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RESEARCH ARTICLE

Metals and PFAS in stormwater and surface runoff in a semi-arid Canadian city subject to large variations in temperature among seasons

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Abstract

Because compounds accumulate through dry periods and enter aquatic systems in just a few seasonal events such as snowmelt and summer storms, surface waters in semi-arid, cold regions, such as the Canadian Prairies, are particularly vulnerable to loading of contaminant from runoff events from surfaces. This study assessed concentrations of metals and selected trace organics entering a river via surface runoff from an urban region and how these semi-arid regions with large seasonal variations in temperature might differ from more temperate regions. Selected potentially harmful elements (PHEs) including, Mn with Cr, Cu, Zn, Ba and U all exceeded guideline discharge values set by the Canadian Council of the Ministers of the Environment (CCME) by as much as 16-fold. Variation among discharges during spring, summer and winter was observed. For example, across the whole city, an estimated 6 kg of zinc was discharged in a spring storm, 36 kg in a summer storm and 17 tonnes in snowmelt. The mass of Zn discharged is similar to the annual loading estimated for Stockholm, Sweden, but in Saskatoon, Saskatchewan, Canada, the bulk of runoff was during snowmelt. The mean sum of poly- and per-fluoroalkyl substances (PFAS) in stormwater was 9.0 ng L^{-1}, which is consistent with concentrations observed in other Canadian cities (6.5–16 ng L^{-1}). These concentrations of PFAS are likely due to dispersed sources and orders of magnitude less than thresholds for toxicity to fish and aquatic invertebrates.

Keywords Inorganic · Organic · Contaminants · Stormwater · Snowmelt · Seasonality · PFAS · North America · Prairies

Introduction

Urban development often involves removal of vegetation and modification of pervious areas with impervious materials, which results in a change in dynamics and compositions of surface water runoff (Goonetilleke et al. 2005). A range of contaminants can accumulate on these surfaces by dry deposition, which can then be mobilised during rainfall or snowmelt (Djukić et al. 2016). Over the last century, humans have generated millions of chemicals and artificially modified distributions of natural elements including metals (Woodruff et al. 2011). Today in most countries, domestic sewage and industrial wastes are closely monitored for a range of chemicals. Such that their release into the environment can be regulated and managed, stormwater however can bypass treatment altogether or diminish the efficacy of combined sewer systems (Kadlec and Knight 1996; Westerbeek-Vopicka 2009). It was calculated that in the Canadian Great Lakes region, annually, 10,000 tonnes of suspended solids, 1000 tonnes of chloride, 100 tonnes of oil and 75 tonnes of

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trace metals were discharged from urban areas (Marsalek and Ng 1989; Marsalek et al. 2008). In terms of discharge volume and solids loads, urban runoff can exceed those associated with municipal wastewater (Biswas 2003).

Potentially harmful elements (PHE, formally known as trace/heavy metals) generally represent the predominant contamination of concern associated with urban runoff (Loganathan et al. 1997; Göbel et al. 2007; Hvitved-Jacobsen et al. 2010; Gasperi et al. 2012). In urban environments, there can be multiple sources of PHEs, including building materials that are a source of zinc (Zn) and pipes used for drinking water that can contribute copper (Cu) or lead (Pb) (Sörme and Lagerkvist 2002). Roads and vehicles are sources of PHEs such as cadmium (Cd), nickel (Ni) and chromium (Cr) (Liu et al. 2014). It is estimated that PHEs from roads and roofs combined represent up to 44% of metals in runoff in urban areas (Hullmann and Kraft 2002).

Most PHE are classified as trace elements because they are typically detected at ng L^{-1} concentrations in aquatic systems. However, in stormwater, concentrations of these elements can be significantly greater and can exceed water quality guidelines (Karlsson et al. 2010). Predicting toxicity of PHEs in surface waters is not simple due to variations in parameters that can affect bioavailability of PHEs, including hardness, alkalinity, pH and organic carbon (Hamelink et al. 1994; Allen and Hansen 1996; Luthy et al. 2003). Furthermore, detection of PHEs is typically limited to the elemental form rather than the environmental state. For example, Cu is an essential micro nutrient; however, it cycles between a reduced Cu (I) and an oxidised state Cu (II); this property has made copper essential in plants and animals, but it can also generate hydroxide and superoxide radicals (Leppard 2013). Due to their toxicity, prevalence and persistence, Pb and Zn are of particular concern in aquatic systems (Stern 2010).

PHEs are not the only contaminants of concern in stormwater, which can contain complex mixtures of organic chemicals. Stormwater represents a significant source of trace organic compounds to aquatic ecosystems (Horner 1994; Buffleben et al. 2002; Rossi et al. 2004). One class of concern are the poly- and per-fluoroalkyl substances (PFAS). Unlike the traditional priority pollutants, because PFASs have a range of uses in urban environments, such as hydraulics, firefighting, paper, textiles and carpets, apportionment of sources for PFAS is difficult. Industrial use of PFAS during manufacture may create point sources, but often, diffuse inputs from domestic use are major contributors to stormwater (Paul et al. 2009). Also, PFASs are much more soluble in water than in many neutral, halogenated organic compounds.

There is no standardised method for management of stormwater. In some cities, sewage and stormwater are in separate flows, while in others, they are combined (Burton Jr and Pitt 2001). Some stormwater systems have retaining ponds that aim to remove suspended solids through sedimentation, but these themselves become sinks of contaminants, and other regions allow sewage and stormwater to go untreated to a receiving water body during periods of high water flow (Kadlec and Knight 1996; Westerbeek-Vopicka 2009). Techniques for remediation of water contaminated with metals and trace organics have utilised waste plant material, such as shells of seeds and coffee production by-products, and others introduced synthetic materials to actively take up hazardous substances (Kumar et al. 2011; Anitha et al. 2015a, b; Cobas et al. 2016; Neeraj et al. 2016; Prabu et al. 2016; Gunasundari and Kumar 2017; Saravanan et al. 2018; Suganya and Kumar 2018). However, adaptation to use in fast-flowing stormwater with no opportunity to optimise for pH, temperature or filtration would create variability in the effectiveness of such options, especially with the sporadic nature of precipitation in prairie regions.

The Canadian Council of Ministers of the Environment (CCME) has produced a series of water quality guidelines for discharge of various waters (industrial, household waste and stormwater) and in 2009 developed a guideline to mitigate episodic events skewing mean discharge values in stormwater (CCME 2001, 2009, 2011). However, these guidelines and recommendations were developed considering moderate climates and relatively homogenous weather patterns and do not take into account more extreme conditions such as in the Canadian Prairies.

The prairies of Canada are characterised by long, cold winters, during which snow can accumulate over 5–6 months with brief but intense rainstorms during summer. These climatic conditions lead to situations of long accumulation and rapid mobilisation of contaminants during runoff events. This can potentially create periods of significant acute toxicological risk to aquatic ecosystems. One representative example of a city situated in the prairies is the city of Saskatoon in Saskatchewan, Canada. Stormwater drainage in the city is via drains not linked to the municipal wastewater system and has limited contaminant management capacity. As the drains are independent of wastewater, samples are not influenced by domestic sewage. Stormwater retention ponds are in use to reduce loading of particle-bound contaminants and slow flow. However, due to the cold winters, the ponds tend to freeze solid so sediments are picked up by the ice or the ponds may be less effective during spring than in temperate regions due to loss of vegetation.

The objectives of this study were to investigate stormwater and runoff discharge for PHE and PFAS within the city of Saskatoon, during two representative episodic runoff events, spring melt and summer storms. PHEs were primary compounds of interest due to their prevalence in stormwater and potential toxicity. Selected PFAS were studied only during snowmelt, representing additional contaminants of concern in urban environments. PFAS (carboxylate and sulfonate PFAS) were selected based on their potential to accumulate in snow solubility in water.

Materials and methods

Chemicals and reagents

Target compounds were 24 PHEs, including beryllium (Be), aluminium (Al), titanium (Ti),vanadium (V), Cr, Fe, manganese (Mn), cobalt (Co), Ni, Cu, Zn, arsenic (As), selenium (Se), strontium (Sr), molybdenum (Mo), Ag, cadmium (Cd), Tin (Sn), antimony (Sb), barium (Ba), mercury (Hg), thallium (Tl), Pb and uranium (U) and 17 PFAS (PFAS details are summarised in supplementary information (SI) Table 1). All solvents used were HPLC or better, and for PFAS, these were distilled or SPE filtered prior to use (SI 1.1 provides further detail on the solvents and reagents quality controls). The certified reference material (CRM) used for confirmation in metal identification was the NIST 1640a from LGC standards (Middlesex, UK).

