Supplement of Biogeosciences, 18, 3029–3052, 2021
https://doi.org/10.5194/bg-18-3029-2021-supplement

Biogeosciences
Open Access

Supplement of

Rain-fed streams dilute inorganic nutrients but subsidise organic-matter-associated nutrients in coastal waters of the northeast Pacific Ocean

Kyra A. St. Pierre et al.

Correspondence to: Kyra A. St. Pierre (k.stpierre@oceans.ubc.ca)

Extended methods

2.2.3 Targeted stream samplings during rainfall events (ctd.)

Sample times were determined by comparing the height of each bottle above low water level to the water levels recorded with an Odyssey water stage logger installed alongside each rack. The pump sampler (Hach Sigma 900 MAX sampler) was pre-programmed to sample based on stream stage over the rising limb and by time over the falling limb, and was remotely triggered during unexpected rainfall events. Water samples collected using the single-stage or pump samplers were typically retrieved from the installations within 12 to 24 hours (20% of samples were retrieved within 36 hours and 5% of samples were retrieved up to 3 days after collection) and transported to the field station in a cool bag where they were processed as above for TDN, TDP, dFe, and DOC, and starting in 2018, NH_4^+, NO_3^-, TP, and TN. To test the reliability of the single-stage sampler method, chemistry results of bottles installed at the same height in all watersheds in 2015, as well as single-stage samples collected concurrently with pump samples at watershed 708, were compared (Table S4). Differences between single-stage sampler bottles were 13.5±4.8%, 37.6±14.8%, 9.9±4.8%, and 3.5±1.1% for dFe, TDP, TDN, and DOC respectively. For the same parameters, differences between the single-stage and pump samplers were 37.9±33.0%, 168.5±39.9%, 13.3±10.1%, and 3.6±2.9%, respectively. While differences in TDP concentrations were large, we note that TDP concentrations were often at or below detection (0.058 µmol L^{-1}), such that small absolute differences (e.g., 0.100 vs. 0.200 µmol L^{-1}) produce large relative ones (100%).

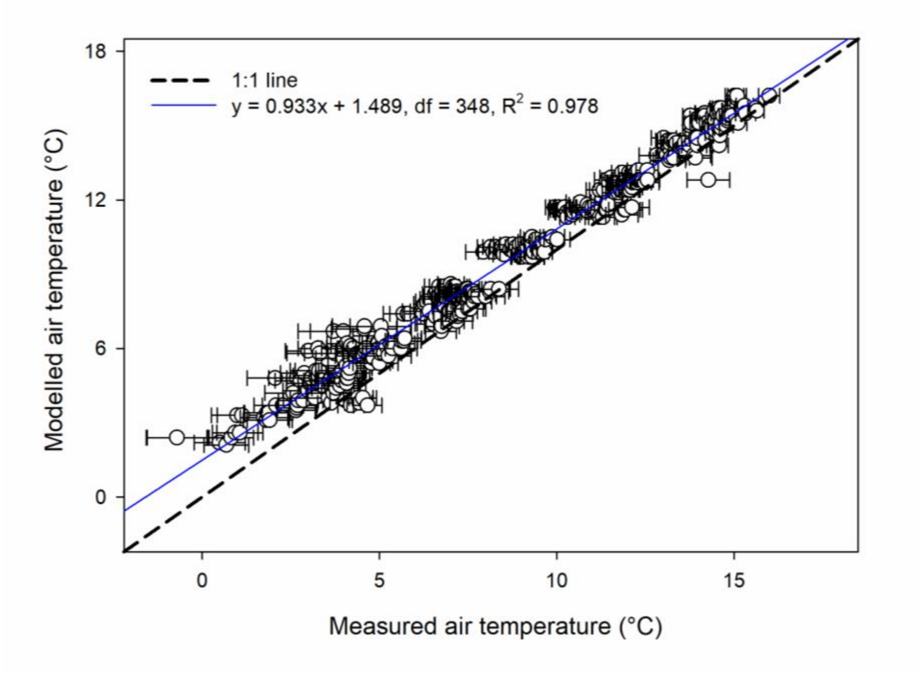

Fig. S1. Station-specific mean monthly measured (± SE) and modeled air temperature on Calvert and Hecate Island between January 2015 and December 2018. Modeled mean monthly air temperatures extracted from the Climate NA spatially downscaled models (climatena.com, Wang et al. 2016) at coordinates corresponding to Hakai weather stations SSN626PWR, SSN1015US, SSN708, SSN819PWR, SSN693PWR, WSN703, and WSN844 (see Table S3).

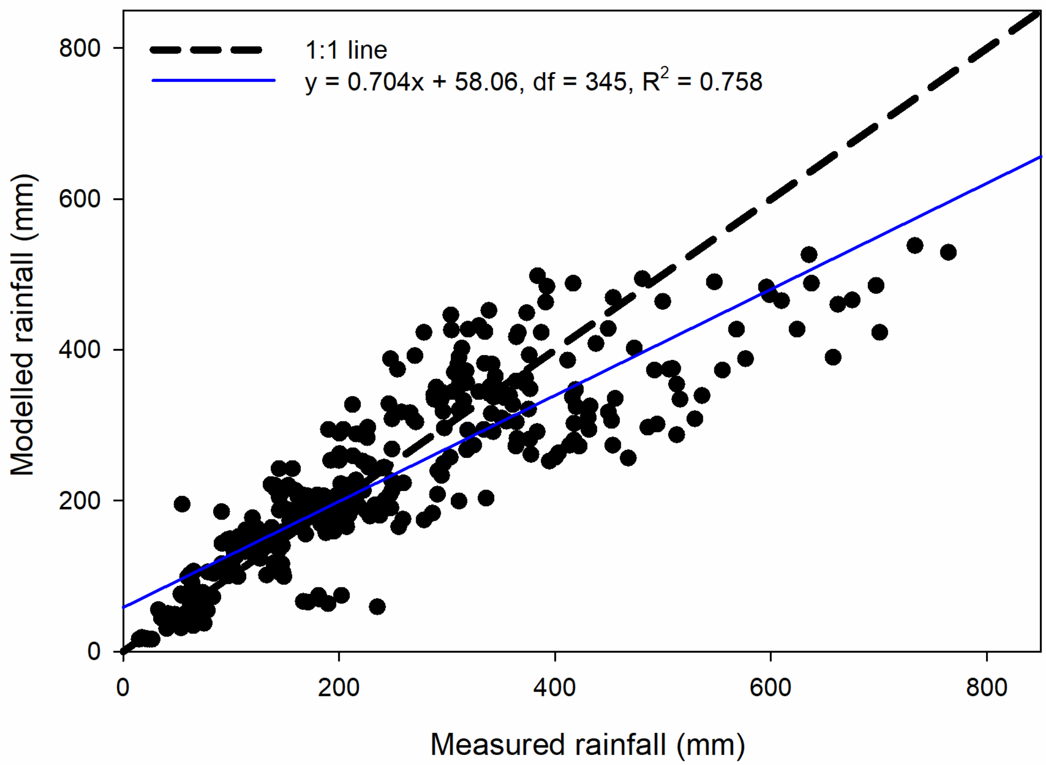

Fig. S2. Station-specific total monthly measured and modeled rainfall on Calvert and Hecate Island between January 2015 and December 2018. Modeled total monthly rainfall extracted from Climate NA (climatena.com, Wang et al. 2016) at coordinates corresponding to Hakai weather stations SSN626PWR, SSN1015US, SSN708, SSN819PWR, SSN693PWR, WSN703, and WSN844 (see Table S3).

