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Contribution of rain events to surface water loading in 3 watersheds in Canada's Alberta Oil Sands region

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ABSTRACT

Study region: In the oil sands region of Canada, hydrology of rivers is strongly influenced by snowmelt and a shifting climate resulting in shortening of snow cover duration and increases in the frequency of rain events.

Study focus: To evaluate the importance of rain events to these rivers, discharge and water quality sampling was conducted at river sites in this region. Two approaches were used to collect water quality samples: (1) event-based automated samplers that triggered repeated sampling in response to 10% increases in surface flow, and (2) an intensive program of routine sampling at daily, weekly or biweekly intervals from April 2013 to January 2014.

New hydrological insights for the region: The importance of rain events as contributors to loading of nutrients and priority pollutants differed temporally. During fall, when baseflow conditions prevailed, average daily loads differed when calculated using routine only versus routine + rain-event data. However, on an annual basis, the inclusion of rain-event sampling did not change pollutant loads. Thus, when assessing loads on an annual basis, rain event sampling may not provide enough benefit to warrant the additional logistical considerations for this remote region. However, when monitoring focuses on capturing fall conditions, efforts should be expanded to include rain event sampling in order to capture spikes in chemical concentration during this ecologically important time period. Predictions of a shorter snow season with more precipitation falling as rain rather than snow reinforce the need to adapt monitoring schemes to ensure that the timing and frequency of water chemistry sampling reflects changing climate and hydrological patterns.

1. Introduction

The hydrology of rivers draining cold regions (i.e., regions with snow and ice for much of the year) is strongly influenced by the annual cycle of snow accumulation followed by snowmelt. In these regions, flows of more than 50% of the annual maximum daily flow occur during snowmelt (Costa and Pomeroy, 2019). Chemical loads also increase during snowmelt (a period generally lasting 2–4 weeks between April and June in northern latitudes) because melt water has limited potential for infiltration through frozen soils (e.g., Rattan et al., 2019). Analyses of long-term historical data are showing, however, significant changes in climatology of cold regions,

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notably an increase in temperature that is greatest during winter, shortening of annual snow cover duration, and an increase in the frequency of rain events (Barnett et al., 2005; Beltaos and Burrell, 2003; Burn, 1994; Prowse and Beltaos, 2002). With a changing climate reported throughout cold regions (Keenan and Riley, 2018), there is significant potential to underestimate chemical loads as the short duration, yet intense, rain events that are now more frequent may deliver more pollutants than previously acknowledged.

Rivers in the oil sands region of northeastern Alberta, Canada experience a climate typical of cold boreal regions, notably a long snow cover period, rapid seasonal snowmelt and intense localized summer and fall rain events (Woo et al., 2008; Monk et al., 2011). This distinct seasonality in climate gives rise to a marked seasonal hydrology: most (> 50%) of the annual flow volume occurs during spring freshet due to melting snow and ice and is followed, with the exception of convective rainstorms that produce 2–3 day spikes in discharge in late summer and early fall, by a slow tapering of streamflow to base conditions that last from November when ice cover starts to form and remains until early April (Bush and Lemmen, 2019). Analysis of long-term data (1948 to 2016) for north-eastern Alberta showed a mean annual increase in temperature of 1.7–3 °C (driven by winter warming), a shift in the timing of precipitation from proportionately less in winter and more in spring (when it falls as rain rather than snow), and a decrease in snow cover during the snow onset period of October to December (Bush and Lemmen, 2019). With warming and changes to precipitation patterns expected to continue or be exacerbated in future (IPCC, 2007), there is a strong likelihood of changes in the timing and magnitude of contaminant transport in streams traversing Canada's oil sands region.

Contaminants in streams draining Canada's oil sands are derived from both natural outcrops of bitumen and mining of buried bitumen deposits. Bitumen is a dense, highly viscous petroleum that contains a mixture of particulate organic material, hydrocarbons, metals and sulfur compounds (WHO, 2004). Whilst contaminants found in bitumen can make their way to surface water via natural pathways (groundwater seeps and erosion of river banks with exposed bitumen deposits), oil sands mining operations have the potential to enhance the transfer of these components to surface waters as a result of both surface runoff, particularly during the construction phase (Alexander et al., 2017), and atmospheric long-range transport during extraction and processing operations (Kirk et al., 2014; Kurek et al., 2013), both of these methods can also facilitate the transport of pollutants outside the watershed. Although early studies reported that concentrations of metals (e.g., As, Cd, Cu, Pb, Ni, Zn) did not differ between river sites downstream of oil sands operations versus those in undeveloped locations (Conly et al., 2007; Headley et al., 2001, 2005), more recent findings show elevated

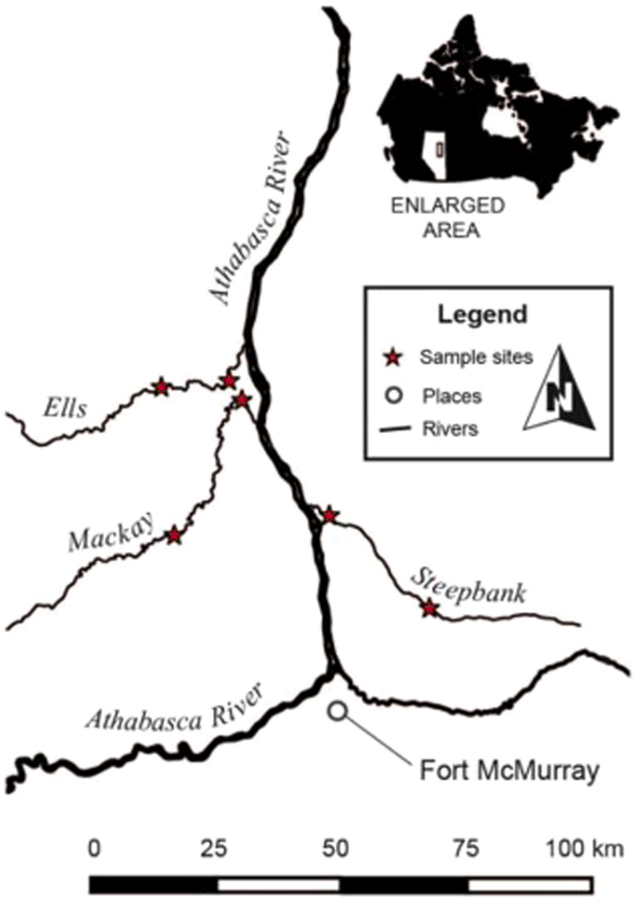

Fig. 1. Study site locations within the oil sands region of Alberta, Canada. Stars indicate locations of study sites along the Ells, Mackay and Steepbank rivers. Stars located mid-reach are those termed upper reach, while those located near the Athabasca River are termed lower reach.

concentrations of 13 priority pollutants (Kelly et al., 2010). The fact that background levels of contaminants can be high due to natural contributions makes it difficult to quantify inputs and has led to conflicting reports about the significance of anthropogenic sources. With a changing climate reported for the oil sands region (Lemmen et al., 2004), there may be a greater need than previously recognized to sample water chemistry during and immediately after rain events in addition to during spring snowmelt and baseflow conditions to better understand the effect of these events on concentrations of pollutants in this region.