Sampling area–Saskatoon

Saskatoon is the largest city in the province of Saskatchewan, Canada. It has a growing population of ~ 261 thousand inhabitants within the city proper covering an area of 170.83 km^2 (Saskatoon 2015). Estimates of the rate of expansion and growth predict that over the next 10–15 years the population could double, leading to a significant increase in pressure on current infrastructures including drinking, waste and stormwater facilities and infrastructure. The city itself is bisected by the South Saskatchewan River, which provides drinking water to a large portion of the central Canadian region (Fig. 1). Mean annual precipitation is 350 mm, with an annual temperature range between − 35 and 35 °C. Snow cover can last as long as 6 months with no or little intermediate melt representing 30–50% of annual precipitation. Summer precipitation typically occurs during a few severe storms.

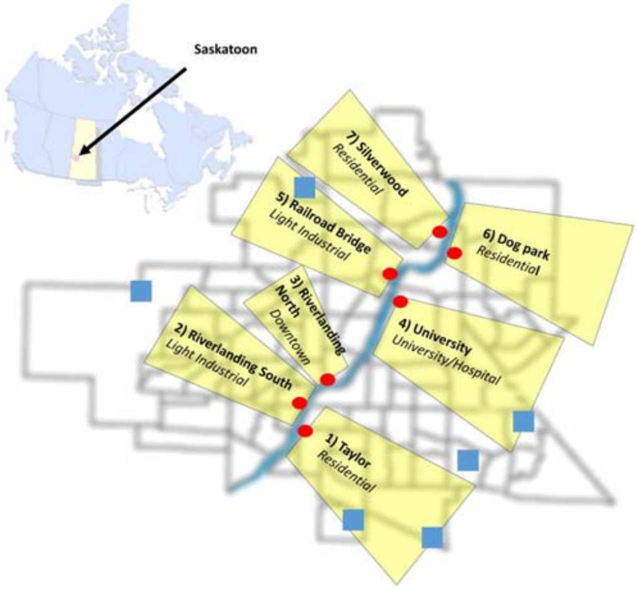

Fig. 1 Sampling locations at stormwater drains (circles). The yellow-shaded region indicates the suspected drainage area for each storm drain. Blue squares are locations of stormwater retention ponds; the size of ponds vary. Each storm drain (1–7) represents the major drains for the whole city

Sample collection

Three periods during which significant runoff events occurred were selected, spring melt (March to April 2013) and after rainstorms in late spring (May) and summer (August) 2012. Samples were collected from storm sewer outfalls along the urban stretch of the South Saskatchewan River that represent various urban developments, including residential, light industrial and retail (Fig. 1). Glass amber bottles (4 L) were used for metal analysis and Nalgene bottles (2 L; high-density polyethylene) were selected for PFAS. Collection was by hand sampling where possible or a pre-cleaned food-grade bucket on a rope during high flow events. For spring and summer storm events, 7 locations (1–7 Locs.) were selected for collection (Fig. 1), while during snowmelt collection, 4 Locs. were identified for daily sampling (Locs. 1, 4, 5 and 7). Due to restricted accessibility, fewer samples were collected in winter. All samples were collected between mid-day and 13:00 with the exception of 1 day during melt when morning and afternoon samples were taken to investigate short-term variance (more detail on the collection methods and locations are provided in SI 1.2.)

Sample extraction and chemical analyses

The focus of this study was limited to assessment of compounds detected in the dissolved phase. All samples were filtered through 0.42-μm filters; polycarbonate for metals and pre-baked glass-fibre for trace organics (GFF; pre-baked at 450 °C for 12 h). Metals were identified by inductively coupled plasma mass spectrometry (ICPMS; Thermo X Series II ICP-MS, Thermo-Scientific, MA USA) (Vardy et al. 2013, 2014). ICPMS was operated in ‘normal’ mode, following EPA method ILM05.2D, with a 40-s flash period followed by a 55-s read delay followed by a 55-s measurement period and 120-wash period per sample. Quantification was performed using an external calibration curve and validated with a CRM and blanks.

Pre-conditioned HLB cartridges (Walters Milford OH) concentrated individual PFAS samples from 1-L water samples. Each sample was fortified with surrogate compounds (listed in SI Table 1). For cleanup, 0.5 g of Envicarb was added to the sample tube and the sample was vortexed for 30 s and shaken for 20 min (min) at 2000 rpm, using a bench shaker (Heidolph MultiReax, Germany) then passed through an Acrodisc syringe filters with 0.2 μm particle size (VWR international BV, Amsterdam). This was then taken to dryness under a gentle N_2 stream and dissolved in 200 μL of MeOH with 0.1% acetic acid containing 50 ng mL^{-1} of $^{13}C_8$-PFOA as internal standard. PFAS were measured by LC-MS/MS (3500 MS AB-SCIEX; ON Canada), using a previously published method (Codling et al. 2014b).

Quality control and analysis

Field and laboratory blanks were generated from nanopure water taken to and from the sample site. All glassware was baked at 450 °C or solvent-rinsed using acetone > hexane > methylene chloride (DCM).

Recoveries of PHEs were determined by use of certified reference material (CRM 1640a), with recoveries between 97.4% for chromium (Cr) and 109% for U, with a maximum standard deviation of 10%. Two exceptions were beryllium (Be; 174%) and vanadium (V; 124%) that both had a high standard deviation of 31 and 18%, respectively. Limits of detection (LOD) was calculated from triplicate laboratory water samples injected at intervals during analysis and calculated as either 3 times the baseline or, if detected, 3 times the peak height. Field blanks were exposed on site that had ± 10% of the laboratory blank with the exception of V whose lab blank was < LOD, while field blanks were ~ 12 μg Kg^{-1}. For Cr, V and Sn the majority of sample sites were < MDL defined as 3 times the mean of the field blanks added to 3 times the standard deviation; metals that were < LOQ (limit of quantification) set at 10 times the baseline were omitted (SI Table 2).

For identification of PFAS, two fragment ions were used along with formulae determined parent mass, and identified compounds were validated against existing literature. The LOD was defined as 3 times the baseline, and LOQ was defined as 10 times the baseline. Where no mass-labelled standard was available for individual PFAS, samples were calibrated by use of compounds with ± 1 carbon chain. Thus, concentrations of these are deemed semi-quantitative. Samples that exceeded the calibration curve were subsequently diluted to fit within the linear range. Average PFAS recoveries of 9 ^{13}C mass-labelled compounds were 74% (31–121). Recovery of shorter chain PFAS was poorer than a longer chain, with these recoveries similar to that seen in previous studies (Skutlarek et al. 2006; Ahrens et al. 2010; Codling et al. 2014a).

Statistical analysis

Pearson's correlation using Excel 2016 (Microsoft 2016) was initially used, but given the small number of samples, statistical significance was limited. Log-transformed concentrations of PHEs were used to offset the large variance inherent in concentrations of compounds like Zn. Simca 14 (Umetrics, Malmö Sweden) was used to perform multivariate analysis; initially, nearest neighbour squared Euclidean for primary relationship identification followed by orthogonal partial least squares discriminant analysis (OPLS-DA) was used to identify relationships between sample locations and observed compounds. OPLS-DA was performed using a minimum of 50% observational tolerance and variance scaling. Non-detected values were not substituted with proxy LOD values.

Results and discussion

PHE overview

Of the 24 PHE studied, concentrations of Be and Ag were typically < LOD, (LODs were 0.38 μg L^{-1} and 0.02 μg L^{-1}, respectively), while concentrations of Ba, Zn, Mn and Sr were the most abundant metals across all sampling events (Fig. 2). Concentrations of Cu, Cr, Al, Mn. and Zn were comparable to those reported in other studies (SI Table 3). While concentrations of Fe appeared to be greater than those reported for other locations. However, the material used at the end of the stormwater pipes in Saskatoon was made of iron and can reflect a localised input. Concentrations of lead (Pb) in this study were significantly less than that seen in other studies of stormwater. However, leaded gasoline accounted for 20% of sales in 1999, but the US and Canada began to phase out leaded gasoline in 1996 and 1993, respectively, so concentrations of Pb observed during older studies can be the result of greater use of leaded fuels ((UNEP) 1999). An additional source of Pb might be from pipes themselves, and lesser concentrations of Pb can be a result of the city of Saskatoon being a young city (founded in 1883), and thus has fewer buildings built before 1950 where lead piping would have been used (Saskatoon 2016).

