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UNDERSTANDING FINE SEDIMENT DYNAMICS IN AQUATIC SYSTEMS

Concentrations and total mass storage of fine sediment, potentially toxic elements (PTEs) and phosphorus in the channel bed of an urban river: a multi-year study

Philip N. Owens[1] · **P. Michael Rutherford**[1]

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Abstract

Purpose Given the rapid growth of people living in urban and peri-urban areas, this study examined the downstream trends in concentrations and determined the total storage of potentially toxic elements (PTEs) and phosphorus (P) associated with fine-grained sediment (0.45 to 63 µm) stored in the channel bed of an urban river.

Materials and methods Samples were collected from seven sites along McMillan Creek (watershed area = 55 km^2) in the city of Prince George, British Columbia, Canada, between 2010 and 2016 using a resuspension approach. Grabs samples were also collected from two key tributaries and a large culvert.

Results and discussion Some elements (e.g., As, Mn and P) decreased in a downstream direction due to inputs from agricultural sources in the headwaters, while others (e.g., Cr, Cu, Pb and Zn) increased downstream reflecting inputs from urban sources in the lower part of the watershed. Several PTEs increased significantly due to a large culvert which supplied road-deposited sediment (RDS) and other urban materials. In some cases (e.g., As, Mn, Zn) PTE concentrations exceeded Canadian sediment quality guidelines (SQGs) for the protection of aquatic organisms. While concentrations were similar for most years, they were elevated in 2016 which may reflect higher rainfall prior to sample collection. The average total storage of fine-grained sediment in the channel bed of McMillan Creek was 155 t (4198 g m^{-2}), while for PTEs this ranged from 0.01 kg (0.0002 g m^{-2}) for Hg to 1130 kg (30.7 g m^{-2}) for Mn.

Conclusions The channel bed of an urban river stored large amounts of fine sediment, PTEs and P, with concentrations that exceeded SQGs for some elements. Given the expected increase of people living in urban and peri-urban areas, more studies are required to assess the impacts of this growth on the amount and quality of fine-grained sediment stored in urban rivers.

Keywords Metals · Anthropogenic activities · Road-deposited sediment · Culvert · Streambed pollution · Nechako

1 Introduction

The world's population is increasing, and a greater proportion of people are living in urban and peri-urban areas. In 2021, 4.46 billion people (57%) were living in urban areas, and this is expected to increase to 6.68 billion people by 2050; the latter value being a 10-times increase since 1950 (United Nations 2018; Statistics Times 2021). The proportion of people living in urban areas varies across the globe, being greatest in North America; at present 83% and expected to grow to 89% by 2050 (United Nations 2018; Statistics Times 2021).

As a consequence, many studies are documenting that streams and rivers in these areas are becoming contaminated with chemicals and fine-grained sediment derived from human activities (for reviews, see Salomons and Förstner 1984; Horowitz 1991; Foster and Charlesworth 1996; Taylor and Owens 2009; Mohanavelu et al. 2022). As urban areas expand, they are utilizing and encroaching on landscapes that were previously under different land cover, such as agriculture and forest. These more-natural landscapes contain streams and rivers that are, or have been, important habitats for aquatic organisms. With this transformation of the landscape, there has been an increase

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✉ Philip N. Owens
Philip.owens@unbc.ca

[1] Department of Geography, Earth and Environmental Sciences, University of Northern British Columbia, Prince George, British Columbia V2N4Z9, Canada

of contaminant loads into urban and peri-urban rivers, leading to detrimental impacts on aquatic organisms in terms of species composition and diversity. In many cases, key species such as salmonids (e.g., salmon, trout) have declined or are no longer present.

In urban landscapes, chemicals are delivered to watercourses via several pathways including sewage treatment works (STWs) and urban runoff. A large portion of these contaminants are in dissolved form but ionic and hydrophobic elements may sorb to sediment, both suspended and on the channel bed, once in the channel. Some contaminants are delivered in particulate form, especially during periods of runoff from impervious surfaces and due to erosion of channel banks. As a consequence, studies have documented sediments in urban rivers with high concentrations of sorbed contaminants including metals/metalloids, persistent organic pollutants (e.g., polycyclic aromatic hydrocarbons), fallout radionuclides, phosphorus and, more recently, micro-plastics, pharmaceutical wastes and personal care products (e.g., Owens et al. 2001; Horowitz and Elrick 2017; Hurley et al. 2018; Mohanavelu et al. 2022; Van Metre et al. 2022). Furthermore, fine-grained sediment (0.45 to 63 µm) itself can be considered a physical contaminant (Owens et al. 2005; Bilotta and Brazier 2008), for example through clogging of river gravels and reducing interactions between surface waters and the hyporheic zone (Packman and MacKay 2003; Shrivastava et al. 2020). Thus, the deposition and storage of sediment and chemicals in channel-bed gravels represents a risk to organisms that live (e.g., invertebrates) or spawn (e.g., salmonids, sturgeon) in such gravels (e.g.,Wood and Armitage 1997; Soulsby et al. 2001; Jones et al. 2012a), as well as plants such as macrophytes (Jones et al. 2012b; Wharton et al. 2017). In addition, fine-grained sediment and associated contaminants can be mobilized by increasing river flows during storm events, floods and freshets, thereby causing problems to organisms that reside in the water column (e.g., phyto- and zooplankton), as well as society through drinking water quality issues.

While numerous studies have documented high concentrations of contaminants in urban rivers, few studies have determined the total mass storage of fine-grained sediment and associated contaminants in urban rivers. In the few studies that have done this (e.g., Walling et al. 2003; Collins et al. 2005; Estrany et al. 2011), it has been shown that the mass storage of sediment and contaminants on the channel bottom can be high. Thus, the objectives of this work are: (i) to determine spatial concentrations of sediment-associated potentially toxic elements (PTEs) and phosphorus (P) in an urban river in British Columbia, Canada; (ii) to assess if concentrations have changed over time; and (iii) to estimate the total mass storage of fine-grained sediment and associated PTEs and P in the channel bed.

