Water and Fine-grained Sediment Assessment in the Capital Region (Edmonton) of the North Saskatchewan River (Canada)

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Abstract

Purpose To better understand the behaviors of sediment-associated metals (Cu, Ni, Cd, Mn, Cr, Pb, Fe, Sr, Mo, and Co), an evaluation of physicochemical parameters and metal speciation on suspended and bedload sediment collected from the North Saskatchewan River was conducted in 2018. Sampling sites were selected within the urban region (Edmonton) to assess the influences of anthropogenic inputs (e.g., municipal waste and/or agrochemical runoff) on water and sediment qualities.

Methods The sequential extraction procedure was modified based on Tessier's method to investigate the association of metals with different fractions of sediments (e.g., exchangeable, carbonate, Fe-Mn oxides, organics, and residual fractions). The mineralogical composition and particle size distribution (<63μm) were measured to help interpret the metal fractionation patterns. Pollution levels were assessed by comparing results with the fresh water and sediment quality guidelines (WQGs and SQGs) published by Environment Canada. Risk assessment code (RAC) was employed to evaluate the bioavailability and potential toxicity of heavy metals.

Results Generally, suspended sediment contains more clay minerals, carbonates and particulate organic carbon than bedload sediment. The size fractionation data indicate that there were more clay-sized particles (<2μm) in suspended sediment. Sr, Cd, and Mo represented appreciable portions in exchangeable fraction. Substantial amounts of Cu, Sr, Cd, Mn, Co, and Pb were associated with carbonate fraction and Co, Pb, Ni, Fe, and Cr were predominantly bound to Fe-Mn oxides and residual fraction. Cu and Mo represented relatively high proportions in oxidizable fraction. For most heavy metals except for Cu and Mo, larger parts of non-residual fractions can be observed in suspended sediments than in bedload sediments. Water quality assessment reveals that all dissolved toxic metals and nutrients were in the environmentally acceptable ranges posted by WQGs. SQGs suggest that the total concentrations of Mn, Ni and Cr in all sediment samples, Cu in bedload samples and Cd in suspended samples were of environmental concern in the present study and can occasionally be associated with adverse biological effects. According to RAC, for both suspended and bedload sediments, Cr, Fe showed low risk, Co and Pb showed medium risk and Mn showed very high risk to the environment. Other metals such as Ni, Mo, Cu, Sr and Cd showed different levels of toxicity to the environment at different sampling sites.

Conclusion This study provides information about the sources, storage patterns (in suspended and bedload sediment), fate and environmental impacts (bioavailability and potential toxicity) of metals in the NSR and helps monitor the anthropogenic influences caused by a large city (Edmonton) to better characterize the contaminant chemistry of the river.

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Chapter 1: Introduction

1.1 North Saskatchewan River (NSR)

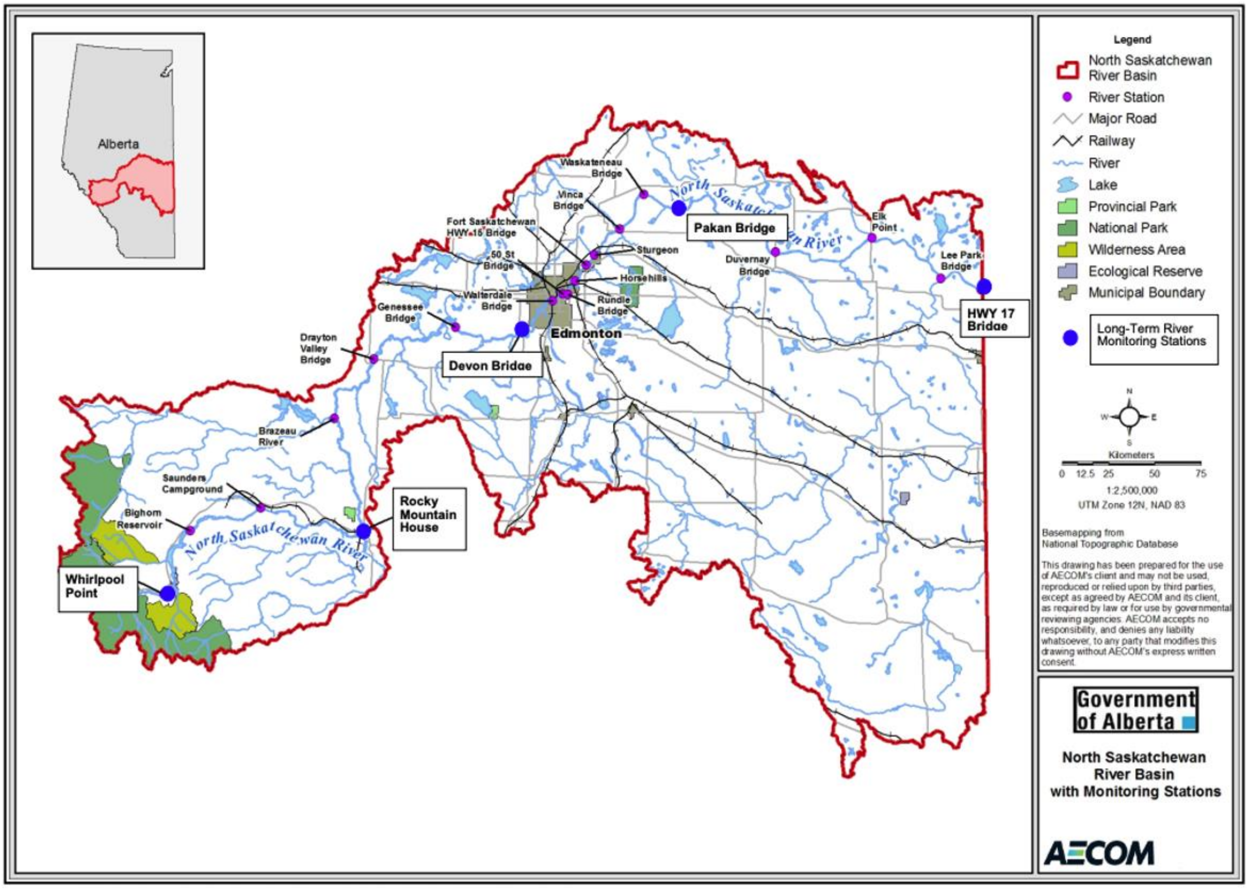


Figure 1.1 The North Saskatchewan River Basin with water monitoring stations (Anderson, 2011)

The North Saskatchewan River (NSR) is one of the major rivers in Alberta and the seventh largest in Canada. It originates at Saskatchewan Glacier in Banff National Park, then descends almost 900 meters in elevation and flows over 1000 kilometers across Alberta (passing through Edmonton) to Saskatchewan (Toomey, 1988) (Figure 1.1). It joins with the South Saskatchewan River in Saskatchewan east of Prince Albert, flows into Lake Winnipeg in Manitoba, and eventually empties into Hudson Bay (Neufeld, 2010). The NSR drains an area of approximately 55,000 km^2, with an average annual discharge at the Alberta/Saskatchewan border of around 7 billion m^3 (Stone, 2012a). Headwaters such as the Brazeau River, the Ram River and the Clearwater River are main water sources of the NSR and generate 90% of the total annual flow (AESRD, 2014), but when they contribute less water, the Sturgeon River and the Vermillion River instead become the main tributaries that contribute flows to the mainstem. Discharge of the NSR is regulated by the Brazeau dam (on the Brazeau River near its confluence with the NSR) and the Bighorn dam (on the mainstem of NSR) (Halliday, 2009). These impoundments constructed in 1961 and 1972, respectively, help redistribute flow to be higher than natural flow in winter and lower than natural flow in summer (AESRD, 2014).

Mean annual temperature of the NSR basin varies between 0.3°C and 3.5°C, with average temperatures in the Rocky Mountains, Edmonton and Alberta/Saskatchewan border approximately -9°C, -13°C and -17°C in January and 13°C, 16°C and 18°C in July (Alliance, 2012). Climate in the basin is semi-arid with annual precipitation up to 1000 mm in the Rocky Mountain headwaters and less precipitation near the interprovincial border (up to 400 mm). By contrast, evaporation rates increase eastward from 500 mm/y (at Rocky Mountain House) to 700 mm/y (at Alberta/Saskatchewan border) (Alliance, 2012). Thodsen et al. (2008) and Walling (2009) indicated that variations of temperature and precipitation in the NSR basin can directly influence the rate, magnitude and variability of suspended sediment and associated pollutants via changes in erosion processes and river discharges, or indirectly influence via changing input patterns from the drainage basin (Stone et al., 2022). As a glacier-fed river, there is more than one type of snowmelt runoff event in the NSR due to the combination of topography and climate. For example, the Rocky Mountain snowmelt usually occurs in late spring or early summer (June/July), while the plain-prairie snowmelt often occurs in April or May (Laceby et al., 2019). Apart from snowmelt runoff contributions, during low flow seasons, the source of base flow is mainly controlled by groundwater recharge (Dumanski et al., 2015; Zaremehrjardy, 2020). Generally, those climatic and seasonal changes can affect the river hydrology and water quality, as well as influence the source and transport of suspended solid and the solid-associated constituents (Laceby et al., 2019; Lu et al., 2013; Milliman and Syvitski, 1992).

In the NSR basin, water flows through a wide variety of natural ecozones such as the Rocky Mountains, Foothills, Boreal Forest, Grassland regions and Central Parkland; each differs with respect to geology, soil, natural vegetation, and surficial deposit. Those differences can cause instant or gradual changes to the river water chemistry (e.g., nutrients, metals, suspended loadings) (Atkinson et al., 2018; Shaw et al., 1994; Stone, 2012a). For example, nutrient levels are typically very low in the headwaters sampled in the Rocky Mountains, while by the time the NSR traverses the Central Parkland Natural Region and flows to the areas downstream, its waters become richer in nutrients and more bio-productive (Anderson, 2011). Geological variation indicates that the mountains and foothills where the NSR originate comprise Palaeozoic to Cretaceous-aged bedrocks of the Cordillera including dolomite, shale, sandstone and siltstones. East of the foothill lies the Paskapoo Formation (non-marine, calcareous sandstones, siltstones and mudstones) and Wapiti Formation (non-marine, sandstone and siltstone with coal beds) (Green, 1972; Shaw et al., 1994). The major surficial deposits and landforms of the NSR comprise morainal, glaciolacustrine, glaciofluvial et al. in the foothill and locally derived glacial till, rocks, recent alluvial deposits in the Interior Plains and the river valley (Bjorge, 1983; Dudas and Pawluk, 1969; Laceby et al., 2019; Shaw et al., 1994; Tokarsky, 1971; Ullman et al., 2016). In addition, longitudinal changes occur when the river passes through successive natural regions since changes in elevation would influence trends and patterns of sediment transportation in the river (Anderson, 2011; Caine, 2014). For instance, the size of river bottom substrates tend to decrease from coarse-grained (cobbles) in the headwaters to fine-grained sediments (silt and clay) in the middle and lower reaches due to decreasing flow velocities in the regions of central parkland and grassland (AESRD, 2014; Anderson, 2011).

The NSR basin also supports human land uses, which include major urban centers such as Rocky Mountain House, Drayton Valley, Edmonton, and Fort Saskatchewan (Figure 1.1) (AESRD, 2014). Around one third of the total population (1.4 million) in the province live in the Capital Region (City of Edmonton and adjacent areas) (Anderson, 2011; Canada, 2022), and along with urbanization, it is expected that the population would increase to 1.7 million in the next 30 years (AESRD, 2014). Other anthropogenic activities, such as infrastructure development, resource exploitation and industry also influence river chemistry (Kienzle, 2012; Schindler and Donahue, 2006; Stone, 2012a). For example, there are several intensively developed areas along the river, such as the oil and gas exploration activities in Drayton Valley area, the coal mining operations in Wabamun area, the power plants in Genesee area, the petrochemical development in Industrial Heartland area (Neufeld, 2010; Pomeroy et al., 2005; Stone, 2012a). In the central and eastern portions of the basin, nutrients derived from agricultural lands are main sources of anthropogenic contaminant discharges to the NSR during spring runoff and heavy rain events (Anderson, 2011).

By the time the NSR reaches Devon and flows through the industrial heartland and Edmonton, water uses are dominated by human consumption, petrochemical processing, and agricultural applications such as livestock watering and some irrigation (Kolter, 2018; Paterson and Nursall, 1975; Wisner et al., 1981). Every year, around 5.5% of Alberta's water supply is sourced from the NSR and most of the treated (municipal and industrial discharges) and untreated water (surface runoff) will be returned to the river at last (Stone, 2012a; Stone et al., 2022). Although the industrial and population growth are managed carefully, point and non-point sources of contaminants are also detected in the water and sediment samples collected downstream of Edmonton (Clearwater, 2010; Neufeld, 2010; Stone et al., 2022), suggesting that more assessments need to be done to better monitor human-derived inputs in the reach of the Capital Region.

1.2 Previous works on the NSR

The North Saskatchewan River supports many land-use activities within its basin that ultimately influence its water quality (AESRD, 2014). In the past few years (from 2007 to 2022), several studies have been conducted to monitor, model, and report the status of the NSR and its tributaries, particularly in the reach of the Capital Region (Table 1.2). In those studies, information has been collected at key locations to quantify temporal and spatial variations of pollutants and their types. Modelling studies have been completed to help predict source and transport patterns of contaminants. New tools have been developed for sample collection and data processing. Details are discussed below:

Table 1.2 Recent studies (from 2007 to 2022) which investigated the status of the NSR and its tributaries

Water quality		
Reference	Time frame	Main contribution
Laceby et al. (2019)	April 1987-Octorber 2017	a. Investigated the potential impact of road de-icers on the concentration of Cl^- in freshwater. b. Examined spatial and temporal variations of major ions along the NSR. c. Predicted major sources of Cl^-.
Bell (2015)	June, August and October 2014	a. Measured water quality (e.g., metals, conductivity, alkalinity) of four tributaries located upstream and downstream of Edmonton. b. Monitored differences in water quality between seasons.
AESRD (2014): Long-term River Network (Low-flow seasons)	January 2007-October 2012	a. Provided long-term records of water quality (e.g., metals, nutrients and dissolved oxygen) in the reach from Clearwater River to Pakan. b. Helped manage the status and trend of the water quality.

AESRD (2014): Short-term (High-flow seasons)	March, June and October 2008; May, July and October 2012	a. Conducted seasonal water quality measurements (e.g., metals, nutrients and dissolved oxygen) along the entire length of the NSR. b. Observed spatial water quality variations as well as point and non-point sources of inputs. c. Distinguished local impacts on the NSR water quality during different seasons and flow levels. d. Included surveys of tributaries along the river to provide datasets for future NSR watershed planning.
AESRD (2014):Datasonde	2007-2012	a. Measured conductivity, pH, temperature, turbidity, and dissolved oxygen every 15min at 7 monitoring sites along the NSR mainstem. b. Recorded daily fluctuations of the water chemistry to better understand the particular variables that have differences between day and night (e.g., oxygen in summer). c. Figured out which day-time sampling site may generate unrepresentative results. d. Recorded seasonal and spatial changes in water chemistry in daytime to provide details for extreme events (e.g., low oxygen levels under ice).
AESRD (2014):Diurnal	October 2011 and 2012	a. Analysed water samples collected during daytime to figure out if there are any differences (e.g., pH, turbidity, dissolved oxygen) between day and night.
Golder (2013a) Golder (2013b) Golder (2013c)	2012	a. Monitored point sources of contaminant from water and sediment samples collected in approved facilities (combined and storm sewers, wastewater treatment plant/ water treatment plant). b. Assessed the improvements of water quality within the city based on Water Quality Index. c. Generated sub–Water Quality Index values for metals, nutrients, bacteria and pesticides. d. Quantified water quality variations within the city under both wet and dry seasons. e. Documented impacts caused by seasonal events (e.g., dry weather and runoff from snowmelt or rain) on the water quality within the reach of Edmonton area. f. Characterized water conditions at the tributary's confluence with the mainstem.

Sediment and Non-fish biota

Reference	Time frame	Main contribution
Stone (2012b); Stone et al. (2022)	Fall 2010-Fall 2011	a. Measured physical (grain size distribution) and chemical (mineralogy and major element composition) properties of fine-grained bedload sediment samples collected in the NSR and its tributaries to investigate the source, transport and fate of sediment-associated contaminants (trace metals and polycyclic aromatic hydrocarbons). b. Evaluated the bioavailability of trace metals. c. Investigated the influences of a large city (Edmonton) on trace metal chemistry in deposited river sediment.