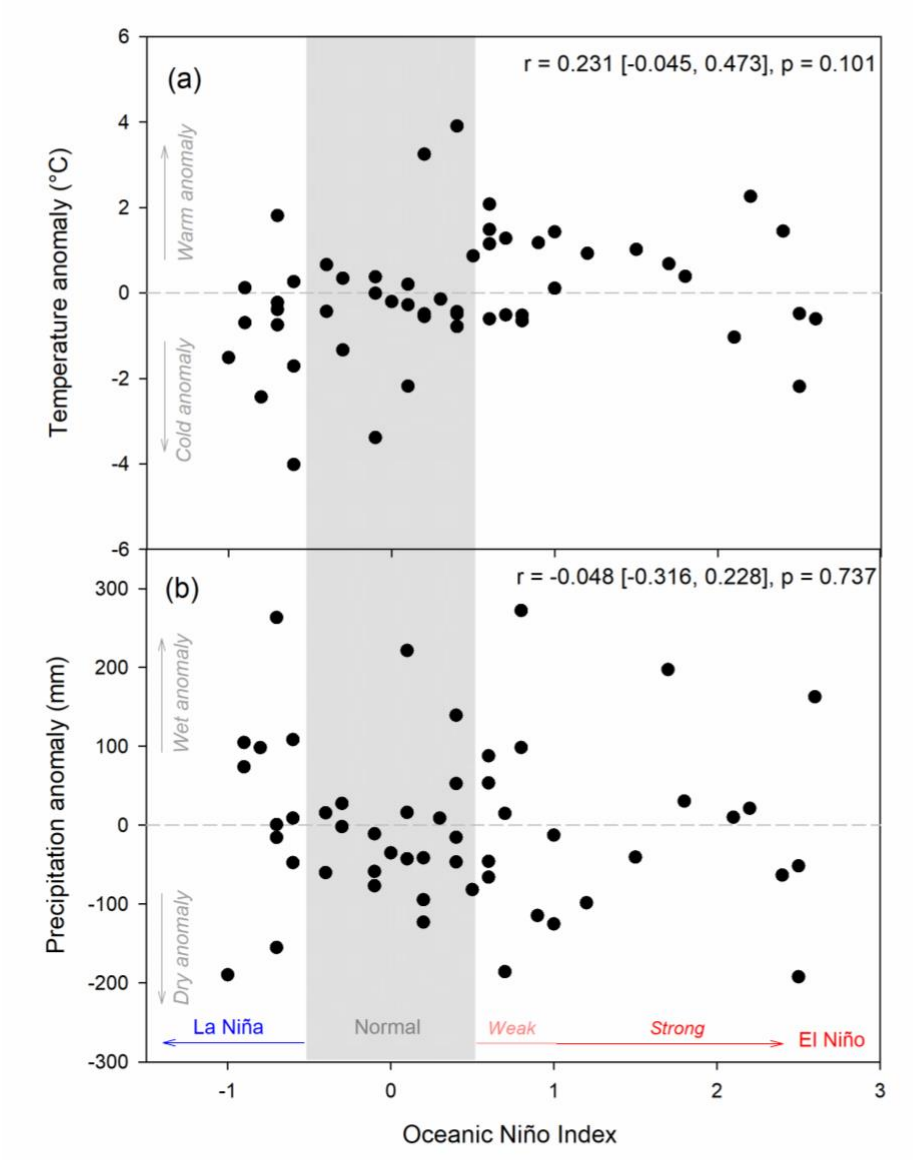

Fig. S3. Monthly mean (n = 7 stations) temperature (a) and precipitation (b) anomalies, relative to the model 1981-2010 normal (ClimateNA; Wang et al., 2016), in relation to the Oceanic Niño Index. Statistics are shown for a Pearson product moment correlation.

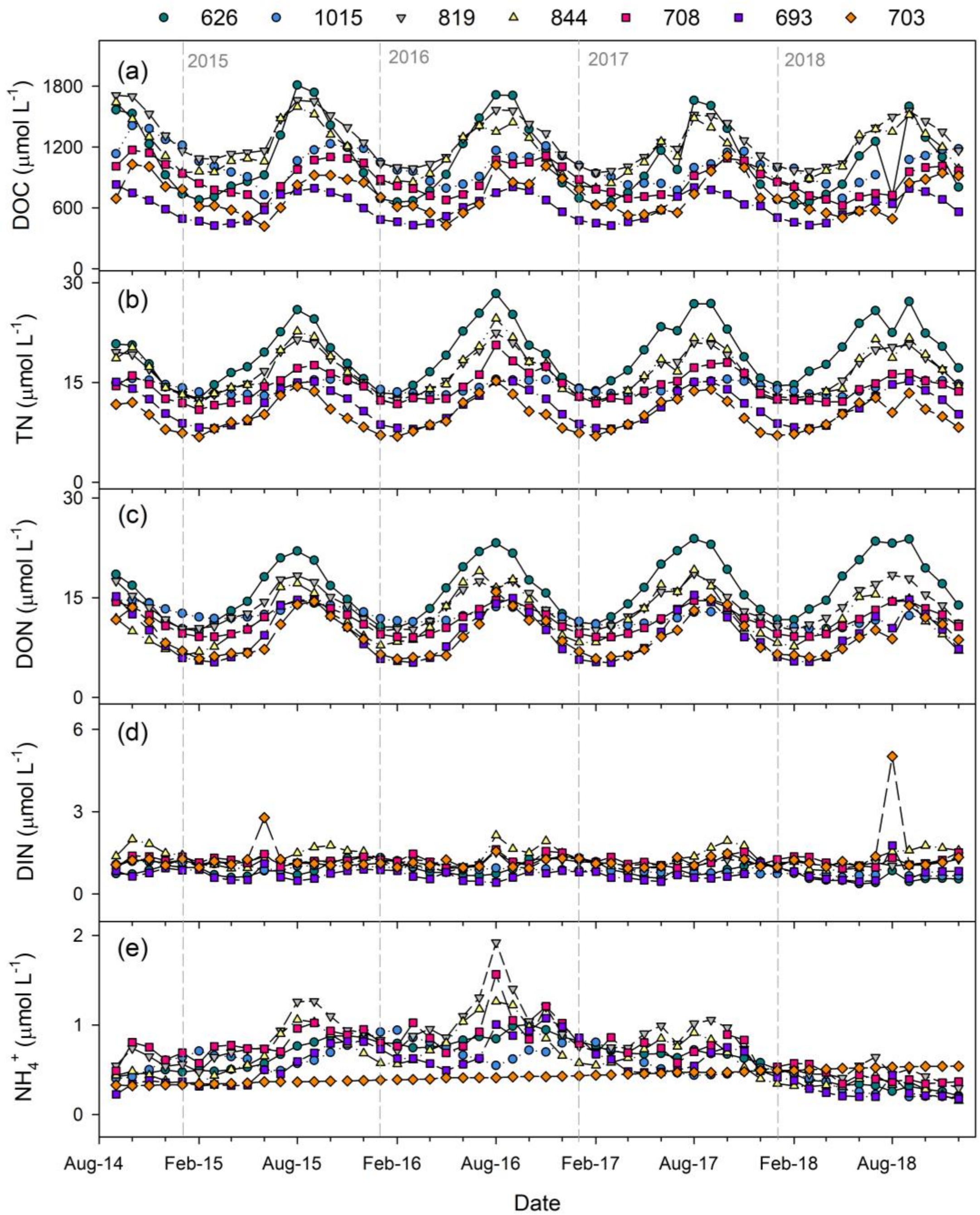

Fig. S4. Monthly flow-weighted nutrient concentrations by watershed over time. Note that the y-axes scales vary between the different constituents.

