.04	1.27	4.29	1.04	37.00	44.38	2.56	66.10
36	24/02/2018 20:00	2	2.07	2.10	6.5	64.7	5653.81	1.21	607.28	5.67	23.89	0.62	10.19	21.56	7.13	4.90	0.68	7.29	385.13	8.87	27.78	144.74	20.61	14.25	5.32	790.08	1.11	3.56	0.93	30.93	36.81	2.01	54.99
37	24/02/2018 23:00	0	1.81	2.21	6.49	65.9	5653.81	1.21	560.53	3.74	6.54	0.44	6.15	23.45	5.99	4.49	4.26	3.43	416.34	13.91	25.33	174.95	18.45	11.20	6.05	634.25	0.92	2.97	0.80	24.65	30.79	1.77	44.30
38	25/02/2018 4:58	2	1.52	2.18	6.5	69.1	3177.35	0.68	517.48	2.52	41.78	0.00	2.69	15.74	6.07	3.38	0.00	4.49	236.77	4.84	19.71	184.15	23.95	10.01	4.07	704.38	0.76	2.39	0.68	19.52	24.31	1.51	35.33
39	25/02/2018 8:05	0	1.9	2.06	6.52	68.3	3177.35	0.68	416.04	4.16	24.03	0.71	13.65	33.36	6.15	3.21	2.90	6.76	1160.97	7.13	30.66	206.48	12.76	29.36	2.92	2639.18	0.38	3.04	0.80	24.99	29.63	1.93	42.95
40	25/02/2018 11:03	0	2.19	1.91	6.54	70	3177.35	0.68	405.96	5.10	0.13	0.53	5.96	23.76	5.77	3.05	2.73	4.01	237.08	2.24	32.07	209.55	19.43	8.65	4.48	584.59	1.00	3.43	0.90	30.07	34.78	2.01	50.91
41	25/02/2018 13:57	0	1.59	1.90	6.52	75.1	3177.35	0.68	410.23	1.82	7.34	0.00	2.88	15.26	4.45	2.56	0.00	2.56	110.13	1.99	24.04	194.05	19.24	5.94	3.65	515.85	0.79	2.62	0.72	22.37	27.87	1.74	41.88
42	25/02/2018 16:57	0	1.37	1.92	6.52	74.3	3177.35	0.68	352.01	1.49	7.87	0.00	5.00	30.69	4.80	2.23	13.29	4.63	362.65	1.55	18.80	194.79	13.35	22.40	1.98	1046.70	0.69	2.16	0.63	17.42	23.42	1.39	32.50
43	25/02/2018 20:00	0	1.45	1.90	6.51	67.6	3177.35	0.68	347.54	3.04	0.00	0.36	5.00	22.82	5.12	2.53	1.02	4.49	568.37	23.08	25.51	239.05	15.70	14.42	1.88	917.81	0.79	2.66	0.70	22.04	25.83	1.63	37.92
44	25/02/2018 22:55	0	2.2	1.92	6.54	62.4	3177.35	0.68	344.91	1.29	13.75	0.00	8.85	15.89	3.97	2.42	0.00	3.43	144.85	7.38	24.44	223.26	6.67	7.98	4.69	703.58	0.86	2.94	0.78	23.93	28.79	1.97	42.81
45	26/02/2018 5:01	0	3.24	1.89	6.57	51.6	2943.72	0.63	314.07	0.92	9.88	0.44	23.85	34.94	3.19	3.11	11.76	2.08	129.09	3.79	36.83	205.81	21.00	49.72	3.86	643.65	1.25	5.02	1.12	41.83	47.88	2.68	71.79
46	26/02/2018 8:04	0	4.18	1.94	6.61	45.9	2943.72	0.63	347.87	1.08	10.14	0.18	0.00	12.75	3.01	3.72	0.00	2.94	68.83	3.94	47.32	209.70	25.32	8.65	2.08	611.90	1.60	6.46	1.39	54.79	64.72	3.71	97.80