AESRD (2014): Long-term River Network (Low-flow seasons)	January 2007-October 2012	a. Provided long-term records of bedload sediment quality (e.g., metals) in the reach from Clearwater River to Pakan. b. Helped manage the status and trend of sediment quality.
Clearwater (2010)	Fall 2007 and 2008	a. Analysed contaminants including nutrients, metals and organic matters in depositional sediments. b. Assessed sediment quality based on CCME Sediment Quality Index. c. Benthic invertebrates were enumerated and identified. d. Epilithic algal were identified and analyzed for *chlorophyll-a* content.
Golder (2014)	August 2010 and 2011	Observed macrophyte density and assessed the biotic/abiotic parameters between a. Devon and Pakan. b. Rocky Mountain House and the Alberta/Saskatchewan border.
Modeling		
Reference	Time frame	Main contribution
Pilechi et al. (2012)	October 2011	a. Described plume mixing patterns of three major effluents (Goldbar, Capital Region, Agrium Redwater Fertilizer). b. Determined the distance required to achieve full mixing of treated wastewater.
TetraTech (2012)	1998-2009	a. Represented non-point sources of sediment, nutrients, trace metals and bacteria. b. Provided a suite of models (e.g., wastewater mass balance model) that intend to evaluate the water quality in the Capital Region. c. Helped build models for land-use management. d. Investigated how hydrological processes influence the water quality in the NSR watershed.
Data processing and Tools		
Reference	Time frame	Main contribution
AEP (2018)	1990-2018	a. Compiled surface water and sediment quality guidelines posted by previous studies and generated guidelines for environmental protection in Alberta.
McDonald (2013)	2000-2011	Based on the data collected from the Long-term River Network, this model provided a useful tool for: a. Selecting variables (except for bacteria) of concern in Devon and Pakan. b. Monitoring effects caused by effluent loadings on water quality in the Capital Region.
Anderson (2011)	2006-2009	Summarized comprehensive information on: a. Point sources of contaminants discharged from the Capital Region into the NSR (e.g., municipal and industrial effluences, tributaries). b. Natural contribution of loadings in the mainstem of NSR and its tributaries.

		c. Sensitivity (water and sediment quality variations) of the NSR to anthropogenic and natural influences.
Kessler (2010)	2000-2008	a. Selected the best tool for loading calculation. b. Provided information on total suspended solids, nutrients, metals and bacteria in the reach of Capital Region. c. Determined the in-stream loads and contributions from point sources (e.g., municipal and industrial effluences, tributaries).
Neufeld (2010)	1950-2009	a. Summarized water quality changes in the NSR (Capital Region) in last 60 years. b. Indicated improvements in water quality in recent years due to upgrades of wastewater treatment plants in Edmonton.

As summarized above, previous studies have provided information on current status of the North Saskatchewan River. In sum, they show:

1. Flow. As a large glacier-fed river, the NSR has more than one flow season caused by natural factors such as snowmelt and precipitation. Those seasonal variations within a year can generate different levels of major ions and total suspended solids from both point and non-point sources. Although two headwater dams (Bighorn and Brazeau) regulate flows to be higher in winter and lower in summer (Halliday, 2009; NSWA, 2010), seasonal impacts on flows are still significant. This results in four distinct patterns: (1) Medium flow season in April and May (spring) from grassland ice melting. (2) High flow season in June and July (early summer) from mountain headwaters due to contributions of snowmelt. (3) Medium flow season in late summer which is treated as the end of the summer flow. (4) Low flow season from September to March (winter), which is the lowest flow occurring in the whole year (AESRD, 2014; TetraTech, 2012).

2. Total suspended solid (TSS). TSS is important for indicating suspended particles in river water columns. During the high-flow season in early summer, TSS increases in the mainstem due to disturbance of surficial geology, erosion of riverbanks and resuspension of bedload sediments. When the river velocity decreases in mid and late summer, suspended solids are mainly supplied by tributaries (AESRD, 2014). In the reach of the Capital Region, seasonal changes were observed by Golder (2013b) who indicated that TSS loadings derived from the City of Edmonton increased from 5,389 kg/day in dry seasons (fall and winter) to 141,242 kg/day in wet seasons (spring and summer), which was mainly caused by inputs from urban tributaries such as the Goldbar Creek and the Whitemud Creek (Golder, 2013a). Additionally, longitudinal changes showed that suspended solids content increased consistently towards downstream of Edmonton (from 130mg/L at Devon to 150mg/L at Pakan) (AESRD, 2014; Golder, 2013b).

3. pH. Water samples collected from the mainstem of NSR (from 2007 to 2012) were naturally alkaline, with a median pH value of 8.3. Anomalies were observed in August and September, when some monitoring sites (e.g., Fort Saskatchewan and Vinca) located downstream of the Capital Region reported pH values >9.0, which exceeded the Alberta Water Quality Guideline (6.5-9) (AESRD, 2014).

4. Dissolved oxygen (DO). DO concentrations measured by Datasondes (from 2007 to 2012) indicate that oxygen contents in the river were generally higher in winter (10-12 mg/L) than in other seasons (8-10 mg/L). When the NSR flows through the Capital Region, DO concentration fluctuated over a wide range (from 1 to 20 mg/L) and showed lower values at all sites downstream of Edmonton Fort Saskatchewan (<6.5 mg/L) and Vinca (< 5mg/L), which were mainly attributed to impacts caused by both aquatic activities (e.g., respiration and photosynthesis by algae and plant) and anthropogenic inputs (e.g., from Wastewater Treatment Plants).

5. Chloride. The Long-term River Network monitoring program conducted from 2007 to 2012 indicate that the median Cl^- concentration in the NSR (3.2 mg/L) was lower than the water quality guidelines (3.6 mg/L) calculated by McDonald (2013). While during local spring runoff in 2008, an increasing concentration (from around 10 to 16 mg/L) of Cl^- was observed downstream of Edmonton, which was mainly attributed to de-icers (sodium chloride, calcium chloride and magnesium chloride) applied on the road during winter (AESRD, 2014; Laceby et al., 2019). In the summer of 2008 and 2012, Cl^- concentrations measured at Fort Saskatchewan (downstream of Edmonton) were relatively high (around 2 mg/L) compared with upstream of Edmonton (1 mg/L), due to influences caused by groundwater or Wastewater Treatment Plant (WWTP) effluents (Golder, 2013c). Anderson (2012) summarized the temporal variations (from 1998 to 2011) of Cl^- and found that there was an increasing trend for chloride levels from Pakan to Devon.

6. Nutrient. During open-water seasons from 2007 to 2012, median concentrations of several nutrients exceeded the Water Quality Guidelines (WQGs), which include total phosphorus (TP) at all monitoring sites (Clearwater River, Devon and Pakan), total dissolved phosphorus (TDP) at Devon, NO_3^-+NO_2^- at Pakan, total organic carbon (TOC) at both Devon and Pakan. Spatial variations of nutrients were observed as follows: 1) From upstream (headwater) to downstream (Alberta/Saskatchewan border), TKN (Total Kjeldahl Nitrogen which include organic nitrogen and ammonia) and TOC increased gradually (from 0.1 to 0.6 mg/L and 1.0 to 5.0 mg/L respectively), with significant elevations (from 0.1 to 0.5 mg/L and 1.0 to 4.0 mg/L respectively) occurring east of Rocky Mountain House. 2) NO_3^-+NO_2^- were at relatively low levels (<100 ug/L) in the upstream reaches (from the headwater to Edmonton), with significant increases (>200 ug/L) occurring downstream of Edmonton. 3) For TP and TDP, both continuous increases (from 20 to 25 ug/L and 5 to 6 ug/L respectively) in the upstream reaches and abrupt high values (from 25 to 50 ug/L and 6 to 8 ug/L) in the Capital Region were observed (AESRD, 2014). Nutrient changes in the upstream of NSR were attributed to nutrient-rich inputs from prairie tributaries and agricultural lands. The loading analysis conducted in the City of Edmonton indicated that the increasing trends of nutrients (e.g., TP, ammonia, ammonium and NO_3^-+NO_2^-) were sourced from GoldBar WWTP in both dry and wet weather conditions (Golder, 2013a). Temporal variations showed that upgrades of WWTPs in the Capital Region were main reasons for the declines in ammonia, NO_3^-+NO_2^- , TN, TP, TDP from 1987 to 2009 (Anderson, 2012).

7. Metals. Water samples collected in the Long-term River Network (2007-2012) showed that several metals (e.g., Pb, Ag and Zn at Devon; Co, Cu at both Devon and Pakan; B, Cd, Fe at Clearwater River, Devon and Pakan) exceeded the WQGs published by Environmental Canada (AEP, 2018). In the 2008 and 2012 short-term surveys (during high flow seasons), dissolved metals showed four spatial trends along the river (AESRD, 2014): 1) No trend (for Be, Fe, Mn, Se, Ag, Th and Sn). 2) Increasing in headwaters and then remaining unchanged in the downstream reaches (for Ba). 3) Continuously increasing trend (for Sb, As, B, Cu, Pb, Li, Ti, U and V). 4) Significant increases downstream of Edmonton (Al, Bi, Cd, Co, Mn, Mo, Ni and Zn) (AESRD, 2014). Golder (2013b) indicated that the increases of metal concentrations in the mainstem can partially attributed to influences from tributaries since the total concentrations of Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Mo, Se, Ag and Zn were observed to be higher than the WQGs in at least one sample collected from tributaries in 2012. Besides, the total concentrations of Al, Mo and Zn in treated effluent samples collected from the Goldbar and Capital Region WWTPs were higher than WQGs, suggesting that wastewater discharges can be one of the reasons for the enrichment of these metals in the NSR (Anderson, 2011).

8. Wastewater mixing pattern. The contaminants (e.g., metals and nutrients) associated with wastewater treatment plants (WWTP) were detected at the opposite bank sampling sites by 6.3 km (for Capital Region WWTP) and 11.6 km (for Goldbar WWTP) from the outfalls. At a sampling site located 92 km downstream of Edmonton, the effluents from WWTPs were observed to be diluted from 60 to 133 times depending on the effluent volumes (from 0.7 m^3/s to 3.2 m^3/s). Accordingly, some contaminants may be undetectable in the laboratory due to the high dilution rates. In addition, the WWTP-related pollutant presented higher concentrations on the south (right) bank compared with the north (left) bank for a very long distance downstream of Edmonton (Pilechi et al., 2012).

Sediment (bedload sediment) quality studies were conducted initially from 2007 to 2008 by Clearwater (2010) at 30 locations on the mainstem (from Rocky Mountain House to the Alberta/Saskatchewan Border) and then from 2010 to 2011 by Stone (2012b) at 20 locations along the NSR (from Rocky Mountain House to Lloydminster) and 10 locations at the confluences of tributaries. The results showed that:

1. Mineralogy. Mineralogical analyses conducted in 2010 and 2011 provide spatial and temporal patterns of mineralogical composition of bedload sediment collected from the mainstem and tributaries of NSR. For example, all sediments consisted of varying concentrations of quartz, albite, microcline, muscovite, chlorite, dolomite, calcite and smectite. Compared with the NSR sediment, tributary sediment had larger proportions of quartz, albite, dolomite and calcite (Stone, 2012b).

2. Particle size. Particle size was measured in both studies (Clearwater, 2010; Stone, 2012b) and the results indicated that sediment samples were dominated by sand and silt, with a small amount of clay. From the data collected in 2007 and 2008, the decrease in particle size was observed from upstream to downstream, showing more silt and clay content in sediment samples collected in Edmonton (downstream). Stone (2012b) indicated that the average diameter of sediment collected in the mainstream was 90 μm compared with 228 μm in tributaries. Temporal variations suggested that the range of particle size measured in 2011 (up to 500 μm) were wider than in 2010 (up to 300 μm).

3. Metal. Extractable and total concentrations of metals were measured in both studies conducted in 2007-2008 and 2010-2011 (Clearwater, 2010; Stone, 2012b). In 2007 and 2008, the concentration for most of the metals showed increasing trend from upstream to downstream of the NSR. Elevated concentrations of Cr, Pb, Mn and Ni were observed at some monitoring sites located downstream of Edmonton. Based on the Interim Sediment Quality Guidelines (ISQG) and Probable Effects Level (PEL), Cd, Cu, Hg and Zn were all below their toxic limits in the sediment samples collected from 2007 to 2008. However, As and Cr concentrations exceeded the ISQG at some sampling sites along the NSR (Clearwater, 2010), indicating that those metals may cause adverse influences to the environment. Stone (2012b) found that Cr (in both 2010 and 2011) and Ni (in 2010) could potentially pose harm to the ecosystem since they exceeded the consensus-based threshold effect concentration (TEC) at sampling sites located downstream of the Capital Region. Temporal variations suggested that compared with 2011, the concentrations of Cu, Hg, Pb, Ni were higher, while the Cr and As were lower in 2010 (Stone, 2012b). Anderson (2011) also showed that higher concentration of metal is likely to coincide with higher TSS levels in high flow seasons (e.g., in summer or spring runoff).

4. Metal fractionation. The metal fractionation data for the NSR and tributary sediments indicated that some metals (Hg in 2010 and 2011, Pb in 2011) were mainly controlled by geological factors (e.g., weathering) since there was no significant change in distribution of these metals in sediments collected from Rocky Mountain House (upstream) through to Lloydminster Ferry (downstream). Other metals (e.g., Ni and Zn) showed increasing trend of extractable fractions (exchangeable, bound to carbonate, bound to Fe-Mn oxides and bound to organic matters) in sediments when the river flows through areas (e.g., Drayton Valley, Edmonton and Fort Saskatchewan) affected by human activities (Stone, 2012b).

As discussed above, studies have been conducted not only on water, but also on sediment, which is considered to be the major transporter for contaminants in aquatic systems (Horowitz, 1991; Owens et al., 2005; Turowski et al., 2010). Compared with bedload sediment, suspended sediment is composed of finer particles and more chemically active components, making it a better carrier for contaminates in natural river water (Horowitz, 2008; Turowski et al., 2010; Walling and Fang, 2003). Moreover, most bedload sediment samples collected along the river were not from the actual places which are affected by contaminants (AESRD, 2014). However, to date (as summarized in Table 1.2), the geochemical and contaminant properties of suspended sediments in the NSR are poorly documented. Such information is required to assess the storage ability of river suspended sediment and evaluate its fate and environmental impacts (toxicity and bioavailability) (Stone, 2012b).

1.3 Objectives

To address the information gap discussed above, suspended sediment samples were collected in 2018 at 8 sites along an 100km reach of the NSR to answer the following questions:

1. What are major differences (physical and chemical) between suspended and bedload sediments?
2. How do bedload and suspended sediments effect behaviors of trace elements in natural water column?
3. Which elements can pose environmental risk to the ecosystem of the NSR and why?

To address these questions, and better understand the behavior of sediment-associated contaminants, this study evaluates physical (grain size distribution) and chemical (mineralogical composition) properties of the sediments (suspended and bedload) and their trace metal distributions. To determine the current status of the NSR and its stressors, assessments for water (major ion, nutrient, anion, trace metal, pH and alkalinity) and sediment (trace metal) quality conditions are provided by comparing with standard values in water and sediment quality guidelines (WQGs and SQGs) (AEP, 2018). Spatial (from upstream of Edmonton to downstream) variations of the geochemical properties (e.g., pH and alkalinity) and contaminants (e.g., metals and nutrients) along the river are presented to discuss the impacts of anthropogenic activities (urbanization). The specific objectives of this study are to:

1.3.1 Assess water and sediment qualities in the NSR with the aid of guidelines.

Anthropogenic wastes containing trace metals, degradable organics, nutrients, domestic effluent, and agricultural waste are main sources of wastewater discharge into rivers (Lenat, 1988). An unexpected change of dissolved matters can directly reflect the source of contaminants such as trace metals and nutrients since they tend to bound to solid particles and will be diluted very quickly within tens of kilometres along the river (Mohiuddin et al., 2010; Pilechi et al., 2012; Prartono et al., 2016). Additionally, it is widely accepted that the long-standing measurement of water quality should be based on assessing the sediment-associated constituents (Förstner, 2004a; Forstner and Wittmann, 1979; Horowitz, 1991; Horowitz, 2008; Lu et al., 2005; Peijnenburg et al., 2007; Tessier et al., 1979). In most aquatic systems, the amount of metals in sediment (including suspended sediments or bedload) can be orders of magnitude higher than those in the dissolved phase (Ankley et al., 1996; Enguix González et al., 2000; Forstner and Wittmann, 1979; Horowitz, 1991; Horowitz, 2008; Sharma et al., 1999; Singh et al., 2005; Srivastava et al., 1994). Thus, acting as both carriers and sinks for contaminants in aquatic environment (Jain, 2004; Singh et al., 2005), river sediments can either pose direct threats to the ecosystem or store heavy metals as reservoirs (Ke et al., 2017; Pratap et al., 2020; Saeedi et al., 2013; Sundaray et al., 2011).

To properly evaluate the levels of pollution in water and sediment, guidelines are essential since they provide consistent, science-based recommendations for the protection of a specific use of water or other aquatic ecosystem components (Al-Mamun and Zainuddin, 2013; Liang et al., 2018; Sousa et al., 2018). Developed from extensive supporting data (AEP, 2018), various statistical techniques (guidelines) have been applied in assessing water and sediment qualities, which update the knowledge of current conditions of rivers and support contaminant loading studies (Chatterjee et al., 2010; Kumar et al., 2016; Vieira et al., 2012; Wang et al., 2017). However, when using environmental quality guidelines, we should be aware that there are limitations which may lead to inadequate understanding of bioavailability and toxicity of sediment-associated contaminants. For example, they do not include guidelines for suspended sediment, which is a better carrier for trace metals and more sensitive to environmental conditions change (Owens et al., 2005; Walling and Fang, 2003).