During snowmelt, six metals (Cr, Mn, Cu, Zn, Ba and U) exceeded guidelines for freshwater quality in Canadian water systems (SI Table 5). For example, the CCME value for Mn is < 50 μg L^{-1} (CCME 2009). This value was exceeded by up to 16-fold in 53% of samples with a mean concentration of 240 μg L^{-1} discharged into the South Saskatchewan River. Since uranium (U) is a naturally occurring mineral of the region (Hecht and Cuney 2000), it might indicate that water from these locations had some exposure to open land. This is substantiated by the drainage area of the university location (Loc. 4) that is surrounded by fields to the north and east. Concentrations of U did not exceed the short-term exposure guidelines, which is 30 μg L^{-1}, but did on 2 occasions for samples from Locs. 1 and 4 that exceed long-term exposure concentrations of 15 μg L^{-1}. U is the only PHE for which both short- and long-term exposure values are provided.

During spring and summer, discharges of the seven metals studied (Cr, Cu, Mo, Ni, Se, U and Zn) exceeded guidelines only for Cr and Cu during spring for two and one sample(s)

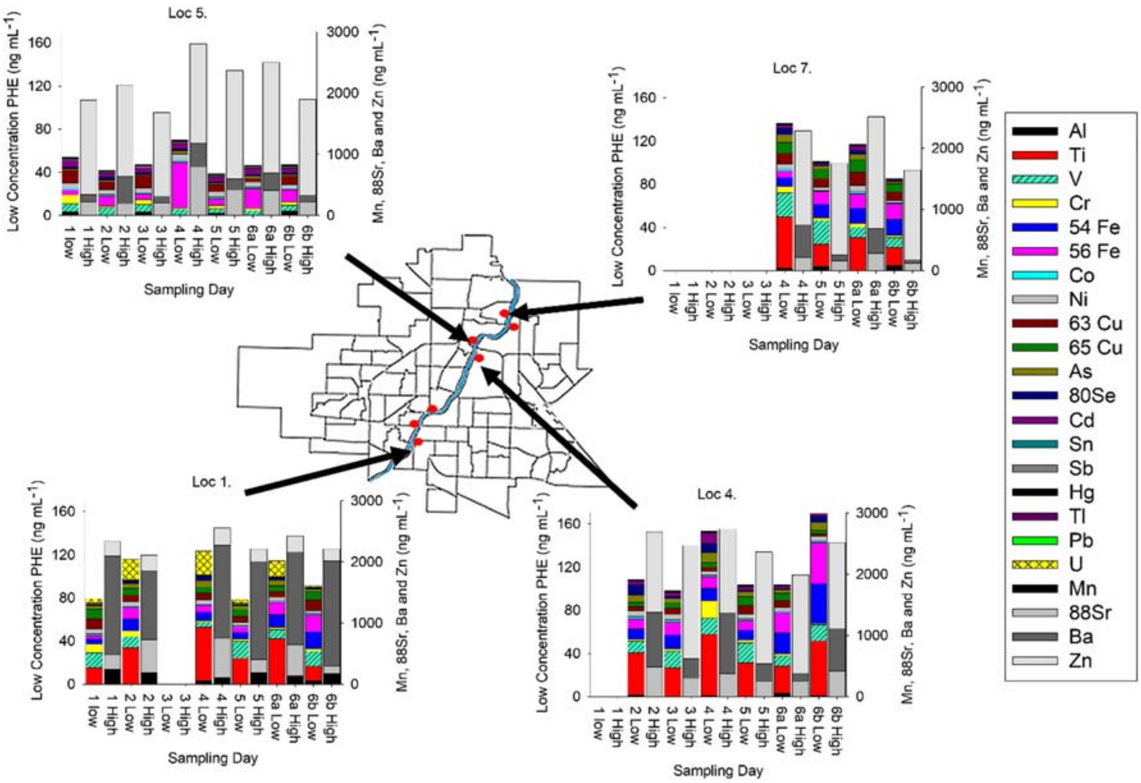

Fig. 2 Stormwater discharge of PHE over a 7-day period at 4 locations (Locs. 1, 4, 5 and 7) during spring melt 2013. PHE of low concentration < 100 ng mL^{-1} are presented in the left *Y*-axis, while Mn, 88Sr, Ba and Zn are in a separate axis; on the *X*-axis, the low concentration PHE are all compounds excluding Mn, Sr, Ba and Zn

respectively. In summer, Cr, Cu and Zn all exceeded guideline concentrations with all locations being above the recommended concentrations for Cu and, with the exception of Loc. 1, Cr. For Zn, however, guideline values were exceeded only at Locs. 2, 3 and 5.

Prediction of hazards posed by concentrations of metals measured in this study was not possible because no accompanying water quality parameters such as other cations and anions, dissolved organic carbon (DOC), alkalinity and hardness were measured. Toxicity of elements in the environment depends on their speciation as well as their potential binding to organic molecules such as DOC. However, based on concentrations of some metals analysed here that exceeded guidelines by up to 16-fold, hazard to local aquatic wildlife cannot be excluded (SI Table 4). Cu and Zn concentrations measured in stormwater after the summer storm and snowmelt, respectively, in this study, exceeded acute LC50 and chronic LC20 values derived for early life stages of white sturgeon from the Columbia River after exposure (Vardy et al. 2014). Acute LC50s for other species like the fathead minnow and juvenile rainbow trout (Vardy et al. 2013) are slightly greater than concentrations measured in runoff. However, to fully understand the potential risks and hazards posed to surface waters, volume and water flow of the river would be needed coupled to the flow from each outfall.

Seasonal variation

There were significant variations in concentrations of all PHEs among these three sampling periods (Fig. 3). When a CV-ANOVA to assess reliability of the OPLS-DA was performed, the Q2 (cum) for the OPLS-DA, which is the cumulative total variation for all x and y variables for the extracted components, the Q2 was > 0.5. This can be regarded as good, and a Q2 > 0.9 as excellent fits (Eriksson et al. 2003). In this study, predictability of the model was good (Q2 of 0.59), with Zn being the most important element, while Mo, U, Cu and Ni all had similar importance in the model and Se being the least important variable. A p value < 0.05 indicates significance, and this was calculated in this study (0.048), which indicated that there was significant difference between the sample periods (Eriksson et al. 2008).

By using masses of PHEs, measured at each storm drain, the volume of precipitation and adjusting for the total city area estimations of the minimum, maximum and median concentrations that could enter the South Saskatchewan River were calculated. Details of the calculation and formula are provided in the SI (SI 1.3, *Area Calculation of Precipitation*). The PHEs Cr, Cu, Mo, Ni, Se, U and Zn were used for comparison. The greatest contribution of PHEs was from metallic zinc that caused melt samples to vary greatly between spring and summer. During the spring storm, between 3 and 20 kg of zinc

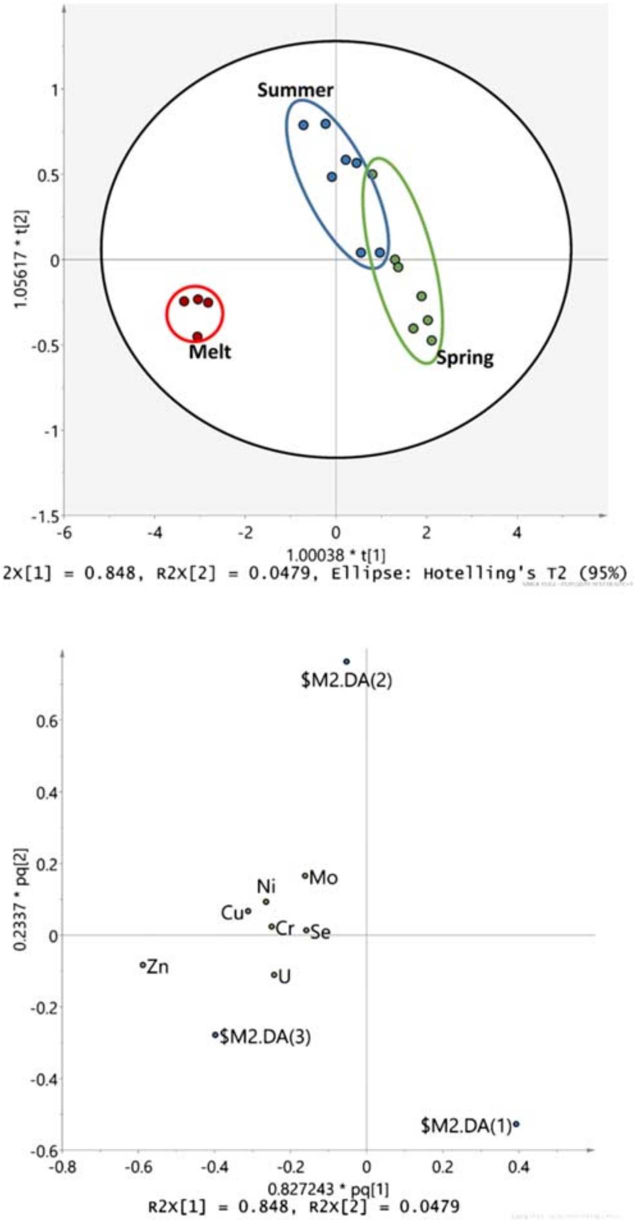

Fig. 3 OPLS-DA plot of spring (green), summer (blue) and snowmelt (red) for all sampling locations for seven metals using the log-transformed results to offset the greater concentrations of Zn