The objective of this study was to examine the influence of rain events on the concentration and load of 12 priority pollutants in the Athabasca Oil Sands region (antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn)) as well as two nutrients (nitrogen (N), phosphorus (P)) for streams draining the Athabasca Oil Sands region of north-western Alberta, Canada. First, we examined the influence of rain events on pollutant concentrations and loads during rain events (i.e., >5 mm within 12–24 daytime period), seasonally (summer and fall) and annually (2013 and 2014). Second, we put these findings into a spatial context and examined differences in loads only between upper and lower reaches of three watersheds with different types (e.g., open pit vs in situ recovery) and areal extent of Athabasca Oil Sands operations. Lastly, we assessed whether collecting event-based samples would increase the accuracy of seasonal or annual load estimations for priority pollutants and macronutrients in these watersheds. Understanding the potential contribution of storm events has important implications for water management and the design of water quality monitoring programs.

2. Materials and methods

2.1. Study design

The study area spanned 55° 52′ 36″ N x 110° 48′ 46.8″ W and 59° 52′ 9″ N x 111° 35′ 8″ W, or an area approximately 30,000 km^2, north of Fort McMurray, AB, Canada (Fig. 1). Water quality of Athabasca River tributaries in Canada's oil sands region is heavily influenced by underlying bedrock, which consists of shale, sandstone and limestone. The waters are moderately hard (average

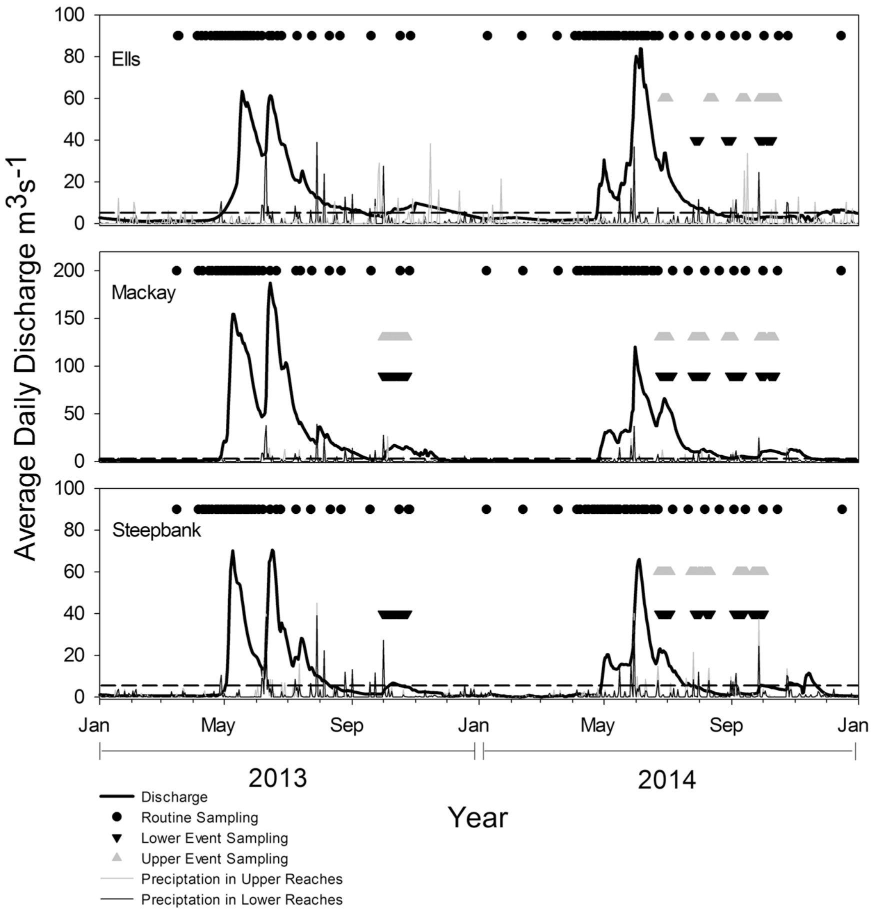

Fig. 2. Average daily discharge and precipitation within the Ells, Mackay and Steepbank rivers in 2013 and 2014. Collection of routine samples are indicated by black circles, while collection of automated event samples is indicated by grey upward triangles (upper reach sampling) and black downward triangles (lower reach sampling). Dashed line indicates 10% above baseflow conditions that would be considered a rain-event.

alkalinity of 113 mg l^{-1} $CaCO_3$) because of their mineral content, particularly Mg^{2+}, Ca^{2+} and bicarbonate (8.9, 29.1 and 137 mg l^{-1} respectively) (Chambers et al., 2018). Concentrations of N and P (indicators of nutrient status) are typically low to moderate, indicative of oligotrophic to mesotrophic conditions (Chambers et al., 2018). Concentration average 0.15 mg l^{-1} total P (TP) and 0.03 mg l^{-1} total dissolved P, and 0.94 mg l^{-1} total N (TN), 0.08 mg l^{-1} N as nitrate+nitrite, and 0.04 mg l^{-1} N as total ammonia (Chambers et al., 2018).

An intensive monitoring program of grab water sampling (referred to as "routine sampling") was conducted over 2 years (2013–2014) by Environment and Climate Change Canada at 6 sites (Fig. 1). Two sites (upper and lower reach) were located along 3 tributaries discharging to the Athabasca River (Steepbank, Mackay and Ells rivers). The program included daily or alternate-day routine sampling during snowmelt (April-May) followed by weekly (June), biweekly (July-August) or monthly sampling (September-November), and then occasional under-ice sampling (~ 3 times/winter). For each site, this resulted in a total of 35 samples in 2013 (9 from summer (May 31 - August 31) and 3 from fall (September 1 - October 30)) and 41 samples in 2014 (10 from summer and 4 from fall). Summer sampling period captured the declining trend of spring snowmelt (Fig. 2).

In addition to routine sampling, an intensive event-based automated sampling program was undertaken at the same sites, though for a shorter time period. From September – October 2013 and June – October 2014, event-based automated samplers (ISCO 6712, Teledyne, NE) were triggered for repeated sampling every 3 (2014) or 6 (2013) hours in response to either: (a) > 5 mm in rainwater (9 pin rain gauge attachment, ISCO 6712, as above), or (b) change in water level (e.g., 2 cm change in depth) over a defined period (e.g., 30-min) measured by pressure transducers (HOBO, Onset Computer Corporation, MA). Once triggered, a 250-ml sample of river water was collected and this procedure was repeated every three (2014) or six (2013) hours for a maximum of 8 samples in a 24-h period, which were composited into two, 1-L sample bottles. Sampling continued until water depth was below the threshold of the original depth measurement. This 'rate of change' program was developed for the three rivers based on average ± 2 SD fluctuations in water level (depth to transducer during the open water sampling period using outlet data collected by the Water Survey of Canada (https://wateroffice.ec.gc.ca/)) and upstream data from pressure transducers collected by Environment and Climate Change Canada. Water depth, rainfall volume, time and date of triggering, and number of samples collected were recorded in 15-minute intervals by the automated sampler (Table 1). Autosamples were retrieved during routine grab sampling from each site after event completion. Sample bottles were replaced with new, acid-washed 1-L bottles, and the automated sampling program was reset. Water samples were preserved on-site if required.