1.3.2 Trace metal distribution in suspended and bedload sediments.

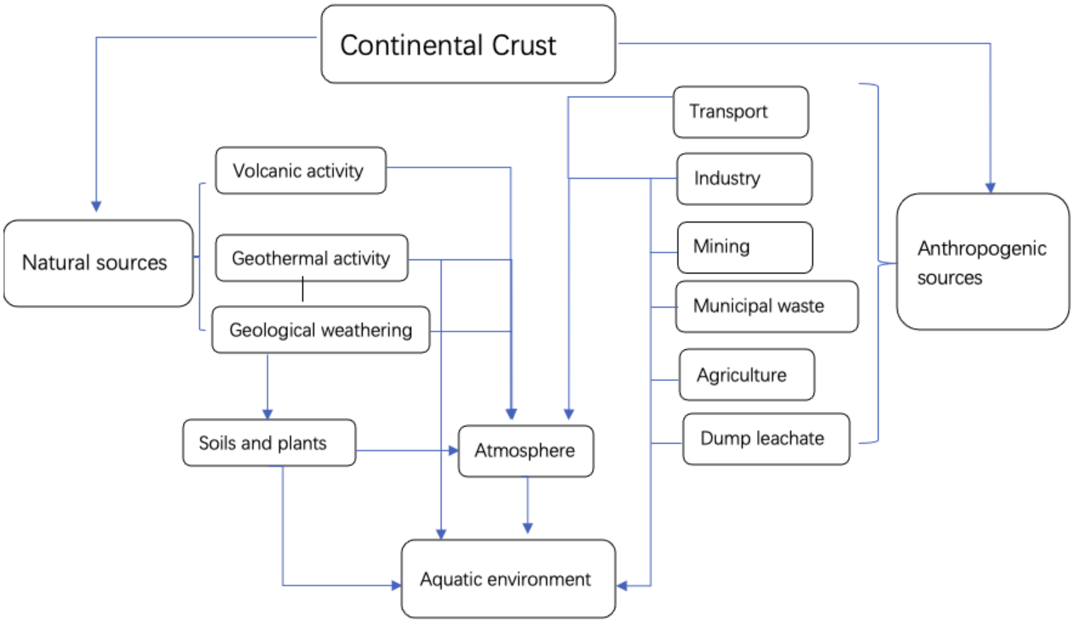


Figure 1.3.2 Pathways of trace metals entering the aquatic system (modified from Gaillardet et al. (2003) and Foster and Charlesworth (1996))

As shown in Figure 1.3.2, trace metals in river water are mainly derived from natural and anthropogenic sources (originally from continental crust). During geochemical processes and human activities, trace metals have multiple pathways entering the river water system and cause environmental problems in both dissolved and particulate forms (Owens et al., 2005). Based on a world river database compilation, Gaillardet et al. (2003) concluded that the majority of metals are transported through solid forms, and only the most mobile elements can be transported in dissolved forms. Jain and Sharma (2001) also indicated that more than 97% of the heavy metals were transported to the ocean through river sediment. Martin and Meybeck (1979) estimated that sediment-associated contribution accounts for more than 90% of the total river-borne flux of elements such as P, Ni, Mn, Cr, Pb, Fe and Al.

During transportation, trace metals associate with river suspended sediments (e.g., minerals, organics) via ion exchange, adsorption, precipitation, and surface complexation (Sakai et al., 1986; Thorne and Nickless, 1981). However, most of the metals are not permanently sequestered onto suspended sediment surfaces, but instead, they can be released into the water or change their aqueous speciation with varying environment conditions (e.g., pH, redox potential, or organic ligand concentrations) (Yuan et al., 2004). Therefore, the mobility and toxicity of metals also depend on their phases in water, and in this regard, it is critical to ascertain the mode of occurrence by which a metal is present in sediments to gain a more precise understanding of the mobility and bioavailability of metals (Liu et al., 2008). This theory is also suitable for fine-grained bedload sediment (<63μm) quality analysis since they can be resuspended from river bed with agitation during high flow seasons or pose threats directly to the local ecosystem by releasing contaminants with changes in environmental conditions (Horowitz, 1991).

Since the mobility and toxicity of metals partially depends on their fractionations in sediment, significant attention has been directed at evaluating metal contamination by applying sequential extraction procedures (Stone, 2012b). Generally, the sequential extraction method is based on the theory that one or more reagents can selectively isolate trace metals in different sediment fractions (Horowitz, 1991). And, when sequential extractions are conducted on sediments or soils, the most mobile metals should be removed first and continue in order of decreasing of mobility (Zimmerman and Weindorf, 2010). For example, the five-step procedure adopted by Tessier et al. (1979) can essentially separate soils and sediments into five different fractions such as exchangeable fraction, carbonates, Fe-Mn oxides, organics and residue (Qiang et al., 1994; Ryan et al., 2008; Shan and Chen, 1993). Depending on different purposes and sample types, the procedure and reagent can be variable. For instance, Ure et al. (1993) reduced the fractions to 4 by combining the exchangeable and carbonate-bound fractions, whereas Miller et al. (1986) split the soil/sediment into 9 fractions for agricultural waste analysis. Accordingly, sequential extraction method provides valuable information for researchers to better understand the transport and fate of sediment-associated metals in natural water systems, which can help develop appropriate strategies for environmental protection and soil remediation (de Andrade Passos et al., 2010; Huang and Kretzschmar, 2010; Nemati et al., 2011; Plan et al., 1997; Rao et al., 2010; Singh et al., 2005; Tessier et al., 1979).

1.3.3 The physical and chemical properties which may affect distribution of trace metals in sediments

The transport capacity of sediment-associated trace metals is influenced by a wide variety of physical attributes such as grain size, surface area, specific gravity, surface charge, bulk density, sheer stress, porosity, and permeability (Horowitz, 1991; James et al., 2006; Zhang et al., 2011). Generally, in natural water systems, grain size is considered to be one of the most important factors controlling a sediments' capacity for accumulating trace metals (Liebens, 2001; Ma et al., 2019; Yao et al., 2015; Zhu et al., 2008). Jones and Bowser (1978) showed that the clay-sized sediments (<2μm) have specific surface areas measured in square meters per gram (m^2/g), while the sand-sized particles have specific surface areas commonly measured in tens of square centimeters per gram (cm^2/g). Because of the larger specific surface areas, finer particles can contain more binding sites on the surface for metal adsorption (Gibbs, 1973; Jenne, 1968; Jenne et al., 1980). Based on this theory, to better understand the presence of trace metals in sediments during transportation in rivers, numerous techniques have been applied to determine the grain-size distribution of various sediment samples and specific grain-size fractions were separated for subsequent chemical analysis (Jain and Sharma, 2001; Priju and Narayana, 2007; Sattarova et al., 2021). As a result, Horowitz (1991) pointed out that there is a strong correlation between decreasing grain size and increasing trace element concentrations. Stone and Collins (2010) indicated that inorganic and organic particulate matters which <63μm are main scavengers for contaminants of concern in aquatic system.

The mobility of sediment-bound trace metals is not only related to the physical properties (e.g., surface area) but also the geochemical composition of sediments (Stone et al., 2022). During river transport, trace metals accumulate onto minerals such as clays, carbonates, Fe-Mn oxides, organic matters, sulfides and silicates through adsorption onto the surface of fine particles, precipitation/co-precipitation with substrates or incorporation in crystalline lattices (Horowitz, 1991). Those processes form different strength of bindings between solid phases and trace metals, which in return, reflect the ability of different capacities for retaining metals (Singh et al., 2005;

Tessier et al., 1979). In addition, the most surface-active components (e.g., Fe-Mn oxides and hydroxides, organic carbon and clay minerals) increase with decreasing grain size (Förstner, 2004b; Förstner and Wittmann, 1981). Horowitz and Elrick (1987) determined the capacity of minerals for trace metals in the following sequence: amorphous Fe oxide> total extractable Fe> total organic carbon> reactive Fe> clay minerals> total extractable Mn> Mn oxides. Accordingly, the physical (grain size distribution) and chemical (mineralogical composition) properties of sediment samples collected in the NSR should be measured to better interpret the concentration and distribution patterns of sediment-associated metals.

1.3.4 The bioavailability and subsequent toxicity of heavy metals with the aid of risk assessment code (RAC)

The risk assessment code was initially proposed by Perin et al. (1985) and supported by the theory that trace metals are bound to different fractions of the sediment with different strengths (Förstner and Wittmann, 1981; Li et al., 1995; Peijnenburg et al., 2007; Sundaray et al., 2011; Tessier et al., 1979). This is important because metals introduced by anthropogenic activities were preferentially accumulated in the exchangeable and carbonate fractions, which can easily equilibrate with the aqueous phase and thus became more bioavailable (Singh et al., 2005). Therefore, to better assess the risk of heavy metals in an aquatic environment, RAC has been applied to scale the percentages of metals in the exchangeable and carbonate fractions (Liu et al., 2008; Perin et al., 1985; Sundaray et al., 2011). For example, Zhang et al. (2017) investigated metal fractionation in sediments of the Pearl River estuary in China, and found that Cd was in the medium to high risk category. Mondal et al. (2020) used RAC to evaluate potential contamination of Ganges River sediment in India, finding that Cu and Cr posted medium to high ecological risk. Moreover, both studies indicated that heavy metals were highly associated with bioavailable fractions in both urban and reclamation-affected river sediment, suggesting that rapid urbanization and industrialization are main reasons for the increase of the active forms of metals (Mondal et al., 2020; Zhang et al., 2017).

1.3.5 The influences of anthropogenic activities (in Edmonton)

Milliman and Syvitski (1992) hypothesized that human activities have significant impacts on global sediment fluxes — the modern estimations are at least 100% higher than 2000 years ago. 40% of the total sediment fluxes are sourced from wastewater discharges, atmospheric fallouts (e.g., road dust), and direct release of fine sediments (Carter et al., 2003; Robertson et al., 2003). Other studies were conducted to determine the anthropogenic sources of river sediments, and they collectively found that most sediment was sourced from topsoil in agricultural fields (especially arable and overgrazed grassland) (Collins et al., 1997; Owens et al.; Walling et al., 1999) and others from forestry, construction and mining activities (Motha et al., 2003).

As the capital city of Alberta, Edmonton has a population of more than 1 million people, making it the fifth-largest city and sixth-largest metropolitan area in Canada (Canada, 2022). The North Saskatchewan River flows through and bisects the city. Water usage and discharge along the river in the industrial heartland and Edmonton region include two water treatment plants, three wastewater treatment plants, agricultural lands and many industries (Figure 2.1.2) (Parks, 2015). This river supports Edmonton and its surrounding communities with drinking water, and the population, industrial and municipal growth along the river are expected to continue (Laceby et al., 2019). Due to the cumulative effects of human activities in urban areas, more contaminants were detected in the water and sediment samples collected from downstream than upstream (Stone et al., 2022). For example, Laceby et al. (2019) indicated that, compared with upstream of

Edmonton (Devon), the concentrations of Cl^-, Na^+ and K^+ detected downstream (Pakan) increased by 5.5, 4.8, and 2.7 times respectively. These elements likely entered the river through the application of salt on road during winter, runoff from agricultural land, as well as effluents from wastewater treatment plants and industries. Stone et al. (2022) investigated the geochemical composition and trace metal speciation of fine-grained bedload sediments collected in the Edmonton area and found that the proportion of extractable Cr in bedload sediments was significantly higher downstream of Edmonton compared with the upstream sites.

Over the years, the city of Edmonton has been one of the main sources of wastewater discharge to the NSR and the water quality in this river had been significantly influenced by municipal wastewater until the Goldbar Wastewater Treatment Plant began operation in 1956 and provided secondary treatment (AESRD, 2014). Then in 1984, the Capital Region Wastewater Treatment Plant was opened to upgrade wastewater treatment ability not only for municipal wastewater but also the storm and combined sewers (Anderson, 2011). Although the ongoing upgrades and implementation of state-of-the-art technologies have provided efficient tools for wastewater treatment (e.g., removal of biological nutrient, UV disinfection and membrane filtration), there are still water contamination issues when the volume of surface runoff exceeds sewer capacity or during a high flow season (Anderson, 2011). Thus, to protect aquatic ecosystem of the NSR, assessments are required to help manage the impacts of urbanization on water and sediment.

Chapter2 Materials and methods

2.1 Water and sediment sampling method

The eight sampling sites are shown in Figure 2.1.1 from Devon to Sturgeon River, and a list of all sample locations are provided in Table 2.1.

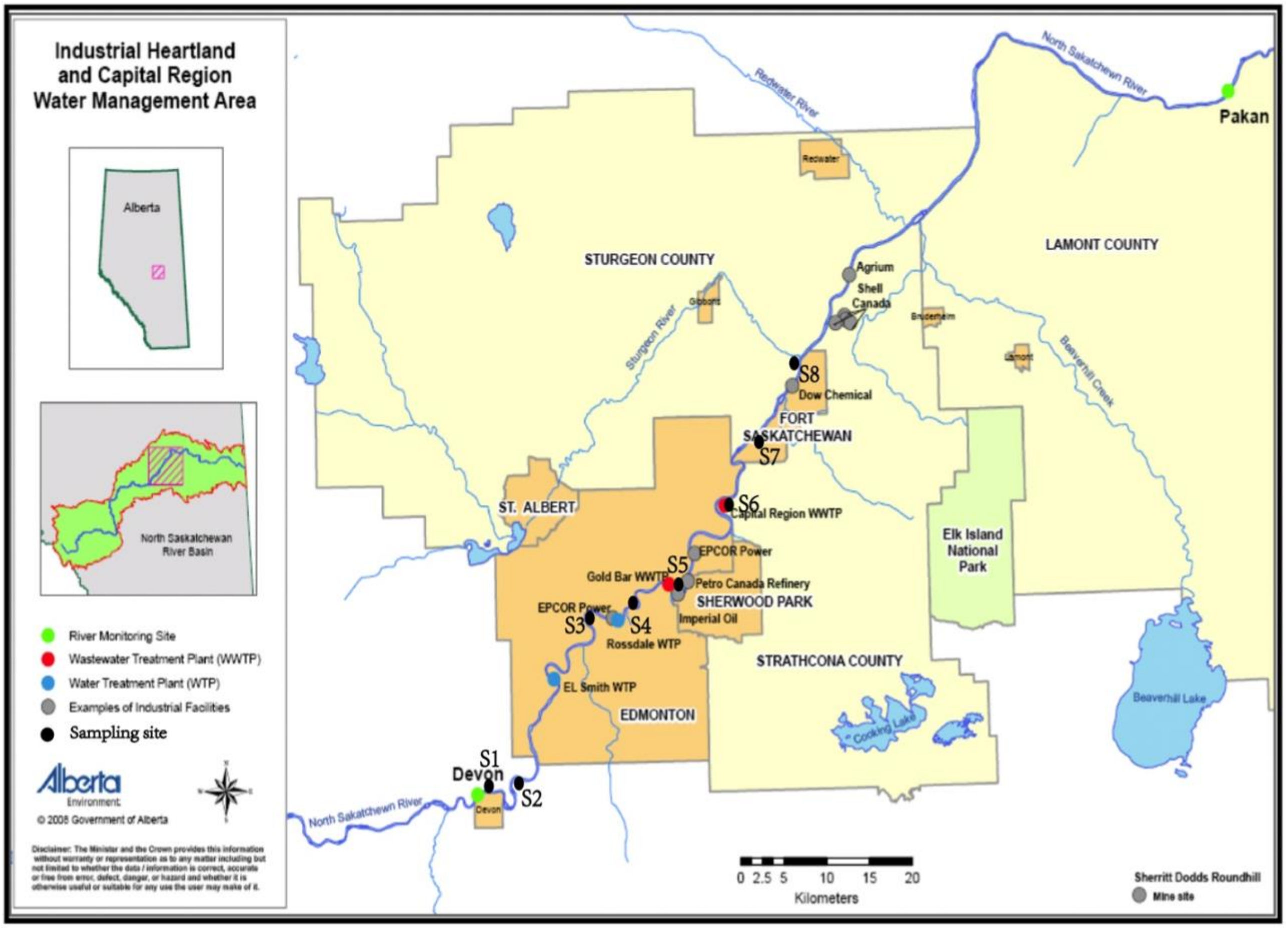


Figure 2.1.1 Sampling sites along the North Saskatchewan River (Modified from McDonald (2013))

Table 2.1 Water and sediment sampling locations on the NSR

Site	Location	Distance from the last monitoring site (km)	Southern/Northern Bank
1	Devon Voyageur Park	0	Southern
2	Shalom Park	7	Southern
3	Willian Hawrelak Park	30	Southern
4	Allan Stein Park	10	Northern
5	Rundle Park (near Gold Bar Wastewater Treatment Plant)	15	Southern
6	Alberta Capital Region Wastewater Treatment Plant	16	Southern
7	Fort Saskatchewan	15	Southern
8	Confluence of the Sturgeon River and the mainstream	10	Northern

As the NSR is typically ice-covered from November to March in Edmonton, all samples were collected in July 2018 as high river flow usually transports large amounts of suspended solids and associated contaminants such as nutrients and metals. (Ashmore and Day, 1988). The turbidity data (Figure 2.1.2) also indicate that the highest flow in 2018 occurred in July.