2 Study area and methods

2.1 Study area

McMillan Creek watershed (area: ~ 55 km^2; mainstem river length: ~ 15 km) is the largest watershed contained within the city of Prince George, British Columbia, Canada (Fig. 1). Prince George is the most northern city in Canada for its size (population = ~ 80,000) and acts as a regional centre for most of the central and northern part of British Columbia; the province is ~ 925,000 km^2. The city expanded rapidly in the 1960s with the creation of several pulp and paper mills to serve the timber industry, which dominates this part of the province. Recently, the city has expanded spatially with a steady influx of people and also diversified with the creation of a university and a range of light industries, many of which serve resource extraction industries such as oil and gas development and metal/metalloid mining. The city lies at the junction of several major transportation routes, including highways and rail networks, and is at the confluence of the Nechako (~ 45,000 km^2) and Fraser (~ 220,000 km^2) Rivers. McMillan Creek is located to the north of the city centre and drains primarily small-scale agricultural land with a low population density in the headwaters, with increasing urbanization downstream including light-industry. Highway 97 (Fig. 1) links southern British Columbia (including Vancouver) to northern British Columbia, Yukon and Alaska. It passes through the western part of the watershed and occurs close to the river in its lower reaches, such that there are several culverts that supply water, sediment and chemicals to the river close to its confluence with the Nechako River.

Given its high latitude (ca. 54°N, 122°W) the watershed has cold winters (annual minimums of about -30 °C) and warm summers (annual maximums of about 30 °C). Annual precipitation is about 650 mm of which a large portion falls as snow. River flows are dominated by the annual freshet which occurs in April to May, with low flows between November and March. There is not a discharge gauging station on the river, so there are no discharge or sediment flux data.

McMillan Creek is a fish-bearing stream, including Chinook salmon (*Oncorhynchus tshawytscha*), bull trout (*Salvelinus confluentus*), rainbow trout (*Oncorhynchus mykiss*) and northern pikeminnow (*Ptychocheilus oregonensis*). Chinook salmon typically spawn in September (NWSRI 2017). Studies (e.g., Jacklin 2007) have determined that aquatic organisms in McMillian Creek such as macroinvertebrates and fish are stressed by contaminants and fine sediment. However, these studies have been based on sampling of the water column and have not assessed the quality and quantity of channel stored material.

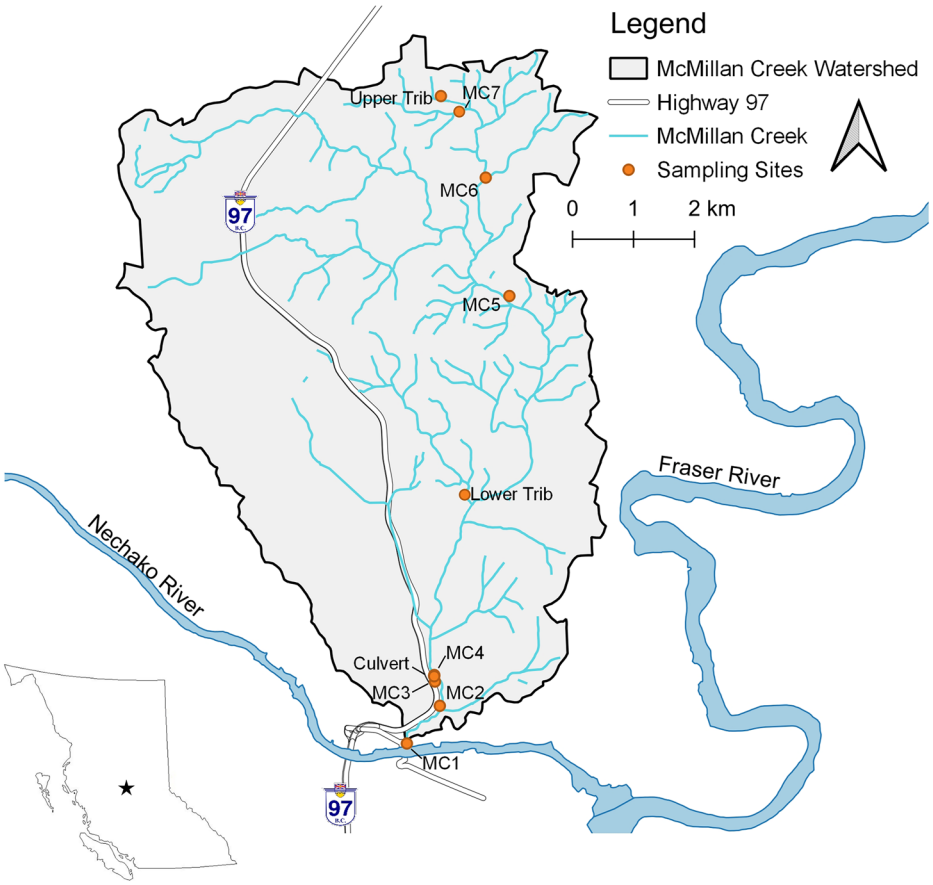

Fig. 1 Location map of McMillan Creek watershed, Prince George, British Columbia, Canada. The main channel bed sampling sites for the period 2010–2016 are MC1 to MC7 with additional grab samples collected from Upper Trib, Lower Trib and Culvert sites

2.2 Methods

Samples of the fine-grained sediment stored on the bottom of the channel bed were collected from seven sites along the mainstem of McMillan Creek in 2010, 2011, 2012, 2015 and 2016. In each year, samples were collected in late September in order to determine concentrations and storage of fine-grained sediment, PTEs and P at the key time for spawning of Chinook salmon, and to assess temporal trends. At each site, a resuspension approach was used (for details, see Lambert and Walling 1988), whereby an open-ended plastic cylinder was pushed into the channel bed – so as to isolate a section of the bed – and a stainless-steel trowel was used to mobilize the fine-grained sediment stored on and within the upper ~ 5 cm of the bed. This approach has been used frequently to sample fine-grained sediment and associated contaminants from the channel bed of shallow (typically < 1 m depth) rivers (e.g., Estrany et al. 2011; Smith and Owens 2014; Pulley et al. 2016; Hurley et al. 2018; McKenzie et al. 2022; Chen et al. 2023). Once resuspended into the water column within the cylinder, sub-samples of the sediment–water mixture were collected and transferred to fill one-third of a 20 L plastic bucket. Three replicate samples were collected at each site so as to encompass some of the local variation, and to also yield a sufficient volume (i.e., 20 L) and thus sediment mass (> 1 g dry sediment) for subsequent property analysis.