47	26/02/2018 10:55	0	4.28	1.94	6.62	45.7	2943.72	0.63	351.22	5.71	8.01	0.53	7.69	27.38	3.81	3.89	25.05	3.91	378.86	3.59	52.33	209.75	27.09	9.50	3.44	616.63	1.71	6.81	1.53	60.19	73.19	3.87	105.11
48	26/02/2018 13:55	6	3.04	2.05	6.62	56	2943.72	0.63	363.19	1.57	0.00	0.27	3.08	15.42	3.19	2.93	0.00	3.04	130.47	3.09	40.48	184.11	25.91	28.00	4.27	546.87	1.26	5.02	1.15	44.79	54.01	3.68	78.55
49	26/02/2018 17:00	26	0.6	2.01	6.4	75.6	2943.72	0.63	345.10	2.87	4.54	0.09	0.77	19.51	7.62	3.46	0.00	3.23	350.11	1.79	25.27	152.17	18.65	9.33	4.38	859.55	0.85	2.96	0.75	25.45	30.31	1.86	42.34
50	26/02/2018 20:00	2	4.16	2.09	6.58	44	2943.72	0.63	432.54	3.97	7.21	0.00	3.08	28.64	4.46	1.89	0.00	4.01	1542.06	16.75	8.78	139.55	8.64	8.82	0.73	534.49	0.29	0.59	0.31	3.63	5.43	0.74	7.73
51	26/02/2018 22:55	0	5.91	2.00	6.68	30.7	4438.94	0.95	510.12	4.14	5.34	0.53	1.54	37.61	3.85	1.54	0.00	3.28	485.93	2.84	9.15	159.77	9.82	18.50	0.31	753.31	0.31	0.51	0.30	3.29	5.77	0.66	7.59
52	27/02/2018 5:01	0	7.55	1.98	6.79	21.3	4438.94	0.95	521.83	4.06	3.07	2.40	4.62	29.43	4.18	1.69	0.17	3.47	403.79	1.65	13.68	212.34	18.26	10.01	1.67	1026.24	0.46	1.16	0.40	9.11	11.91	1.07	15.85
53	27/02/2018 8:00	0	7.52	1.92	6.77	17.9	4438.94	0.95	466.84	2.70	20.02	0.71	1.54	21.40	4.81	3.67	4.94	4.25	763.08	2.39	52.92	189.54	22.77	13.74	5.84	1961.81	1.66	6.55	1.47	57.58	67.24	3.65	99.51
54	27/02/2018 11:00	0	7.44	1.94	6.76	13.7	4438.94	0.95	502.85	2.49	29.76	0.36	5.77	20.14	5.99	4.67	0.00	2.65	198.53	1.30	73.35	157.30	31.02	11.20	8.65	827.15	2.31	9.83	2.14	89.90	103.56	5.47	153.33

Table A1. (cont.) - Raw data

Sample #	Date and time	Rain (mm)	Salinity (ppt)	^{222}Rn (dpm L^{-1})	pH	DO (% sat)	Discharge (m^3 day^{-1})	Runoff (mm)	DOC (µmol L^{-1})	Al (µmol L^{-1})	As (nmol L^{-1})	Cd (nmol L^{-1})	Cr (nmol L^{-1})	Cu (nmol L^{-1})	Fe (µmol L^{-1})	Mn (µmol L^{-1})	Ni (nmol L^{-1})	Pb (nmol L^{-1})	Zn (nmol L^{-1})	Hg (nmol L^{-1})	B (µmol L^{-1})	Si (µmol L^{-1})	V (nmol L^{-1})	Co (nmol L^{-1})	Mo (nmol L^{-1})	Ba (nmol L^{-1})	Ca (mmol L^{-1})	Mg (mmol L^{-1})	K (mmol L^{-1})	Na (mmol L^{-1})	Cl (mmol L^{-1})	S (mmol L^{-1})	Br (µmol L^{-1})
55	27/02/2018 14:06	0	7.46	1.92	6.76	12.2	4438.94	0.95	552.68	1.88	27.63	21.35	11.35	21.40	3.86	4.87	3.75	4.39	261.24	2.39	87.16	160.64	26.50	16.46	8.34	824.46	2.71	12.19	2.57	108.23	128.86	6.39	191.56