Samples were analyzed for nutrients (total N and P) and a suite of total metals, metalloids and non-metals considered priority pollutants (Sb, As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl and Zn) or previously studied in detail in the region (e.g., https://www.epa.gov/eg/toxic-and-priority-pollutants-under-clean-water-act; Kelly et al., 2010). All samples were analyzed at Environment and Climate Change Canada's National Laboratory for Environmental Testing (NLET) facility using nationally recognized analytical standards and procedures (Environment Canada, 2012). Routine samples were analyzed for the above as well as an additional 143 parameters. This study focuses on the 14 total parameters that were analyzed as part of both the routine and automated sampling programs.

Table 1
Frequency of rainfall events sampled during summer (June to August) 2014 and fall (Sept – Oct) 2013 and 2014 in upper and lower reaches of the Ells, Mackay and Steepbank rivers in Canada's oil sands region.

			Event-Based Sampling		
River	Site	Average Discharge[a,b] m^3/s (% high flow)	Number of events sampled (% of Total)[c]	Amount of rainfall captured vs missed (mm)[c] (% captured of total during sampling months)	Duration sampled AVG hrs ± SE (Total-d)
2013 (Sept – Oct)					
Ells	upper	NA	NA	NA	NA
	lower	NA	NA	NA	NA
Mackay	upper	4.2 (23%)	2 (67% of 3)	45.4 vs 15.8 (74%)	576.0 ± 0.0 (24-d)
	lower	8.7 (19%)	2 (50% of 4)	45.2 vs 20.2 (69%)	576.0 ± 0.0 (24-d)
Steepbank	upper	NA	NA	NA	NA
	lower	3.4 (25%)	2 (50% of 4)	45.1 vs 30.7 (59%)	576.0 ± 0.0 (24-d)
2014 (Jun – Aug)					
Ells	upper	15.6 (19%)	1 (17% of 6)	6.6 vs 90.38 (7%)	168.0 ± 0.0 (14-d)
	lower	23.4 (39%)	2 (33% of 6)	25.0 vs 74.5 (25%)	156.0 ± 12.0 (13-d)
Mackay	upper	15.8 (19%)	3 (50% of 6)	45.3 vs 52.7 (46%)	232.0 ± 48.7 (29-d)
	lower	33.1 (35%)	3 (50% of 6)	39.5 vs 60.3 (40%)	232.0 ± 92.3 (29-d)
Steepbank	upper	12.4 (49%)	6 (43% of 14)	68.5 vs 56.7 (55%)	264.0 ± 48.0 (33-d)
	lower	15.1 (43%)	2 (33% of 6)	31.5 vs 69.6 (31%)	216.0 ± 48.0 (27-d)
2014 (Sept – Oct)					
Ells	upper	2.1 (28%)	1 (12% of 5)	11.9 vs 85.7 (12%)	312.0 ± 144 (26-d)
	lower	3.0 (36%)	2 (29% of 7)	39.7 vs 60.0 (40%)	120.0 ± 48.0 (15-d)
Mackay	upper	3.7 (28%)	1 (21% of 5)	20.9 vs 78.5 (21%)	136.0 ± 32.0 (17-d)
	lower	7.7 (23%)	4 (57% of 7)	41.8 vs 57.9 (42%)	192.0 ± 36.7 (24-d)
Steepbank	upper	2.9 (8%)	1 (33% of 3)	54.4 vs 43.7 (55%)	264.0 ± 24.0 (22-d)
	lower	3.5 (26%)	4 (57% of 7)	61.0 vs 38.4 (61%)	300.0 ± 12.0 (25-d)

[a] Average discharge and % high flow calculated using a combination of: 1 Indications of Hydrological Alteration (IHA) software http://www.conservationgateway.org;

[b] 2 Water Survey of Canada; http://wateroffice.ec.gc.ca/, as well as upstream pressure transducer data collected by Environment and Climate Change Canada;

[c] 3 For more information on rain events see Environment and Climate Change Canada: http://climate.weather.gc.ca/.

2.2. Determining load in tributary sites

Load, expressed as kg per day, was calculated on a daily interval as the product of concentration C and average daily discharge Q (see Kerr et al., 2016, Moatar and Meybeck, 2005, Eq. 1). As concentrations were not measured every day for the entire study period, the standard midpoint interpolation method was used to estimate daily loads between routine water quality sampling dates (e.g., Moatar and Meybeck, 2005, Eq. 2). Seasonal loads for a given temporal period (i.e., for a season or for the duration of a rain event) were calculated as the integration of the daily load for a fixed time period (δt). There were no differences in how load was calculated between grab and autosamples.

$$\text{Daily load} = Ci \cdot Qi \tag{1}$$

$$\text{Seasonal load} = \sum_{i=1}^{n/\delta t} Ci \cdot Qi \cdot \delta t \tag{2}$$

Daily discharge data were obtained from Water Survey of Canada (WSC; http://wateroffice.ec.gc.ca/) or Alberta's Regional Aquatics Monitoring Program (RAMP; http://www.ramp-alberta.org/ramp.aspx) for each of the three lower reach sites. Discharge data were not available for upper reach sites and so discharge was estimated using an indirect approach. At all six sites, a pressure transducer logger (HOBO, Onset Computer Corporation, MA) was deployed that measured water level and temperature at 30-min intervals. Atmospheric pressure was also monitored concurrently at each site and these observations were used to correct the pressure readings recorded by the HOBO logger, resulting in pressure readings for each site that represented water depth. A watershed-specific correction factor was calculated for each site as the ratio of daily water levels measured at the lower reach gauged versus the upper reach ungauged site for further details see Alexander et al. (2017); Wasiuta et al. (2019). In brief, these correction factors were determined by scaling discharge data from outlet sites by drainage area and water level at upper reach sites. Pressure transducers were also directly connected to autosamplers to trigger sampling based on changes in water level (described above).

Geographic Information Systems (GIS) were used to determine catchment size at both upper and lower reach sites. Base layers were compiled from public sources (e.g., NRCan Atlas of Canada v6, http://atlas.nrcan.gc.ca) whereas Athabasca Oil Sands areas, agreements, leases, boundaries, mineable area and approval boundaries were compiled from the former Energy Resource Conservation Board (ERCB), now the Alberta Energy Regulator (AER), and were formerly available from Alberta Energy (e.g., https://www.energy.alberta.ca/). All GIS data were analyzed using QGIS (http://www.qgis.org/).

2.3. Statistical approaches

Descriptive statistics (mean and standard error, SE) were used to compare concentrations of nutrients and priority pollutants across all sites for both routine and event-based samples. Because routine monitoring was conducted more frequently during snowmelt and less frequently (weekly to monthly) during the remaining open-water period, we expressed concentrations on three seasonal time scales: (1) snowmelt (March 1 – May 31), (2) summer (June 1 – August 31), and (3) fall (September 1 – October 31) in both 2013 and 2014. The summer and fall sampling times coincided with deployment of autosamplers for event-based sampling. Both concentrations and loads across all sites were assessed for normality using Shapiro-Wilks test for normality with the shapiro.test function in R (R Core Team, 2020). The data were found to deviate significantly ($p < 0.05$) from normal (even after transformation) and therefore non-parametric analyses were employed for further statistical analyses. Concentrations were evaluated for correlation with discharge using Spearman ranked correlation tests with the cor.test function in R (R Core Team, 2020). Metrics were considered to be correlated with discharge if Rho > 0.5 and $p < 0.01$. Differences in concentration between routine samples collected during summer and fall and event-based samples were calculated using Kruskal-Wallis tests computed with the kruskal.test function in R (R Core Team, 2020). Post-hoc tests, where appropriate, were evaluated using the Bonferroni adjustment.