The total storage of fine-grained sediment, PTEs and P at each site was determined for 2011, 2012 and 2015 using the approach described by Walling et al. (2003). The mass of resuspended sediment within the cylinder was determined based on the sediment concentration and total volume of water in the cylinder, the latter based on the water depth and cross-sectional area of the cylinder. The sediment concentrations were determined from a 1 L grab sample collected at the time of resuspension and passed through a 0.45 µm filter in the laboratory. From the mass of sediment retained on the filter paper, the mass of fine-grained sediment stored on the channel bed was determined (i.e., g m^{-2}). Total storage for each reach – which was defined as the channel bed between two consecutive sampling sites – was estimated by extrapolating the average sediment mass storage at the two sites by the reach area. The area of a reach was determined from 10 measurements of channel bed width at each site and the distance between consecutive sites obtained from maps, GPS and Google Earth. Total fine-grained sediment storage (i.e., < 63 µm fraction) for the whole mainstem was determined by

summing values for all reaches. The total masses of PTEs and P were determined using the approach described above for sediment and the average PTEs and P concentration of sediment for the two consecutive sites which define the upper and lower ends of each reach (Walling et al. 2003).

In addition to the samples collected at the seven sites along the mainstem, grab samples were also collected from three additional sites during most of the years when resuspension samples were collected (i.e., 2010 to 2016). The grab samples from these additional sites were used to help examine spatial trends in PTEs and P concentrations but were not used to estimate total sediment and contaminant mass storage. The upper grab sample site (Upper Trib; Fig. 1) is a headwater tributary that is confluent with the main stem near site MC7 and thus is representative of material in the agricultural part of the watershed. A lower tributary between sites MC4 and MC5 represents material delivered to the creek from the middle of the watershed. The lowest grab sample site is a large culvert that drains Highway 97 and delivers solids and liquids directly into McMillan Creek between sites MC3 and MC4. To further assess the effect of this large culvert in delivering sediment and chemicals to McMillan Creek, a more intensive set of samples were collected from upstream (n = 2), downstream (n = 7) and within (n = 2) the culvert in October 2018, using the resuspension approach described above.

Upon return to the laboratory, the sediment−water mixture in the 20 L buckets were left to settle for 48–72 h, the supernatant water was siphoned off, and the remaining wet sediment slurry, along with the grab samples, were oven dried at 60 °C. The dried sediment was carefully disaggregated with a mortar and pestle and then passed through a 63 µm stainless steel sieve. The < 63 µm fraction was analysed for trace elements using ICP-MS after aqua regia digestion at a commercial laboratory (ALS, Vancouver, British Columbia) or at Northern Analytical Laboratory Services (NALS) at University of Northern British Columbia (Prince George, Canada). Attention is focused on the metals/metalloids As, Cd, Cr, Cu, Hg, Mn, Pb and Zn and the nutrient P given the concerns associated with these PTEs in urban systems, including issues associated with cultural eutrophication (e.g., Foster and Charlesworth 1996; Sutherland 2000; Owens and Walling 2002; Tansel and Rafiuddin 2016). Samples were also analysed for Al to assist with normalization due to differences in particle size composition between samples from different sites. A check on the suitability of using Al as a normalizing element, assessed by correlating Al with other normalizing elements (i.e., Ca and La), gave Pearson correlation coefficients of > 0.9, thereby confirming the suitability of using Al.

For each sample, three replicate readings were undertaken, and the average reading was used. ALS perform instrument and method QA/QC which includes using method blanks, laboratory control samples and a reference material standard (EnvironMAT SS-2 soil standard) during each set of 20 samples. At NALS, continuous calibration blanks (0 ppb) and calibration verifications checks (500 ppb multi-element standard) were run every 20 samples to confirm instrument stability (for more details on the analysis at NALS, see Owens et al. 2019). An additional standard (Canadian Certified Reference Material Till-3 from Cobalt, Ontario) was also run during each sample batch. Estimates of analyte recovery based on spiked laboratory controls were typically in the range 90 to 110%. Replicate analysis of a reference standard had relative standard deviation (RSD) values of between 0.5 and 2.2%, except for Hg where RSD was 9%, due to the low concentrations.

Samples were analysed for absolute particle size composition using a Malvern Mastersizer 3000 laser diffraction particle size analyser at NALS after removal of organic matter, and chemical (sodium hexametaphosphate) and ultrasonic dispersion. The values reported are d_{50} (median particle size) and specific surface area (SSA: the total surface area of particles divided by the total weight, calculated within the Malvern software assuming the particles are spherical and non-porous). Organic matter content was determined by loss-on-ignition (LOI) at 550 °C.

2.3 Statistical analysis

Difference in properties (i.e., element concentrations, particle size parameters, organic matter content) between sites were assessed used the Mann–Whitney U-test using a 95% probability of significance (i.e., $p = 0.05$). It is important to recognize that the low sample numbers limits the statistical power of this test.