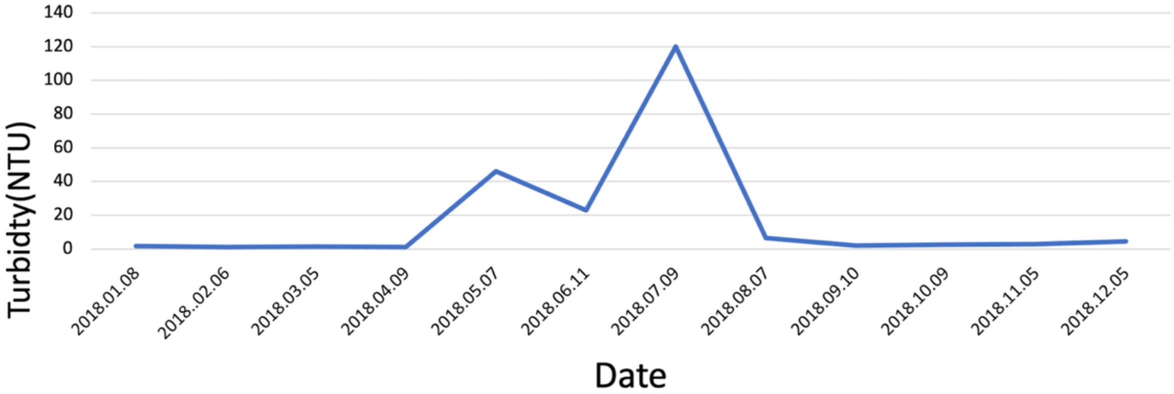


Figure 2.1.2 The turbidity data from the Water Survey of Canada’s National Water Data Archive Station AB05DD0010 (Devon)

Water samples were collected approximately 30 cm below the water surface, with high density polyethylene bottles that were acid washed three times.

Bedload sediments were directly sampled from shallow water about 10 m away from the riverbank. All samples were randomly collected (3 times) at each sampling point from sediment surface to a depth of about 30 cm. All samples were sealed in clean polyethylene bags and preserved in a cooled box on site before they were carried to the laboratory.

Suspended samples were collected in the form of suspension with acid rinsed buckets (20 L) from the surface of the water down to a depth of around 1 m (see supplementary, Figure S1).

2.2 Water analysis

Once transported to the laboratory, all water samples were preserved in a refrigerator at 3-4°C. 0.45μm filters were used to remove solid particles in the water and concentrated HNO_3 was added to bring the pH of the samples down to 2.0.

After pre-treatment (filtration, acidification, dilution), part of the water samples was analyzed using an Agilent 8800 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to quantify the concentration of major and trace metals in the NSR. Other water samples were sent to the Natural Resources Analytical Laboratory (NRAL), Department of Renewable Resources, at the University of Alberta for analysis of dissolved organic carbon (DOC), total and dissolved nitrogen (TN, DN), anions, nitrate/nitrite. Apparatuses are summarised in Table 2.2.

Table 2.2 Apparatuses used to measure dissolved contaminants

Dissolved P, S, Ca, Mn, Fe, Gu, Zn, As, Sr, Se, Mo, Pb, Cd, Cr, Co	Agilent 8800 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
Anions (phosphate, chloride, sulfate)	Dionex Ion Chromatography (IC) DX600
DOC and TN	Shimadzu TOC-V CHS/CSN Model Total Organic Carbon Analyzer
Nitrate/Nitrite	SmartChem Discrete Wet Chemistry Analyzer, Model 200
Alkalinity	Automated continuous titrator, Metrohm Titrando 905

2.3 Sediment analysis

2.3.1 X-ray diffraction (XRD) analysis

After drying in an oven (40℃) for over 24 h, around 0.5 g of each sample was weighted and then ground in anhydrous ethanol with a McCrone Micronizing Mill for 4 minutes. Samples were then air-dried in a desiccator for about 24 h and disaggregated by agate mortar and pestle. The ion-exchange process was carried out on sediment samples at room temperature with 100mL of 1M $CaCl_2 \cdot 2H_2O$. The suspension was shaken mechanically for 24h before separation of the solid fraction. In the last step, samples were rinsed three times with deionized water and disaggregated again with the agate mortar and pestle.

For the XRD processes, a humidifier was applied to control the relative humidity in the range of 20-80% (Bish et al., 2003), and at the beginning and end of each patten collection, relative humidity was recorded.

2.3.2 Sequential weight loss on ignition (LOI)

The sequential weight loss on ignition (LOI) method is widely used to determine organic and inorganic carbon (carbonate) contents in river sediments (Bengtsson and Enell, 1986; Dean, 1974; Heiri et al., 2001). At around 500°C, organic carbon is oxidized to carbon dioxide (CO_2) and ash, and at around 800°C carbonate minerals breakdown into CO_2 (Heiri et al. (2001). Based on this theory, several studies were conducted to measure C contents in sediment and found that the weight losses during those two reactions are correlated to the amount of organic carbon and carbonate in the original sample (Dean, 1974; Heiri et al., 2001).

The protocol of LOI in this study was modified from Heiri et al. (2001), Bengtsson and Enell (1986), Dean (1974) and Wang et al. (2011). To avoid instrumental errors, crucibles were rinsed by deionized water three times and placed in a mechanical oven (Thermo Scientific™, Heratherm Mode) at 105°C for more than 48 h until they reached solid weights. Then, 100 mg samples were weighed (METTLER TOLEDO, XPR Micro and Ultra-Microbalance) and dried overnight (12 h) in the same oven at 105 °C. After that, for the first step, samples and crucibles were placed in a box furnace (Thermo Scientific™, Lindberg/Blue) and heated to 550 °C for 12 h to combust organic carbon to ash and CO_2. The following equation was used to calculate LOI (Heiri et al., 2001):

$$LOI_{550}=((DW_{105}-DW_{550})/DW_{105})*100$$

Where LOI_{550} represents weight loss at 550 °C (%), DW_{105} (g) represents the dry weight of the sample before heating to 550 °C. After cooling to room temperature in a desiccator, sample and crucible were weighted again to get the DW_{550} (g). The furnace was then reheated to 950 °C for 12 h and the amount of CO_2 evolved from carbonate minerals can be calculated as:

$$LOI_{950}=((DW_{550}-DW_{950})/DW_{105}) *100$$

Where LOI_{950} represents LOI at 950 °C (%), DW_{550} (g) and DW_{950} (g) are the dry weights of samples after heating to 550 °C and 950 °C respectively. DW_{105} (g) is the dry weight of initial sample. When calculating weight loss in this step, Bengtsson and Enell (1986) indicated that the molar mass of CO_2 and CO^{3-} are 44 g/mol and 60 g/mol, thus the weight loss by LOI at 950 °C multiplied by 1.36(60/40) theoretically match the initial weight of carbonate in the original sample. This also implies that inorganic carbon = 0.273 × LOI_{950} (the fraction of C in CO_2) (Dean, 1974).

2.3.3 Sieving and laser diffraction particle size analyzer

Bedload sediment coarser than 63 μm was separated by sieving (see supplementary, Figure S2). To avoid contamination from metallic sieves, non-metallic sieves were used in this section (Horowitz, 1991; Sakai et al., 1986). First, 70-100 g dried and ground bedload sediment samples were weighed and put into a vertical nylon nest of 7 sieves with opening of 2 mm, 1 mm, 710 μm, 500 μm, 250 μm, 125 μm, 63 μm. Then the sieve box was set onto a shaker with continuous vibration for 1 h. Dry weight of each size range (Table 2.3.3) was then recorded, and samples were stored in a refrigerator at -20 °C for subsequent analysis.

Table 2.3.3. Classification of grain sizes (Panchuk, 2019)

		Clast name	Diameter Range
Coarse-grained		Boulder	Larger than 256mm
		Cobble	64mm-256mm
		Pebble	2mm-64mm
Medium-grained	Sand	Coarse	500μm-2mm
		Medium	250μm-500μm
		Fine	63μm-250μm
Fine-grained		Silt	2μm-63μm
		Clay	Smaller than 2μm

For bedload sediment finer than 63 μm and suspended sediment, 100 mg of each sample was weighed, and a laser diffraction particle size analyzer (Malvern, Mastersizer3000) was used to deduce the size, surface area and volume distribution patterns of particles in each sample.

2.3.4 Total digestion and sequential extraction of heavy metals

Most sequential extraction methods follow similar procedures with little variation, and here, a five-step extraction method adopted by Tessier et al. (1979) was used as a basic frame and some modifies were made to suit our samples and testing apparatus:

Under a fume hood, bedload samples were dried for seven days, then ground and sieved to isolate the particles that are smaller than 63 μm after a portion of the sample was taken for textural analysis (sand, silt, clay, and gravel percentages, section 2.3.3). Suspended samples were filtered by vacuum filtering system through 0.45 μm filter upon arriving back at the lab. Then the solid phase was air dried under the room temperature and scraped with a spatula before being homogenized (see supplementary, Figure S3). All sediment samples were stored in Falcon tubes at around -20 °C before the following total digestion and sequential extraction analysis (Horowitz, 1991; Horowitz, 2008; Horowitz and Elrick, 2017).

Extractive reagents were prepared in advance based on áVan Rees (1995), Li et al. (1995), Wilson et al. (2006), Tessier et al. (1979) and von Gunten et al. (2017), details are as follows (Table 2.3.4):

Table 2.3.4 Selected reagents employed in sequential extraction

Solution 1	0.5M magnesium chloride ($MgCl_2$)
Solution 2	1M sodium acetate ($C_2H_3NaO_2$)
Solution 3	0.04M hydroxylammonium hydrochloride ($NH_2OH \cdot HCl$)
Solution 4a	0.02M nitric acid (HNO_3)
Solution 4b	30% hydrogen peroxide (H_2O_2)
Solution 4c	3.2M ammonium acetate ($C_2H_3O_2NH_4$)

Heavy metal fractionations were measured by modified sequential extraction scheme (Figure 2.3.4) and these fractions were divided into five categories (the quantities of extraction reagents below refer to 0.3 g sediment samples):

Step 1. (Exchangeable Metals): 4.8 mL solution1 was added into each polyethylene tube to extract the sediment at room temperature. The solution was then carefully adjusted pH to 7 using pH Meter and then put on a rotary shaker for 20 mins.

Step 2. (Metals Bound to Carbonates): 4.8 mL solution2 was added into each tube to react with the residue from Step 1. At room temperature, pH was adjusted to 5 with acetic acid. After that, continuous agitation was maintained by rotary shaker for 5 h.

Step 3. (Metals Bound to Iron and Manganese Oxides): The residue from Step 2 was extracted with 12 mL solution3. Samples were then put on a preheated oven (96 °C) for 6 h with occasional agitation every hour.

Step 4. (Metals Bound to Organic Matter): For each tube, 1.8 mL solution 4a and 3 mL 4b were added, and the mixture was adjusted to pH=2 using HNO_3 and heated to 85°C for 2 h with occasional agitation every hour. After 2 hours, 1.8 mL solution4b was added to react with the mixture of solution at the same temperature for 3 h with occasional agitation. After cooling, 3 mL solution4c and 2.4 mL deionized water were added, samples were then put on the rotary shaker for 30 mins.

Step 5. (Residual Metals): In the last step, the residue from Step 4 was transferred into a more resilient PTFE tube and digested with a mixture of 65 % HNO_3, 30 % H_2O_2 and 70 % HF to obtain a total metal concentration. Specifically, 5 mL 65 % HNO_3 and 5 mL 30 % H_2O_2 were added into each tube, and samples were then moved to the hotplate and heated to 120 °C with lids sealed for 1 h. After that, 2 mL hydrofluoric acid was added in each tube and temperature was increased to 130 °C until nearly dry of the solution (around 3.5 h). Finally, 20 mL 4.5 % H_3BO_3 was added to dissolve the residue at 130 °C for 1 h.

H_3B0_3 was added in the last step of sequential extraction to (1)remove HF and improve safety for sample handling, (2)better recover the elements by reducing volatilization losses (e.g., Si) and solubilizing metal fluoride complexes (e.g., Ca, Al and Mg), (3)increase detection limits for Inductively Coupled Plasma(ICP) analysis (Wilson et al., 2006).

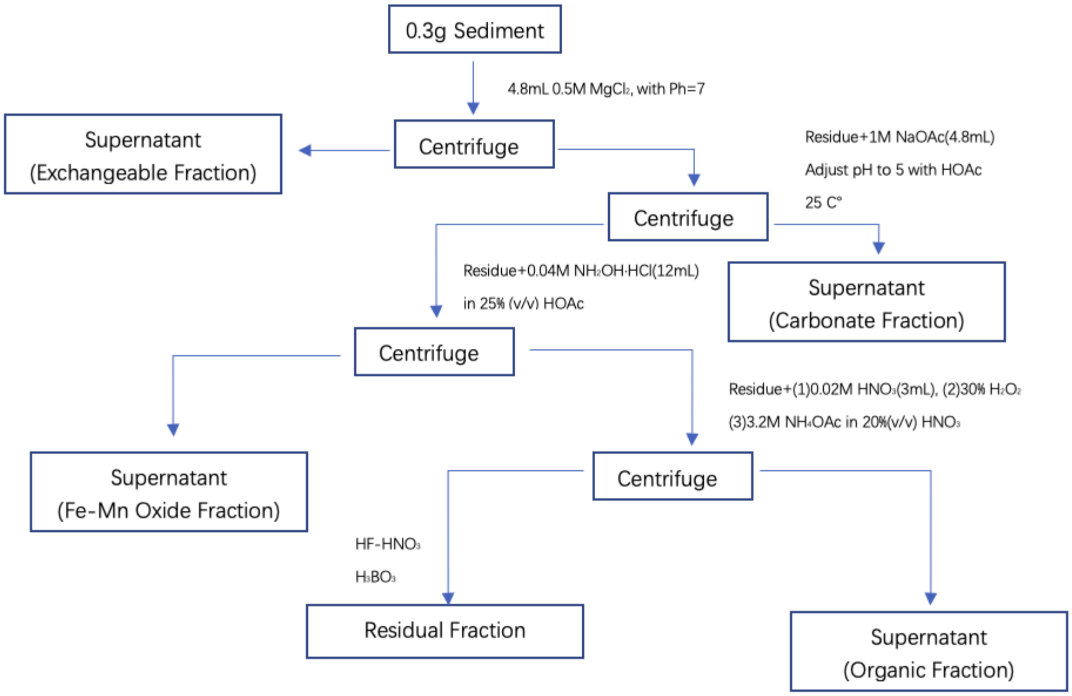


Figure 2.3.4 Modified chart of the speciation scheme of sediments (Martin and Meybeck, 1979; Tessier et al., 1979; Wilson et al., 2006)

After each extraction step, to minimize the loss of solid materials, the supernatant solution was separated by centrifugation (Thermo Scientific™, LYNX) at 15000 rpm for 15 mins. The supernatant solution was then extracted with a pipette and diluted with a mixture of 2 % HNO_3 and 0.5 % HCl. The solution was filtered (0.45 µm) for trace metals (Zn, Cu, Ni, Cd, Mn, Cr, Pb, Fe, Sr, Co, Mo) and analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Also, after exposing the solids to extractive solutions in each step, deionized water (Milli-Q Millipore, 18.2 MΩ/cm resistivity) was used to rinse the residue three times along with the same centrifugation processes before the next extractive solution was introduced. Blanks were included to avoid contamination of extractive reagents and help monitor instrumental errors. Each sample was performed in triplicate.

Accuracy of the metal concentrations in sediment samples were determined through repeated analysis of STSD-3 and the results were found to be within ± 5% of certified values. STSD-3 is a mixture of stream sediment samples collected in Ontario and British Columbia to represent typical stream sediments from various geochemical environments in Canada. The recommended values of 65 elements are given by thirty-five laboratories.

The concentration of trace elements measured by total digestion were compared with the sum of the metal concentrations in each individual fractions (exchangeable, carbonate, Fe-Mn oxides, organic, residual fractions), and the results showed good agreement for all trace elements. The detection limits are summarized in Table 2.3.5:

Table 2.3.5 The ICP-MS detection limit for different metals

Element	Detection limit (µg/L)
Zn	1.110
Cu	0.140
Ni	0.280
Cd	0.007
Mn	0.470
Cr	0.380
Pb	0.010
Fe	1.260
Sr	0.050
Mo	0.007
Co	0.020

2.4 Pollution extent and risk assessment

The Water Quality Guidelines (WQGs) include guidelines for general features (e.g., pH, temperature and hardness), nutrients, metals, petroleum hydrocarbons and mixtures. For the protection of aquatic life, both long-term and short-term guidelines are provided. The long-term guidelines are levels of condition that should result in negligible risk of adverse effects on growth, reproduction, or survival of aquatic biota, which is more stringent than the short-term guidelines (AEP, 2018). In this study, the risk assessment code (RAC) was used to classify bioavailable fractions (exchangeable and carbonate-bound fraction) and non-bioavailable fractions of heavy metals in sediment samples. According to the RAC guidelines (Perin et al., 1985) summarized in Table 2.4.1, for any trace metal, less than 1 % participation of total metal in exchangeable and carbonate fractions is considered to be safe to the environment. The percentage of bioavailable fractions within 1-10 %, 11-30 % and 31-50 % represents low, medium, and high risk to the environment, respectively, whereas larger than 50 % means the environment is under very high risk of pollution.

Table 2.4.1 Risk assessment code (Perin et al., 1985)

Category	Risk	Metal in carbonate and exchangeable fractions (%)
1	No Risk	<1
2	Low Risk	1-10
3	Medium Risk	11-30
4	High Risk	31-50
5	Very High Risk	>50

For sediment quality guidelines (SQGs), the Interim Sediment Quality Guidelines (ISQG) and Probable Effects Level (PEL) are listed separately to indicate different levels of contamination (Table 2.4.2). Comparison between the total concentration and the SQGs can help us better understand the toxic level of a specific trace metal.