56	27/02/2018 16:57	0	7.53	1.86	6.76	11.8	4438.94	0.95	575.83	1.27	21.09	0.27	9.62	14.95	3.30	3.82	0.00	3.67	259.87	1.50	79.75	157.04	37.49	10.52	8.76	614.23	2.46	10.60	2.25	96.46	110.41	6.23	175.59
57	27/02/2018 19:57	0	7.44	1.87	6.77	10.5	4438.94	0.95	562.75	2.61	12.28	0.36	8.08	15.74	3.12	3.32	0.00	2.56	54.30	0.75	73.95	129.32	36.51	5.43	7.61	464.95	2.10	8.92	1.99	83.62	97.29	4.70	151.20
58	27/02/2018 10:55	0	7.21	1.84	6.76	11.2	4438.94	0.95	565.77	1.26	28.30	0.36	0.96	10.07	3.67	4.43	2.56	3.09	237.08	1.50	88.45	179.91	46.52	12.22	6.67	646.70	2.89	11.96	2.61	112.04	132.82	6.51	197.13
59	28/02/2018 5:08	0	7.01	1.87	6.97	2.01	2383.01	0.51	576.97	1.38	48.45	0.00	4.81	10.07	4.28	4.32	0.51	3.38	145.30	2.24	91.98	162.91	40.44	7.30	12.51	840.11	2.84	12.09	2.61	111.69	132.34	6.41	200.88
60	28/02/2018 7:56	0	6.8	1.82	6.97	2.3	2383.01	0.51	587.96	1.92	49.38	0.27	2.50	14.32	3.60	4.25	0.00	3.47	442.64	2.04	93.64	168.93	36.51	23.08	9.38	852.35	2.81	12.01	2.55	113.05	128.73	6.64	197.01
61	28/02/2018 10:57	0	6.55	1.82	7.03	2.27	2383.01	0.51	575.51	2.93	42.71	0.00	1.73	13.85	3.68	3.63	0.00	4.34	425.36	1.65	82.09	175.22	23.56	14.93	11.36	787.46	2.44	10.22	2.38	99.51	117.57	5.54	180.37
62	28/02/2018 16:54	0	6.2	1.86	6.91	2.36	2383.01	0.51	499.50	1.51	36.71	0.27	4.23	11.49	4.45	3.49	4.94	2.94	165.80	1.60	71.00	173.34	25.91	4.92	11.78	769.19	2.26	9.34	2.05	85.89	100.62	5.19	149.90
63	28/02/2018 10:55	0	6.1	1.93	6.85	3.06	2383.01	0.51	457.66	1.40	16.28	0.09	0.19	15.58	4.88	3.11	0.00	3.81	688.44	4.34	53.62	170.87	25.52	11.03	7.30	1162.99	1.74	7.22	1.56	63.73	73.65	3.99	109.99
64	1/03/2018 4:58	0	5.9	1.95	6.95	4.1	1635.40	0.35	468.36	1.03	21.76	0.00	8.27	11.17	3.11	3.37	0.00	2.75	233.86	1.50	67.62	172.27	25.72	8.99	7.30	676.20	2.14	8.99	1.95	80.87	93.79	5.02	139.03
65	1/03/2018 11:02	0	5.72	1.98	6.7	25.8	1635.40	0.35	514.53	1.05	0.13	0.36	2.69	8.81	2.90	1.99	0.00	4.10	130.47	2.24	42.31	109.23	15.90	2.38	6.46	391.91	1.29	5.62	1.24	50.16	57.92	3.18	84.68
66	1/03/2018 20:00	0	2.73	1.84	6.68	64.2	1635.40	0.35	361.56	1.18	12.41	0.44	0.00	15.74	2.82	1.69	5.07		451.82	1.69	35.16	189.65	19.43	9.50	12.92	882.86	1.30	4.60	1.09	41.62	47.54	2.88	65.63