3 Results

3.1 Spatial variations of PTEs and phosphorus concentrations

Although there are variations between years (discussed further in Section 3.2), there are consistent trends over the sampling period 2010 to 2016 with some elements (e.g., Cr, Cu, Pb and Zn) increasing in concentration with increasing distance downstream, while other elements (e.g., As, Mn and P) decrease in concentration in a downstream direction (Fig. 2). Some elements, such as Cd and Hg, show no consistent downstream trend. Thus, the average (n = 5 years; mean ± 1 standard deviation) P content for channel bed sediment at the most upstream site (site MC7) was 2995 ± 235 µg g^{-1}, whereas the value for the most downstream site (site MC1) was 1491 ± 125 µg g^{-1}. In the case of As, equivalent values were 147 ± 7 µg g^{-1} (site MC7) and 12.8 ± 2.3 µg

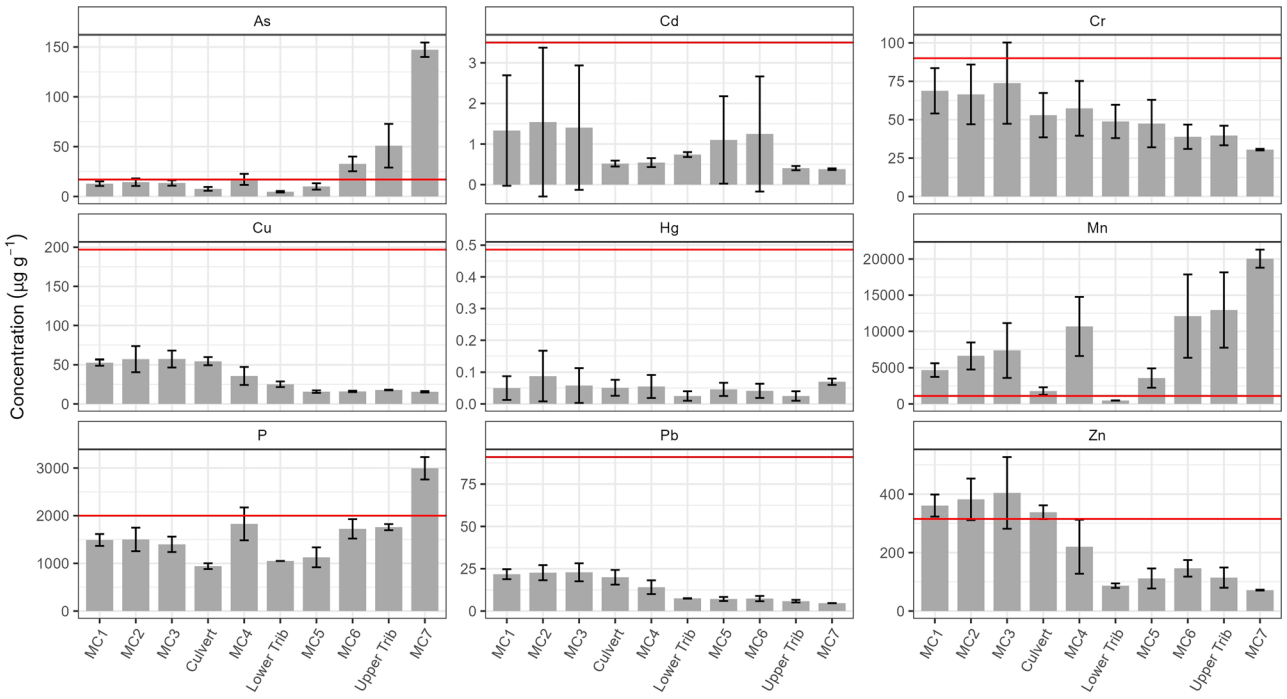

Fig. 2 Concentrations (average ± 1 standard deviation) of PTEs and P on channel-bed stored sediment collected from 10 sites in McMillan Creek watershed for the period 2010–2016. Also shown (red horizontal line) is the probable effects level (PEL) sediment quality guideline for the protection of aquatic organisms for the PTEs or an equivalent guideline for P

g^{-1} (site MC1). For both elements, these differences were statistically significant ($p < 0.05$). However, for most elements, concentrations increased with distance downstream being greatest in the urban part of the watershed. Thus, Zn increased from 71.5 ± 1.5 µg g^{-1} at site MC7 to a maximum of 404 ± 123 µg g^{-1} at site MC3, while Pb increased from 4.65 ± 0.05 µg g^{-1} to 22.9 ± 5.3 µg g^{-1} at sites MC7 and MC3, respectively, and these differences were statistically significant ($p < 0.05$).

For those elements that increased downstream, there was often a pronounced increase below a large culvert that enters McMillian Creek between sites MC3 and MC4, with concentrations at MC3 (i.e., below the culvert) being similar to the grab samples collected from the culvert (Fig. 2). These patterns suggest that not only do some PTE concentrations increase in the urbanized part of the watershed but that the culvert is a main source of these. For the samples collected upstream, within and downstream of the culvert in 2018 (Table 1), concentrations were similar to those collected during the period 2010–2016 (Fig. 2) for equivalent sampling sites. For most PTEs (i.e., Cd, Cr, Cu, Pb and Zn) concentrations were highest for the samples taken within the culvert and the effect of the culvert was to increase concentrations for samples collected downstream of it (i.e., MC3), especially for Cu, Pb and Zn. For Mn and P, the culvert appeared to dilute concentrations, whereas for As the effect of the culvert was less clear. The upstream and downstream of the culvert differences were statistically significant ($p < 0.05$) for Cu, P, Pb and Zn. The Lower Trib site also had lower concentrations for some elements (e.g., As, Mn, P, Zn) than the main river, and may have had a similar diluting effect.