Table 2.4.2 Classification of sediment quality guidelines and their effects (AEP, 2018)

<ISQG	Not associated with adverse biological effects.
ISQG - PEL	May occasionally be associated with adverse biological effects.
>PEL	Frequently associated with adverse biological effects.

Additionally, a Lowest Effect Level (LEL) guideline (Persaud et al., 1993) was introduced to complement some missing data.

Chapter3 Results and Discussions

3.1 Physicochemical parameters of the NSR water

3.1.1 Major ions and general properties

Major ions

Concentrations of major ions in the NSR and Water Quality Guidelines (WQGs) are summarized in Table 3.1.1. The median concentrations of cations and anions in the NSR are in the order of calcium (Ca^{2+}) > magnesium (Mg^{2+}) > sodium (Na^{+}) > potassium (K^{+}) and HCO_3^- (bicarbonate) > SO_4^{2-} (sulfate) >Cl^- (chloride), respectively. HCO_3^- was estimated based on the alkalinity since it would be the predominant form of inorganic carbon at the pH range between 7.6 and 8.5 (Langmuir, 1997). According to Table 3.1.1, the median open-water major ions were all below their WQGs (chronic and acute). Spatial variations indicate that, generally, from Devon Voyageur Park (S1) to Fort Saskatchewan (S7), the concentrations of Mg^{2+}, Na^{+} and K^{+} increased from 15.18, 4.07 and 0.83 mg/L to 16.28, 7.07 and 1.45 mg/L, respectively. Similarly, in the same reach, Cl^- and SO_4^{2-} increased from 1.17 to 4.44 mg/L and 41.00 to 51.93 mg/L respectively. At S8, all major ions showed relatively lower concentrations compared with the S7.

Table 3.1.1 Concentration of major ions and general properties of the NSR

Sampling Site	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	pH	Temperature (℃)	Alkalinity (mg/L)
site1 (S1)	41.14	15.18	4.07	0.83	1.17	41.00	8.36	17.30	133.86
site2 (S2)	40.90	15.06	4.05	0.82	1.00	41.16	8.27	17.50	136.62
site3 (S3)	40.36	15.03	5.81	1.08	0.48	47.12	7.64	18.20	130.73
site4 (S4)	41.50	15.43	4.87	0.93	1.86	45.18	7.70	18.70	128.42
site5 (S5)	42.28	15.77	5.01	0.95	0.34	46.38	7.74	18.00	134.07
site6 (S6)	40.61	15.34	6.32	1.23	4.44	48.45	7.91	19.00	131.27
site7 (S7)	42.35	16.28	7.07	1.45	3.77	51.93	8.51	19.00	132.01
site8 (S8)	40.90	15.96	4.87	0.98	1.73	48.44	8.50	19.20	133.23
Maximum	42.35	16.28	7.07	1.45	4.44	51.93	8.51	19.20	136.62
Minimum	40.36	15.03	4.05	0.82	0.34	41.00	7.64	17.30	128.42
Median	41.02	15.39	4.94	0.96	1.45	46.75	8.09	18.45	132.62
Average	41.25	15.51	5.26	1.03	1.85	46.21	8.08	18.36	132.53
Standard deviation	0.74	0.45	1.07	0.21	1.50	3.73	0.37	0.72	2.49
Long-Term (Chronic)	N/A	N/A	N/A	N/A	120.00	309.00	6.50-9.00	N/A	> 20
Short-Term (Acute)	N/A	N/A	N/A	N/A	640.00	N/A	N/A	N/A	N/A

Long-term, levels of the condition that should result in negligible risk adverse effects on aquatic biota in an indefinite period, data from WQGs (AEP, 2018).
Short-term, levels of the condition that should result in no lethality for most aquatic biota during intermittent and transient period, data from WQGs (AEP, 2018).

Previous studies showed that multiple anthropogenic activities caused spatial and temporal variations of major ions (e.g., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, CO_3^{2-} and HCO_3^{-}) in the reach of the Capital Region (AESRD, 2014; Anderson, 2011; Laceby et al., 2019). For example, Laceby et al. (2019) indicated that during spring runoff (in April and May), sodium chloride (salt applied on road as de-icing agents) and other chloride-containing compounds (e.g., $MgCl_2$, $CaCl_2$) are major sources (54%) of chloride in the NSR, while softener brines from WWTPs and fertilizers from agricultural land can also cause pronounced increases of major ions (e.g., Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}) downstream of Edmonton (AESRD, 2014; Golder, 2013c). In summer (sampling season in this study), Golder (2013c) indicated that Cl^{-} concentrations measured at individual outfalls (e.g., effluents from WWTPs) were still high (from 143 mg/L to 218 mg/L). In June and July, elevated levels of Cl^- in water samples collected in tributaries such as Whitemud Creek (60-100 mg/L, between S2 and S3), Goldbar Creek (60-80 mg/L, between S4 and S5) and Sturgeon River (around 60 mg/L, S8) were observed in wet weather conditions due to flushing of salts in soils (Golder, 2013c). Accordingly, the increasing trend of major ion concentrations between S1 and S7 can be attributed to high chloride-containing inputs from WWTPs and tributaries. Additionally, Pilechi et al. (2012) found that WWTP-related contaminants presented higher levels on the south bank than the north bank in the reach of the Capital Region, which can explain the obvious decreases of major ion concentrations at S8 (which is located on the north bank at the upstream of the Sturgeon River month) (Figure 2.1.1).

pH and alkalinity

Aqueous pH is affected by multiple factors including dissolved/suspended pollutants and biological activities (Shaw et al., 1994). Generally, there was no significant change in pH along the NSR (Table 3.1.1). Relatively high pH values were found in sampling sites near Devon at around 8.3 (S1 and S2) and sites located downstream of the WWTPs at around 8.5 (S7 and S8), while other monitoring sites showed lower pH values, ranging from 7.64 to 7.91 (S3-S6). Alkalinity refers to acid-neutralizing capacity of water (Dickson, 1992) and the buffering ions include carbonate, bicarbonate, borates, phosphates, and silicates etc. (Clesceri et al., 1989). The alkalinity values were stable (stand deviation = 2.49) along the river, with a relatively lower value at S4 (Allan Stein Park, 128.42 mg/L).

According to the WQGs, all pH and alkalinity values were in the environmentally acceptable range. In this study, S1 and S2 showed their pH at 8.36 and 8.27, which confirms the results from the Long-term River Network conducted between 2007 and 2012 which indicated that the median pH in the reach of the Capital Region (from Devon to Pakan) was around 8.3 (AESRD, 2014). Bell (2015) measured pH values of four tributaries in Edmonton area (e.g., Wedgewood Creek, Horsehills Creek, Sturgeon River and Red River) and found that pH in the Wedgewood Creek (7.99, between S2 and S3) and Horsehills Creek (7.93, between S5 and S6) were all below the values measured at S1, S2, S7 and S8, which provides a likely reason for lower pH between S3 and S6 (from 7.64 to 7.91). For sampling site 7 and 8, previous studies showed that individual values sometimes exceeded the WQGs of 9.0 at WWTPs and Fort Saskatchewan (S7) (AESRD, 2014). Thus, the relatively high pH values (8.51 at S7 and 8.50 at S8) were most likely due to the cumulative contribution of alkaline materials and nutrients from the WWTPs. By stimulating algal growth, nutrients can indirectly influence the rates of algal photosynthesis and respiration in above areas, causing higher pH values during daytime through the consumption of CO_2 (reaction 1).

$$[1]\ CO_2 + H_2O \rightarrow CH_2O + O_2$$

This hypothesis is proved by the spatial trends of both periphyton biomass and dissolved oxygen levels measured between Devon and Pakan (AESRD, 2014). The Datasonde data (measured every 15 minutes) also showed biological influences by presenting diurnal fluctuations (higher during the day and lower during the night) of pH in the study area (AESRD, 2014).

3.1.2 Trace metals

Trace elements, especially heavy metals, are among the most common pollutants because of their toxicity, persistence, and non-degradability in the environment (Morley et al., 1993; Singh et al., 1999). In natural rivers, elevated concentration of dissolved heavy metals can be used to reflect the source of the pollutant (e.g., effluent from WWTPs) since they tend to bond to solid particles in aquatic system and can be diluted very quickly within tens of kilometres along the river (Mohiuddin et al., 2010; Pilechi et al., 2012).

In this study, dissolved nickel (Ni), cadmium (Cd), chromium (Cr) and cobalt (Co) were below detection limits. Concentrations of dissolved manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), strontium (Sr), molybdenum (Mo) and lead (Pb) are presented in Table 3.1.2. Generally, the median levels of those heavy metals follow the sequence of Sr (338.50 µg/L) > Zn (6.18 µg/L) > Fe (3.38 µg/L) > Mo (0.85 µg/L) > Mn (0.72 µg/L) > Cu (0.40 µg/L) > Pb (0.11 µg/L). Significant fluctuations were observed in Pb, Zn and Mn, with the maximum values 45, 32 and 16 times higher than the minimum values.

Table 3.1.2 Concentration of dissolved metals (µg/L) in the NSR

Sampling Site	Mn	Fe	Cu	Zn	Sr	Mo	Pb
site1 (S1)	0.50	3.27	0.31	9.13	327.47	0.69	0.07
site2 (S2)	0.48	2.87	0.23	2.69	324.99	0.66	0.05
site3 (S3)	1.49	7.10	0.76	1.13	332.73	1.96	0.28
site4 (S4)	1.66	3.79	0.82	13.72	335.56	0.86	0.75
site5 (S5)	1.81	3.72	0.59	1.73	341.43	1.15	0.14
site6 (S6)	0.95	2.83	0.46	4.86	349.67	0.85	1.80
site7 (S7)	0.14	3.48	0.33	7.50	378.36	0.90	0.06
site8 (S8)	0.11	0.85	0.23	36.99	372.35	0.72	0.04
Maximum	1.81	7.10	0.82	36.99	378.36	1.96	1.80
Minimum	0.11	0.85	0.23	1.13	324.99	0.66	0.04
Median	0.72	3.38	0.40	6.18	338.50	0.85	0.11
Average	0.89	3.49	0.47	9.72	345.32	0.97	0.40
Standard deviation	0.69	1.73	0.23	11.81	20.15	0.43	0.61
Long-Term (Chronic)	50	300.00	7.00	61.00	N/A	73.00	4.00
Short-Term (Acute)	N/A	N/A	21.00	550.00	N/A	N/A	N/A

Long-term, levels of the condition that should result in negligible risk adverse effects on aquatic biota in an indefinite period (AEP, 2018),data from WQGs.

Short-term, levels of the condition that should result in no lethality for most aquatic biota during intermittent and transient period (AEP, 2018), data from WQGs.

Dissolved Cu in aquatic system is mainly from weathering of copper minerals (Shaw et al., 1994). Its background concentration is usually below 20 μg/L, and human activities may cause higher levels in river water (Linder et al., 1998). According to Table 3.1.2, the concentration of dissolved Cu was relatively low at sampling site located upstream of Edmonton (Devon Voyageur Park, S1, 0.31 μg/L). Towards downstream, it increased from S2 (Shalom Park, 0.23 μg/L) to S4 (Allan Stein Park, 0.82 μg/L), then decreased gradually from S4 to S8 (Sturgeon River mouth, 0.23 μg/L). Compared with WQGs (7 μg/L), dissolved Cu showed no adverse effects on aquatic biota.

Dissolved Fe can be released into the water column through weathering of sulfide minerals (e.g., pyrite) and leaching from sandstones (Fantle and DePaolo, 2004). Anthropogenic sources include burning of coke and coal, acid mine drainage, mineral processing etc. (Müller et al., 2006). In water samples collected from Devon Voyageur Park (S1), the average concentration of dissolved iron was 3.27 μg/L. From Shalom Park (S2) to Willian Hawrelak Park (S3), it increased from 2.87 μg/L to 7.10 μg/L, then dropped from 7.10 μg/L to 3.48 μg/L (S7) and showed its lowest value at S8 (0.85 μg/L). According to the WQGs (300μg/L), all the data collected from the mainstem were lower than the guidelines.

For Pb, compared to natural enrichment pathways in the aquatic environment, anthropogenic inputs play a more important role. For example, Del Rio-Salas et al. (2012) indicated that industrial and municipal discharges and urban runoff, as well as the atmospheric deposition caused by vehicle and industrial emissions, can increase the Pb concentration in surface waters. According to Table 3.1.2, the concentration of dissolved Pb showed an upward trend from S1 to S4 (0.07-0.75 μg/L), then it was diluted to 0.14 μg/L at S5. The peak value of 1.80 μg/L was found at S6. After that, the concentration of dissolved lead decreased again to 0.06 μg/L at S7 and

0.04 µg/L at S8. According to the WQGs (4 µg/L), all the data collected from the mainstem were lower than it.

Dissolved Mn mainly comes from soil, sediments, rocks and human-derived sources such as industrial discharges (Li et al., 2014). In this study, dissolved Mn increased along the mainstem from 0.48 µg/L (S2) to 1.81 µg/L (S5) and then dropped to 0.11 µg/L (S8). The highest value of dissolved manganese was 1.81µg/L, which is much lower than the standard value suggested by WQGs (50µg/L).

The main sources of dissolved Mo in aquatic environment include weathering of igneous and sedimentary rocks and utilization of fertilizers (Novotny and Peterson, 2018). The highest concentration (1.96 µg/L) was observed in water samples collected at S3 (Hawrelak Park). Another peak was found in water samples collected in Rundle Park (S5, 1.15 µg/L). According to WQGs (73.00 µg/L), all the data collected from the mainstem were lower than it.

Natural weathering and human activities will increase the concentration of Sr in river water (Shaw et al., 1994). Although not actively mined in Canada, Sr can be released into water column through pathways such as by-product of other mining operations and industrial effluents (Health, 2018). According to Table 3.1.2, dissolved Sr showed no significant change in concentration along the river. Generally, it increased from upstream at around 325 µg/L to downstream at around 370 µg/L. There are no WQGs for Sr, but according to the consultation document developed by Health (2018), the maximum acceptable concentration of 7000 µg/L is proposed for total strontium in drinking water. All the data were lower than that value.

Dissolved Zn is widely distributed in natural environment and it can be sourced from natural inputs (geochemical weathering of rocks) and/or anthropogenic inputs (Davis et al., 2001).

Generally, compared to the long-term guideline (61 µg/L), the mean concentration of dissolved Zn in the NSR was low (9.72 µg/L). However, there was a dramatic increase in zinc concentration between S7 and S8 (from 7.50 µg/L to 36.99 µg/L), indicating that there were additional inputs of Zn between those two sites.

Table 3.1.3 The enrichment pattern of dissolved metals

Sampling Site	S1	S2	S3	S4	S5	S6	S7	S8
			Mn	Mn	Mn			
			Fe	Fe			Fe	
			Cu	Cu	Cu			
	Zn			Zn				Zn
			Mo		Mo		Mo	
			Pb	Pb		Pb		

Elevated levels of dissolved metal in the surface water are efficient signatures for targeting anthropogenic sources (AESRD, 2014). In Table 3.1.3, the three highest concentrations of Mn, Fe, Cu, Zn, Mo and Pb were selected as indicators of the contaminant sources. Sr is excluded since it showed constant increasing trend from S1 to S8, which can be related to natural factors (AESRD, 2014). Those metals display their highest concentrations in three main areas: S1, S3-S5 and S6-S8. The three main sources of metals include:

(1) inputs from tributaries: Golder (2013b) collected water samples from tributaries in the Capital Region in 2012 and found that the increases of dissolved metals in the mainstem are partially related to tributary influences. Specifically, the previous study indicated that metal levels were higher in Whitemud Creek (between S2 and S3), Mill Creek (between S3 and S4) and Goldbar Creek (between S4 and S5), Horsehills Creek (between S5 and S6) and Sturgeon River (S8).

(2) inputs from municipal/industrial wastewaters or WWTPs: Golder (2013b) indicated that higher concentrations of dissolved Mo and Zn were observed in treated effluent from Goldbar and Capital Region WWTPs.

(3) sediment-associated metals: when environmental conditions change (e.g., salinity, pH, redox potential), heavy metals which were bound to solid particles can be released into the water column (Yuan et al., 2004). In this study, the total concentrations of Fe and Cu in sediment (both suspended and bedload) followed the opposite pattern (lower values at S3, S4 and S5) (Table 3.2.4), indicating that the elevated levels of dissolved Fe and Cu found at S3, S4 and S5 were associated with sediment-bound species. As summarized above, other metals were more related to inputs from tributaries and effluents from human-derived activities (Table 3.1.4).

Table 3.1.4 Possible sources of dissolved metals

Inputs from tributaries	Inputs from municipal/industrial wastewaters or WWTPs	Sediment-associated metals
Mn, Zn, Mo, Pb	Mn, Zn, Mo, Pb	Fe, Cu

3.1.3 Nutrients

Nitrogen

Nitrogen is one of the essential nutrients for the growth of aquatic algae, cyanobacteria and macrophytes (Lu et al., 2009). In natural water systems, total dissolved nitrogen (TDN) includes inorganic forms such as nitrite (NO_2^-), nitrate (NO_3^-), ammonia/ammonium (NH_3/NH_4^+) and organic forms such as amino acids, amines and proteins (Shaw et al., 1994). Dissolved inorganic nitrogen (DIN) is one of the most bioavailable forms of nitrogen and mainly dominated by anthropogenic inputs (Dagg et al., 2004; Meybeck, 1982; Turner et al., 2003). In natural rivers, increasing DIN (e.g., NO_2^-, NO_3^-, NH_3/NH_4^+) can directly influence the growth of primary producers (e.g., plant and algae) and cause environmental problems (Grizzetti et al., 2011).