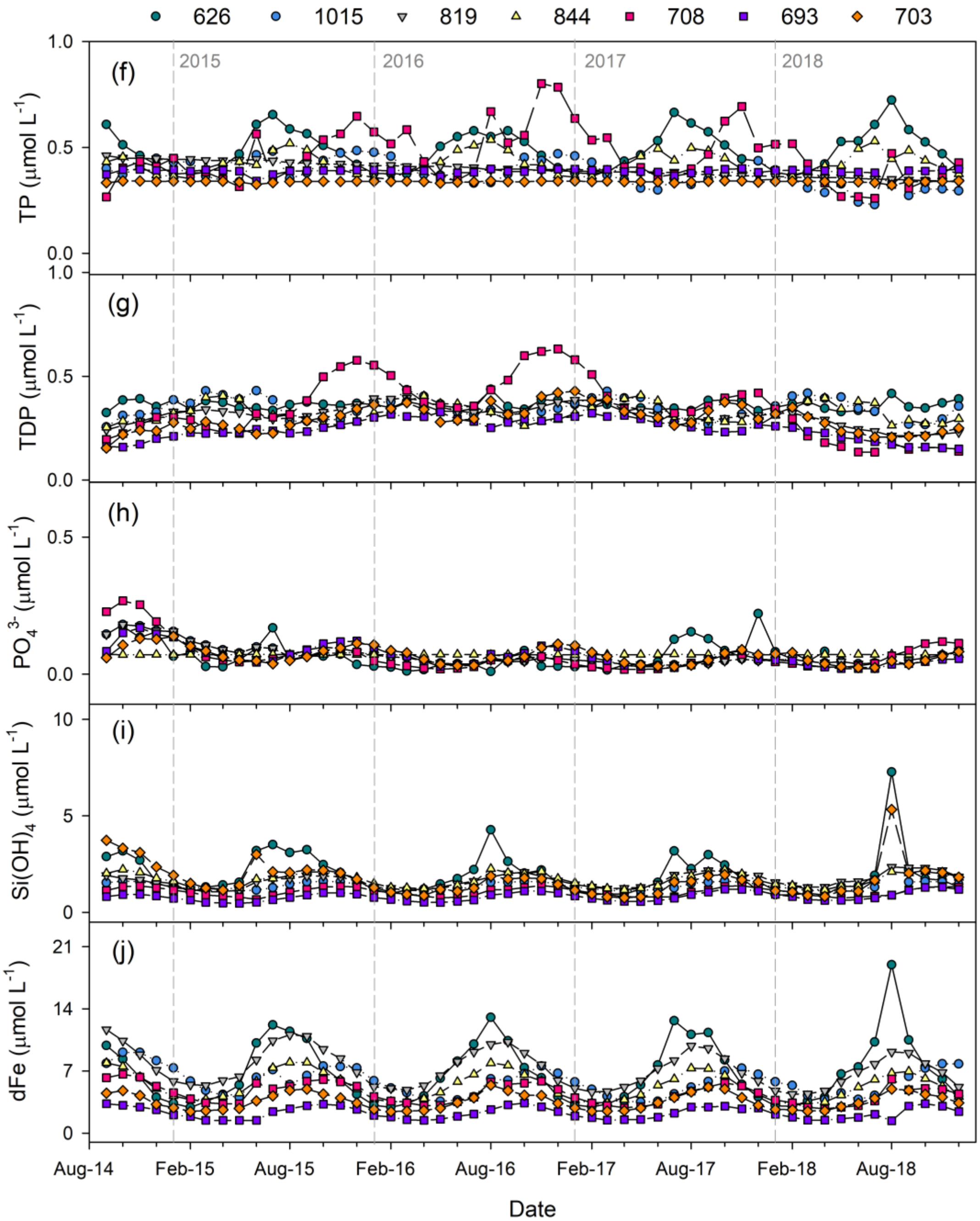

Fig. S4 (ctd). Monthly flow-weighted nutrient concentrations by watershed over time. Note that the y-axes scales vary between the different constituents.

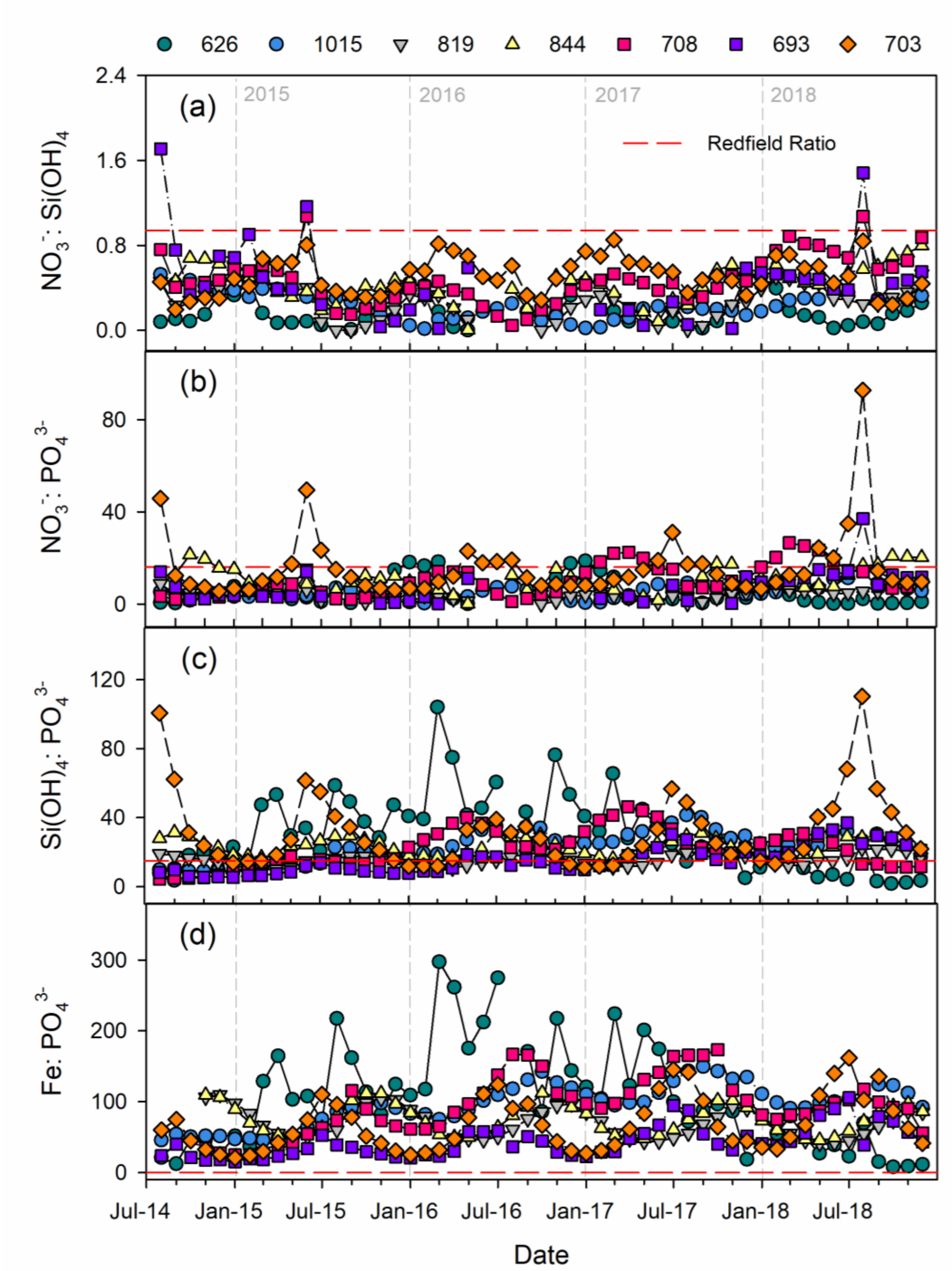

Fig. S5. Stoichiometric ratios (mol mol^{-1}) of the freshwater fluxes by watershed over time. Ratios calculated based on the monthly fluxes for each watershed.