Loads were analyzed in two different ways in order to discern the importance of spatial differences (reach scale) versus seasonal gradients. First, we assessed the short-term significance of rain events by comparing daily loads calculated using routine samples only versus event-based samples averaged over the duration of rain events (i.e., >5 mm within 12–24 day period), with the data grouped by season (summer versus fall), year (2013 versus 2014) and spatial position in the watershed (upper versus lower reach). Secondly, we assessed the seasonal significance of rain events by comparing average daily loads calculated for an entire season using routine samples versus routine samples supplemented with event-based samples, with the data again grouped by season (summer versus fall versus annual), year (2013 versus 2014) and spatial position in the watershed (upper vs lower reach). We then calculated average daily loads over the entire time scale at each site and compared using Kruskal-Wallis tests. The percent error of the estimates calculated for the routine samples compared with routine + event-based estimates was then calculated to quantify the differences between the methods of measuring loads.

3. Results

3.1. Hydrology

All three rivers showed similar hydrological properties during both study years (Fig. 2). Discharge was greatest during snowmelt, with flow during this period accounting for 62–68%, 69–75% and 69–71% of annual flow in the Ells, Mackay and Steepbank rivers, respectively. By comparison, snowmelt flows in the three watersheds for the last ~40-years averaged 55 ± 4%, 56 ± 3% and 46 ± 3% of total annual flow in the Ells (1975–2017), Mackay (1971–2015) and Steepbank (1972–2015) rivers, respectively (Alexander and

Chambers, 2016).

Sizable rain events (>5 mm) occurred after initial snowmelt during spring, summer and fall in all three catchments (Fig. 2). Rainfall events > 5 mm occurred on up to 4 occasions during autosampler deployment in 2013 and up to 17 occasions in 2014 (Table 1). Events averaged 14.95 ± 1.88 mm in fall 2013, 8.93 ± 0.49 mm in summer 2014, and 12.23 ± 1.34 mm in fall 2014. For a given stream and season, event-based sampling captured 17–67% of the > 5 mm rain events and 7–74% of the rain volume. The number of events captured were greater in 2013 (50–67%) than 2014 (8–57%). In 2014, there were higher capture rates for the Mackay and Steepbank watersheds as compared to the Ells (Table 1, Fig. 2).

3.2. Temporal comparisons in concentrations

Concentrations of 12 priority pollutants and two nutrients varied considerably among seasons (snowmelt, spring and fall) across the two study years (Table 2). Average daily concentrations were often correlated (Rho ≥ 0.5, P < 0.05) with discharge: all 14

Table 2

Average concentration and standard error (SE) of nutrients and 12 USEPA identified priority pollutants as determined using routine (R) or event-based (E) sampling during snowmelt (March 1 – May 30, 2013 and 2014), summer (May 31 – August 31, 2014), and fall (September 1 – October 30, 2013 and 2014) for the Ells, MacKay and Steepbank rivers. Also shown are the number (and frequency) of exceedances of Canadian guidelines for the protection of aquatic life (http://ceqg-rcqe.ccme.ca/en/index.html). Significantly higher values (p < 0.05, Kruskal-Wallis tests) between routine and event-based sampling for both summer and fall are highlighted in grey. Concentrations correlated with discharge (Spearman Ranked Correlations) are bolded.

	R – Snowmelt			R – Summer			E – Summer			R – Fall			E – Fall		
	AVG	SE	Guideline (% obs.)	AVG	SE	Guideline (% obs.)	AVG	SE	Guideline (% obs.)	AVG	SE	Guideline (% obs.)	AVG	SE	Guideline (% obs.)
2013		(N=113)			(N = 65)			(N = 263)			(N=8)			(N=72)	
Nutrients (mg/L)															
TN	**1.25**	0.05	-	**1.03**	0.05	-	-	-	-	0.95	0.09	-	**0.97**	0.03	-
TP	**0.30**	0.03	-	**0.15**	0.02	-	-	-	-	0.06	<0.01	-	**0.11**	0.01	-
Priority pollutants (µg/L)															
Sb	**0.08**	0.01	-	**0.05**	<0.01	-	-	-	-	**0.02**	<0.01	-	**0.08**	0.01	-
As	**2.63**	0.28	5 (14%)	**1.76**	0.23	5 (1%)	-	-	-	0.80	0.07	5 (0%)	1.25	0.06	5 (0%)
Be	**0.18**	0.02	-	**0.08**	0.01	-	-	-	-	**0.02**	<0.01	-	0.06	<0.01	-
Cd	**0.04**	<0.01	0.09 (12%)	**0.02**	<0.01	0.09 (0%)	-	-	-	0.01	<0.01	0.09 (0%)	0.03	0.02	0.09 (1%)
Cr	**4.41**	0.57	8.9 (15%)	**1.96**	0.32	8.9 (1%)	-	-	-	**0.26**	0.03	8.9 (0%)	1.29	0.09	8.9 (0%)
Cu	**4.66**	0.54	2 (47%)	**2.14**	0.31	2 (17.7%)	-	-	-	0.55	0.09	2 (0%)	1.24	0.07	2 (13%)
Pb	**2.43**	0.32	2 (40%)	**1.01**	0.17	2 (4%)	-	-	-	0.13	0.02	2 (0%)	0.64	0.05	2 (0%)
Ni	**5.51**	0.63	65 (0%)	**3.03**	0.36	65 (0%)	-	-	-	0.96	0.12	65 (0%)	2.01	0.10	65 (0%)
Se	**0.21**	0.02	1 (2%)	**0.14**	0.01	1 (0%)	-	-	-	0.10	0.01	1 (0%)	0.14	<0.01	1 (0%)
Ag	**0.03**	<0.01	0.25 (0%)	**0.01**	<0.01	0.25 (0%)	-	-	-	<0.01	<0.01	0.25 (0%)	0.01	<0.01	0.25 (0%)
Tl	**0.05**	0.01	0.8 (0%)	**0.02**	<0.01	0.8 (0%)	-	-	-	**<0.01**	<0.01	0.8 (0%)	**0.01**	<0.01	0.8 (0%)
Zn	**14.07**	1.83	7.0 (46%)	**6.01**	0.91	7 (13.3%)	-	-	-	**1.06**	0.22	7 (0%)	5.04	0.04	7 (24%)
2014		(N = 121)			(N = 65)			(N = 263)			(N = 23)			(N = 235)	
Nutrients (mg/L)															
TN	**1.10**	0.04	-	**0.98**	0.04	-	**0.83**	**0.01**	-	**0.65**	0.04		**0.70**	0.01	-
TP	**0.19**	0.02	-	**0.16**	0.02	-	**0.07**	**<0.01**	-	0.04	<0.01		**0.04**	<0.01	-
Priority pollutants (µg/L)															
Sb	**0.07**	<0.01	-	**0.06**	<0.01	-	**0.06**	**<0.01**	-	0.03	<0.01	-	0.05	<0.01	-
As	**1.53**	0.15	5 (3%)	**1.90**	0.22	5 (8%)	**0.36**	0.09	5 (<1%)	0.73	0.03	5 (0%)	**0.83**	0.01	5 (0%)
Be	**0.08**	0.01	-	**0.11**	0.02	-	**0.05**	**<0.01**	-	0.01	<0.01	-	**0.02**	<0.01	-
Cd	**0.03**	<0.01	0.09 (7%)	**0.03**	<0.01	0.09 (0%)	**0.01**	<0.01	0.09 (0%)	<0.01	<0.01	0.09 (0%)	**0.01**	<0.01	(<1%)
Cr	**2.01**	0.27	8.9 (2%)	**2.74**	0.46	8.9 (8%)	**1.14**	**0.09**	8.9 (0%)	0.16	0.02	8.9 (0%)	**0.53**	0.12	8.9 (1%)
Cu	**2.43**	0.28	2 (37%)	**2.92**	0.47	2 (37%)	**1.42**	**0.09**	2 (24%)	0.57	0.08	2 (4%)	**0.61**	0.04	2 (2%)
Pb	**1.18**	0.16	2 (16%)	**1.41**	0.25	2 (20%)	**0.66**	**0.06**	2 (6%)	**0.09**	0.01	2 (<1%)	**0.18**	0.02	2 (<1%)
Ni	**3.09**	0.33	65 (0%)	**3.97**	0.56	65 (0%)	**2.33**	**0.19**	65 (0%)	0.97	0.07	65 (0%)	**1.32**	0.09	65 (0%)
Se	**0.13**	0.01	1 (<1%)	**0.17**	0.02	1 (0%)	**0.11**	**<0.01**	1 (0%)	0.08	<0.01	1 (0%)	**0.08**	<0.01	1 (0%)
Ag	**0.01**	<0.01	0.25 (0%)	**0.02**	<0.01	0.25 (0%)	**0.01**	**<0.01**	0.25 (0%)	< 0.01	<0.01	0.25 (0%)	**<0.01**	<0.01	0.25 (0%)
Tl	**0.02**	<0.01	0.8 (0%)	**0.03**	<0.01	0.8 (0%)	**0.01**	**<0.01**	0.8 (0%)	<0.01	<0.01	0.8 (0%)	**<0.01**	<0.01	0.8 (0%)
Zn	**7.20**	0.95	7.0 (26%)	**8.22**	1.41	7 (31%)	**5.35**	**0.40**	7 (22%)	0.79	0.07	7 (0%)	**1.54**	0.13	7 (2%)