Table 3.1.5 Concentration of dissolved nutrients in the NSR

Sampling Site	DOC (mg/L)	DON (mg/L)	NH_3/NH_4^+ (ug/L)	NO_2^- (ug/L)	NO_3^- (ug/L)	PO_4^{3-} (ug/L)	pH
site1 (S1)	17.74	0.11	61.81	N/A	106.74	N/A	8.36
site2 (S2)	18.13	0.14	53.82	N/A	114.10	N/A	8.27
site3 (S3)	21.34	0.22	2.04	N/A	125.54	N/A	7.64
site4 (S4)	18.19	0.14	31.34	2.08	169.02	1.94	7.70
site5 (S5)	19.08	0.17	8.06	4.14	105.62	3.86	7.74
site6 (S6)	16.00	0.31	15.68	8.04	777.19	7.51	7.91
site7 (S7)	17.75	0.57	110.06	38.66	1774.77	36.10	8.51
site8 (S8)	13.14	0.19	50.04	3.14	327.15	2.93	8.50
Maximum	21.34	0.57	110.06	38.66	1774.77	36.10	8.51
Minimum	13.14	0.11	2.04	2.08	105.62	1.94	7.64
Median	17.94	0.18	40.69	4.14	147.28	3.86	8.09
Average	17.67	0.23	41.61	11.21	437.52	10.47	8.08
Standard deviation	2.37	0.15	35.42	15.51	586.68	14.48	0.37
Long-Term (Chronic)	N/A	N/A	138.00-1200.00	20.00-60.00	3000.00	N/A	6.50-9.00
Short-Term (Acute)	N/A	N/A	N/A	60.00-180.00	124000.00	N/A	N/A

Long-term, levels of the condition that should result in negligible risk adverse effects on aquatic biota in an indefinite period (AEP, 2018),data from WQGs.
Short-term, levels of the condition that should result in no lethality for most aquatic biota during intermittent and transient period (AEP, 2018),data from WQGs.

Table 3.1.5 reveals that the NO_3^- (147.28 μg/L) exhibited the most abundant dissolved inorganic form of nitrogen in the study area, which was followed by NH_3/NH_4^+ and NO_2^- (40.69 μg/L and 4.14 μg/L). DON showed its maximum value at 570 μg/L and minimum value at 110 μg/L in the same reach.

Nitrite is an intermediate, partially oxidized anion, which can be oxidized rapidly to nitrate, forming the more stable and abundant species of nitrogen (Grizzetti et al., 2011). Along the NSR, nitrite and nitrate increased gradually from Devon Voyageur Park (S1) to Alberta Capital Region Wastewater Treatment Plant (ACRWWTP) (S6) (from 0 to 8.04 μg/L and 106.74 to 777.19 μg/L respectively). Then dramatic increases were observed at S7 (Fort Saskatchewan) (from 8.04 to 38.66 μg/L and 777.19 to 1774.77 μg/L respectively) (Table 3.1.5). In the same reach, the concentration of dissolved organic nitrogen (DON) also showed an increasing pattern from S1 (0.11 mg/L) to S7 (0.57 mg/L). Ammonification generates ammonia (NH_3) and ammonium (NH_4^+) from organic nitrogen, and total ammonia (NH_3/NH_4^+) can cause adverse effects on aquatic species such as fish (Anderson, 2011). According to Table 3.1.5, the concentration of total ammonia fluctuated in the study area with three peaks at S1 (61.81 μg/L), S4 (31.34 μg/L) and S7 (110.06 μg/L), which were nearly 2 to 55 times higher than S3, S5, S6 (2.04, 8.06 and 15.68 μg/L). At S8, all dissolved species of nitrogen were significantly lower than S7.

Phosphate and dissolved organic carbon

Phosphorus is the nutrient that most often limits productivity of aquatic biotas in freshwater ecosystems (Shaw et al., 1994). It occurs in organic and inorganic compounds and in particulate and dissolved forms. Dissolved inorganic phosphorus (DIP) is considered to be the most bioavailable form of phosphorus and high concentration of DIP (orthophosphate or PO_4^{3-}) in natural river water can be attributed to anthropogenic inputs (Dagg et al., 2004; Meybeck, 1982; Turner et al., 2003). In the NSR, DIP followed similar longitudinal trends to that of nitrogen. It was below the detection limit at S1, S2 and S3, and increased gradually from S4 (1.94 μg/L) to S6 (7.51 μg/L) and reached its peak at S7 (36.10 μg/L). Then it dropped to 2.93 μg/L at S8 (Table 3.1.5).

The natural sources of dissolved organic carbon (DOC) in fresh river water include leaching of humic substances and degradation of plant and animal materials (Shaw et al., 1994).

Lu et al. (2009) and Shaw et al. (1994) demonstrated that municipal and industrial wastewaters and runoff from agricultural land can also increase DOC in surface waters. According to Table 3.1.5, DOC levels remained stable along the mainstem of the NSR. Only a slight increase was found between S2 and S3, from 18.13 to 21.34 mg/L.

Generally, dissolved nitrogen, phosphate and organic carbon were all below their WQGs (chronic and acute), while several nutrients (e.g., NO_2^- and NO_3^-) showed their potential toxicity as their maximum values were approaching the chronic levels (38.66/60 and 1774.77/3000 μg/L respectively) at S7 (Fort Saskatchewan). The spatial trends of nutrient contents in river water can be confirmed by previous studies. For example, the Long-Term River Network program (2007-2012) indicated that, in open water seasons (April-October), the median values of NO_2^- /NO_3^- and TDP increased from around 7 to 300 μg/L and 6 to 8 μg/L respectively, while the DOC showed no significant change between Devon and Pakan (AESRD, 2014). The synoptic surveys conducted in 2008 and 2012 indicated that concentrations of NH_3/NH_4^+, NO_2^- /NO_3^-, DON, DOC and TP were significantly higher at sampling site located at Fort Saskatchewan (S7) compared to other sites located upstream and downstream of S7 (Golder, 2013c). The loading analysis program (from 2008 to 2012) revealed that the Goldbar WWTP is the predominant source of NH_3/NH_4^+, NO_2^- /NO_3^-, DON, DOC and TP to the NSR within the city in wet seasons, which was also confirmed by Kessler (2010), who found that the WWTPs (both Goldbar and Alberta Capital Region) were major contributors for nitrogen and phosphorus in dissolved forms.

WWTP-related pollutants showed distinct right bank-left bank differences in concentration in the Edmonton area since both Goldbar WWTP and Alberta Capital Region WWTP discharge their effluents on the right bank (south bank), which leads to lower levels of total ammonia, nitrite/nitrate and DON in water samples collected from centre channel or north bank (e.g., S8)

(Anderson, 2011). The unexpected high level of NH_3/NH_4^+ observed at S4 (31.31 μg/L, in north-bank samples) was less likely related to WWTPs and needs more assessment in the future.

3.2 Physicochemical parameters of the NSR sediment

3.2.1 Mineralogical composition and organic carbon content

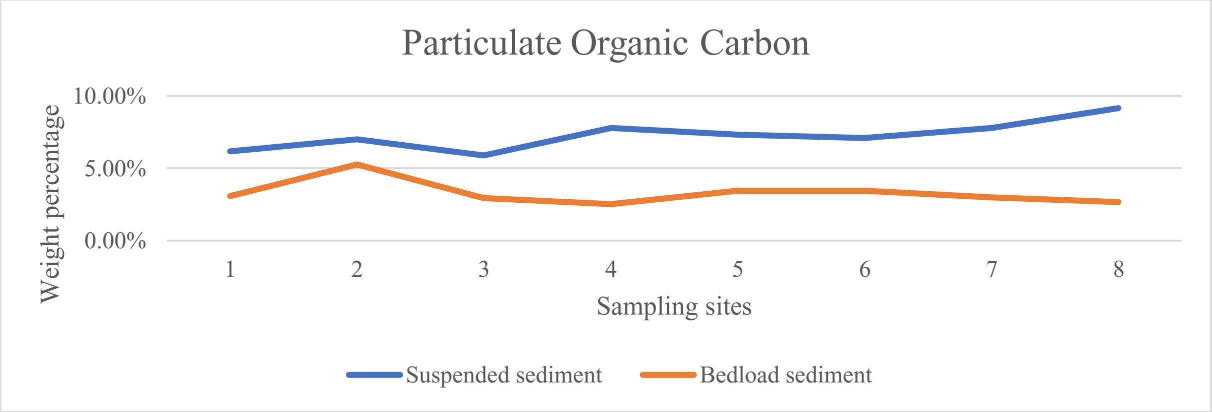
The mineralogical composition of both suspended and bedload sediments in this study are summarized in Table 3.2.1. Sediment samples were composed of various types of minerals such as quartz, feldspar (albite), micaceous phyllosilicates (muscovite), carbonates (dolomite and calcite), clay minerals (smectite), and amorphous parts (e.g., organics and Fe-Mn oxides/hydroxides).

According to Table 3.2.1, in both suspended and bedload sediments, quartz accounted for the largest portion at 31.12% and 40.76% respectively. The amorphous group represented similar percentages in suspended and bedload samples, accounting for 15.82% and 13.71% respectively. By comparing differences between suspended and bedload sediments, carbonates (e.g., dolomite and calcite) were markedly higher in suspended sediments (33.45 %) than in bedload sediments (17.06 %). For albite and muscovite, higher percentage of those minerals were found in bedload samples, while suspended sediments contained more smectite than bedload sediments. The Loss on Ignition (LOI) experiments reveal that the mean concentration of particulate organic carbon was higher in suspended sediments (7.20%) compared with in bedload samples (3.04%) (Figure 3.2.1).

Table 3.2.1 Mineralogy of the NSR sediments in this and previous studies (% by weight)

	Quartz	Albite	Muscovite	Dolomite	Calcite	Smectite	Amorphous
NSR bedload sediments (this study)	40.76	18.03	6.33	10.80	6.26	4.11	13.71
NSR suspended sediments (this study)	31.12	4.78	4.23	17.01	16.44	10.6	15.82
NSR mainstem (Stone et al., 2022)	33.80	11.20	4.4	12.70	7.10	3.00	16.3
NSR tributaries (Stone et al., 2022)	38.00	10.70	3.5	16.40	14.40	2.00	13.4

Figure 3.2.1 The percentage of particulate organic carbon in suspended and bedload sediments



3.2.2 Particle size distribution

Textural compositions of bedload sediments are shown in Table 3.2.2, and the size distribution of fine particles (<63 µm) as well as their specific surface area are summarized in Table 3.2.3. According to Table 3.2.2, particles smaller than 250 µm, which include fine sand (63-250µm) as well as silt and clay (<63µm) fractions, accounted for the largest part of bedload sediments at all sampling sites, ranging from 75.35% to 98.47%. As grab samples of bedload sediments were used in this section, spatial variations in grain size (especially in the fractions smaller than 250 µm) were significant and random among the 8 sampling sites (Table 3.2.2). Stone and Saunderson

(1992) found that in suspensions, the <63 μm fraction accounts for 60% to 99% of total particles, which implies that those fine-grained materials settled on the stream bed can be resuspended and transported under various flow conditions (e.g., spring melt and storm flow) and settle down again in other places via physical, chemical, or biological processes (e.g., flocculation) (Black et al., 2002; Dade et al., 1990; Liss et al., 2004; Stone and Collins, 2010).

Table 3.2.2 Textural composition (%) of bedload sediments collected in the NSR

Sites Size	Larger than 2mm (Pebble)	500μm -2mm (Coarse Sand)	250-500μm (Medium Sand)	63–250 μm (Fine Sand)	Smaller than 63μm (Silt and Clay)	Total weight of sample(g)
1 (upstream)	0.00	0.00	1.53	43.41	55.06	119.79
2	0.06	0.85	3.76	28.06	67.26	70.04
3	2.10	3.97	6.92	54.48	33.12	120.11
4	10.14	3.32	4.42	66.97	15.15	149.9
5	11.10	6.41	6.63	50.83	24.52	150.66
6	0.37	0.43	2.02	38.75	58.41	60.48
7	0.18	0.20	4.57	79.26	15.78	150.12
8 (downstream)	2.84	1.10	1.32	49.34	45.38	100.14

The <63μm fraction was divided into three categories (clay, silt, sand) (Table 3.2.3). The average clay fraction in suspended sediments was around 70 % compared to around 57 % in bedload sediments. By contrast, bedload sediments contained more silt fraction (around 43 %) than suspended sediments (around 30 %). Differences in particle size characteristics between suspended and bedload sediments were not significant because large amounts of bedload sediments can be disturbed and re-enter the suspension under high turbulence conditions (Horowitz, 1991).

Table 3.2.3 Size fractionations of fine-grained suspended and bedload sediments

	Clay (<2μm)	Silt (2-50μm)	Sand (>50μm)	Specific surface area (m*m/kg)
Suspended sediment				
Average (%)	69.18	30.80	0.02	341.71
Min	63.04	26.42	0.01	260.50
Max	73.57	36.95	0.04	390.90
Median	70.16	29.82	0.02	349.25
Stdev	3.68	3.68	0.01	47.62
Bedload sediment (<63 μm)				
Average (%)	56.91	43.07	0.02	316.95
Min	51.53	24.30	0.01	245.60
Max	75.67	48.45	0.03	503.50
Median	54.87	45.13	0.02	298.60
Stdev	7.99	8.00	0.01	80.97

Sediment composition and grain size are important factors that directly influence how researchers interpret information of environmental pollutants (Clearwater, 2010). Normally, suspended sediment can concentrate and transport more pollutants than bedload sediment since it contains a larger portion of finer particles (clay-sized fraction) (Table 3.2.3). As particle size decreases, the specific surface area will increase (Horowitz, 1991). This is important because sediments with larger surface areas per unit mass will have more binding sites on the surface to concentrate and transport heavy metals and other sediment-bound contaminants (Stone et al., 2022). According to Table 3.2.3, the median specific surface area of suspended sediment was 349.25 m^2/kg, while that of bedload sediment was 298.60 m^2/kg. Moreover, grain size can cause further impact on mineralogy since clay minerals, organic matters, and Fe-Mn oxides are preferentially concentrated in the finer size fractions (Förstner, 2004a; Horowitz, 1991).

Previous studies conducted in 2010 and 2011 (Table 3.2.1) summarized the mineralogical composition of bedload samples collected along the NSR (mainstem and tributaries) in the areas with different regional and local geology, soil type and weathering rate (Stone, 2012b), and found that the bedload sediments contain less clay minerals (3% in mainstem samples and 2% in tributary samples) than suspended sediment in this study (10.6%). This comparation confirms the differences in particle size between bedload and suspend sediments, which in return, indicates that with different physical (grain size, surface area) and chemical (mineralogy) properties, suspended sediment can be a better scavenger for contaminants in the NSR.

Stone (2012b) also found that in low flow seasons (low flow open water and ice cover periods), bedload sediment, which mainly consist of silt and sand size particles with low levels of organic matter, might make the tracking of sediment-associated contaminants more difficult. Since during low flow season, the deposition zones of those bedload sediment are usually not the original contaminated areas. Thus, in low flow season, suspended sediment can better reflect the contaminant chemistry of the NSR. However, in natural river system, situations are much more complicated. For example, the organic matter has two major forms in aquatic environment: (1) surface coating that tends to concentrate on various minerals and finely dispersed particles (Förstner and Wittmann, 1981); (2) and separate particles associated with large size fractions (Horowitz, 1991). Similarly, iron and manganese oxides commonly occur as surface coatings in aquatic systems (Horowitz, 1991). The clay minerals, apart from being direct sorbents for trace elements, they can also act as mechanical substrates and form organic and hydrous Fe-Mn oxides coatings to bind metals (Förstner, 2004b). Thus, those different forms of absorbents might lead to unexpected results and recognizing the limitations of the natural samples can help us better interpret the data collected from polluted areas.

3.2.3 Sediment quality assessment and urbanization effects

Sediment quality assessment

Suspended and bedload sediment samples were analysed for total concentrations of Cu, Ni, Cd, Mn, Cr, Pb, Fe, Sr, Mo, and Co. According to Table 3.2.4, the mean concentrations (µg/g) of Ni, Cd, Mn, Cr, Pb, Fe, Mo, and Co in suspended sediments were 29.97, 0.46, 546.54, 74.44, 16.34, 43449.33, 173.98, 1.49, 8.80, respectively, while in bedload sediments those same metals were 21.91, 0.30, 412.19, 51.75, 13.68, 30967.56, 0.88, 7.38, respectively. By contrast, Cu and Sr were more enriched in bedload sediments (114.95 and 189.32) than in suspended sediments (16.98 and 173.98), which implies that the presence of trace metal in sediments can not be simply interpreted by differences in grain size and mineralogical composition. In natural environment, metals can enter aquatic ecosystem naturally through biogeochemical cycles or from anthropogenic sources (Gaillardet et al., 2003). Ip et al. (2007) indicated that dissolved trace metals in the river water can be scavenged and accumulated in both suspended and bedload sediments through geochemical processes (e.g., adsorption, co-precipitation). When environmental conditions change (e.g., pH, redox potential), those sediments will act as potential secondary sources of metal contamination in river water (Forstner and Salomons, 1980).