entered the river (median concentration of 6 kg), while in summer, 16–309 kg was estimated (median of 36 kg). In winter, estimates for runoff from snowmelt were 13–16 tonnes (median 16 tonnes). In comparison, Stockholm Sweden, with an area of 215.4 km^2, had an estimated annual loading of 17 tonnes of metallic zinc (Palm and Östlund 1996). The annual loading of zinc to Sydney Harbour Australia was estimated to be 17.7 tonnes (Birch and Rochford 2010). For Sydney Harbour (Australia), loadings of Cr, Cu and Ni were estimated to be 0.5, 1.7 and 1.1 tonnes, compared with 0.3, 0.4 and 0.3 from Saskatoon, SK, during this study. Elevated concentrations of Zn were not surprising given its presence in a range of urban building materials, and it is the most water soluble of the PHEs. In the aquatic environment, 30–50% of zinc is in the dissolved phase. In a study conducted at the University of Maryland in the USA, it was found that Zn was often present at concentrations several orders of magnitude greater than Pb, Cu or Cd in building materials including bricks, painted wood, metals and concrete (Santore et al. 2001). Zn is also used as a filler in car tires that is lost during wear, so this can also be a significant source for this metal (Davis et al. 2001). Given that the greatest concentration was observed in snowmelt runoff, it may be that this has accumulated in the snowpack, perhaps due to tire wear and tear. The variation observed between summer and spring may reflect a buildup from dry deposition and accumulation, with differences simply a factor of time between wet events (i.e. rainfall, snowmelt or previous storms).

Agencies of the Canadian Government measures river flow across the country. Station code 05 HG 001 measured the discharge flow of the South Saskatchewan River at Saskatoon. The discharge was 104–123, 83–89 and 290–323 m^3 s^{-1} for spring, summer and snowmelt respectively. By adjusting the total input to surface water flow, an approximate normalisation was performed. Even taking into account the greater river flow concentrations in surface water during melt for Zn would still be two to three orders of magnitude greater than at other times. However, for most other PHEs, only a 10-fold greater concentration was observed between median concentrations, and comparing maximum values in spring and summer to mean winter, there is close approximation.

Intensive snowmelt study of PHEs

The pattern of discharge of PHEs, studied over 7 days (M1–7) of snowmelt across four locations (Locs. 1, 4, 5 and 7; Fig. 2 for PHE), indicated that a classic discharge pattern of more soluble compounds were present in the 'first flush' of melt, and the less soluble would be released as time progresses (Meyer et al. 2011).

At each location, the mean for each day was investigated for discharge patterns during melt (SI Table 5). Pearson's correlations, where 1.0 indicates a strong correlation and zero no correlation, were used in the assessment. The slope of the trend was also calculated such that positive values would indicate an increase in time while negative values would indicate a decrease from the first sample. As no flow rates were available for individual drains, calculation of loadings was not possible and a low number of samples did not allow for testing of the statistical significance.

For individual samples, Loc. 5 exhibited a poor correlation, either positive or negative for most PHEs, which was caused by a peak observed on the 4th day of sampling. This storm drain is near a light industrial region and has a stormwater retention tank built to control discharge that might affect concentrations. Loc. 5 also was unique in having a near stable concentration of tin (Sn) entering from that storm drain at a mean concentration of 1.3 μg L^{-1} that were several orders of magnitude greater than those at other locations were where a mean of 0.04 μg L^{-1} was observed. Location 7 had the greatest correlations both positive and negative but with just four samples, this is not valid for assessment. Fe and Al indicated strong positive correlations with melt progression with the exception of Loc. 5 (r^2 0.12 and r^2 0.27 for Fe and Al respectively). Ni has a strong negative correlation ($r^2 > 0.63$ in 3 out of 4 samples). Other PHEs have either poor correlation or positive and negative correlation between individual locations.

Mean concentrations at all locations for each sample day were used to assess the overall trend of discharge into the South Saskatchewan River. A strong positive correlation was observed for Fe (r^2 0.70) and negative correlations for Co (r^2 0.51), Ni (r^2 0.88), Zn (r^2 0.65) and Sn (r^2 0.59). Since Co and Zn are among the most soluble metals, the observed decrease in concentrations might be a direct result of compounds washing out of snowpack. While the increase observed for Fe may be a result of the increase in solubility as temperatures increased.

PFAS

PFASs were studied for 7 days of melt (M6 to M13) in 2013 to understand better the loading of these compounds and their variability with snowmelt (Fig. 4). Samples are labelled from M6 to align dates with PHE collected during the same period. Of the 17 compounds this study focussed upon, perfluoro-n-butanoic acid (PFBA), perfluoro-n-undecanoic acid (PFUnA), perfluoro-n-dodecanoic acid (PFDoA), sodium Perfluoro-1-decanesulfonate (PFDS), perfluoro-1-octanesulfonamide (FOSA) and perfluoro-1-octanesulfonamidoacetic acid (FOSAA) were not detected above the LOD.

In a laboratory study of PFAS in a melting snowpack, it was shown that the elution sequence of each compound was determined by their physical-chemical properties with the more soluble compounds eluting first and those more associated with particles last (Plassmann et al. 2011). In the field, this process was less clear (Codling et al. 2014a). In Japan, a first flush effect following rainfall revealed concentrations of PFAS exceeding 100 ng mL^{-1} for specific compounds (Zushi and Masunaga 2009). Though the first flush was not captured in this study, concentrations observed for individual PFAS reflect those reported in other Canadian cities where individual PFASs were between 6.5 and 14.0 ng L^{-1} (Plassmann et al. 2011). For the two most commonly described PFAS, no observable effect concentrations (NOECs) for specific aquatic species typically range from 0.53 to 46.9 mg L^{-1} for perfluoro-n-octanoic acid (PFOA) and 0.05 to 206 mg L^{-1} for perfluoro-n-octanesulfonic acid (PFOS), depending upon species. Thus, concentrations of PFAS measured in this study are not likely to pose a risk to ecological receptors in receiving water bodies, as these concentrations were orders of magnitude below those having previously reported being biologically active (Tobiszewski and Namieśnik 2012).

With the exception of PFBA, PFHpA and PFHxA, concentrations observed from the first sampling to the last decrease with time (SI Table 7). This indicates that the PFASs are being washed from the snowpack. Unfortunately, during this study, the ‘first flush’ event where potentially the maximum observed concentrations of water-soluble PFAS might have been measured was missed. For Locs. 1, 4 and 5, strong negative correlations were observed for PFOA ($r^2 > 0.57$) and a strong positive correlation for PFBA ($r^2 > 0.8$). PFBA being one of the most soluble compounds to find that concentrations increase with time is difficult to interpret unless the warming period is mobilising secondary sources such as ice. Taking the average of each day of sampling, however, no linear trend was observed for sample day and concentrations measured (SI Table 7).

Variability in snowmelt sampling during a day

During snowmelt, sampling temperatures ranged from 10 °C to below freezing during the night, which resulted in different flow rates of stormwater from morning to evening (SI Figure 1). On day 6 (M6), samples for both metals and PFAS were collected at the same four locations (Locs. 1, 4, 5 and 7). There were clear differences in concentrations of PHE among locations. Concentrations of U, Mn and Co were greater in the morning compared with the afternoon, while concentrations of PFOA and Cu tended to be greater in the afternoon (SI Figures 2 and 3). There are many factors that might have caused these differences, including the greater flow rate mobilising more particles or changing the pH, thus altering the solubility of the compounds within the storm drain system. In a laboratory study of PFAS, ageing of snowpack and thus the specific surface area might be key in how PFAS elute from a snowpack (Meyer et al. 2011; Plassmann et al. 2011). However, in the environment, many features such as ice layers can affect how compounds can move through a snowpack (Codling et al. 2014a).