parameters were correlated with discharge during snowmelt and summer for both 2013 and 2014, and a more variable number (2–13 parameters) during fall. Comparison of concentrations with Canadian Water Quality Guidelines for Protection of Aquatic Life (CCME, 2017) showed that As, Cd, Cr, Cu, Pb, Se, and Zn from individual samples exceeded guidelines during both event and routine sampling regimes, albeit to varying degrees (Table 2). Routine samples collected during spring snowmelt had the highest number of exceedances: 7 of 10 parameters exceeded guidelines with a frequency of 2–46% of samples. In contrast, routine samples collected during fall had the lowest frequency of exceedances: only 2 of 10 parameters exceeded guidelines, with a frequency of < 3% of samples. Exceedances occurred more frequently for event-based samples than routine samples during fall: 3 exceedances with a frequency of 1–24% in event-based samples versus 0 exceedances in routine samples during fall 2013 and, similarly, 5 exceedances with a frequency of < 1–2% in event-based samples versus 2 exceedances with a frequency of < 1–4% in routine samples during fall 2014. There were more exceedances (5 vs 4) with higher frequency (8–31% vs <1–24%) in routine samples in the summer than event-based (Table 2).

Comparison of routine versus event-based samples showed that during fall, event samples had, on average, greater concentrations (Tables 2 and 3). During fall, 14 of 14 comparisons in 2013 and 8 of 14 comparisons in 2014 were greater for event-based sampling. The opposite was true during summer 2014: 11 of 14 comparisons were greater for routine sampling whereas none were greater for event-based sampling. The parameters most likely to show elevated concentrations associated with fall event samples were Sb, Be, Cd, Cr, Pb and Zn, whereas during summer, highest concentrations were observed for TN, TP, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag and Tl from routine samples.

3.3. *Temporal and Spatial pattern in loads*

Average daily loads estimated for the duration of rain events differed when calculated using routine-only samples versus event-based samples from the same time period (Tables 4a and 5). Rain-event loads were greater ($P < 0.05$) when calculated using event-based samples (as opposed to routine samples) for a total of 48 of 84 comparisons (57%, all data combined). When examined seasonally, daily loads during rain events were greater when calculated using event-based samples versus routine samples for 46 of 56 (82%) fall comparisons (2013 and 2014 data combined) but only 2 of 28 (7%) summer comparisons. Spatially, there was no observable difference between the frequency of greater loads calculated using event-based samples as compared to routine samples for upper (24 of 41 (57%)) versus lower (24 of 41 (57%)) reaches. Certain parameters often had greater loads during rain events when calculated using event-based samples, for example Sb, Cd, Cr, Pb, Ag, Tl and Zn (Tables 4a and 5).

Although inclusion of event-based samples resulted in greater estimates of daily loads during fall rain events (Tables 4a and 5), the influence of event sampling on load estimates was dampened when incorporated into a longer time period. Thus, when daily loads at lower reach sites were expressed for an entire season, only 6 of 14 (46%) comparisons during fall 2013, 0 of 14 (0%) comparisons during summer 2014, and 5 of 14 (36%) comparisons during fall 2014 were greater with inclusion of event-based samples (Tables 4b and 6). Similar results were found for upper reach sites whereby the influence of event-based sampling on daily loads was dampened when the time period was extended from days (i.e., an event) to an entire season. Moreover, on an annual basis, average daily loads exhibited no differences when calculated using samples from routine monitoring versus a combination of routine plus event-based sampling (0 of 14 comparisons annually; Table S1).

4. Discussion

Analysis of chemical loads in three rivers draining Canada's Alberta Oil Sands region showed that the contribution of rain events to loading of nutrients and priority pollutants differed temporally. During fall, when baseflow conditions prevailed, daily loads averaged over a rain event were significantly greater when event-based samples (as compared to only routine samples) were included in calculations. These improved estimates were particularly evident for parameters such as Sb, Cd, Cr, Pb, Ag, Tl and Zn. In contrast, the inclusion of summer and fall rain-event samples did not change annual pollutant loads because of the overwhelming influence of snowmelt on annual loads. Overall, this study supports the prevailing view that in the oil sands region of Alberta, the contribution from spring snowmelt to annual loads is profound. Thus, if the purpose of water quality sampling is to accurately estimate annual loads, then intensive monitoring during freshet followed by intermittent monitoring during other seasons is appropriate, given the short-lived effect of summer and fall rain events on chemical concentrations. However, studies investigating seasonal phenomena (e.g., aquatic

Table 3
Comparison of concentrations measured in event-based (E) versus routine (R) samples, with sampling sites grouped temporally as fall or summer. Comparisons are based on comparing E versus R concentrations for a given parameter and site such that the number of comparisons equals 14 parameters x 3 streams (2 streams in fall 2013) x 2 sites per stream (upper and lower).