67	2/03/2018 8:07	0	3.88	1.79	6.76	55.4	1121.42	0.24	415.81	0.88	7.21	0.27	0.19	25.49	2.83	1.47	0.00	4.83	104.47	1.69	49.14	209.80	15.12	5.77	8.96	600.17	1.57	6.11	1.42	54.46	65.47	3.55	91.59
68	2/03/2018 19:57	0	4.37	1.82	6.77	64.6	1121.42	0.24	419.24	1.28	11.61	0.18	3.65	42.17	2.08	1.30	0.00	6.95	229.12	2.39	53.82	203.88	27.29	6.96	12.61	732.99	1.80	7.04	1.58	62.77	75.17	4.16	105.93
69	3/03/2018 10:00	0	4	1.72	6.75	36.5	794.34	0.17	411.96	1.05	21.22	0.36	2.50	12.27	1.84	1.08	0.00	3.52	146.68	1.50	51.83	182.59	23.75	5.09	8.44	676.12	1.59	6.52	1.47	58.12	68.03	3.82	101.20
70	4/03/2018 10:40	0	3	1.71	6.77	55	560.71	0.12	383.67	2.36	24.96	0.44	3.46	11.17	1.60	1.11	0.51	2.94	216.89	1.15	50.79	178.01	24.73	6.45	15.11	736.64	1.55	5.78	1.37	52.90	60.98	3.39	89.68
71	5/03/2018 9:50	0	3.57	1.74	6.89	61.2	373.81	0.08	425.24	1.24	26.29	0.18	9.81	14.32	1.25	0.75	0.00	3.57	105.38	1.30	51.51	197.44	22.38	3.73	9.28	511.41	1.59	5.95	1.49	57.31	68.73	3.66	100.17
72	6/03/2018 9:33	28	0.75	1.81	6.67	78.7	1775.58	0.38	303.31	1.33	7.61	10.23	0.96	18.10	2.62	1.02	0.00	2.80	216.58	0.45	16.17	199.21	7.85	4.75	11.36	502.01	0.68	1.60	0.50	12.40	16.67	1.33	21.85
73	6/03/2018 13:20	53	0.21	1.85	6.54	87.1	1775.58	0.38	672.65	6.96	17.06	10.96	2.50	31.69	6.89	1.85	7.84	3.55	245.01	0.18	4.60	110.88	10.42	9.20	7.29	535.34	0.26	0.36	0.21	2.23	2.35	0.43	3.22
74	6/03/2018 17:05	2	0.15	2.27	6.34	90.6	1775.58	0.38	694.99	8.72	20.86	0.14	3.71	28.94	4.33	1.63	9.49	5.30	1012.82	0.24	5.01	111.39	10.31	9.93	3.84	2374.38	0.20	0.31	0.23	1.86	2.18	0.35	2.76
75	7/03/2018 6:50	20	0.17	2.37	6.39	92.1	14905.49	3.19	444.53	5.26	16.60	0.17	3.71	22.71	2.94	0.71	12.01	1.99	268.34	0.12	4.64	157.01	7.30	7.55	3.55	744.57	0.23	0.36	0.23	2.10	2.27	0.38	3.05
76	7/03/2018 11:30	0	0.18	2.19	6.45	96.3	14905.49	3.19	373.74	5.72	20.58	0.14	5.14	127.31	3.42	0.71	5.32	16.08	519.10	0.23	4.71	175.08	10.05	12.10	3.67	631.98	0.24	0.38	0.23	2.32	2.54	0.42	3.29
77	7/03/2018 17:00	0	0.19	2.13	6.47	93.2	14905.49	3.19	336.44	2.95	17.71	0.17	4.00	16.38	2.83	0.64	6.01	1.55	180.59	0.08	4.69	142.24	8.05	6.50	2.93	622.66	0.21	0.41	0.24	2.45	2.58	0.41	3.51