This study opened multiple avenues for further exploration into stormwater in semi-arid Canadian cities. Concentrations of PFAS and PAHs (unpublished data) indicated that there is a need to further investigate the concentrations of organic contaminants in stormwater outflow, especially employing emerging technology such as high-resolution mass spectrometers. Exceedances of CCME guidelines for metals during each sampling period requires sampling over a greater period during a single event and also over multiple storm events to understand the total input from each storm and the annual

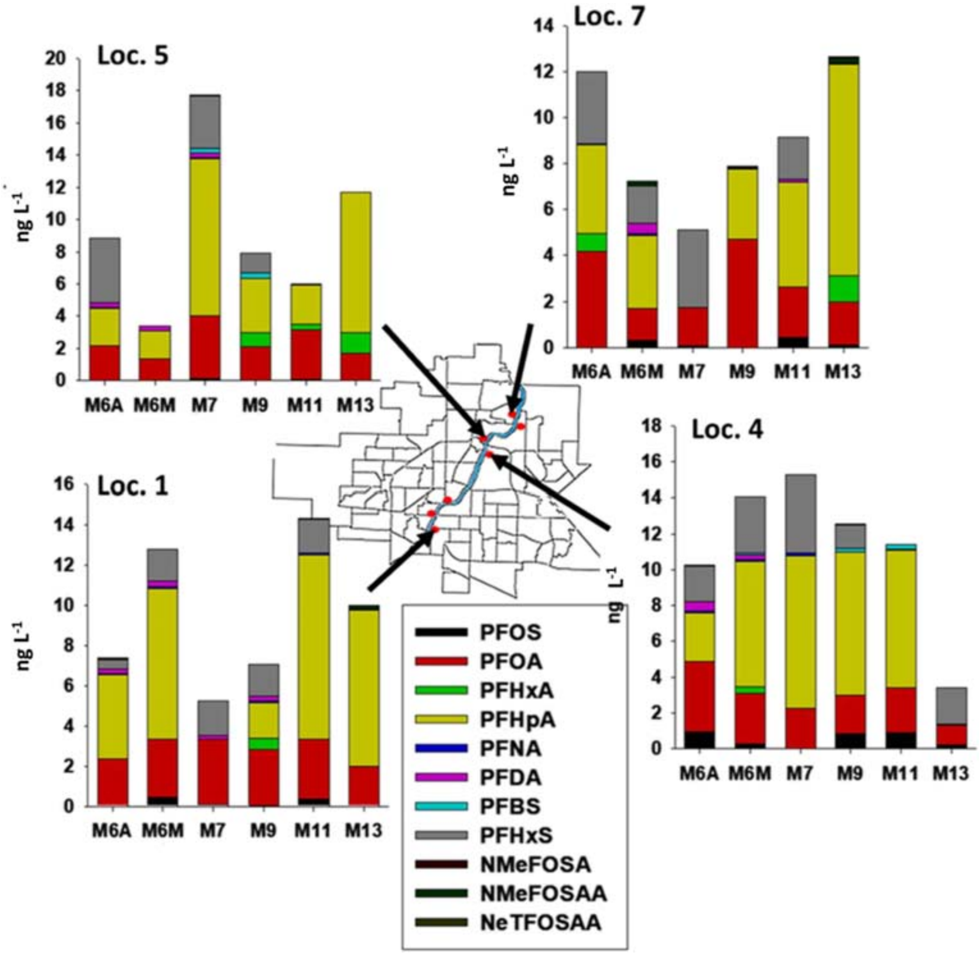

Fig. 4 Poly- and per-fluorinated compounds (PFAS) in stormwater from snowmelt during 7 days of sampling in 2013, at 4 locations within the city of Saskatoon (Locs. 1, 4, 5 and 7). For M6, morning and afternoon samples were collected, while for all other days, a mid-day collection was performed

mean input. For winter, accumulation of snow samples should be measured across the city along with the stormwater to gauge the actual input from snow and the melt behaviour to stormwater input.

Conclusions

Cold, semi-arid climates such as the Canadian Prairies face unique challenges with regard to monitoring and assessment of contaminants introduced into surface water through stormwater runoff. In fact, these cryospheric and dry systems are of particular risk of periodic influxes of contaminants because summer storms and winter snow accumulation represent predominant factors in discharge after significant and extended accumulation periods of substances on urban surfaces. This study demonstrated that the periodic runoff events due to snowmelt or summer storms represent significant sources for metals and select organic pollutants that can exceed current water quality guidelines by up to 16-fold for Cr and 15-fold for Mn. The current approach in monitoring contaminant inputs from stormwater into surface waters does not consider events occurring in dry and cold climates that are characterised by summer storms and snowmelt, and thus does not capture these important events. Therefore, to advance our understanding of the larger picture of stormwater as a significant source of contaminants to surface waters, these extreme conditions need to be taken into account. Further work will be needed to identify if the discharge poses a threat to aquatic health and to determine the long-term trends in stormwater contamination through a more systematic approach. However, to enable a more realistic assessment of the potential risks associated with PHEs and organic contaminants in stormwater in a cryospheric environment, a more detailed approach is needed. Additional focus that measures additional water quality parameters are needed to enable prediction of toxicological risks of metals using the biotic ligand model (Santore et al. 2001), as well as consider overall loadings and dilution in the receiving water body and interactions with organic contaminants (Gauthier et al. 2014). Furthermore, more resolution in sampling is needed to identify fully some of the trends that were loosely defined through this preliminary assessment.

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Supplementary Information

Metals and PFAS in Storm Water and Surface Runoff in a Semi-arid Canadian City Subject to Large Variations in Temperature among Seasons.

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SI 1. Detailed Methods

SI 1.1 Chemicals

Methanol (MeOH) tested prior to analysis for PFAS extraction and was identified as having perfluoro-n-octanoic acid (PFOA) contamination after a 1000 fold concentration. Therefore all MeOH used was first distilled, testing identified no PFAS above the LOD following distillation. Nano pure water used for PFAS extraction or analysis was subject to solid phase extraction (SPE) through Oasis WAX cartridges prior to use (6 cc 150 mg Waters, Milford MA, USA). The water after passing through the SPE was collected and tested for PFAS and no PFAS were identified above the LOD. Extraction for PFAS and PAHs was through Oasis HLB cartridges (6 cc 600 mg Waters Milford MA, USA). Sodium sulphate and Envicarb used in the clean-up of samples were from Sigma Aldrich (Oakville Ontario, Canada). The certified reference material (CRM) used for confirmation in metal identification was the USEPA 23 metals from LGC standards (Middlesex, UK).

SI 1.2. Sample Collection

Three periods during which significant runoff events occurred were selected, spring melt (March to April 2013), and after rainstorms in late spring (May) and summer (August) 2012. In winter all precipitation is in the form of snow that is retained until spring melt and in summer the dominate precipitation is rainstorms. These samples represent non-normal events, however, during the year, most storm sewers have no flow so during water flow events accumulated contaminants are mobilized and are discharged directly into the South Saskatchewan River.

All bottles were pre-washed with acetone, hexane, methyl chloride and methanol in series and left in a fume hood to dry. The use of MeOH as final rinse was due to its miscibility with water and DCM. During collection, each bottle was rinsed three times with water from the sample site. Most samples were collected by hand on site though where flow rate and environmental factors prevented a pre-cleaned bucket on a rope was used.

SI 1.3 Area Calculation of precipitation

In order to assess the variability between snowfall and storm events samples were adjusted to the precipitation volume. During May and August, 2012 storm events 50 mm and 43 mm of rainfall was recorded respectively. Snow was adjusted to snow water equivalent (SWE) by taking the average density of wind packed snow as 470 kg m^{-3} and an average depth of 1.1 m (Equation 1).

$$SWE\ (L) = D\ (m) * \text{f}(kg\ m^2)\ \ (1)$$

Water volume was then calculated for the whole city municipality taking an area of 170.83 km^2. Factoring this in an estimate water equivalent of 7.2 x 10^{10} L is calculated. However, the city of Saskatoon took 22’000 trucks of snow from the city (Saskatoon 2014). Assuming this is aged snow with a density of 470 kg m^{-3} and a truck has an average volume of 20 m^3 it may carry 7510.3 L per truck or 1.65 x 10^8 L removed during winter of 2012-2013. Thus, the meltwater volume was adjusted to account for this loss. Final volumes of precipitation was estimated at 8.5 x 10^9, 7.5 x 10^9 and 7.2 x 10^{10} L for spring, summer and winter meltwater respectively. It is expected some overestimation due to some percolation into the soils but during first melt the ground remains frozen and after long dry periods the heavy rain does not soak well into dry soils.