The downstream increases in the concentrations of some PTEs may also reflect changes in particle size of the sediment. The average (±1SD) d_{50} and SSA of the analysed sediment collected at site MC7 were 30 ± 3 µm and 245 ± 39 m^2 g^{-1},

Table 1 Effect of a large culvert on concentrations of PTEs and P on stored channel bed sediment collected from McMillan Creek in 2018

Element	Upstream concentration (n = 2[a]) (µg g^{-1})	Culvert concentration (n = 2[b]) (µg g^{-1})	Downstream concentration (n = 7[a]) (µg g^{-1})
As	21.9	21.3	24.3
Cd	1.5	1.82	1.80
Cr	62.5	80.3	71.5
Cu	34.7	101.0	79.0
Mn	17,400	8454	16,700
P	2600	1692	1970
Pb	14.6	31.8	20.3
Zn	231	635	587

[a]Each sample is a composite of several taken within 5 m using the resuspension approach

[b]Each sample is a composite of several grab samples

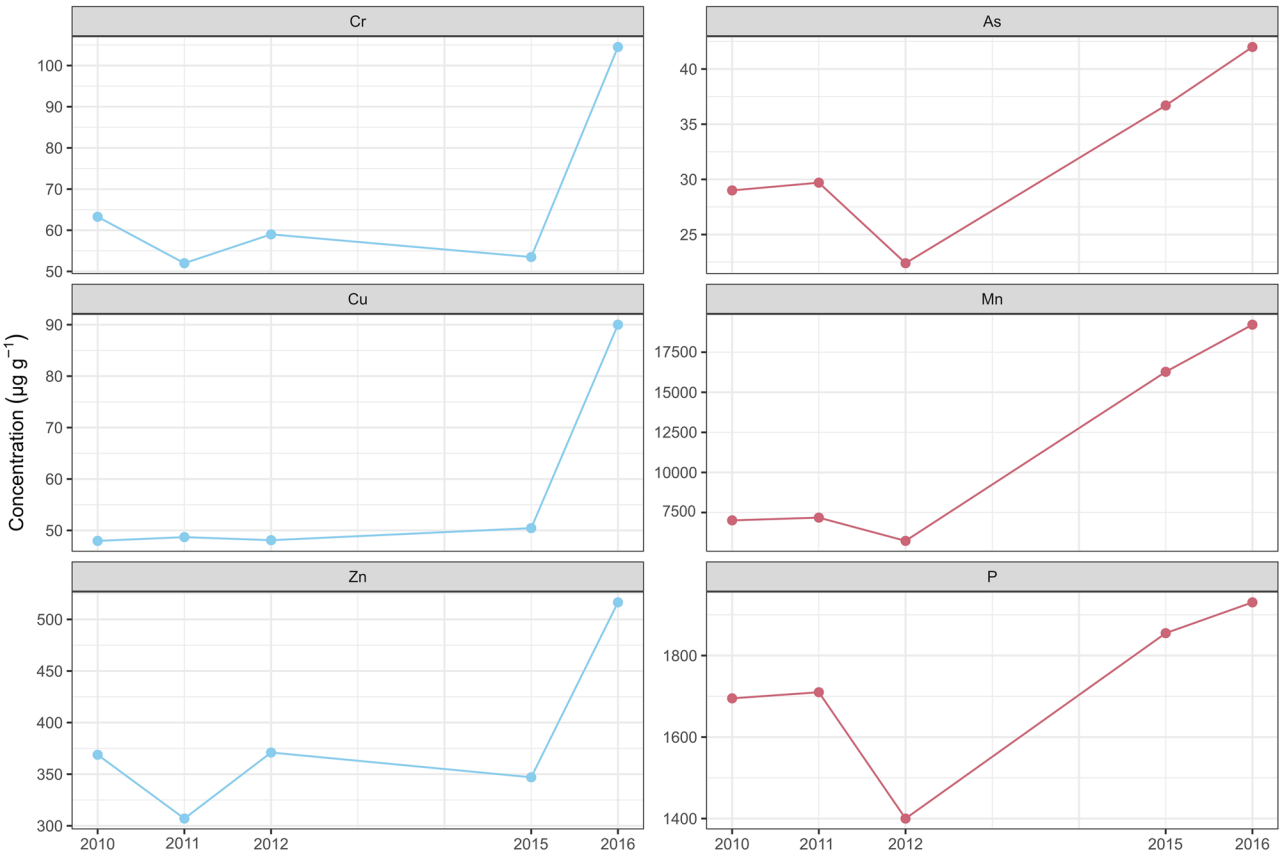

Fig. 3 Temporal changes in PTEs and P concentrations for the study period (2010–2016) for example elements that either increase downstream (Cr, Cu and Zn at site MC2; left column) or decrease downstream (As, Mn and P at site MC6; right column). Note the years with consistently high or low concentrations

respectively, and these values are statistically different ($p<0.05$) than those at site MC1; 16 ± 6 µm and 471 ± 82 m^2 g^{-1}, respectively. The sediment collected from the culvert (<63 µm fraction) was coarser than that collected from the river, with average d_{50} and SSA of 35 ± 10 µm and 231 ± 59 m^2 g^{-1}, respectively, compared to 23 ± 7 µm and 344 ± 62 m^2 g^{-1}, respectively, for site MC4, although this was not statistically different ($p>0.05$). This resulted in noticeable changes between sites MC4 and MC3 (i.e., upstream and downstream of the culvert), although these were not statistically different ($p>0.05$). In the case of organic matter content, there was not a clear downstream trend although the highest average value for a site was recorded for the upstream tributary site (Upper Trib; 25%) and values for sites MC6 and MC7 were > 14%. The lowest average value was 7.5% for site MC3, again likely due to the supply of organic-poor, minerogenic material from the culvert (LOI = 1.8%).

3.2 Temporal variations in PTEs and phosphorus concentrations

In most cases, while there were temporal variations in PTEs and P concentrations over the study period, there was no consistent pattern for the years 2010, 2011, 2012 and 2015. Thus, some sites had the highest element values in some years, while for other sites the highest values were in different years. However, 78% of the PTEs and P were highest for the samples collected in 2016. Figure 3 shows examples from an upstream and a downstream site for a selection of elements that either decreased (As, Mn, P) or increased (Cr, Cu, Zn) in a downstream direction. In all cases, concentrations were greatest in 2016; this is discussed further in Section 4.1.

3.3 Channel bed storage of PTEs and phosphorus

Table 2 gives total storage of fine-grained sediment, PTEs and P in the channel bed of McMillan Creek for the years when this was determined (i.e., 2011, 2012 and 2015). The average fine-grained sediment storage for the three years was 155 t, while that for the trace elements ranged from 0.01 kg for Hg to 1130 kg for Mn. When expressed per unit surface area of the channel bed, equivalent values were 4198, 0.0002 and 30.7 g m^{-2} for sediment, Hg and Mn, respectively.