Time Period	Number of measurements used to estimate sig. differences in parameters		Parameters E > R	E:R	Parameters with E:R ≥ 3
	E	R			
Fall					
2013	72	8	14 of 14 (100%)	2.98	Sb, Be, Cd, Pb, Zn
2014	235	65	8 of 14 (57%)	1.65	Cr
Summer					
2013	NA	NA	NA	NA	NA
2014	263	23	0 of 14 (0%)	NA	NA

Table 4
Comparison of event-based (E) versus routine (R) average daily loads calculated using routine samples only or routine + event (E + R) samples for samples collected during rain events, fall, summer or annually. E = event, R = routine.

Time Period and Site Location	Number of measurements used to estimate sig. differences in parameters	Variables E > R	Average E:R across parameters	Parameters with E:R≥ 3	
a. Average daily load during rain events calculated using E versus R data					
Fall 2013					
Upper Reach	24	14 of 14 (100%)	4.56	TP, Sb, Be, Cd, Cr, Pb, Ni, Ag, Tl, Zn	
Lower Reach	49	13 of 14 (93%)	3.13	Sb, Cd, Cr, Pb, Ag, Tl, Zn	
Summer 2014					
Upper Reach	67	2 of 14 (14%)	2.61	Zn	
Lower Reach	53	0 of 14 (0%)	NA	NA	
Fall 2014					
Upper Reach	64	8 of 14 (57%)	1.40	NA	
Lower Reach	63	11 of 14 (79%)	2.02	Cr	
b. Average daily load for entire season calculated using E + R versus R data					
Time Period and Site Location	Number of measurements used to estimate sig. differences in parameters		E + R>R	Average E + R:R across parameters	Parameters with E:R ≥ 3
	R	E + R			
Fall 2013					
Upper Reach	61	37	13 of 14 (93%)	2.82	Be, Cr, Pb, Ag, Tl, Zn
Lower Reach	122	98	6 of 14 (46%)	2.40	Pb
Summer 2014					
Upper Reach	280	270	0 of 14 (0%)	NA	NA
Lower Reach	360	347	0 of 14 (0%)	NA	NA
Fall 2014					
Upper Reach	215	215	0 of 14 (0%)	NA	NA
Lower Reach	181	181	5 of 14 (36%)	1.29	NA

chemistry during summer or fall), guideline exceedance, or life-history stage of a particular organism likely need to consider the magnitude of spikes in concentrations and loads associated with summer and fall rainstorms.

Previous studies examining temporal variation in metal concentration in water bodies in the oil sands region of Alberta have focused on either longer (seasonal or annual: e.g., Alexander and Chambers, 2016; Headley et al., 2005; Kurek et al., 2013) or very short (Gerner et al., 2017; Guéguen et al., 2011; Lavoie et al., 2012; Shotyk et al., 2017) time scales. Our results highlight the importance of including precipitation events in estimates of metal loads during periods of lower flow. Notably, our results showed that during fall, concentrations of nutrients and priority pollutants were higher for event-based samples compared to routine samples. As a result, daily loads during fall were greater using calculated event-based vs routine samples for 0 – 93% of comparisons. However, when event-based data were incorporated into a longer-term annual dataset, the seasonal event signal was lost: 0% of parameters were significantly higher for event-based + routine as compared to just routine sampling. Our analysis focused on 36 individual events and, for every event, direct comparison was made between loads calculated using routine only versus routine + rain-event data. Given that this study was conducted during the latter part of a more than 25-year increase in precipitation in the region, we might expect to see even greater import of seasonal contributions in the future due to climate change (see Alexander et al., 2017, http://wateroffice.ec.gc.ca).

The above finding is also consistent with reports from the literature showing that precision differs when calculating loads on a seasonal versus annual basis. For example, Kerr et al. (2016) showed that precision in measurements of solute loads for southern Ontario streams differed between annual and monthly sampling such that precision was generally lower for seasonal load estimates relative to annual. Further, Kerr et al. (2016) reported that highly soluble solutes that were positively correlated with discharge during spring flow periods tended to have a positive bias in annual load estimation whereas less soluble compounds were more likely to be underestimated. In our study, annual loads of many solutes were dominated by spring melt contributions, such that seasonal loads would be influenced by baseflow and precipitation events making them inherently more variable. Similarly, Headley et al. (2005) observed higher concentrations of metals in tributaries of the oil sands region during spring versus fall. While these studies did not evaluate the influence of precipitation events, Droppo et al. (2019), also working in Canada's oil sands region, showed elevated hydrocarbons in runoff following fall rain events, such that average daily loads were up to 4.1 fold higher for event-based samples as compared to routine sampling. In our study, significantly greater loads were calculated using routine + event-based data for the fall sampling period (e.g., Sb, Be, Pb, and Zn in both 2013 and 2014), resulting in higher load estimates than would otherwise be observed from routine monitoring in the region. Our findings, and those of others, show that over short time scales, routine sampling may easily miss substantial contributions of elements or increase variability in solute measures if major rain events are not captured.

Despite previous studies identifying differences in chemical concentrations between upper and lower reach sites along tributaries draining the oil sands region (e.g., Headley et al., 2005), we did not find a consistent effect of inclusion of rain event samples on loads

Table 5
Comparison of average summer (May 1 – August 31, 2013 and 2014) and fall (September 1 – October 31, 2013 and 2014) average daily load (kg/day) of nutrients and total metals at the upper and lower reaches of Ells, Mackay and Steepbank Rivers combined, as determined from routine monitoring (R) or event-based storm sampling (E). Significantly higher differences between routine and event-based fall average daily loads within each reach are indicated by gray shaded boxes as determined by a Kruskal-Wallis test. The percent difference was calculated for loads that were identified as significant.