An assessment was made by comparing mean values of total metal concentrations with the freshwater sediment's quality guidelines (SQGs) published by Environmental Canada (AEP, 2018) and Persaud et al. (1993). According to Table 3.2.4, for both suspended and bedload sediments, Cr showed higher values than the Interim Sediment Quality Guideline (ISQG), but it did not exceed the Probable Effect Level (PEL), indicating that Cr only occasionally poses a potential adverse effect to the biology in the river. Ni was observed to have higher values than the Lowest Effect Level (LEL) in all sediment samples, indicating that the river water was marginally polluted by Ni in the reach of the Capital Region. Other metals such as Fe, Co, Sr, Mo and Pb were safe to the aquatic environment.

Metals distributions were also found between suspended and bedload sediment samples. For example, Cu was higher than the ISQG in bedload samples collected from 7 sampling sites (except for S8), indicating its potential toxic effects, while that in suspended sediments showed no harm to the environment. By contrast, some metals showed their higher values in suspended sediments. Specifically, Mn was found to be higher than the LEL in suspended samples collected from 7 sites (except for S3), while in the bedload samples only S2 showed higher Mn concentration than the LEL. Similarly, Cd exceeded the LEL in suspended samples collected from S2, while depositional Cd showed no harm to the environment (Table 3.2.4). Overall, the above results lead to the conclusion that toxic metals such as Cr, Mn, and Ni in both suspended and bedload samples, Cu in bedload samples, and Cd in suspended samples may cause toxic effects on biosphere of the NSR.

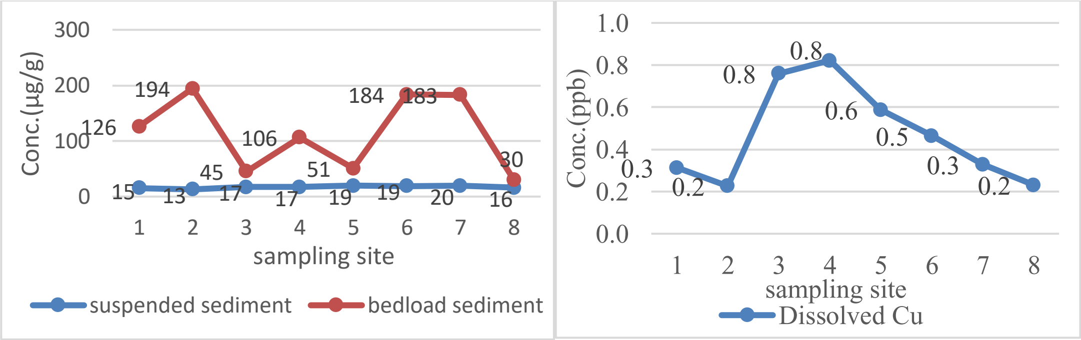
Table 3.2.4 Total concentration of heavy metals and Sediment Quality Guidelines

Metal (μg/g)	Cr	Mn	Fe	Co	Ni	Cu	Sr	Mo	Cd	Pb
ISQG(μg/g)	37.3	N/A	N/A	N/A	N/A	35.70	N/A	N/A	N/A	35.00
PEL(μg/g)	90	N/A	N/A	N/A	N/A	197.00	N/A	N/A	N/A	91.30
LEL(μg/g)	N/A	460	N/A	50	16.00	N/A	N/A	5	0.60	N/A
Suspended sediments										
site1 (S1)	71.99	493.42	45314.15	9.22	26.34	15.26	174.06	1.10	0.37	15.20
site2 (S2)	70.08	523.99	43492.79	8.86	26.82	12.95	175.29	1.27	1.00	15.19
site3 (S3)	71.97	402.94	42164.38	8.01	33.43	17.21	200.84	1.54	0.41	17.18
site4 (S4)	72.41	515.36	44291.05	8.64	25.63	17.04	162.08	1.40	0.37	16.93
site5 (S5)	73.40	548.55	45576.75	9.20	29.02	19.29	162.88	1.49	0.47	18.08
site6 (S6)	77.43	617.38	49761.73	9.96	29.34	18.83	191.48	1.41	0.33	17.97
site7 (S7)	77.18	704.44	40546.83	8.84	28.56	19.60	180.25	2.15	0.35	15.85
site8 (S8)	81.04	566.26	36446.97	7.66	40.66	15.69	144.99	1.56	0.41	14.28
Maximum	81.04	704.44	49761.73	9.96	40.66	19.60	200.84	2.15	1.00	18.08
Minimum	70.08	402.94	36446.97	7.66	25.63	12.95	144.99	1.10	0.33	14.28
Median	72.91	536.27	43891.92	8.85	28.79	17.13	174.67	1.45	0.39	16.39
Average	74.44	546.54	43449.33	8.80	29.97	16.98	173.98	1.49	0.46	16.34

Standard deviation	3.71	88.86	3921.90	0.72	4.95	2.28	17.62	0.31	0.22	1.41
Bedload sediment										
site1 (S1)	48.28	387.85	30394.67	7.15	22.82	125.92	188.69	0.96	0.41	11.41
site2 (S2)	54.53	505.88	35137.04	8.61	25.02	194.41	198.24	0.85	0.39	19.62
site3 (S3)	53.18	416.13	31621.77	7.98	25.13	45.19	197.85	0.87	0.26	14.14
site4 (S4)	48.69	419.53	29157.41	6.90	19.31	106.46	186.92	0.80	0.29	12.52
site5 (S5)	54.43	403.80	29240.79	7.02	20.03	50.61	184.98	0.90	0.28	12.84
site6 (S6)	52.77	386.86	32270.49	7.29	20.93	183.71	185.13	0.79	0.26	14.06
site7 (S7)	54.19	409.39	31631.71	7.45	22.83	183.07	188.05	1.27	0.29	12.90
site8 (S8)	47.93	368.07	28286.60	6.67	19.20	30.21	184.67	0.61	0.24	11.93
Maximum	54.53	505.88	35137.04	8.61	25.13	194.41	198.24	1.27	0.41	19.62
Minimum	47.93	368.07	28286.60	6.67	19.20	30.21	184.67	0.61	0.24	11.41
Median	52.98	406.59	31008.22	7.22	21.88	116.19	187.49	0.86	0.28	12.87
Average	51.75	412.19	30967.56	7.38	21.91	114.95	189.32	0.88	0.30	13.68
Standard deviation	2.93	41.59	2194.97	0.63	2.40	67.68	5.58	0.19	0.06	2.58

Urbanization effects

Figure 3.2.3 The total concentration of Cu in sediments and dissolved phases



In this study, distinct longitudinal fluctuations of Cu were observed in water and sediment samples collected along the river (Figure 3.2.3). From S1 (Devon Voyageur Park) to S2 (Shalom Park), Cu precipitated from the water column and presented increasing trend in bedload sediments (from 126 to 194 µg/g); as a result, Cu in suspended sediments and dissolved phases decreased from 15 to 13µg/g and 0.3 to 0.2µg/L, respectively, in the same reach. From S2 to S5 (Rundle Park), bedload Cu showed a decreasing trend (from 194 to 51 µg/g), while suspended and dissolved Cu increased from 13 to 19µg/g and 0.3 to 0.5µg/L, indicating the possible release of Cu from the bedload sediments. East of S5, the depositional and suspended Cu increased to S7 (Fort Saskatchewan) (from 51 to 183 µg/g and 19 to 20µg/g respectively). By contrast, the concentration of dissolved Cu in water column dropped consistently among those sites (from 0.5 to 0.2µg/L), which might suggest that the adsorption and precipitation were the main controls of Cu from site 5 to 7. At S8, suspended and dissolved Cu (16 µg/g and 0.2 µg/L) were almost equal to the values observed at S1 (15 µg/g and 0.3 µg/L), from S7 to S8, Cu in bedload sediments also dropped from 183 to 30 µg/g, which might indicate that there was little accumulation/precipitation of Cu at S8. Overall, in June and July, bedload sediment acted as a reservoir for Cu and the majority processes of releasing and accumulating of Cu happened within the study area. This finding also confirms the results from Stone et al. (2022) who indicated that Cu concentrations were lower in bedload samples collected downstream of Edmonton.

3.2.4 Metal speciation

Results of the sequential extraction carried out on suspended and bedload sediments showed that trace metals (Cu, Ni, Cd, Mn, Cr, Pb, Fe, Sr, Mo, Co) displayed different degrees of association with the five targeted fractions (see supplementary, Table S1).

Figure 3.2.4 Cu fractionations in the sediment samples

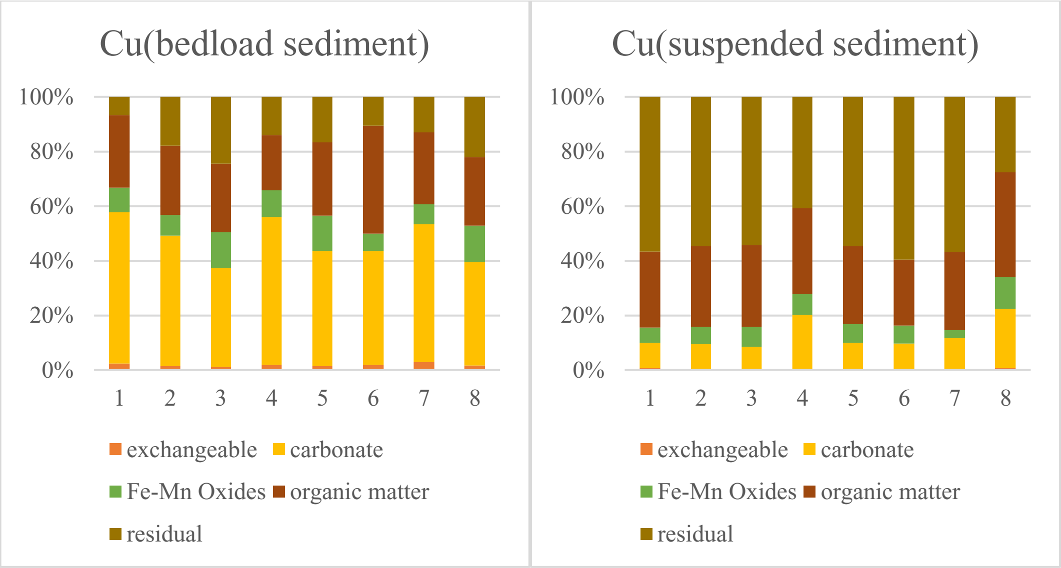
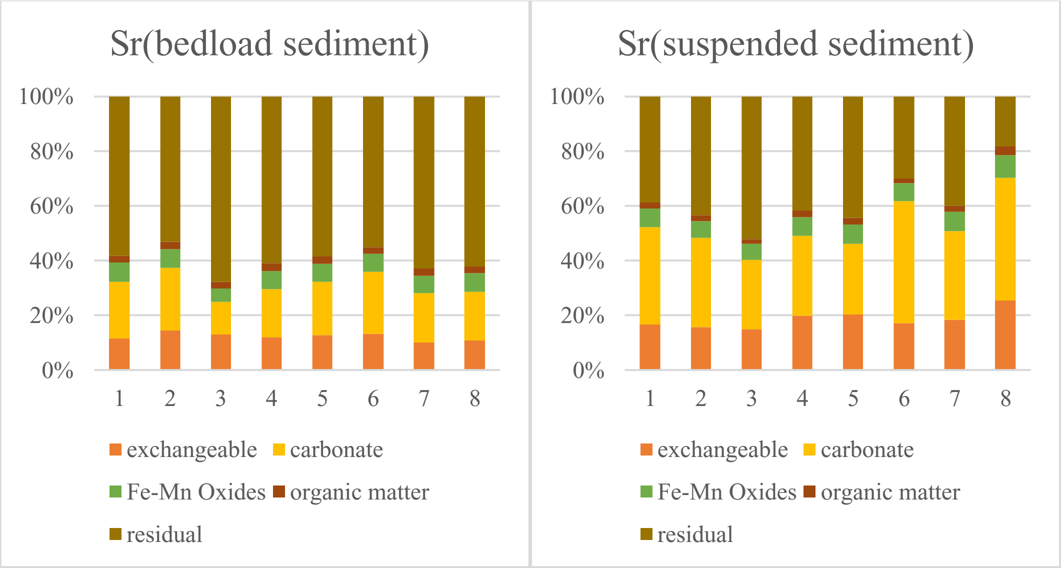


Figure 3.2.4 reveals distribution patterns of Cu in suspended and bedload sediments. The partitioning of Cu within different fractions in bedload sediments were as follows: carbonate (45.64%) > organic matter (26.86%) > Fe-Mn oxides (9.97%) > residual (15.67%) > exchangeable (1.85%). While in suspended sediments, different fractionations were observed as: residual (50.69%) > organic matter (29.73%) > carbonate (12.22%) > Fe-Mn oxides (6.86%) > exchangeable (0.49%) (Table S1). Compared with other metals, a larger proportion of Cu was organically bound in suspended and bedload sediments. This is consistent with the results from previous studies conducted in polluted areas (Dhanakumar et al., 2013; Jain et al., 2008; McBride, 1994; Okbah et al., 2005; Pagnanelli et al., 2004; Palleiro et al., 2016; Zhang et al., 2017), which indicated that Cu can be preferably fixed with particular organic matter (POM) in river sediments.

Zhang et al. (2017) found a strong correlation between organically bound Cu and organic carbon content in surface sediments collected in the Pearl River Estuary, China, indicating that organic carbon is one of the major components for Cu retention in sediments. Under oxic conditions, organically bound copper can re-enter the overlying water column with the mineralization of the host organic matter and cause environmental problems (Jain et al., 2008). The sequential extraction data also indicate that more carbonate-bound Cu (average) was found in bedload sediments (45.64%) than in suspended sediments (12.22%), which reflects the accumulation pattern of Cu in the study area.

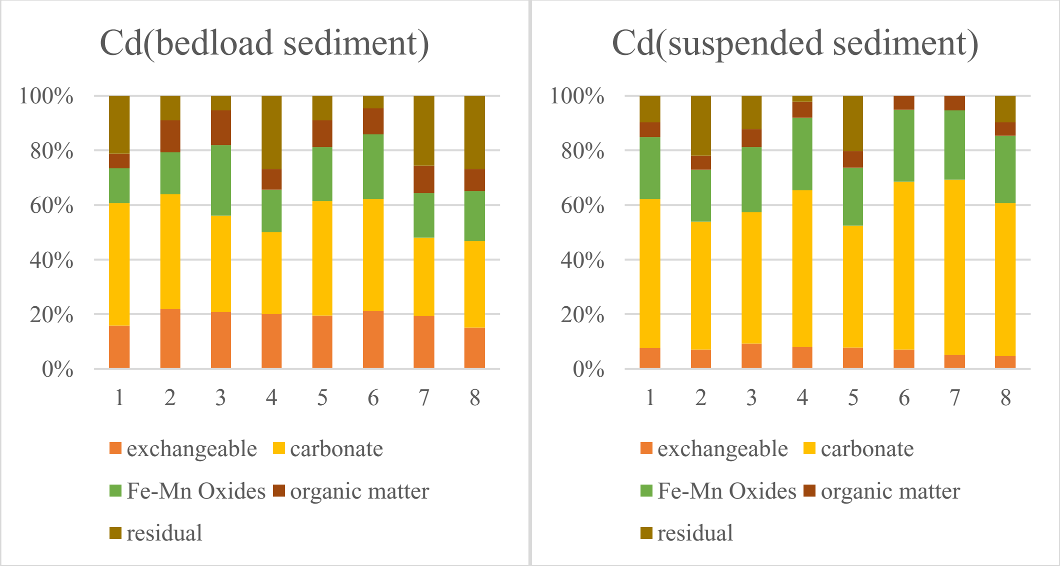
Figure 3.2.5 Sr fractionations in the sediment samples



The sequential extraction results for Sr show similar patterns among the 8 sampling sites (Figure 3.2.5), with more non-residual Sr found in suspended sediments (47.88%-81.75%) than in bedload sediments (32.29%-46.92%). For both bedload and suspended sediments, Sr was enriched in exchangeable and carbonate fractions. Many researchers found that the interaction between Sr and sediments during transport is mainly through cation exchange at pH<9 (Bouzidi et al., 2015). For example, Kilincarslan Kaygun et al. (2017) and Stone et al. (2022) reported that finer particles, such as natural clay minerals, organic carbon and Fe-Mn oxides and hydroxides, have high adsorption efficiency for trace elements. Thus, with higher proportions of clay minerals and organic carbon, suspended sediments may act as a more efficient adsorbents, which can bind more Sr in the exchangeable fraction (Harrison et al., 1981; Modak et al., 1992; Nriagu, 1979; Singh et al., 2005). High flow season can also affect metal intake by bedload sediments from anthropogenic sources (Prartono et al., 2016) and lead to small fraction of exchangeable Sr in bedload sediments. For the carbonate fraction, it is suggested that strontium and calcium have similar chemial properties and can form strontianite ($SrCO_3$) in basic medium (Bouzidi et al., 2015).

Compared with other heavy metals, Sr is the only metal which shows a larger exchangeable fraction in suspended sediments (14.90%-25.39%) than in bedload sediments (10.11%-14.57%). This phenomenon was explained by Mondal et al. (2020) who demonstrated that higher bioavailable fractions of metals in suspended sediments is related to short period of contamination and/or relatively short distance between sampling sites and the source of pollutant.