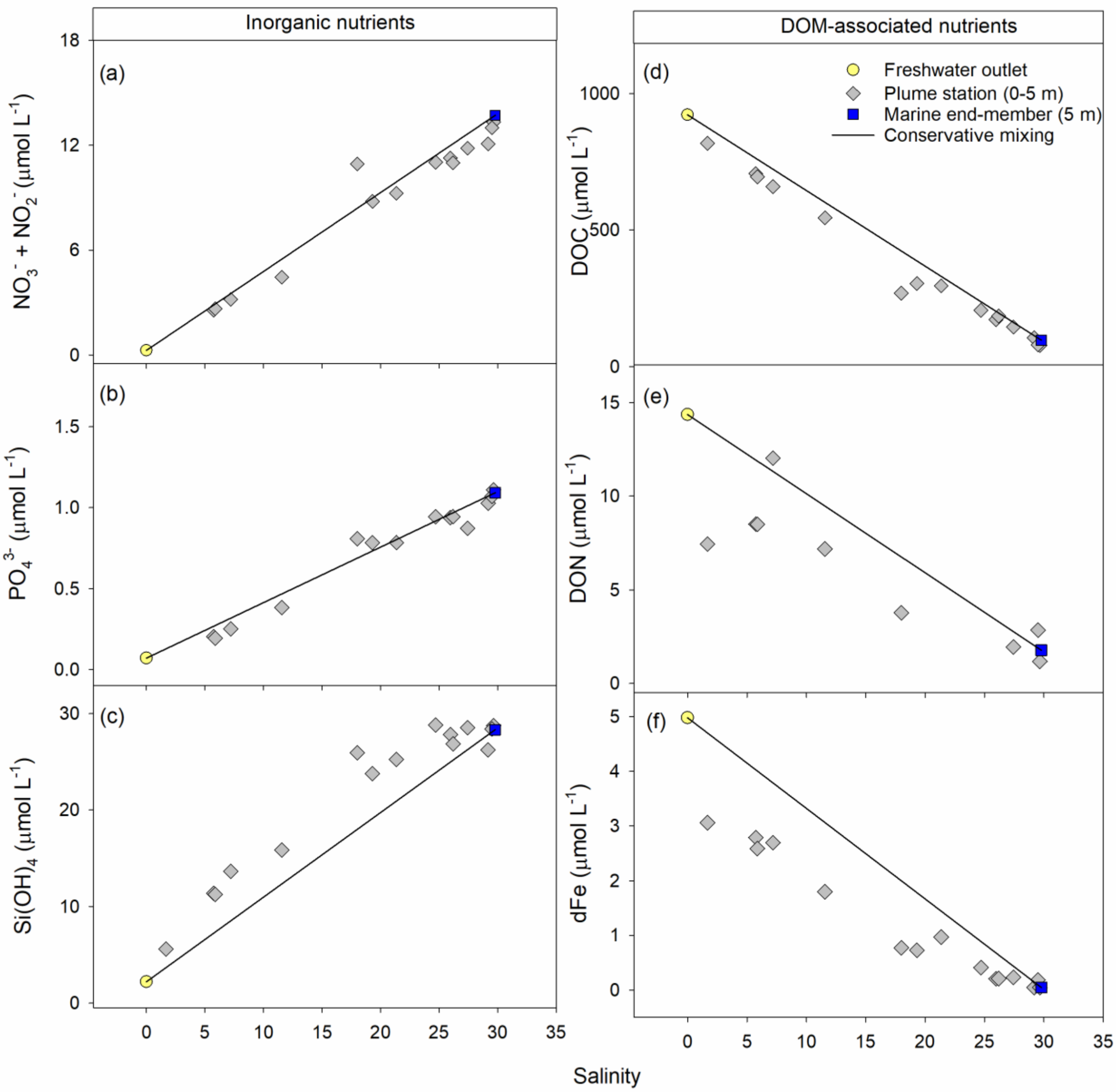

Fig. S6. Nutrient concentration mixing plots across the freshwater plume (0, 1 and 5 m at six stations) at the outlet of watershed 703 for the 135 mm rainfall event on 19-Sept-2015 (day 2 of 8-day event). Combined nitrate-nitrite (NO_3^-+NO_2^-; panel a), phosphate (PO_4^{3-}; panel b), silicic acid ($Si(OH)_4$; panel c), dissolved organic carbon (DOC; panel d), dissolved organic nitrogen (DON; panel e), and dissolved iron (dFe; panel f) are shown. Freshwater and marine end-members are the mean concentration at watershed 703 for the month of September and the plume sample with the highest salinity, respectively.