78	8/03/2018 7:15	0	0.22	1.97	6.5	86.7	10279.65	2.2	286.07	2.19	11.24	0.11	2.46	16.41	2.91	0.58	4.19	1.91	248.65	0.14	4.77	178.83	5.73	5.57	3.35	642.01	0.28	0.44	0.24	2.68	2.91	0.44	4.03
79	8/03/2018 18:27	0	0.23	1.93	6.56	90.8	10279.65	2.2	266.28	1.59	9.65	0.12	2.63	13.23	2.89	0.63	3.20	0.94	217.05	0.16	5.01	188.37	6.01	5.90	3.64	754.13	0.28	0.47	0.24	2.86	3.01	0.49	4.30
80	9/03/2018 8:22	0	0.23	1.91	6.57	86.8	7803.19	1.67	274.91	1.04	7.43	0.12	1.85	12.42	2.44	0.48	4.74	0.96	158.88	0.19	5.02	202.47	5.57	6.50	6.50	511.00	0.30	0.49	0.24	2.86	2.92	0.50	4.30
81	9/03/2018 16:45	4	0.24	1.89	6.63	92.1	7803.19	1.67	0.00	1.05	11.44	0.05	2.85	12.23	2.91	0.53	3.70	0.98	99.11	0.11	5.07	175.05	7.44	9.50	8.24	521.11	0.35	0.52	0.25	3.04	3.21	0.58	4.31
82	10/03/2018 13:20	6	0.24	1.80	6.7	107.1	5980.89	1.28	238.26	0.62	6.38	0.05	2.19	9.39	2.23	0.38	2.83	0.93	191.11	0.31	4.73	164.09	4.73	7.36	8.94	630.98	0.33	0.50	0.23	2.83	2.97	0.52	4.37
83	11/03/2018 18:09	10	0.25	1.90	6.65	89	4252.04	0.91	208.31	0.63	6.87	0.11	3.33	10.83	2.76	0.36	3.39	1.79	139.97	0.10	4.93	188.34	6.01	6.04	6.21	493.12	0.34	0.54	0.24	3.13	3.32	0.57	4.68
84	12/03/2018 10:01	0	0.25	1.81	6.69	101	2943.72	0.63	233.70	0.65	6.07	0.13	2.25	34.95	3.25	0.38	2.90	1.22	72.30	0.10	4.81	214.21	5.95	5.43	6.85	478.70	0.34	0.54	0.25	3.10	3.30	0.53	4.73
85	13/03/2018 11:45	0	0.26	1.75	6.64	91.4	2055.93	0.44	223.92	0.51	7.46	0.22	3.12	9.87	2.66	0.67	3.31	2.69	83.44	0.28	4.91	203.79	5.67	5.75	4.59	525.05	0.33	0.55	0.25	3.24	3.33	0.55	4.74
86	14/03/2018 11:02	0	0.26	1.76	6.62	84.8	1401.77	0.3	227.90	0.36	5.57	0.09	1.06	8.01	2.27	0.63	1.94	0.99	84.22	0.27	4.97	209.80	5.48	5.18	4.81	490.73	0.34	0.57	0.25	3.39	3.50	0.55	4.94
87	15/03/2018 9:22	0	0.27	1.86	6.64	78.9	981.24	0.21	221.23	0.32	6.91	0.29	2.38	9.21	2.11	0.57	4.58	1.15	210.42	0.05	5.13	205.44	3.24	5.70	4.33	735.94	0.33	0.58	0.26	3.38	3.65	0.52	5.00
88	16/03/2018 10:20	0	0.27	1.85	6.64	78.1	700.89	0.15	198.96	0.29	6.66	0.04	1.40	8.62	2.22	0.57	3.51	0.75	53.33	0.07	5.10	204.94	3.85	4.63	3.94	476.06	0.33	0.59	0.26	3.45	3.75	0.57	5.19
89	17/03/2018 14:40	0	0.28	1.56	6.81	107.2	467.26	0.1	242.74	0.65	8.61	0.08	1.77	7.84	2.34	0.46	3.87	1.63	199.07	0.14	5.16	203.05	5.69	5.67	3.80	611.61	0.30	0.61	0.26	3.62	3.88	0.57	5.13