SI Tables

SI Table 1: PFAS Screened for in this study and the mass-labeled recovery standards.

SI Table 2: Metal ratio meltwater, spring and summer samples win the minimum and maximum ratio against the CCME guidelines.

Si Table 3: Comparison of concentrations of metals in stormwater.

SI Table 4: Water quality guidelines for metals from the Canadian Council of Ministers of the Environment (CCME), United States Environment Protection Agency, World Health Organization (WHO), BIS (ISI) Environment Center, Indian Council on Medical Research (ICMR), Central Pollution Control Board (CPCB). CCME values are based upon freshwater concentrations under short-term exposure where possible or long-term where no short-term values are available. Cu, Pb, and Ni are all based upon a water hardness or 180 mg L^{-1}.

SI Table 5 Metal concentrations over the spring melt.

SI Table 6: The Pearson correlation between sample day and concentration observed during the melt. With if the correlation is positive (increases with melt period) or negative (decreases with melt) given by + for the increase and – for the decrease.

SI Figures

SI Figure 1: The nearest neighbour cluster for PHEs during snowmelt. Clusters are derived from squared Euclidean distance calculations in the hieratical single linkage. The full cluster is shown in the cut out while a more zoomed in groupings is placed below for easier sample identification. M and A placed after the melt (M) 6 are for morning and afternoon samples taken on the same day. Calculations were done using The Unscrambler X software (Camo Norway).

SI Figure 2: Images from the 6th day of stormwater sampling during melt (M6) for the morning (left) and the late afternoon (right) from the University (UNI) sample location.

SI Figure 3: Morning and Afternoon Variability of metals from M6 snowmelt for low concentration metals (A) and those more abundant (B). Positive values are those where morning concentrations were greatest and negative where afternoon water had greater concentration. The Y-axis represents the variation between the two-time points.

SI Figure 4: PFOA variability between morning and afternoon sampling on M6.

SI Tables

SI Table 1: PFAS Screened for in this study and the mass-labeled recovery standards. The instrument detection limit (IDL) is calculated as 3 times the baseline.**Abrev**

	Perfluoroalkyl compounds	**Cas No.**	**Formula**	**Mass**	Parent Ion	Daughter	IDL (ng mL-1)
PFBA	Perfluoro-n-butanoic acid	375-22-4	$C_4HF_7O_2$	214.0396	213	169	1
PFHxA	Perfluoro-n-hexanoic acid	307-24-4	$C_6HF_{11}O_2$	314.0552	313	269	0.1
PFHpA	Perfluoro-n-heptanoic acid	375-85-9	$C_7HF_{13}O_2$	364.063	363	319	0.1
PFOA	Perfluoro-n-octanoic acid	335-67-1	C8HF15O2	414.0708	413	369	0.5
PFNA	Perfluoro-n-nonanoic acid	375-95-1	$C_9HF_{17}O_2$	464.0786	463	419	1
PFDA	Perfluoro-n-decanoic acid	335-76-2	$C_{10}HF_{19}O_2$	514.0864	513	469	0.1
PFUnA	Perfluoro-n-undecanoic acid	218-165-4	$C_{11}HF_{21}O_2$	564.0942	563	519	1
PFDoA	Perfluoro-n-dodecanoic acid	335-76-2	$C_{12}HF_{23}O_2$	614.102	613	569	0.1
PFBS	Potassium Perfluoro-1-butanesulfonate	29420-49-3	$C_4F_9SO_3K$	338.1901	299	99	1
PFHxS	Sodium Perfluoro-1-hexanesulfonate	2832-45-3	$C_6F_{13}SO_3Na$	422.0972	399	99	1
PFOS	Sodium Perfluoro-1-octanesulfonate	2795-39-3	$C_8F_{17}SO_3Na$	522.1129	499	99	0.5
PFDS	Sodium Perfluoro-1-decanesulfonate	13419-61-9	$C_{10}F_{21}SO_3Na$	622.1285	599	99	0.5
Perfluorinated precursors							
FOSA	Perfluoro-1-octanesulfonamide	1691-99-2	$C_8H_2F_{17}NO_2S$	499.15	498	78	1
MeFOSA	N-methylperfluoro-1-octanesulfonamide	24448-09-7	$C_9H_4F_{17}NO_2S$	513.17	512	169	1
FOSAA	Perfluoro-1-octanesulfonamidoacetic acid		$C_{10}H_4F_{17}NO_4S$	557.18	556	498	1
MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid		$C_{11}H_8F_{17}NO_4S$	571.21	570	419	1
EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid		$C_{12}H_8F_{17}NO_4S$	585.24	584	419	1
Mass Labelled Recovery Standards							
NaPFHxS [M+4]	sodium perfluoro-1-hexane [$^{18}O_2$]sulfonate		$C_6F_{13}S^{18}O_2{}^{16}ONa$	426.0968	403	103	
NaPFOS [M+4]	sodium perfluoro-1- [1,2,3,4-$^{13}C_4$]octanesulfonate		$^{13}C_4{}^{12}C_4F_{17}SO_3Na$	526.0823	503	99	
PFBA [M+4]	perfluoro-n-[1,2,3,4-$^{13}C_4$] butanoic acid		$^{13}C_4HF_7O_2$	218.009	217	172	
PFHxA [M+2]	perfluoro-n-[1,2-$^{13}C_2$] hexanoic acid		$^{13}C2^{12}C_4HF_{11}O_2$	316.0399	315	270	
PFOA [M+4]	perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid		$^{13}C_4{}^{12}C_4HF_{15}O_2$	418.0402	417	372	
PFNA [M+5]	perfluoro-n-[1,2,3,4,5-$^{13}C_5$] nonanoic acid		$^{13}C_5{}^{12}C_4HF_{17}O_2$	469.0404	468	423	
PFDA [M+2]	perfluoro-n-[1,2-$^{13}C_2$] decanoic acid		$^{13}C_2{}^{12}C_8HF_{19}O_2$	516.0711	515	470	
PFUdA [M+2]	perfluoro-n-[1,2-$^{13}C_2$] undecanoic acid		$^{13}C_2{}^{12}C_9HF_{21}O_2$	566.0789	565	520	
PFDoA [M+2]	perfluoro-n-[1,2-$^{13}C_2$] dodecanoic acid		$^{13}C_2{}^{12}C_{10}HF_{23}O_2$	616.0867	615	570	

SI Table 2 Metal concentrations over the spring melt. The LOD (limit of detection) includes instrumental and sample digestion procedures. Certified reference material (1640a) and blanks were used for digestion and analytical procedures. Be and V did not pass instrumental QA/QC (quality assurance/quality control).