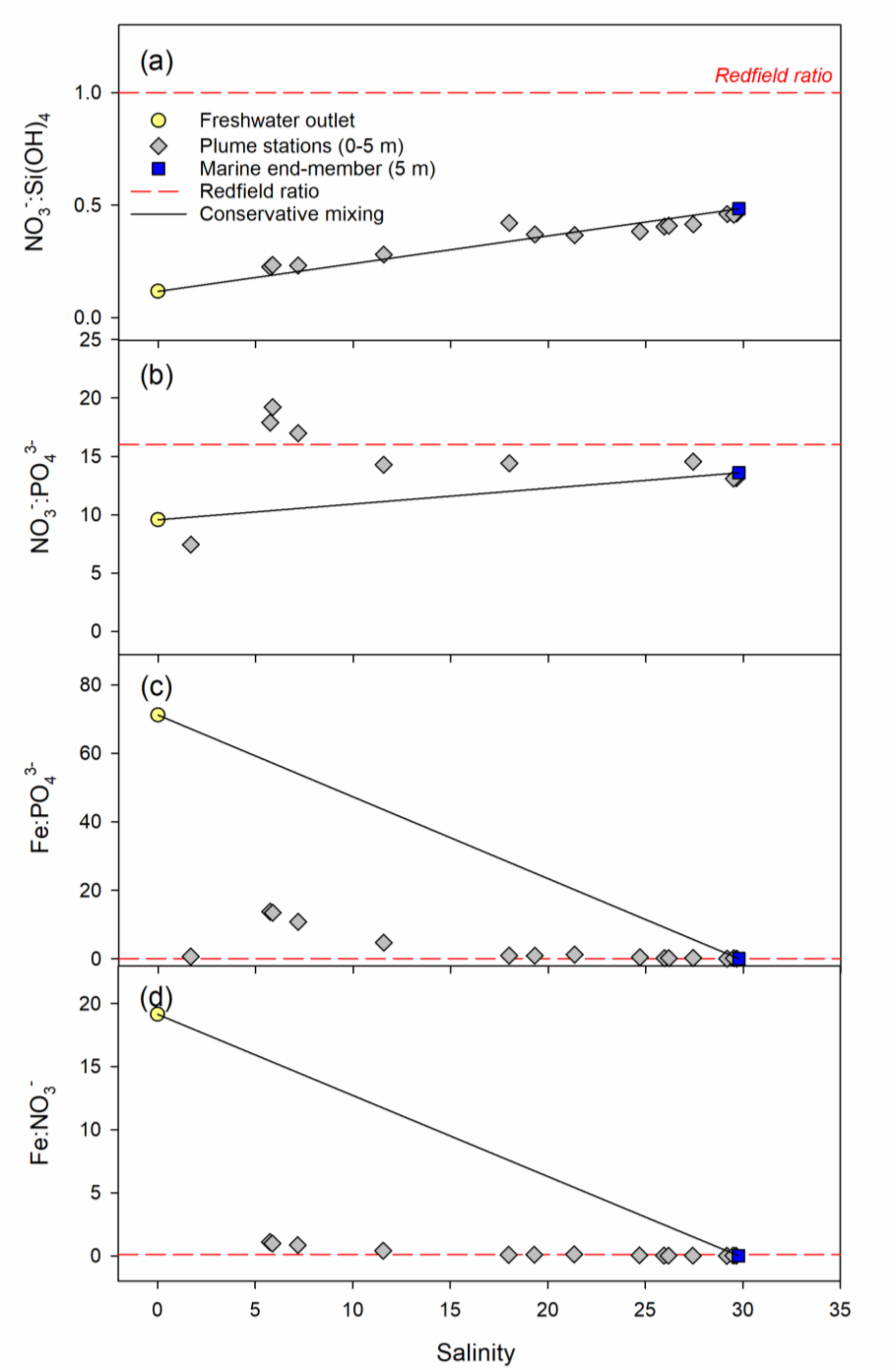

Figure S7. Stoichiometric ratios across the freshwater plume (0, 1 and 5 m at six stations) at the outlet of watershed 703 during the rainfall event on 19-Sept-2015. Freshwater and marine end-members are the mean concentration at watershed 703 for the month of September and the plume sample with the highest salinity, respectively.

Table S1. Marine sampling station information.

Station	Latitude (°N)	Longitude (°W)	Depth (m)	Record
Meay Channel				
MEA02	51.6754	128.0876	54	Jan-15 to Feb-16
MEA03	51.6847	128.0873	55	Aug-14 to Nov-14
MEA04	51.6928	128.0693	8	Aug-14 to Feb-16
Kwakshua Channel				
KC1	51.6545	128.1289	8	Jan-15 to Nov-18
KC7	51.6535	128.0464	168	Aug-14 to Feb-16
KC10	51.6505	127.9516	345	Aug-14 to Feb-16
KC11	51.6507	128.0253	78	Aug-14 to Feb-16
KC12	51.6504	128.0700	22	Aug-14 to Feb-16
KC13	51.6472	128.1199	9	Aug-14 to Feb-16
KC14	51.6487	127.9961	44	Aug-14 to Feb-16
KC15	51.6569	128.0034	28	Aug-14 to Feb-16
KC16	51.6563	128.0419	35	Aug-14 to Feb-16
Pruth Bay				
PRUTH	51.6554	128.0913	70	Aug-14 to Nov-18

Table S2. Analytical methods and laboratories by chemical constituent.

Constituent	Constituent name	Period	Data *	Instrument/Formula	Analytical Lab [a]	Detection limit ($\mu mol\ L^{-1}$)
TN	Total nitrogen	2014-19	Fresh	Lachat QuickChem QC8500	BASL	0.500
TDN	Total dissolved nitrogen	2014-19	Fresh	Lachat QuickChem QC8500	BASL	0.500
NH_4^+	Ammonium	2014-19	Fresh	Lachat QuickChem QC8500	BASL	0.214
NO_3^-+NO_2^-	Combined nitrate-nitrite	2014-15	Both	Lachat QuickChem QC8500	BASL	0.143
		2015-19	Both	Lachat QuickChem QC8500	U.B.C.	0.036
*DIN**	*Dissolved inorganic nitrogen*	*2014-19*	*Fresh*	*DIN* = $NH_4^+ + NO_3^- + NO_2^-$	-	-
*DON**	*Dissolved organic nitrogen*	*2014-19*	*Fresh*	*DON = TDN - DIN*	-	-
TP	Total phosphorus	2014-19	Fresh	Lachat QuickChem QC8500	BASL	0.045
TDP	Total dissolved phosphorus	2014-19	Fresh	Lachat QuickChem QC8500	BASL	0.058
PO_4^{3-}	Phosphate	2015-19	Both	Lachat QuickChem QC8500	U.B.C.	0.032
DOC	Dissolved organic carbon	2014-19	Fresh	OI Analytical Aurora 1030W TOC analyser (wet oxidation)	ACSL	
		2014-19	Mar	OI Analytical Aurora 1030W TOC analyser (high temperature combustion)	Ján Veizer	
Fe	Dissolved iron	2014-19	Fresh	ICP-OES	ACSL	0.090
$Si(OH)_4$	Dissolved silica	2014-19	Both	Lachat QuickChem QC8500	U.B.C.	0.100

* Data availability for monthly surveys of freshwater (Fresh), marine (Mar) or both (Both) for each chemical parameter.

[a] BASL, Biogeochemical Analytical Service Laboratory in the Department of Biological Sciences at the University of Alberta (Edmonton, AB, Canada). U.B.C., Marine Zooplankton and Micronekton Laboratory in the Department of Earth Oceans and Atmospheric Sciences (Vancouver, B.C., Canada). ACSL, Analytical Chemistry Services Laboratory, Ministry of Environment and Climate Change Strategy (Victoria, BC, Canada). Ján Veizer, Ján Veizer Stable Isotope Facility at the University of Ottawa (Ottawa, ON, Canada). UCDavis, University of California Davis Stable Isotope Facility (Davis, CA, USA).

Table S3. Characteristics of the seven study watersheds and freshwater outlet streams.

	Watershed characteristics				Stream characteristics			Weather station info			
Watershed ID	Area (km^2)	Slope (%)	Lakes (% area)[2]	Wetlands (% area)[2]	Annual Q ($x10^6$ m^3; ±SE)[3]	Temperature (°C; ± SE)	pH (± SE)	Weather station ID	Elevation (m.a.s.l.)[4]	Latitude (°N)	Longitude (°W)
626	3.2	21.7	4.7	48.0	6.07 ± 0.25	11.10 ± 0.52	5.31 ± 0.14	SSN626PWR	13	51.6408	128.1219
1015	3.3	34.2	9.1	23.8	5.44 ± 0.22	11.74 ± 0.69	5.36 ± 0.10	SSN1015US	17	51.6906	128.0653
819	4.8	30.1	0.3	50.2	8.25 ± 0.45	9.41 ± 0.50	4.42 ± 0.07	SSN819PWR	79	51.6619	128.0419
844	5.7	32.5	0.3	35.2	11.83 ± 0.15	9.43 ± 0.52	4.47 ± 0.07	WSN844	90	51.6614	127.9975
708	7.8	28.5	7.5	46.3	16.11 ± 0.62	11.95 ± 0.62	5.01 ± 0.10	SSN708US	12	51.6486	128.0684
693	9.3	30.2	4.4	42.8	30.46 ± 0.99	12.03 ± 0.65	4.83 ± 0.09	SSN693PWR	51	51.6442	127.9978
703	12.8	40.3	1.9	24.3	39.36 ± 1.49	9.04 ± 0.54	5.41 ± 0.09	WSN703	42	51.6433	128.0228
Total gauged	46.9	32.7	3.7	37.1	117.53 ± 3.60	-	-	-	-	-	-
Total[1]	69.6	-	-	-	174.50 ± 5.33	-	-	-	-	-	-

[1] Total values obtained by multiplying the total gauged values, when relevant by 1.484.
[2] Watershed coverage statistic calculation described in Gonzalez Arriola et al. 2015 and Oliver et al. 2017.
[3] Standard error (SE) on annual Q: variability around annual discharge estimate across 4 calendar years (2015-2018).
[4] Elevation: elevation in metres above sea level of stream sampling station.

Table S4. Results of tests comparing rack sample bottles and rack and pump sampler chemistry during rainfall events in 2015.