90	18/03/2018 14:30	0	0.3	1.56	6.85	112.3	327.08	0.07	230.68	0.27	8.94	0.21	1.40	7.93	2.34	0.46	2.57	0.74	249.37	0.10	5.72	200.65	5.14	5.26	4.39	872.09	0.34	0.61	0.27	3.79	4.05	0.56	5.46
91	19/03/2018 12:10	0	0.31	1.72	6.67	76.1	233.63	0.05	230.54	0.62	7.89	0.09	0.90	7.73	2.69	0.83	2.78	0.99	121.87	0.39	5.44	204.34	4.40	4.89	4.48	556.76	0.36	0.62	0.28	3.84	4.13	0.58	5.45
92	20/03/2018 13:10	0	0.34	1.66	6.76	84.7	140.18	0.03	230.77	0.28	9.93	0.43	1.29	8.36	2.70	0.87	2.90	0.97	322.41	0.51	6.11	200.08	6.38	16.36	4.92	388.04	0.37	0.67	0.29	4.34	4.61	0.59	6.34
93	21/03/2018 11:40	4	0.33	1.75	6.68	63.9	186.90	0.05	246.94	0.25	8.53	0.11	2.00	8.23	2.61	0.80	2.56	0.76	92.15	0.37	5.65	186.10	5.42	5.23	5.01	524.46	0.38	0.64	0.28	4.20	4.43	0.59	5.82
94	22/03/2018 11:31	8	0.32	1.78	6.7	64.4	1962.48	0.42	258.26	0.23	7.14	0.09	0.90	7.87	2.96	0.67	4.38	0.69	79.09	0.08	5.35	189.83	5.46	6.87	5.41	476.62	0.37	0.64	0.28	4.05	4.11	0.60	5.76
95	23/03/2018 10:11	16	0.31	1.81	6.71	67.8	4111.86	0.88	266.84	0.44	8.76	0.06	2.21	8.99	3.35	0.58	3.44	1.51	166.24	0.10	5.47	178.74	4.22	5.06	4.61	671.52	0.37	0.60	0.27	3.82	3.92	0.58	5.51
96	24/03/2018 11:07	149	0.12	2.33	6.36	96.7	17381.95	3.72	384.27	5.51	23.04	0.10	4.29	20.49	2.33	0.50	4.43	2.27	596.25	0.22	4.10	89.92	10.89	6.14	2.11	658.77	0.16	0.25	0.20	1.49	1.65	0.25	2.25
97	24/03/2018 16:02	12	0.12	2.27	6.3	93.1	17381.95	3.72	289.53	7.22	24.36	0.15	3.42	22.94	2.98	0.49	6.01	2.50	426.14	0.13	3.93	134.46	9.15	8.93	2.57	658.85	0.17	0.26	0.19	1.57	1.72	0.27	2.24
98	25/03/2018 13:40	0	0.17	1.84	6.51	100	10560.00	2.26	287.67	3.30	16.31	0.16	22.52	17.12	3.22	0.64	11.16	3.57	1027.07	0.32	4.70	150.70	9.30	8.38	3.05	1266.77	0.23	0.37	0.21	2.18	2.28	0.36	3.41
99	26/03/2018 15:40	0	0.2	1.88	6.6	96.5	6588.32	1.41	505.18	1.30	7.29	0.09	1.98	30.15	2.38	0.33	3.59	2.32	866.40	0.23	4.83	194.77	5.34	5.46	7.29	1089.66	0.26	0.42	0.21	2.40	2.54	0.43	3.67
100	27/03/2018 10:13	0	0.21	1.83	6.63	92.7	4158.59	0.89	558.07	0.94	12.04	0.05	1.23	19.70	2.24	0.23	2.85	1.35	95.82	0.17	4.37	121.14	5.71	5.06	11.59	464.19	0.30	0.45	0.22	2.52	2.62	0.46	3.72
101	28/03/2018 13:45	0	0.23	1.95	6.73	104.5	1962.48	0.42	357.76	0.75	11.56	0.07	1.73	17.42	2.94	0.31	3.05	1.26	98.62	0.15	4.38	206.00	6.24	4.95	14.21	464.55	0.33	0.49	0.23	2.82	3.04	0.53	4.16