Final Results (ug/kg)	**Be**	**Al**	**Ti**	**V**	**Cr**	**54 Fe**	**Mn**	**56 Fe**	**Co**	**Ni**	**63 Cu**	**65 Cu**	**Zn**	**As**	**80Se**	**88Sr**	**Mo**	**Ag**	**Cd**	**Sn**	**Sb**	**Ba**	**Hg**	**Tl**	**Pb**	**U**
A rerun of June 28																									
Blank water Chem	<LOD	<LOD	<LOD	<LOD	1.0	2.4	0.3	2.8	<LOD	<LOD	0.7	0.9	5.0	<LOD	<LOD	0.3	0.1	<LOD	<LOD	0.2	0.1	6.7	0.1	0.0	0.1	<LOD
Taylor M4 Apr. 1/13	<LOD	3.6	49.2	4.2	1.8	7.4	107.1	7.3	1.1	3.7	5.7	6.0	279.5	6.1	3.9	649.7	2.1	<LOD	0.4	0.1	0.5	1516.0	0.3	0.0	0.2	22.2
University M4 Apr. 1/13	<LOD	<LOD	57.6	14.8	16.7	11.4	376.9	10.4	1.7	3.6	3.6	4.5	62.3	9.1	8.0	984.4	10.4	<LOD	0.4	0.1	0.6	1378.0	0.2	0.0	0.1	18.0
Silverwood M4 Apr. 1/13	<LOD	2.5	47.2	22.4	5.9	8.1	212.1	6.2	1.6	4.9	9.5	10.2	327.6	7.3	5.8	527.5	3.1	<LOD	0.4	0.1	0.9	1543.0	0.1	0.0	0.2	14.4
Taylor M5 Apr. 3/13	<LOD	<LOD	24.0	15.6	2.3	5.9	187.8	5.2	1.1	3.2	5.6	6.2	202.1	3.6	0.9	213.2	2.3	<LOD	0.2	0.0	0.8	1609.0	0.2	0.0	0.1	3.6
Silverwood M5 Apr. 2/13	<LOD	4.0	20.3	22.0	2.6	12.7	157.7	11.9	1.1	2.9	8.1	8.4	143.1	2.9	0.9	101.1	2.0	<LOD	0.2	0.1	0.8	1493.0	0.1	0.0	0.1	0.9
University M5 Apr. 2/13	<LOD	<LOD	31.4	18.4	2.5	9.3	257.9	8.8	1.6	4.3	8.0	8.5	270.3	4.3	1.4	278.2	3.4	<LOD	0.3	0.0	1.0	1827.0	0.2	0.0	0.2	3.7
University M6 Afternoon Apr. 3/13	<LOD	3.3	24.8	9.6	2.2	19.1	258.6	18.8	1.4	3.3	6.6	6.8	146.2	2.9	0.7	123.6	2.5	<LOD	0.2	0.0	0.9	1606.0	0.1	0.0	0.2	1.2
Taylor M6 Morning Apr. 3/13	<LOD	<LOD	42.1	8.3	2.3	11.7	142.0	11.5	1.1	3.6	4.9	5.5	265.2	5.1	2.0	504.7	2.0	<LOD	0.3	0.0	0.6	1513.0	<LOD	0.0	0.2	14.8
University M6 Morning Apr. 3/13	<LOD	<LOD	51.6	15.1	1.1	36.9	416.5	37.9	1.7	4.3	2.3	3.2	300.2	7.2	5.6	687.6	2.7	<LOD	0.4	0.0	0.6	1415.0	<LOD	0.0	0.2	14.2
Silverwood M6 Morning Apr. 3/13	<LOD	<LOD	30.7	9.6	3.4	13.9	279.8	13.6	2.0	5.6	12.1	12.0	270.0	5.0	3.6	412.2	3.8	<LOD	0.3	0.1	1.0	1821.0	<LOD	0.0	0.3	7.5
Silverwood M6 Afternoon Apr. 3/13	<LOD	5.3	16.1	9.3	2.1	14.6	116.2	14.4	0.9	2.1	7.6	7.8	90.2	1.9	0.5	63.8	1.5	<LOD	0.1	0.1	0.6	1459.0	<LOD	0.0	0.2	0.4
Taylor M6 Afternoon Apr. 3/13	<LOD	3.3	13.1	13.6	3.0	15.7	174.9	15.7	1.2	2.6	10.0	7.4	192.4	2.5	0.6	115.4	2.0	<LOD	0.1	0.0	0.8	1725.0	<LOD	0.0	0.2	1.1
Silverwood M7 Apr. 4/13	<LOD	4.8	16.3	7.2	1.5	13.5	97.6	14.0	0.8	1.9	6.7	7.0	84.1	1.9	0.5	65.3	1.4	<LOD	0.1	0.0	0.6	1553.0	<LOD	0.0	0.1	0.6
University M7 Apr. 4/13	<LOD	<LOD	37.8	5.6	1.7	21.0	303.6	21.4	1.5	3.7	5.1	5.6	206.2	4.7	4.4	465.6	2.6	<LOD	0.3	0.0	0.7	1557.0	0.1	0.0	0.2	8.7
Taylor M7 Apr. 4/13	<LOD	13.8	30.3	5.9	1.5	34.3	246.4	36.5	1.4	3.4	6.6	7.1	182.6	3.6	1.2	314.1	2.2	<LOD	0.3	0.0	0.6	1587.0	<LOD	0.0	0.2	7.1
University M2 Mar. 30/13	<LOD	<LOD	40.6	10.8	1.6	9.9	484.3	9.0	2.4	5.2	4.0	3.7	252.1	7.0	9.5	895.6	3.3	<LOD	0.4	0.0	0.7	1305.0	0.2	0.0	0.2	21.5
Taylor M1 Mar. 29/13	<LOD	<LOD	15.1	14.1	7.9	4.6	245.8	3.3	1.6	4.5	9.5	9.0	238.4	3.0	1.2	231.8	3.8	<LOD	0.2	0.0	1.0	1618.0	0.1	0.0	0.2	4.0
Silverwood M2 - Blank Mar. 30/13	<LOD	100.7	<LOD	11.4	1.1	2.5	0.2	2.1	<LOD	<LOD	<LOD	<LOD	18.7	<LOD	<LOD	0.4	0.1	<LOD	<LOD	0.0	0.1	8.2	<LOD	0.0	0.0	<LOD
Taylor Blank M1 Mar. 29/13	<LOD	<LOD	<LOD	14.3	1.1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.2	0.1	<LOD	<LOD	<LOD	0.1	7.1	<LOD	0.0	0.0	<LOD
University M3 Mar. 31/13	<LOD	<LOD	26.5	15.4	2.4	12.6	301.8	12.1	2.1	5.0	5.6	5.2	293.0	3.9	1.9	320.8	3.8	<LOD	0.2	0.0	1.1	1847.0	0.1	0.0	0.2	5.5
Taylor M2 Mar. 30/13	<LOD	<LOD	33.5	10.5	5.2	11.0	190.5	10.6	1.4	4.0	6.3	6.5	253.1	4.4	2.3	537.1	2.7	<LOD	0.3	0.0	0.6	1129.0	0.1	0.0	0.2	18.6
QA/QC Instrumental Certified Reference Material (n=3)																									
Instrumental QAQC	173.8%	102.6%		124.9%	100.7%	97.4%	95.8%	98.9%	100.9%	101.9%	101.3%	98.6%	97.4%	104.8%	99.8%	99.9%	103.1%	100.1%	100.0%		97.1%	99.8%		99.1%	100.1%	109.0%
stdev	31.5%	2.8%		18.9%	1.1%	2.8%	1.9%	3.0%	1.3%	2.4%	2.1%	1.6%	1.7%	1.8%	1.6%	1.1%	1.6%	2.5%	2.1%		1.1%	1.9%		2.2%	2.2%	9.5%
LOD (ug kg^{-1})	0.38	2.31	9.64	0.11	0.05	1.01	0.17	0.76	0.08	1.50	0.29	0.18	1.17	0.70	0.25	0.05	0.05	0.02	0.03	0.02	0.01	0.04	0.10	<0.01	0.01	0.01

SI Table 3: Comparison of concentrations of metals in stormwater. * is the data from this current study

Source area	**Cu** ug L^{-1}	**Cr**	**Fe**	**Al**	**Pb**	**Zn**	Mn	Comments	**Ref:**
Urban runoff (Saskaoon Ca. melt 2013)	6.9	3.6	14.1	5.1	0.2	213.6	239.9	filtered	*
Urban runoff (Saskatoon Ca. spring 2011),	2.3	1.5	N/A	N/A	N/A	3.2	N/A	filtered	*
Urban runoff (Saskatoon Ca. Summer 2011),	9.5	2.7	N/A	N/A	N/A	26.4	N/A	filtered	*
Highway runoff, (Cincinati USA)	13–279	6–28	0.043–0.58	6–229	13–21	209–14,786		filtered	[1, 2]
Highway runoff (Brays Bayou, Houston USA)	0.61	1.8	0.07	n/a	n/a	26.75		filtered	[3]
Street runoff, (USA, 87 locations)	280	9.9	n/a	3.08	43	58		Unfiltered	[4]
Street runoff, (USA, 87 locations)	3.8	1.8	n/a	0.88	2	31		filtered	[5]
Residential and Highway	16.6 (3-65)	15.2 (5-30.3)	3.6 (0.2-20.8)	1.5 (0.1-7.1)	14.6 (5-38.1)	66.8 (7.8-201)	73.1 (6.8-562)	filtered	[6]
Urban Stormwater Runoff (Dunedin, New Zealand)					2.4 (0.4-5.9)	6.3 (1-41)			[7]
Stormwater, (LA, USA)	5.9-37	2.1-20			1.2-16	32-320		non-filtered	[8]
Strasbourg (France)	9.6-12.2	<5			6.6-22	176-206			[9]
South Saskatchewan River*	1.4	<0.5	51.5	0.056	<0.1	1.7	13		[10]

- River water concentration

SI Table 4 Metal ratio meltwater, spring and summer samples win the minimum and maximum ratio against the CCME guidelines.