	Upper										Lower									
	R - Summer		E - Summer		Diff	R - Fall		E - Fall		Diff	R - Summer		E - Summer		Diff	R - Fall		E - Fall		Diff
	AVG	SE	% Diff	SE		AVG	SE	AVG	SE		AVG	SE	AVG	SE		AVG	SE	AVG	SE	
2013																				
TN	-	-	-	-		356.52	41.37	659.57	19.73	1.9x	-	-	-	-		661.13	64.41	742.30	71.80	
TP	-	-	-	-		21.41	2.55	88.58	9.14	4.1x	-	-	-	-		42.39	4.11	77.67	9.39	1.8x
Sb†	-	-	-	-		11.41	1.83	39.12	13.39	3.4x	-	-	-	-		19.48	2.32	68.45	8.87	3.5x
As	-	-	-	-		0.30	0.03	0.82	0.07	2.7x	-	-	-	-		0.54	0.05	0.84	0.09	1.6x
Be†	-	-	-	-		6.95	0.95	36.82	3.79	5.3x	-	-	-	-		15.33	1.70	44.42	4.96	2.9x
Cd†	-	-	-	-		2.96	0.39	10.04	0.97	3.4x	-	-	-	-		5.76	0.61	20.07	9.15	3.5x
Cr	-	-	-	-		0.12	0.02	0.86	0.10	7.2x	-	-	-	-		0.21	0.03	1.00	0.13	4.8x
Cu	-	-	-	-		0.40	0.06	0.79	0.08	2.0x	-	-	-	-		0.39	0.04	0.98	0.11	1.1x
Pb	-	-	-	-		0.06	0.01	0.42	0.05	7.0x	-	-	-	-		0.10	0.01	0.49	0.06	4.9x
Ni	-	-	-	-		0.35	0.04	1.26	0.10	3.5x	-	-	-	-		0.68	0.07	1.58	0.16	2.3x
Se†	-	-	-	-		41.94	5.04	77.91	3.31	1.9x	-	-	-	-		65.99	7.01	111.58	8.57	1.7x
Ag†	-	-	-	-		0.72	0.10	5.29	0.56	7.3x	-	-	-	-		1.34	0.13	5.88	0.73	4.4x
Tl†	-	-	-	-		1.07	0.16	8.85	1.03	8.3x	-	-	-	-		2.25	0.30	9.92	1.22	4.4x
Zn	-	-	-	-		0.60	0.09	3.57	0.50	6.0x	-	-	-	-		0.96	0.12	3.77	0.50	3.9x
2014																				
TN	753.54	78.70	712.85	93.90		176.22	17.15	192.00	16.99		1416.58	196.29	1466.24	251.18		318.08	34.81	350.24	35.24	
TP	71.25	8.87	69.80	10.74		11.71	1.09	12.30	1.09		130.22	19.22	112.50	20.76		19.41	2.09	20.79	2.04	
Sb†	22.91	3.63	45.98	6.62		7.46	0.56	10.73	1.41	1.4x	45.65	5.87	75.43	11.96		12.92	1.12	18.71	1.32	1.5x
As	0.91	0.10	1.36	0.32	2.0x	0.18	0.01	0.20	0.01	1.1x	1.75	0.24	1.77	0.28		0.33	0.03	0.39	0.03	
Be†	29.96	5.1	54.72	10.05		2.61	0.32	3.28	0.36		64.09	10.86	85.97	16.24		5.16	0.66	9.38	1.15	1.8x
Cd†	8.42	1.26	14.61	2.56		1.02	0.10	1.55	0.16	1.5x	17.69	2.80	18.23	3.38		2.13	0.25	4.75	1.55	2.2x
Cr	0.68	0.13	1.41	0.27		0.05	0.01	0.08	0.01	1.6x	1.46	0.26	2.06	0.40		0.10	0.01	0.46	0.20	4.6x
Cu	0.90	0.15	1.47	0.26		0.10	0.01	0.11	0.01		1.93	0.31	2.80	0.55		0.22	0.02	0.38	0.05	1.7x
Pb	0.35	0.06	0.87	0.17		0.02	<0.01	0.03	<0.01	1.5	0.75	0.13	1.13	0.22		0.05	0.01	0.10	0.01	2.0x
Ni	1.39	0.21	2.19	0.36		0.21	0.02	0.23	0.02	1.1x	3.36	0.56	3.58	0.61		0.45	0.04	0.84	0.15	1.9x
Se†	86.68	10.49	82.82	11.30		17.00	0.99	18.68	1.15		168.34	23.82	146.24	22.38		31.67	2.81	39.87	2.66	1.3x
Ag†	4.96	0.89	8.07	1.55		0.34	0.03	0.50	0.05	1.5x	10.80	1.87	12.32	2.47		0.68	0.07	1.21	0.14	1.8x
Tl†	8.29	1.52	15.94	3.07		0.55	0.05	0.70	0.07		16.04	2.72	21.79	4.03		1.29	0.14	2.04	0.24	1.6x
Zn	2.25	0.38	7.21	1.33	3.2x	0.21	0.02	0.36	0.04	1.7x	5.19	0.87	7.66	1.41		0.38	0.05	0.75	0.08	2.0x

from upper and lower reach sites. Observations of average loads calculated from routine vs event-based samples showed that differences in measured parameters between the upper and lower reach sites was largest during fall 2014 when more parameters (79%) were significantly higher for event-based sampling than routine in lower reaches as compared to the upper reach (57%). In contrast, during both fall 2013 and summer 2014, more parameters had significantly higher routine than event-based loads in the upper reaches (100% and 14% respectively) as compared to the lower reaches (93% and 0% respectively). The lack of a clear spatial pattern could be due to a combination of natural and anthropogenic conditions. First, the Ells and Mackay rivers are surface water dominated (45–81%) whereas the Steepbank River has a sizable groundwater contribution (50% groundwater versus 23% surface water) (Gibson et al., 2016). This is consistent with the basic drainage patterns of these watersheds: the upper tributaries of the Ells and Mackay run parallel with the lower catchments, suggesting that these rivers overlay pronounced localized faults resulting in rapid changes in catchment grade (Fig. 1, see Gordon et al., 2004) whereas the Steepbank has a more U-shaped drainage pattern and is known to deeply incise multiple geological strata of varying soft and hard consistencies (Prior et al., 2019). Second, the extent of oil sands development differs among the watersheds. Specifically, the percent of developed land relative to total watershed area is 3.79%, 1.06% and 0.68% for the Steepbank, Ells and Mackay, respectively, with an even greater comparative difference when only the upper catchment area is considered (1.54%, 0.79% and 0.16% for the Steepbank, Ells and Mackay, respectively). Third, muskeg-type habitats are present in these watersheds, particularly in the upper portions of catchments (see Atlas of Alberta Lakes, 1990; Mitchell and Prepas, 1990), and can confound water storage and drainage patterns. Complex interactions between the land and surface waters likely contribute to differences in the response of upper catchments to rain events, resulting in variable "fill and spill" responses. As the present study was conducted over a limited timescale, additional study over multiple years is needed to establish the factors affecting spatial patterns in watershed chemistry.

In Canada's oil sands region, fall water quality monitoring was until recently the norm, with the focus on sampling during base flow but not during rain events (e.g., Culp et al., 2021; Hatfield Consultants Partnership, 2009). This sampling period was chosen on the assumption that any pollutants lost as a result of mining operations were likely transported by seepage or overland flow pathways and thus would be present in highest concentrations during baseflow. Effective monitoring of northern river systems requires knowledge not only of optimal sampling locations, but also of optimal timing. Our results highlight the importance of sampling during rain events, especially during autumn baseflow periods, in order to capture peak concentrations, determine frequency of guideline exceedance, and investigate the importance of seasonal flux. Collection of a single, base-flow measure of water during biological sampling overlooks both longer term periods (e.g., preceding months to entire seasons) and fall rain events to which sampled organisms are exposed. If rain events are not sampled during periods dominated by baseflow, there is a bias toward lower concentrations and loads of nutrient and

Table 6
Comparison of average summer (May 1 – August 31, 2013 and 2014) and fall (September 1 – October 31, 2013 and 2014) average load (kg/day) of nutrients and total metals at the upper and lower reaches of Ells, Mackay and Steepbank Rivers combined, as determined from routine monitoring (R) or event-based storm sampling + routine monitoring (E + R) over the entire time period. Significantly higher differences between routine and routine + event-based fall average daily loads within each reach are indicated by gray shaded boxes as determined by a Kruskal-Wallis test. The percent difference was calculated for loads that were identified as significant.