		% difference				
Date/time collected	Watershed	DOC	Fe	Si	TDP	TDN
Between rack sampler bottles at same height						
21-Jul-2015 08:00	703	4.1	6.9	1.1	25	10.8
29-Aug-2015 11:50	626	1.7	1.4	0.4	38.9	3.7
29-Aug-2015 13:50	708	5.2	20.2	0.9	120	10.4
29-Aug-2015 14:30	844	2.3	0.8	1.6	31.6	4.2
29-Aug-2015 17:11	693	0.1	533.3*	9.3	0	37.3
30-Aug-2015 04:20	819	2.4	26.7	1.3	9.1	0
30-Aug-2015 18:30	1015	8.8	24.9	0.9	38.5	3.2
Mean ± SE	All	3.5 ± 1.1	87.7 ± 74.4 13.5 ± 4.8*	2.2 ± 1.2	37.6 ± 14.8	9.9 ± 4.8
Between rack and pump sampler chemistry results						
10-Oct-2015 18:05	708	6.5	70.8	1.6	128.6	3.2
11-Oct-2015 22:20	708	0.7	4.9	0.4	208.3	23.4
Mean ± SE	All	3.6 ± 2.9	37.9 ± 33.0	1.0 ± 0.6	168.5 ± 39.9	13.3 ± 10.1

* Mean calculated without outlier (Watershed 693 on 29-Aug-2015 17:11).

Table S5. LOADEST log-linear model statistics by watershed and nutrient species.

Nutrient	Species	Watershed	No. obs.	Model	R^2	Bias (%)	PLR [a]	*E* [b]
Carbon	DOC	1015	106	9	99.6	0.76	1.01	0.97
	DOC	626	115	8	99.2	-2.08	0.98	0.92
	DOC	693	107	6	97.8	0.89	1.01	0.94
	DOC	703	144	6	98.1	-0.63	0.99	0.95
	DOC	708	248	7	98.6	2.16	1.02	0.95
	DOC	819	135	9	99.4	0.35	1.00	0.95
	DOC	844	119	9	99.0	-1.15	0.99	0.96
Nitrogen	TN	1015	72	4	98.8	0.34	1.00	0.96
	TN	626	70	7	98.3	4.54	1.04	0.92
	TN	693	68	4	98.2	0.13	1.00	0.99
	TN	703	75	4	97.4	1.57	1.02	0.87
	TN	708	74	9	98.8	2.57	1.03	0.92
	TN	819	79	4	98.5	1.62	1.02	0.92
	TN	844	67	4	98.1	0.73	1.01	0.93
	TDN	1015	103	7	99.4	0.00	1.00	0.97
	TDN	626	110	9	99.1	-1.87	0.98	0.92
	TDN	693	103	9	99.0	-0.16	1.00	0.91
	TDN	703	132	4	98.0	-1.18	0.99	0.93
	TDN	708	242	9	98.8	1.50	1.02	0.95
	TDN	819	135	4	99.2	1.16	1.01	0.95
	TDN	844	115	4	99.0	1.49	1.02	0.95
	DIN	1015	45	3	94.0	0.56	1.01	0.78
	DIN	626	43	9	95.2	-0.62	0.99	0.88
	DIN	693	41	4	90.0	-10.63	0.89	0.38
	DIN	703	43	2	72.7	-10.40	0.90	0.51
	DIN	708	49	2	94.5	7.59	1.08	0.70
	DIN	819	50	2	83.2	6.57	1.07	0.08
	DIN	844	45	6	83.9	-1.61	0.98	0.45
	NH_4^+	1015	69	9	87.8	4.36	1.04	0.52
	NH_4^+	626	69	9	86.9	2.73	1.03	0.90
	NH_4^+	693	66	9	88.5	3.90	1.04	0.22
	NH_4^+	703	74	3	77.7	-21.5	0.79	0.19
	NH_4^+	708	74	9	87.7	8.08	1.08	0.73
	NH_4^+	819	79	9	84.9	0.33	1.00	0.67
	NH_4^+	844	66	9	83.4	-0.50	1.00	0.65
	DON	1015	43	7	99.3	-0.58	0.99	0.97

Nitrogen (Ctd.)	DON	626	39	7	98.6	5.67	1.06	0.95
	DON	693	38	6	99.0	-1.50	0.99	0.97
	DON	703	36	4	98.2	-0.32	1.00	0.92
	DON	708	46	4	99.5	-1.32	0.99	0.95
	DON	819	53	6	98.9	-0.07	1.00	0.98
	DON	844	44	9	99.2	-0.67	1.00	0.98
Silicic acid	$Si(OH)_4$	1015	55	4	98.6	-2.11	0.98	0.96
	$Si(OH)_4$	626	52	8	88.6	4.19	1.04	0.91
	$Si(OH)_4$	693	54	7	96.7	-0.23	1.00	0.82
	$Si(OH)_4$	703	67	9	90.0	1.96	1.02	0.95
	$Si(OH)_4$	708	51	4	97.4	-1.66	0.98	0.88
	$Si(OH)_4$	819	67	7	97.3	2.70	1.03	0.89
	$Si(OH)_4$	844	58	6	95.6	0.89	1.01	0.91
Phosphorus	TP	1015	73	9	94.5	1.07	1.01	0.77
	TP	626	69	4	92.2	-3.48	0.97	0.80
	TP	693	67	1	95.3	2.31	1.02	0.30
	TP	703	76	1	95.3	-9.32	0.91	0.64
	TP	708	74	9	91.9	12.37	1.12	0.70
	TP	819	81	3	92.7	6.79	1.07	0.81
	TP	844	67	4	91.6	0.66	1.01	0.67
	TDP	1015	94	6	94.1	-7.79	0.92	0.49
	TDP	626	108	2	97.1	-3.05	0.97	0.79
	TDP	693	101	9	96.4	-0.15	1.00	0.76
	TDP	703	132	9	94.6	2.33	1.02	0.77
	TDP	708	239	9	92.9	1.95	1.02	0.49
	TDP	819	116	9	96.7	2.65	1.03	0.89
	TDP	844	106	4	96.1	-3.07	0.97	0.58
	PO_4^{3-}	1015	28	9	98.4	0.11	1.00	0.95
	PO_4^{3-}	626	30	9	88.6	-9.60	0.90	0.54
	PO_4^{3-}	693	33	8	88.7	-49.21	0.51	0.16
	PO_4^{3-}	703	31	8	93.5	-7.75	0.92	0.57
	PO_4^{3-}	708	29	9	94.1	-6.27	0.94	0.52
	PO_4^{3-}	819	31	1	90.1	8.70	1.09	0.49
	PO_4^{3-}	844	39	1	90.6	5.36	1.05	0.66
Iron	Fe	1015	91	9	98.7	0.58	1.01	0.95
	Fe	626	96	6	97.6	-8.49	0.92	0.86
	Fe	693	89	6	97.5	1.87	1.02	0.84
	Fe	703	116	6	98.1	-0.73	0.99	0.93

Fe	708	162	8	98.4	-0.18	1.00	0.73
Fe	819	112	8	98.9	-3.60	0.96	0.96
Fe	844	96	7	98.8	-1.49	0.99	0.98

[a] Partial Load Ratio (PLR, Stenback et al. 2011) quantifies bias in the estimated loads, where PLR > 1.0: overestimation, and a PLR<1.0: underestimation.

[b] Nash-Sutcliffe Efficiency Index (*E*, Nash and Sutcliffe 1970), where E = 1.0: perfect fit, E = 0.0: load estimate = mean, and E < 0: observed mean is a better estimate than the model.

[c] All models were constructed from data collected between 01-Aug-2014 and 31-Mar-2019, with the exception of PO_4^{3-}, for which only data after 01-Jan-2015 were included.