Metal	**CCME (ug L^{-1})**	**Meltwater**	**Spring**	**Summer**
Sb	6	0.14 (0.09, 0.22)		
As	10	0.36 (0.16, 0.91)		
Ba	1000	1.59 (1.38, 1.83)		
Cd	1	0.25 (0.11, 0.40)		
Cr	1	3.35 (1.16, 6.70)	1.46 (0.66, 5.16)	2.68 (0.95, 4.92)
Co	4	0.33 (0.20, 0.47)		
Cu	4	1.62 (0.17, 2.50)	0.57 (0.13, 1.84)	2.38 (1.54, 5.11)
Fe	300	0.05 (0.02, 0.11)		
Pb	7	0.02 (0.02, 0.03)		
Mn	50	5.28 (1.95, 5.87)		
Hg	1	0.2 (0.11, 0.54)		
Mo	73	0.05 (0.02, 0.14)		
Ni	150	0.02 (0.01, 0.04)		
Se	50	0.04 (0.01, 0.16)		
Tl	0.8	0.02 (0.01, 0.05)		
Sn	300	<0.01		
U	30	0.19 (0.01, 0.74)	0.1 (0.02, 0.18)	0.2 (0.04, 0.37)

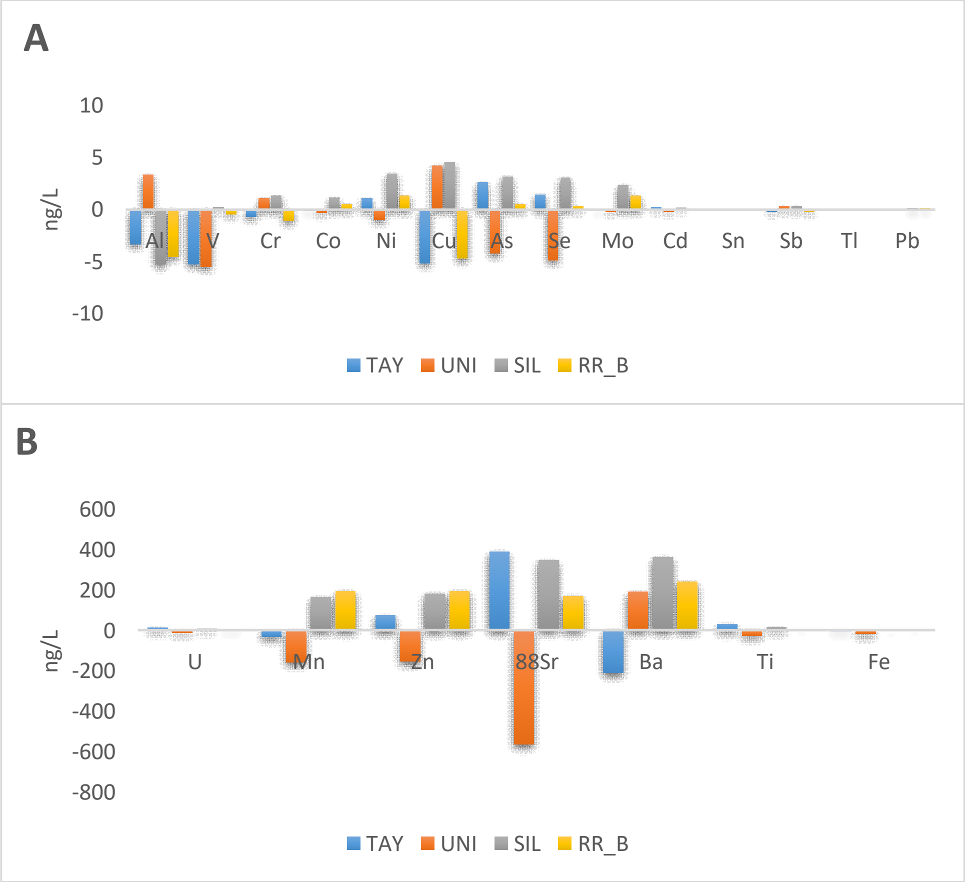
SI Table 5: Pearson correlation between sample day and concentration observed during the melt. With if the correlation is positive (increases with melt period) or negative (decreases with melt) given by + for the increase and – for the decrease.

	Loc 1 (n=6)	Loc 4 (n=6)	Loc 5 (n=7)	Loc 7 (n=4)	Average
PHEs					
Al	0.55(+)		0.27(+)	0.77(+)	0.38(+)
Ti	0.04(+)	0.00(-)		0.69(-)	0.03(+)
V	0.13(-)	0.15(-)	0.84(-)	0.87(-)	0.09(-)
Cr	0.78(-)	0.02(-)	0.35(-)	0.79(-)	0.47(-)
Mn	0.01(-)	0.38(-)	0.07(+)	0.58(-)	0.70(+)
Fe	0.48(+)	0.53(+)	0.12(+)	0.79(+)	0.01(-)
Co	0.3(-)	0.81(-)	0.04(+)	0.50(-)	0.51(-)
Ni	0.81(-)	0.63(-)	0.16(-)	0.65(-)	0.88(-)
Cu	0.2(-)	0.05(+)	0.31(-)	0.35(-)	0.29(-)
Zn	0.37(-)	0.02(-)	0.02(-)	0.74(-)	0.65(-)
As	0(+)	0.11(-)	0.11(+)	0.73(-)	0.01(+)
Se	0.05(-)	0.21(-)	0.07(-)	0.62(-)	0.05(-)
Sr	0.03(-)	0.21(-)	0.01(-)	0.59(-)	0.03(-)
Mo	0.67(-)	0.06(-)	0.03(-)	0.61(-)	0.38(-)
Cd	0(-)	0.04(-)		0.80(-)	0.01(+)
Sn	0.07(+)	0.02(-)	0.20(+)	0.72(-)	0.59(-)
Sb	0.13(-)	0.01(-)	0.40(-)	0.84(-)	0.34(-)
Ba	0.2(+)	0.03(+)	0.48(+)	0.14(+)	0.22(+)
Hg	0.35(+)	0.25(-)			0.12(+)
Tl	0.06(+)	0.82(+)	0.76(+)	0.63(-)	0.17(-)
Pb	0.09(+)	0.02(+)	0.38	0.11(-)	0.27(+)
U	0.04(-)	0.28(-)	0.04(-)	0.59(-)	0.04(-)
PFAS					
PFOS	0.53(-)	0.07(-)	0.15(-)	0.14(-)	0.06(-)
PFOA	0.57(-)	0.79(-)	0.64(-)	0.09(-)	0.47(-)
PFHxA	0.4(+)				0.27(+)
PFHpA	0.00(-)	0.35(+)	0.26(+)	0.41(+)	0.11(+)
PFNA	0.18(-)	0.00(-)	0.92(-)	0.71(-)	0.78(-)
PFDA		0.76(-)			0.92(-)
PFBS	0.82(+)		0.97(+)		0.43(+)
PFHxS	0.61(-)	0.52(-)	0.23(-)	0.56(-)	0.22(-)
NeTFOSAA				0.69(-)	0.04(-)

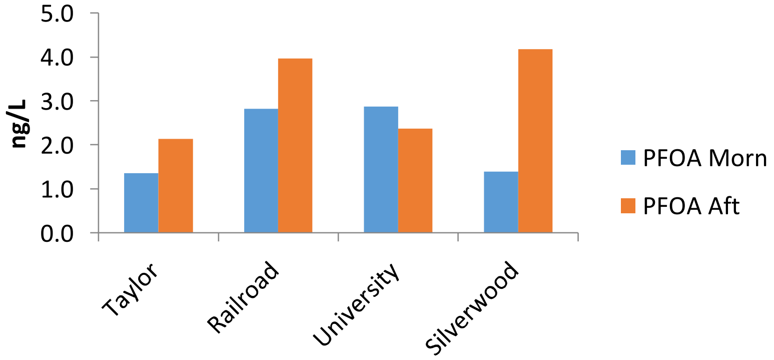
SI Figures

SI Figure 1: Images from the 6th day of stormwater sampling during melt (M6) for the morning (left) and the late afternoon (right) from the Univerity (UNI) sample Loc. 5.

SI Figure 2: Morning and Afternoon Variability of metals from M6 snowmelt for low concentration metals (A) and those more abundant (B). Positive values are those where morning concentrations were greatest and negative where afternoon water had greater concentration. The Y-axis represents the variation between the two-time points.



SI Figure 3: PFOA variability between morning and afternoon sampling on M6.



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