Table 2 Total storage of fine-grained sediment (0.45 to 63 µm) and associated PTEs and P on the channel bed of McMillan Creek on a particular day in September 2011, 2012 and 2015. The values of average storage per unit surface area (g m^{-2}) are also shown

Year	Sediment (t)	As (kg)	Cd (kg)	Cr (kg)	Cu (kg)	Hg (kg)	Mn (kg)	P (kg)	Pb (kg)	Zn (kg)
2011	116	2.90	0.05	4.97	2.23	0.005	668	178	0.94	13.4
2012	203	4.54	0.08	8.18	3.70	0.015	1735	308	1.67	24.4
2015	146	2.70	0.08	5.30	2.40	0.009	986	201	0.97	19.0
Average	155	3.38	0.07	6.15	2.78	0.010	1130	229	1.20	18.9
Average storage (g m^{-2})	4198	0.09	0.002	0.167	0.08	0.0002	30.7	6.22	0.03	0.51

4 Discussion

4.1 Temporal and spatial patterns in PTEs and phosphorus concentrations

There were distinct downstream trends in PTEs and P concentrations which reflect anthropogenic activities in the watershed. For those elements that were higher at headwater sites (e.g., As, Mn and P), which is dominated by agricultural land and ranching, it may reflect agricultural amendments and products, such as P associated with fertilizers (e.g., ammonium phosphate, $(NH_4)_3PO_4$) and manures. Manganese is essential for plant growth and Mn deficiency can be a serious problem (Alejandro et al. 2020), and therefore is often addressed through the addition of fertilizers (e.g., manganese sulphate, $MnSO_4$), manures, other amendments, or through soil pH adjustment (Adriano 2001). Arsenic is used in some pesticides. Concentrations of As, Mn and P were higher at site MC7 compared to the Upper Trib site suggesting that the part of the watershed draining into site MC7 is the main source of these elements.

For those PTEs that increased downstream, this likely reflects inputs from urban and industrial sources including culverts, such as the large one between sites MC3 and MC4. Culverts are known to deliver water and sediment from the urban road network to rivers, such as road-deposited sediment (RDS). Numerous studies (e.g., Carter et al. 2003; Poleto et al. 2009; Devereux et al. 2010) have determined that RDS can represent a significant amount of the fluvial sediment transported and stored in urban river systems. Not only is RDS an important source of sediment in urban streams but it is also an important source of PTEs; for reviews, see Hanfi et al. (2020) and Haynes et al. (2020).

In terms of variations over the different sampling years, generally PTEs and P concentrations were consistent over time, with the exception of 2016, when concentrations were markedly greater (Fig. 3). The exact reason for this is unknown, however rainfall for the period prior to sample collection was greatest in 2016. For the four months June to September, total precipitation during 2016 was 266 mm and this was greater than the average for 2010, 2011, 2012 and 2015 (211 mm). This may have caused greater runoff and erosion in the headwaters, and more surface runoff and mobilization of RDS and other contaminant sources in the lower reaches of the watershed. Other studies (e.g., Carter et al. 2003; Mohanavelu et al. 2022) have also identified that rainfall (and snowmelt) events are important in supplying chemicals to urban rivers by connecting the terrestrial component of the watershed to the channel network. In addition to RDS, rainfall events also increase the movement of water, sediment and chemicals through sewer and septic systems and industrial effluents.

It is important to recognize that samples were not collected during 2013 and 2014, which limits a comprehensive assessment of temporal trends over the full 2010 to 2016 period. In addition, samples were only collected in late September for each year, so it is not possible to examine how concentrations and storage may have varied during the year. It is likely that both would vary considerably during differ seasons and also different hydrological events. During the main winter period in Prince George (e.g., November to March) it is likely that the delivery of sediment and chemicals to McMillan Creek would be minimal due to the cold temperatures (i.e., below freezing) and frozen nature of the river corridor. During this period, it is logistically difficult to sample the channel bed and thus determine concentrations and storage of sediment, PTEs and P. Ideally, future work would assess variations over the full year to identify the times of the year when concentrations are greatest. This, in addition to the spatial trends described above, would help determine the likely hydrological and geomorphological processes and human activities that supply sediment and chemicals to the river. In turn, such information could assist with developing and implementing mitigation options, such as road sweeping and nature-based solutions such as urban buffers and wetlands (e.g., Irvine et al. 2023).

4.2 Effects of variations in sediment particle size and organic matter content on downstream trends

While there are clear downstream trends in the concentrations of PTEs and P (Fig. 2), as explained in Section 3.1 there were variations in the particle size and

organic matter content of the fine-grained sediment stored in the river gravels. Studies (e.g., Horowitz 1991; Herngren et al. 2006; Tansel and Rafiuddin 2016; Unda-Calvo et al. 2019) have shown that some elements preferentially bind to the finer fractions of sediment and organic matter. Thus, Stone and Droppo (1996) found that concentrations of Cu, Pb and Zn were greatest in the finest fractions of sediment from the channel bed of two rivers in Ontario, Canada. Variations in particle size and organic matter content might, therefore, influence the spatial interpretations described above. To examine this further, concentrations of PTEs and P were normalized by multiplying the concentration of an element at a specific site by the ratio of the SSA for site MC7 divided by the SSA for the specific site. In other words, values were adjusted to reflective difference in SSA using MC7 as a reference. The same exercise was undertaken using Al instead of SSA to normalize concentrations relative to site MC7. In all cases, the downstream trends described above and shown in Fig. 2 still hold, but the magnitude of the difference between sites changed. This is illustrated in Fig. 4 using As (decreases downstream) and Zn (increases downstream) as examples. Thus, the downstream increase in some PTEs (i.e., Cr, Cu, Pb and Zn) may partly be due to decreases in the size of the sediment – itself due to hydraulic sorting – and concomitant increases in specific surface area and thus more sorption sites. While this partly explains the absolute downstream patterns shown in Fig. 2, and is therefore a useful exercise, care must be taken in altering raw concentration data to explain patterns.