Table S6. Characterisation of rain events over the whole period of record near sea level, based on the weather station at the outlet of watershed 626.

Criteria	Whole period		2015		2016		2017		2018	
	No.	%	No.	%	No.	%	No.	%	No.	%
≥ 0.2 mm d^{-1}	1067	66.1	241	66.0	252	68.9	247	67.7	230	63.0
≥ 5 mm d^{-1}	604	37.4	140	38.4	142	38.8	137	37.5	126	34.5
≥ 15 mm d^{-1}	291	18.0	63	17.3	65	17.8	70	19.2	65	17.8
≥ 25 mm d^{-1}	150	9.2	37	10.1	36	9.8	33	9.0	27	7.4
≥ 50 mm d^{-1}	39	2.4	8	2.2	11	3.0	6	1.6	8	2.2
≥ 75 mm d^{-1}	8	0.5	2	0.5	3	0.8	2	0.5	0	0
≥ 100 mm d^{-1}	1	0.06	0	0	1	0.3	0	0	0	0
Total no. days*	1614	-	365	-	366	-	365	-	365	-
Frequency of multi-day events			No.	mm [a]	No.	mm [a]	No.	mm [a]	No.	mm [a]
4-5 days			3	21-49	10	12-164	6	20-106	7	7-71
6-7 days			6	53-157	3	10-108	5	43-69	5	52-114
8-9 days			5	58-149	2	58-219	3	23-129	1	96
10-14 days			2	180-265	3	51-155	2	92-160	3	80-223
≥ 15 days			3	175-346	5	152-508	3	324-567	3	237-490
Longest event (days)			23	[Dec.]	21	[Mar.]	47	[Mar.]	25	[Jan.]
4+ day event size [b]			No.		No.		No.		No.	
< 50 mm			3	-	8	-	7	-	4	-
50-100 mm			5	-	6	-	5	-	9	-
100-200 mm			8	-	4	-	4	-	2	-
200-400 mm			3		4	-	1	-	2	-
≥ 400 mm			0	-	1	-	2	-	2	-

* Total number of days within the period of interest. Whole period = 1-Aug-2014 to 31-Dec-2018.

[a] mm : Total rainfall in mm over the multi-day event.

[b] Frequency of rainfall events (more than 4 days long) by total rainfall.

Table S7. Summary statistics for measured nutrient concentrations (in μmol L^{-1}) in fresh and marine waters.

	MARINE (0 – 5 m)			**FRESHWATER**					
	Measured			**Measured [b]**			**Flow-weighted [c]**		
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range
DOC	72.64	63.95	7.87 - 965	954	911	47.0 - 3130	959	941	420 - 1810
TN	-	-	-	14.07	13.71	4.57 - 43.84	14.67	14.18	6.84 - 28.35
TDN	-	-	-	14.12	13.71	4.71 - 40.69	13.27	12.68	5.99 - 27.53
DON	-	-	-	12.18	11.91	2.44 - 25.25	12.13	11.88	5.25 - 23.86
DIN	-	-	-	1.19	0.93	0.17 - 5.58	1.06	1.05	0.37 - 5.01
NO_3^-+NO_2^- [a]	8.18	6.92	0.01 - 22.39	0.48	0.14	<D.L. - 5.30			
NH_4^+	-	-	-	0.56	0.43	<D.L. - 6.43	0.61	0.56	0.15 - 1.92
TP	-	-	-	0.39	0.32	0.02 - 2.58	0.41	0.39	0.23 - 0.80
TDP	-	-	-	0.31	0.29	0.03 - 2.32	0.32	0.32	0.13 - 0.63
PO_4^{3-}	0.78	0.78	<D.L. - 2.50	0.11	0.06	<D.L. – 1.09	0.09	0.07	0.01 - 0.96
$Si(OH)_4$	18.67	19.55	0.02 - 40.70	1.67	1.33	0.23 - 37.89	1.48	1.31	0.47 - 8.21
dFe	-	-	-	5.79	5.16	0.34 - 24.4	5.11	4.56	1.38 - 18.94

[*] For constituent-specific detection limits (D.L.), see Table S2.

[a] Because NO_3^-+NO_2^- fluxes were poorly modelled, flow-weighted concentrations of NO_3^-+NO_2^- were determined by subtracting the flow-weighted concentration of NH_4^+ from DIN for each month.

[b] Measured freshwater concentrations summarise all samples collected in the seven watersheds between May 2014 and November 2018.

[c] Flow-weighted concentrations summarise the monthly statistics across all seven watersheds between August 2014 and December 2018.

Table S8. Results of linear mixed effects models comparing marine nutrient concentrations over time. p-values are shown (α = 0.05).

	Year (2015-18)	Month (Jan-Dec)	Year*Month
Degrees of freedom	3	11	33
DOC	0.926	0.960	0.960
NO_3^-+NO_2^-	**<0.001**	**<0.001**	**<0.001**
$Si(OH)_4$	**<0.001**	**<0.001**	**<0.001**
PO_4^{3-}	**<0.001**	**<0.001**	**<0.001**

Table S9. Results of linear mixed effects models comparing flow-weighted freshwater nutrient concentrations over time. p-values are shown (α = 0.05).

	Year (2015-18)	Month (Jan-Dec)	Year*Month
Degrees of freedom	3	11	33
DOC	0.567	**<0.001**	0.355
TN	0.987	**<0.001**	0.532
TDN	0.963	**<0.001**	0.995
DON	0.988	**<0.001**	0.999
DIN	0.672	0.121	**<0.001**
NH_4^+	**<0.001**	**<0.001**	**<0.001**
NO_3^-+NO_2^-	0.238	**0.002**	**<0.001**
$Si(OH)_4$	0.885	**<0.001**	**0.009**
TP	0.795	0.441	0.999
TDP	**0.025**	0.711	0.559
PO_4^{3-}	0.615	0.994	0.953
Fe	0.818	**<0.001**	0.999

Table S10. Range of freshwater yields of DOC, TN, DON, NO_3^-, $Si(OH)_4$, PO_4^{3-}, and Fe across the 7 watersheds with reference to literature values shown below.

		Annual yields (kg km^{-2} y^{-1})						
Watershed	Area (km^2)	DOC	TN	DON	DIN	$Si(OH)_4$	PO_4^{3-}	dFe
626	3.2	18,300 - 25,100	446 - 518	368 - 423	15.7 - 32.3	62.1 - 105	1.94 - 17.06	469 - 642
1015	3.3	18,700 - 23,700	309 - 374	239 - 319	15.0 - 24.5	58.7 - 72.3	2.21 - 5.01	471 - 616
819	4.8	22,700 - 29,300	345 - 450	283 - 358	25.9 - 34.5	68.4 - 89.0	5.34 - 6.59	517 - 774
844	5.7	25,500 - 27,800	433 - 484	270 - 345	38.1 - 43.5	93.2 - 104	4.49 - 4.73	500 - 617
708	7.8	19,600 - 25,500	352 - 471	279 - 352	34.4 - 43.1	59.6 - 72.6	2.68 - 5.48	410 - 580
693	9.3	20,500 - 24,000	439 - 525	338 - 409	31.8 - 34.5	66.4 - 88.0	4.22 - 9.67	381 - 440
703	12.8	24,900 - 30,500	340 - 434	319 - 411	44.4 – 54.1	111 - 150	5.29 - 8.79	496 - 625
Kwakshua Channel	69.6	22,200 – 26,900	378 - 463	304 - 381	33.6 - 40.9	84.5 - 95.7	5.17 - 6.90	462 - 596