102	29/03/2018 10:20	0	0.23	2.02	6.69	93.8	1355.04	0.29	287.01	0.62	10.85	0.12	2.15	12.72	2.72	0.23	2.91	1.06	461.93	0.04	4.59	167.10	5.69	4.65	13.54	794.47	0.33	0.47	0.22	2.74	2.92	0.51	4.16
103	30/03/2018 11:14	0	0.23	1.94	6.86	121.6	934.51	0.2	272.85	0.43	9.57	0.08	1.04	11.58	2.41	0.18	2.90	0.74	91.42	0.10	4.29	201.43	8.03	4.89	13.65	461.72	0.34	0.48	0.22	2.73	2.75	0.53	4.16
104	31/03/2018 11:32	0	0.24	1.92	6.8	103.1	654.16	0.14	258.62	0.39	14.31	0.18	2.77	10.73	2.32	0.25	2.59	20.86	373.72	0.03	4.62	189.34	6.48	4.26	6.52	611.60	0.36	0.52	0.23	2.97	3.07	0.56	4.28
105	1/04/2018 12:01	0	0.24	1.89	6.44	109.1	467.26	0.1	258.62	0.44	13.35	0.06	2.27	10.43	2.48	0.23	2.47	0.90	81.31	0.05	4.53	198.15	5.67	4.80	17.11	478.76	0.38	0.54	0.23	3.06	3.21	0.60	4.30
106	2/04/2018 10:16	0	0.26	1.96	6.73	5.49	327.08	0.07	258.22	0.42	9.29	0.13	1.90	8.50	2.42	0.19	2.93	1.01	814.82	0.29	5.19	201.93	5.32	5.19	16.56	1227.99	0.38	0.55	0.24	3.19	3.47	0.60	4.53
107	3/04/2018 11:01	0	0.27	2.02	6.8	6.69	233.63	0.05	254.25	0.01		0.04	7.50	8.78	0.20	0.01	13.15	0.95	105.49	105.49	189.58	0.01	4.33	4.33	480.36	742.54	0.00	0.57	0.24	3.37	3.45	0.58	5.01

Table A2. Variance of 2 extracted components of PCA.

Total Variance Explained

Extraction Sums of Squared Loadings		
Total	% of Variance	Cumulative %
16.223	45.064	45.064
3.440	9.556	54.620

Table A3. Component correlation matrix from 2 extracted components of PCA.

Component	1	2
1	.978	.210
2	.210	-.978

Extraction Method: Principal
Component Analysis.
Rotation Method: Varimax with
Kaiser Normalization.

Table A4. Rotated component matrix correlations from PCA.

Rotated Component Matrix[a]

	Component	
	1	2
S	.986	.098
Mg	.985	.114
Cl	.985	.118
Na	.983	.135
K	.981	.148
Ca	.981	.139
Br	.980	.158
B	.977	.146
Conductiv	.970	.193
NOx	-.935	-.274
NH4	-.849	-.173
V	.827	-.086
pH	.790	.010
Rn222	-.789	-.215
Salinity	.767	.437
Si	-.751	.083
Fe	-.748	-.269
Mo	.714	-.161
Zn	-.691	.047
P	.390	.280
As	.352	.331
Al	-.280	.000
Cu	.264	.056
Hg	-.173	-.105
Pb	-.040	.014
Runoff	-.107	-.875
Flow	-.107	-.875
Rainfall	.105	-.601
Mn	-.124	.512
DOSat	.210	-.494
Ni	.016	.444
DOC	.337	.431
Ba	.229	.399
Cr	.166	.352
Co	.018	.233
Cd	.185	.214

Extraction Method: Principal Component Analysis.