Unlike particle size composition (e.g., SSA), which changed consistently with distance downstream, there was not a clear pattern for organic matter content. The only major differences between the sites were for the Upper Trib site and the culvert, where values were noticeable higher and lower than the other sites, respectively.

4.3 Comparison to sediment quality guidelines

It is possible to assess if the PTEs and P associated with stored fine-grained channel bed sediment in McMillan Creek are likely to have adverse effects on aquatic organisms by comparing values to Canadian sediment quality guidelines (SQGs) determined for the protection of sediment-dwelling benthic organisms (CCME 1999; BCMECCS 2021a). While there is not presently an SQG for P (CCME 1999; BCMECCS 2021a, b), earlier studies in Canada (e.g., Persaud et al. 1993) suggested that 2000 µg g^{-1} could be used as a guide for adverse effects on aquatic organisms, although this should be treated with caution. While many are essential trace elements (e.g., Cr, Cu, Mn, Zn) and nutrients (e.g., P), they can be toxic and/or have detrimental effects at elevated concentrations. Other trace elements (e.g., As, Cd, Hg, Pb) have no known biological function and can be toxic even at low concentrations.

Figure 2 shows that in most cases (e.g., Cd, Cr, Cu, Hg, Pb), average values are below the probable effects level (PEL), meaning that they are unlikely to have adverse effects on aquatic organism that live in, or utilize (i.e., for

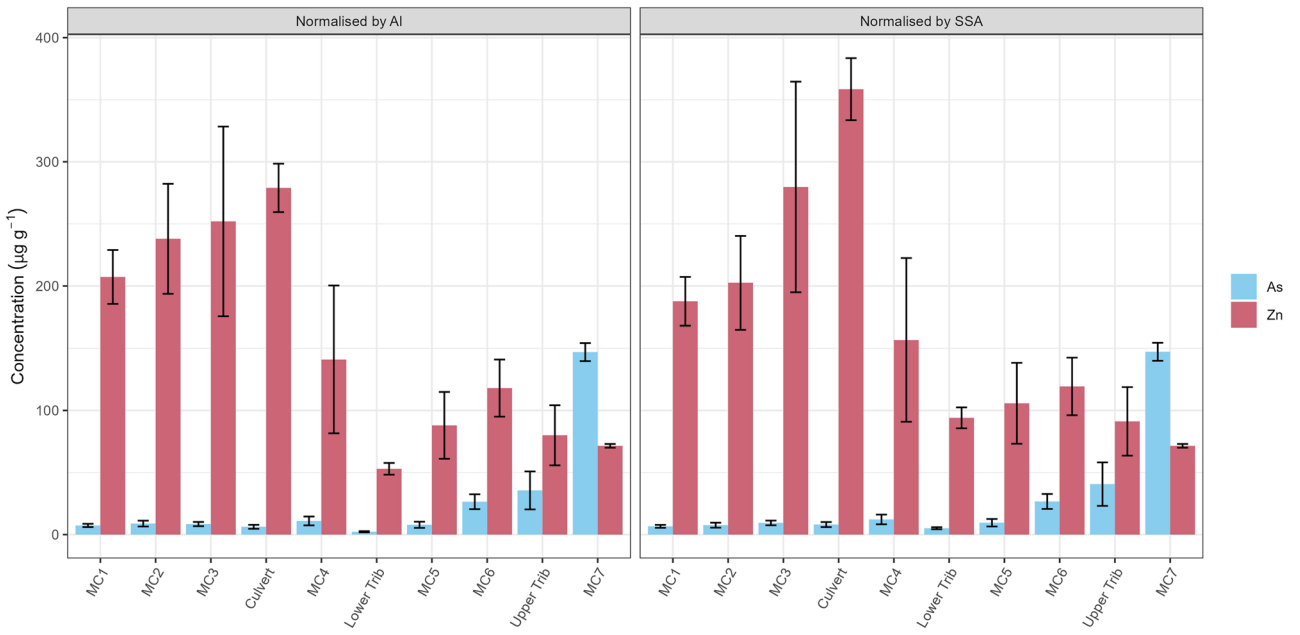

Fig. 4 Downstream trends in As and Zn concentrations. Values have been normalized by Al and SSA relative to site MC7 in order to assess the effects of changes in particle size composition on element concentrations

Table 3 Comparison of the storage of fine-grained sediment and associated PTEs and P in the upper layers of the channel bed of McMillan Creek with other studies that have used the same sampling approach

Location	Sediment ($g\ m^{-2}$)	As ($g\ m^{-2}$)	Cd ($g\ m^{-2}$)	Cr ($g\ m^{-2}$)	Cu ($g\ m^{-2}$)	Hg ($g\ m^{-2}$)	Mn ($g\ m^{-2}$)	P ($g\ m^{-2}$)	Pb ($g\ m^{-2}$)	Zn ($g\ m^{-2}$)	Reference
McMillan Creek, BC, Canada	4198	0.09	0.002	0.167	0.08	0.0002	30.7	6.22	0.03	0.51	This study
River Exe, UK	400										Lambert and Walling (1988)
River Ouse, UK[a]	162										Walling et al. (1998)
River Tweed, Scotland[b]	560										Owens et al. (1999)
Aire, Calder, Swale Rivers, UK[c]	334	0.05			0.05			0.93	0.14	0.25	Walling et al. (2003)
Several rivers in UK[d]	1442		0.0012	0.0276	0.046			1.65	0.077	0.23	Collins et al. (2005)
Pang, Lambourne, Tern Rivers UK[e]	1780							1.91			Ballantine et al. (2009)
Na Borges, Mallorca[f]	2375			0.027	0.094				0.015	0.207	Estrany et al. (2011)
Sanginjoki River, Finland[g]	1132										Marttila and Kløve (2014)

[a]Average for 10 sites. Mainly rural/agricultural

[b]Average for 12 sites. Mixed agricultural with some urban areas

[c]Average for 5 rivers (45 sites) watershed area 160 to 425 km^2, mainly agricultural