	Upper										Lower									
	Routine Summer		E + R - Summer		% Diff	Routine Fall		E + R - Fall		% Diff	Routine Summer		E + R - Summer		% Diff	Routine Fall		E + R - Fall		% Diff
	AVG	SE	AVG	SE		AVG	SE	AVG	SE		AVG	SE	AVG	SE		AVG	SE	AVG	SE	
2013																				
TN	-	-	-	-		298.89	27.81	418.11	34.17	1.4x	-	-	-	-		450.78	36.85	495.61	40.12	
TP	-	-	-	-		19.39	2.11	45.82	5.94	2.4x	-	-	-	-		28.98	2.41	42.49	4.73	
Sb†	-	-	-	-		8.20	1.13	19.10	43.84	2.3x	-	-	-	-		13.37	1.27	30.85	4.39	2.3x
As	-	-	-	-		0.27	0.03	0.48	0.05	1.8x	-	-	-	-		0.40	0.03	0.55	0.05	
Be†	-	-	-	-		5.45	0.61	17.20	2.54	3.2x	-	-	-	-		9.13	1.02	19.81	2.69	2.2x
Cd†	-	-	-	-		2.58	0.30	5.37	0.66	2.1x	-	-	-	-		3.56	0.35	5.39	0.64	
Cr	-	-	-	-		0.09	0.01	0.38	0.06	4.2x	-	-	-	-		0.14	0.01	0.42	0.07	
Cu	-	-	-	-		0.28	0.04	0.44	0.05		-	-	-	-		0.25	0.02	0.47	0.06	
Pb	-	-	-	-		0.05	0.01	0.19	0.03	3.8x	-	-	-	-		0.07	0.01	0.21	0.03	3.0x
Ni	-	-	-	-		0.30	0.03	0.65	0.08	2.2x	-	-	-	-		0.50	0.04	0.83	0.09	1.7x
Se†	-	-	-	-		32.83	3.09	46.99	4.09	1.4x	-	-	-	-		42.63	4.32	57.59	5.80	
Ag†	-	-	-	-		0.67	0.09	2.47	0.37	3.7x	-	-	-	-		1.01	0.09	2.68	0.37	
Tl†	-	-	-	-		0.84	0.10	3.90	5.08	4.6x	-	-	-	-		1.60	0.15	4.33	0.63	2.7x
Zn	-	-	-	-		0.44	0.06	1.61	0.28	3.7x	-	-	-	-		0.65	0.07	1.64	0.25	2.5x
2014																				
TN	1279.96	96.03	1232.70	94.84		477.20	49.80	456.92	48.90		2065.54	189.95	2118.73	196.29		308.29	19.16	319.25	19.42	
TP	224.02	30.63	215.13	30.33		34.41	4.76	31.96	4.72		421.48	60.90	432.76	62.28		18.36	1.15	18.83	1.15	
Sb†	78.38	10.25	81.82	10.16		13.16	2.00	15.12	2.04		156.64	21.47	168.89	22.30		13.22	0.58	15.23	0.65	1.2x
As	2.39	0.29	2.46	0.30		0.41	0.04	0.39	0.04		4.53	0.58	4.71	0.60		0.31	0.02	0.33	0.02	
Be†	141.79	22.10	144.62	22.11		11.39	2.01	11.73	2.02		286.67	42.00	300.76	42.93		4.45	0.35	5.90	0.51	1.3x
Cd†	30.28	4.26	31.01	4.26		3.92	0.68	3.98	0.69		73.91	12.71	78.75	13.47		1.78	0.13	2.66	0.56	
Cr	3.61	0.57	3.71	0.57		0.30	0.06	0.30	0.06		7.11	1.04	7.46	1.06		0.09	0.01	0.21	0.07	
Cu	3.71	0.56	3.77	0.56		0.30	0.04	0.31	0.04		7.88	1.15	8.37	1.19		0.19	0.01	0.24	0.02	1.3x
Pb	1.82	0.29	1.71	0.29		0.13	0.03	0.15	0.03		3.94	0.61	4.18	0.63		0.05	<0.01	0.07	0.01	1.4x
Ni	4.93	0.70	5.02	0.70		0.52	0.06	0.52	0.64		10.05	1.35	10.45	1.38		0.43	0.02	0.56	0.06	
Se†	204.39	22.84	197.52	22.72		39.24	3.82	37.32	3.77		419.41	55.56	432.83	57.77		20.52	1.51	33.36	1.52	
Ag†	19.73	2.93	20.04	2.94		1.79	0.29	1.78	0.29		42.21	6.31	44.32	6.53		0.58	0.04	0.76	0.06	
Tl†	38.98	5.95	40.00	5.96		3.57	0.79	3.67	0.79		88.88	14.06	94.29	14.62		1.11	0.07	1.36	0.10	
Zn	10.54	1.62	11.63	1.64		1.12	0.21	1.22	0.22		23.22	3.57	24.75	3.70		0.37	0.03	0.49	0.04	1.3x

priority pollutant loads. Monitoring programs that sample during baseline conditions in order, for example, to successfully capture aquatic biota would benefit from incorporating the additional chemical variability associated with rain events.

5. Conclusions

The contribution of rain events to chemical daily loads varies temporally. During fall, when baseflow conditions prevailed, average loads were lower when calculated using routine only data versus routine + rain-event data. However, on an annual basis, the inclusion of rain-event sampling did not significantly change estimated pollutant loads, largely because of the overwhelming influence of snowmelt on annual load estimates. Temporal scaling of the influence of rain events on elemental loads has implications for the design of water and ecological quality monitoring programs. If a sampling campaign spans only a few days or weeks, it is critical that all streams be sampled during similar weather conditions so as to avoid misleading comparisons of chemistry from streams sampled during or following a rain event versus streams sampled under dry or even drought-like conditions (Alexander et al., 2020; Headley et al., 2005). In the cold regions of northern Alberta, Canada, our results showed that under the present climatological conditions, the contribution of rain events to seasonal or annual element loads is negligible if a sampling campaign spans months or years. However, if a sampling campaign focuses only on baseflow conditions and neglects rain events (e.g., during fall), concentrations and loads for the event and even the entire baseflow period can be seriously under-estimated, which may have important implications for assessments of the health of aquatic biota. Evidence presented here showcases this importance with respect to exceedances of water quality guidelines, where more parameters showed exceedances, and with greater frequency during fall for event-based sampling regimes as compared to the more standard 'routine sampling'.

Climate change models predict warmer temperatures (by 5 °C annually and as much as 8 °C in winter), a 1–2 week advance in snowmelt, an increase in precipitation quantity (by 20% overall and by 30% during winter) and variability (more extreme with more precipitation occurring in fewer days) in Canada's oil sands region by the end of this Century (IPCC, 2007; Jiang et al., 2017). The predictions of a shorter snow season with more precipitation falling as rain rather than snow reinforce the need for adaptive management of monitoring programs to ensure that in future, the timing of water chemistry sampling is consistent with the changing pattern in frequency and intensity of precipitation.

CRediT authorship contribution statement

Kathryn Thomas was involved with data curation, formal analysis, methodology, writing original draft, reviewing and editing. Alexa Alexander-Trusiak was involved with conceptualization of the project, data curation, funding acquisition, investigation, methodology, project administration, supervision, reviewing and editing of the written paper. Patricia Chambers was involved with conceptualization of the project, funding acquisition, methodology, project administration, supervision, reviewing and editing of the written paper.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ejrh.2022.101028.

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