Reference	Region/ecotype	DOC	TN	DON	DIN	$Si(OH)_4$	PO_4^{3-}	dFe
Alvarez-Cobelas et al., 2008	Global	-	1 - 20,630	10 - 479	(0.02-10,645)*	-	-	-
	Coniferous forests	-	228 ± 289	-	-	-	-	-
	Deciduous forests	-	917 ± 1861	-	-	-	-	-
Seitzinger et al., 2005 †	Global	1490	-	67	218	-	10	-
	North America	1031	-	101	126	-	5	-
Dürr et al., 2011	Global	-	-	-	-	3300	-	-
	North America	-	-	-	-	2200	-	-
Meybeck, 1982	Global (mean)	2150	-	100	40	-	4.5	-
	Global (range)	2000 -14,000	-	-	(10 - 200)*	-	0.5 - 10	-
§ See notes on derivation.	Global (range)	-	-	-	-	-	-	0.84 - 8.39
Sugai and Burrell, 1984	SE Alaska	7900 - 13,300	-	-	160 - 367	-	5.6 - 6.2	340 - 420
Fellman et al., 2021	SE Alaska	-	-	229 - 401	5.3 -19.8	-	10.7 - 12.6	-

† – NEWS global biogeochemical model outputs.
* - range of NO_3^- exports (DIN = NO_3^- + NO_2^- + NH_4^+).
§ Range of dFe yields derived from dFe fluxes in De Baar and De Jong (2001) and Krachler et al. (2005), using global riverine drainage basin area to the oceans from Meybeck (1982).

Table S11. Pearson product moment correlations between dissolved organic carbon (DOC) and other nutrients in freshwater ecosystems.

	All samples				Watersheds*						
	r	t	df	p[1]	626	1015	819	844	708	693	703
TN	0.63	19.09	554	<0.05	0.65	0.47	0.72	0.81	0.33	0.46	0.40
TDN	0.74	34.39	989	<0.05	0.81	0.43	0.74	0.83	0.56	0.55	0.50
DON	0.72	17.66	296	<0.05	0.64	0.48	0.83	0.85	0.41	0.85	0.77
DIN	-0.16	-2.90	322	<0.05	0.02	-0.03	-0.02	0.15	-0.03	-0.10	-0.42
NO_3^-+NO_2^-	-0.27	-5.98	474	<0.05	-0.05	0.05	-0.15	0.04	0.02	-0.13	-0.38
NH_4^+	0.15	3.41	542	<0.05	-0.01	-0.07	0.18	0.23	0.08	<0.01	0.19
TP	0.10	2.40	556	<0.05	0.08	0.06	-0.06	0.06	0.05	0.02	0.09
TDP	0.11	3.28	939	<0.05	0.08	-0.11	-0.19	-0.01	0.21	-0.16	0.14
PO_4^{3-}	0.10	2.33	526	<0.05	-0.08	0.18	-0.11	0.32	0.20	0.08	-0.15
$Si(OH)_4$	0.07	1.35	391	0.18	0.06	0.18	0.35	0.16	0.53	0.60	-0.15
dFe	0.61	22.07	813	<0.05	0.47	0.46	0.69	0.62	0.36	0.47	0.23

[1] Note that p-values are reported here across all samples, but are not used in the interpretation of the results due to the high sample size (df + 1). r > ± 0.20 are highlighted in purple for positive correlations, and in pink for negative correlations.

* Statistically significant watershed-specific correlations are bolded, based on a Bonferroni-corrected α of 0.001.

Table S12. Loadings of nutrients on to the first two principal component (PC) axes using scaling 2. Note that PC1 was multiplied by -1 for ease of interpretation in Fig 5. Bolded numbers indicate the dominant parameters contributing to each PC.

	PC1 (50.0%)	PC2 (13.8%)	PC3 (11.7%)
DOC	**-2.09**	0.15	-0.23
TN	**-2.25**	0.16	0.21
TDN	**-2.30**	0.15	0.05
DON	**-2.16**	0.41	0.42
DIN	-0.30	-0.43	**-2.12**
NH_4^+	-1.11	**-1.59**	-0.28
TP	-1.52	**-1.03**	0.56
TDP	-0.60	**-1.78**	0.58
PO_4^{3-}	-0.85	**0.93**	0.91
$Si(OH)_4$	-1.58	0.70	**-1.03**
dFe	**-2.22**	0.34	-0.17

References

Alvarez-Cobelas, M., Angeler, D. G., and Sánchez-Carrillo, S.: Export of nitrogen from catchments: A worldwide analysis, Environ. Pollut., 156, 261-269, https://doi.org/10.1016/j.envpol.2008.02.016, 2008.

De Baar, H. J. W., and De Jong, J. T. M.: Distributions, sources and sinks of iron in seawater, in: The Biogeochemistry of Iron in Seawater, edited by: Buffle, J., and van Leewen, H. P., IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, 2001.

Dürr, H. H., Meybeck, M., Hartmann, J., Laruelle, G. G., and Roubeix, V.: Global spatial distribution of natural riverine silica inputs to the coastal zone, Biogeosciences, 8, 597-620, 10.5194/bg-8-597-2011, https://doi.org/10.5194/bg-8-597-2011, 2011.

Fellman, J. B., Hood, E., D'Amore, D. V., and Edwards, R. T.: Streamflow variability controls N and P export and speciation from Alaskan coastal temperate rainforest watersheds, Biogeochemistry, https://doi.org/10.1007/s10533-020-00752-w, 2021.

Gonzalez Arriola, S., Frazer, G. W., and Giesbrecht, I. J. W.: LiDAR-derived watersheds and their metrics for Calvert Island. Hakai Institute (Ed.), http://dx.doi.org/10.21966/1.15311, 2015.

Krachler, R., Jirsa, F., and Ayromlou, S.: Factors influencing the dissolved iron input by river water to the open ocean, Biogeosciences, 2, 311-315, https://doi.org/10.5194/bg-2-311-2005, 2005.

Meybeck, M.: Carbon, nitrogen, and phosphorus transport by world rivers, Am. J. Sci., 282, 401-450, https://doi.org/10.2475/ajs.282.4.401,1982.

Nash, J. E., and Sutcliffe, J. V.: River flow forecasting through conceptual models part I — A discussion of principles, Journal of Hydrology, 10, 282-290, https://doi.org/10.1016/0022-1694(70)90255-6, 1970.

Oliver, A. A., Tank, S. E., Giesbrecht, I., Korver, M. C., Floyd, W. C., Sanborn, P., Bulmer, C., and Lertzman, K. P.: A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia, Biogeosciences, 14, 3743-3762, https://doi.org/10.5194/bg-14-3743-2017, 2017.

Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., and Bouwman, A. F.: Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application, Global Biogeochem. Cycles, 19, GB4S01, https://doi.org/10.1029/2005GB002606, 2005.

Stenback, G. A., Crumpton, W. G., Schilling, K. E., and Helmers, M. J.: Rating curve estimation of nutrient loads in Iowa rivers, Journal of Hydrology, 396, 158-169, https://doi.org/10.1016/j.jhydrol.2010.11.006, 2011.

Sugai, S. F., and Burrell, D. C.: Transport of Dissolved Organic Carbon, Nutrients, and Trace Metals from the Wilson and Blossom Rivers to Smeaton Bay, Southeast Alaska, Can. J. Fish. Aquat. Sci., 41, 180-190, https://doi.org/10.1139/f84-019, 1984.

Wang, T., Hamann, A., Spittlehouse, D., and Carroll, C.: Locally Downscaled and Spatially Customizable Climate Data for Historical and Future Periods for North America, PLoS One, 11, e0156720, https://doi.org/10.1371/journal.pone.0156720, 2016.