[d]Average for 16 sites. Mixed agricultural with some urban areas

[e]Average for 16 sites. Mainly agricultural

[f]Average for 8 sites. Mainly rural but with a moderate population density and sewage treatment works

[g]Average for 14 sites

spawning), channel bed sediments. However, it should be noted that for Cd and Cu values for some individual samples are close to or slightly exceed the PEL threshold. In the case of As, Mn, Zn and P, values for some sites are above PEL thresholds. For Zn (PEL = 315 µg g^{-1}) this applies to the downstream sites, especially those below the culvert (MC1 to MC3). For As (PEL = 17 µg g^{-1}) and P (guideline value = 2000 µg g^{-1}) the upstream sites exceed the guidelines. In the case of Mn, average values for all sites, with the exception of the Lower Trib site, exceed the PEL threshold (1100 µg g^{-1}). As such, Mn may be the main element of concern in McMillan Creek. Background (i.e., non-contaminated) soils in the Prince George area, and other parts of British Columbia, can have Mn concentrations greater than 1500 µg g^{-1} (BCMECCS 2021b). As these values are for bulk soil samples, then it is expected that concentrations would be greater in the < 63 µm fraction.

4.4 Comparison of fine sediment, PTEs and phosphorus storage to other studies

While there are numerous studies that have determined the concentrations of contaminants, like PTEs, and nutrients (e.g., N and P) in channel bed sediments, very few studies have determined the storage of such materials (i.e., g m^{-2}). Table 3 compares the values obtained for this study with those from other studies that have used the same sampling approach (i.e., resuspension following Lambert and Walling 1988). Comparison with studies using the same approach is important because inevitably different approaches are likely to yield different amounts and sizes of sediment. In the case of the resuspension approach, fine-grained sediment is typically remobilized from the upper ca. 5 cm of the channel bed, reflecting the nature of the approach. Other approaches such as freeze-coring and gravel infiltration baskets/bags (e.g., Petts et al. 1989; Petticrew et al. 2007; Harper et al. 2017) sample from different depths and often different types of bed material, thereby limiting the appropriateness of comparing with values from this study. Similarly, it is important to recognize that even though the same approach was used in the studies presented in Table 3 that there will be sources of error and variability associated with different operators and variations in equipment type (e.g., size of sampling device). However, Duerdoth et al. (2015) have shown that the resuspension approach used here is a reasonably reliable way to quantity the storage of fine sediment and associated chemicals in river gravels, and that operator error is low. Most variability arises from differences in channel characteristics such as morphology (e.g., thalweg vs channel edges, pools vs riffles etc.). In this study, the widths of the channel at the various sites are relatively low (range 1.4 to 5.2 m) and replicates were collected at each site to account for local spatial variation. In addition, samples were collected at approximately the same site each year, and at the same time of year, thereby limiting some sources of error and uncertainty.

Table 3 shows that the average amount of fine-grained sediment stored in the channel bed of McMillan Creek (4198 g m^{-2}) is relatively high compared to other studies which range between 162 and 2375 g m^{-2}. This may reflect the urban nature of the contributing watershed compared to the other watersheds which are primarily agricultural and rural. Owens et al. (2011) determined that the total amount of RDS stored on the road network of the city of Prince George during June and October of 2009 was 764 and 204 t, respectively, of which the < 63 µm fraction represented 49 and 9.8 t, respectively. They identified that the finer fraction of the RDS would likely make its way into local creeks and rivers, especially during rainfall and snowmelt events. These values compare to the average amount of fine sediment stored in McMillan Creek of 155 t (Table 2) which includes other urban sources of material as well as soil erosion of fields and channel bank erosion. Other studies (e.g., Franz et al. 2014) have shown that material from urban construction sites can be an additional source of sediment in urban rivers.

Table 3 also shows that the amounts of PTEs and P stored in the channel bed are similar to the few studies that have determined this. Given the lack of other studies, it is difficult to make any generalizations. However, storage of some PTEs (i.e., As, Cd, Cr, Zn) and P are greater in McMillan Creek than in other rivers where there are equivalent data.

5 Conclusion

This study demonstrated that fine-grained sediment deposited and stored in the channel bed of an urban river in Prince George, British Columbia, was enriched in PTEs and P. Some elemental concentrations were higher in headwater areas reflecting agricultural and rural sources, while others appeared in elevated concentrations in the lower reaches due to inputs from urban and industrial sources. In particular, a large culvert appeared to be a significant source of Cr, Cu, Pb and Zn. This may be due to inputs of runoff and road-deposited sediment and associated PTEs. While there was not a clear temporal trend, PTEs and P concentrations were highest in 2016 and may reflect higher than average rainfall in the months preceding sample collection.

Average concentrations of As, Mn and Zn exceeded sediment quality guidelines for the protection of aquatic organisms at several sites, while guidelines were approached or exceeded for Cr and P for some individual samples. The implications of this, is that stored fine-grained sediment in the channel bed of McMillan Creek may be detrimental to benthic organisms like invertebrates

and fish that live and/or spawn in river gravels like Chinook salmon.

The total storage of fine-grained sediment in the channel bed of McMillan Creek was greater than that determined for other studies, which may be due to the urbanized nature of this watershed. There was also significant total storage of PTEs, especially Mn and P. Given the limited number of studies that have determined such storage of contaminants using the same sampling approach, it is difficult to draw conclusions from this. Although the approach used here has its limitations − such as the depth of water that it can be operated in − it is a low-cost and simple way to both collect the fine-grained sediment stored in the channel bed and to estimate the storage of sediment and contaminants. Thus, it is recommended that it can be used more widely for applications such as: (i) initial assessments to identify reaches and rivers at risk; (ii) monitoring over time to determine trends; (iii) regional and national surveys; and (iv) assisting with the identification of the types and locations of mitigation options. The number of people living in urban and peri-urban areas is expected to increase substantially in the next few decades. Thus, more studies are required to assess how this will impact the amount and quality of sediment in urban rivers.

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Declarations

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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