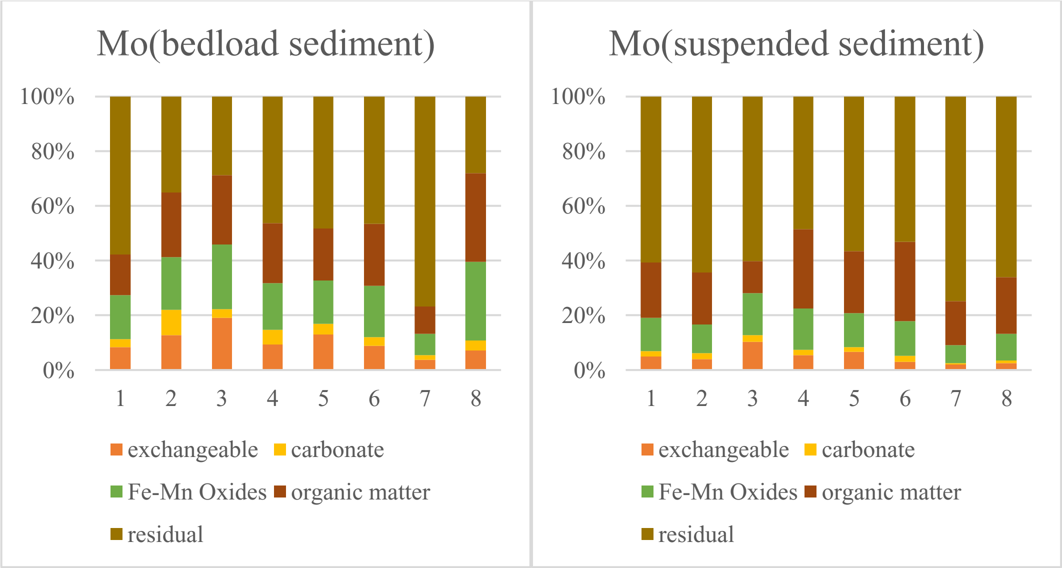
Figure 3.2.6 Cd fractionations in the sediments



Distribution patterns of Cd indicate that it was predominantly bound to the exchangeable (7.14%-19.30%), carbonate (36.88%-54.11%) and Fe-Mn oxides phases (18.74%-23.72%) (Figure 3.2.6). To explain this phenomenon, Modak et al. (1992) and Förstner and Wittmann (2012) indicated that Cd has a special affinity with carbonate and can coprecipitate with carbonate minerals in alkaline environment (Ahdy and Youssef, 2011). Previous studies also showed similar distribution patterns of Cd in sediments (Boughriet et al., 2007; Ianni et al., 2000; Korfali and Davies, 2004). For example, Tessier et al. (1979) found a large amount of Cd in the exchangeable and carbonate fractions in Yamaska and St. Francois River sediments, Canada. Okbah et al. (2005) and Singh et al. (2005) showed that more than 50% of total Cd contents were associated with the exchangeable and carbonate fractions. Modak et al. (1992) demonstrated that Cd has a special affinity for clay minerals since their ionic radii are similar to those of potassium metal primarily associated with clay minerals. Additionally, through electrostatic attraction on the sediments colloid surface, Cd can adsorb on the surface of solid particles (Li et al., 2009; Sims and Kline, 1991).

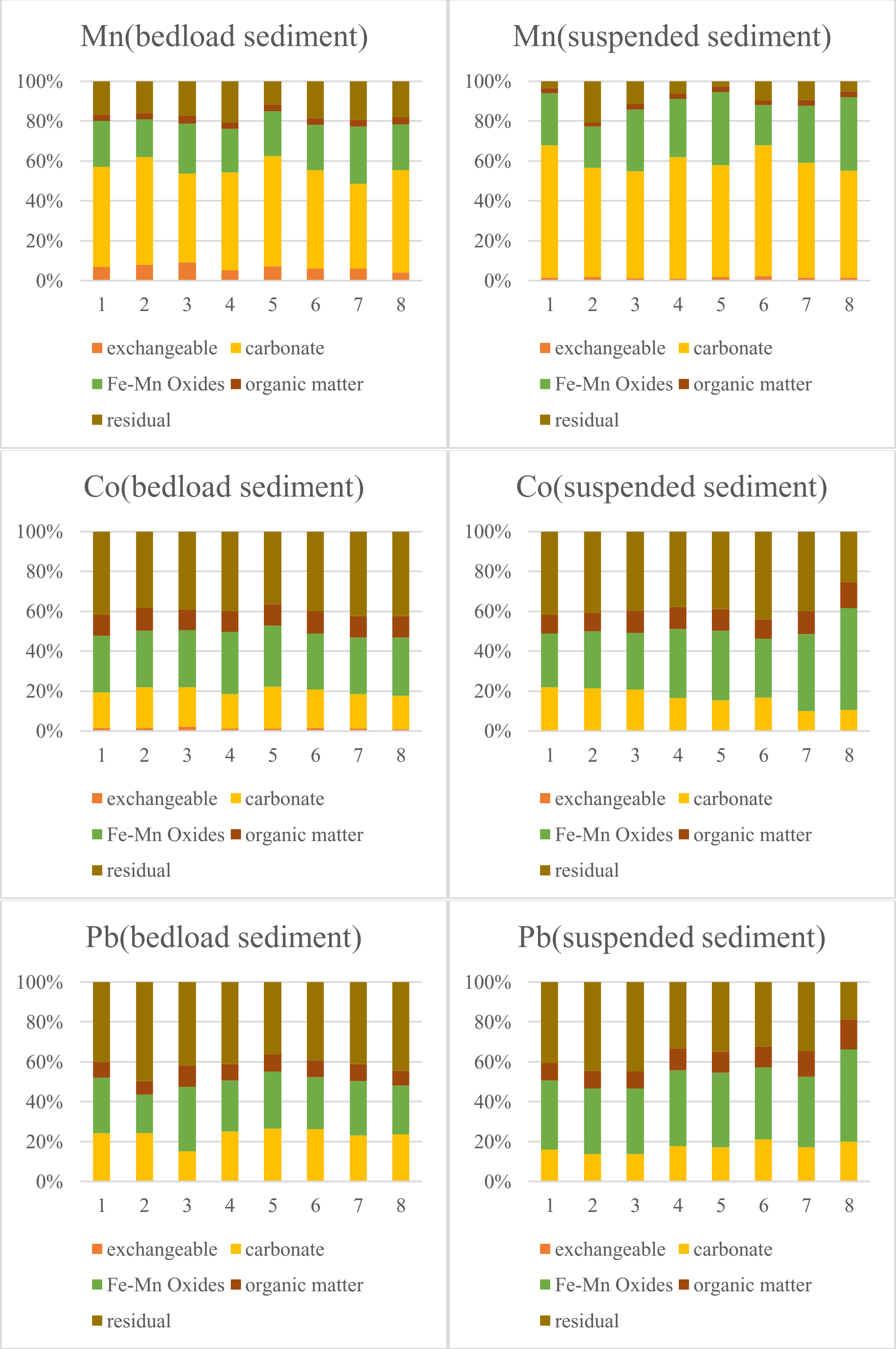
As the most unstable host fraction for trace metals, the exchangeable Cd can easily become dissolved in the water column when environmental conditions change. For example, previous studies indicated that lower pH and higher ionic strength will inhibit Cd adsorption onto clay minerals (Gu and Evans, 2007; Gu and Evans, 2008; Gu et al., 2010). Hao et al. (2020) tested three different clay minerals (kaolinite, illite and montmorillonite) and found that montmorillonite (the most abundant form of smectite in river sediments) has a relatively high sensitivity to changes in environment, displaying more than 30% of Cd loss from river to the ocean conditions. In this study, less exchangeable Cd was observed in suspended sediments (4.59%-9.28%) than in bedload sediments (15.26%-22.07%), which might relate to the low concentration of dissolved Cd (below detection limit in the study area) and the relatively stable environment for bedload sediments (Anderson, 2011; Anderson, 2012). By contrast, a higher proportion of carbonate-bound Cd was found in suspended sediments (44%-64%) than in bedload sediments (28%-44%), which might be attributed to higher carbonate mineral contents in suspended sediments. In urban areas, there are several ways for Cd to enter the aquatic system, which include the phosphate fertilizer from agricultural areas nearby the river (Huang et al., 2004; Sundaray et al., 2011) and Cd emission from road traffic (Sundaray et al., 2011). According to Figure 3.2.6, Cd was predominately accumulated in carbonate fraction and can be released into the water column with a slight lowering of pH (Ghrefat et al., 2012).

Figure 3.2.7 Fractionations of Mo in the sediments



As shown in Figure 3.2.7, Mo was likely to be retained in bedload sediments in the following order: residual (45.91%) > organic matter (21.19%) > Fe-Mn oxides (18.44%) > exchangeable (10.28%) > carbonate (4.18%). Similarly, in suspended sediments, fractionations were observed as: residual (60.52%) > organic matter (21.06%) > Fe-Mn oxides (11.82%) > exchangeable (4.87%) > carbonate (1.73%). The majority of Mo occurred in the residual phase and lesser extent in the organic phase, suggesting that it formed various complexes with organic hydroxy compounds (Borovec, 1993).

Figure 3.2.8 Fractionations of Mn, Co and Pb in the sediments



For Mn, Co and Pb, more than 50 % of those three metals were extracted in the exchangeable, carbonate, and Fe-Mn oxides fractions. According to Figure 3.2.8, little variation was found spatially in the 8 sampling sites or between suspended and bedload samples. The Mn extracted from carbonate fraction could come from the dissolution of Mg/Ca carbonates, as Mn can substitute for Mg in dolomite and Ca in calcite (Gao et al., 2010; Rath et al., 2009; Shan and Chen, 1993; Sundaray, 2007; Zhang et al., 1988). The Fe-Mn oxides fraction was one of the main non-residual fractions for bonding Mn, Co and Pb in river sediments since the metal oxides have a high affinity to heavy metals through adsorption, flocculation and co-precipitation (de Andrade Passos et al., 2010; Iwegbue et al., 2009; Rath et al., 2009; Venkateswaran et al., 2007). Changes in pH and redox potential can remobilize Mn, Co and Pb associated with carbonates and Fe-Mn oxides and cause adverse effects on aquatic biotas (Jain et al., 2008).

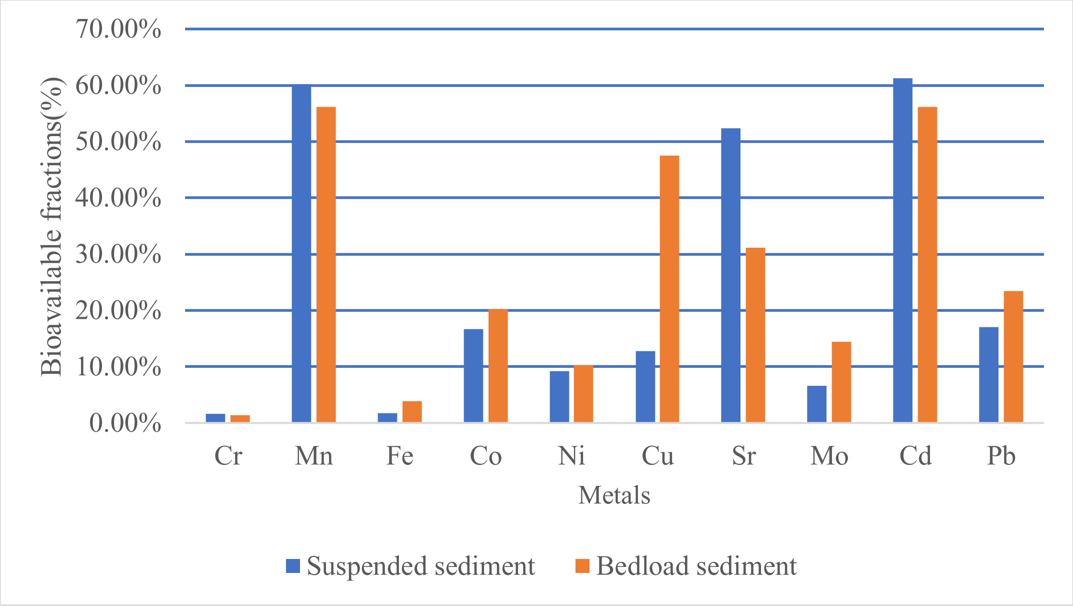
Figure 3.2.9 Fractionations of Ni, Fe and Cr in the sediments

According to Figure 3.2.9, Ni, Cr and Fe were predominantly bound to the residual fraction (nearly 50% for Ni, 70% for Fe and 90% for Cr on average). This phenomenon indicates that these three metals are strongly associated with crystalline silicate lattices and are expected to be chemically stable and biologically inactive (Tessier et al., 1979; Xiao et al., 2015). Prartono et al. (2016) and Rodrigues and Formoso (2006) indicated that the labile fractions (exchangeable, carbonate, Fe-Mn oxides, organic fractions) of trace metals mainly originate from human-derived inputs, while metals associated with the non-labile (residual) fraction mainly come from natural processes (Yu et al., 2001). Thus, the data strongly suggest that predominant Ni, Fe and Cr in both suspended and bedload sediments were from the erosion of lithogenic bedrock. Other forms of Ni, Fe and Cr were associated with carbonate, Fe-Mn oxides and organic phases, which may be attributed to anthropogenic inputs (e.g., industrial effluent and urban runoff).

3.2.5 Bioavailability and toxicity of heavy metals

Figure 3.2.10 depicts the bioavailable fractions (%) of metals in suspended and bedload sediments of the NSR. The concept of bioavailable fraction is based on the sum of exchangeable fraction and carbonate-bound fraction since these fractions of metals can be easily released into water column and utilized by aquatic plants and animals (Owens et al., 2005).

Figure 3.2.10 Bioavailable fractions (exchangeable and bound to carbonate) of the river samples



Based on the RAC criteria (Table 2.4.1), for both suspended and bedload sediments, Cr, Fe fell in the low-risk category (1-10%), while Co and Pb showed medium risk (11-30%) to the river's biota. Mn was in the very-high-risk category (>50%) since more than 55% of it was found in exchangeable and carbonate fractions.

According to Table 3.2.5, some metals were at higher toxic levels in the bedload sediments. For example, half of the sampling sites (2,3,5,6) had Ni and 7 sampling sites (1,2,3,4,5,6,8) had Mo in the medium-risk (11-30%) category, while in suspended sediments, Ni and Mo were posing low risk (1-10%) to the aquatic environment in most of the sites. Similarly, bedload Cu showed high to very high risk (>30% ~ >50%), while suspended Cu posed low to medium risk (1-30%) to the biota. Different distribution patterns were observed for Sr and Cd which showed larger bioavailable fractions in suspended sediments than in bedload sediments. For example, suspended Sr was in the high to very-high-risk category (>30% ~ >50%), while in bedload samples, Sr posed medium to high risk (11-50%). Suspended Cd showed very high risk (>50%) at all sites, while in bedload sediments, site 4,7 and 8 showed less toxicity, falling in the high-risk (31-50%) category.

Table 3.2.5 Bioavailable fractions (%) in suspended and bedload sediments

	Cr	Mn	Fe	Co	Ni	Cu	Sr	Mo	Cd	Pb
Suspended sediments										
Site1 (S1)	1.59%	67.78%	1.88%	21.95%	9.75%	9.99%	52.35%	6.81%	62.26%	15.93%
Site2 (S2)	1.47%	56.68%	1.70%	21.45%	8.58%	9.38%	48.25%	6.29%	21.37%	13.65%
Site3 (S3)	1.56%	54.89%	1.27%	20.92%	9.29%	8.40%	40.32%	12.77%	57.26%	13.65%
Site4 (S4)	1.45%	61.95%	1.77%	16.69%	12.76%	20.15%	49.00%	7.35%	65.47%	17.75%
Site5 (S5)	1.37%	58.10%	1.65%	15.30%	8.73%	9.99%	46.14%	8.32%	52.41%	17.05%
Site6 (S6)	1.62%	67.99%	1.72%	16.89%	8.40%	9.68%	61.86%	5.20%	68.62%	21.11%
Site7 (S7)	1.53%	59.15%	1.77%	10.08%	7.76%	11.74%	50.69%	2.60%	69.32%	17.04%
Site8 (S8)	1.96%	58.20%	2.14%	10.50%	8.47%	22.35%	70.19%	3.50%	60.87%	20.05%
Maximum	1.96%	67.99%	2.14%	21.95%	12.76%	22.35%	70.19%	12.77%	69.32%	21.11%
Minimum	1.37%	54.89%	1.27%	10.08%	7.76%	8.40%	40.32%	2.60%	52.41%	13.65%
Median	1.54%	58.62%	1.75%	16.79%	8.65%	9.99%	49.84%	6.55%	61.56%	17.04%
Average	1.57%	60.22%	1.74%	16.72%	9.22%	12.71%	52.35%	6.60%	61.26%	17.03%
Standard deviation	0.18%	5.24%	0.24%	4.66%	1.55%	5.38%	9.43%	3.15%	6.41%	2.68%
Bedload sediment										
Site1 (S1)	1.80%	57.05%	4.20%	19.47%	9.37%	57.71%	32.32%	11.38%	60.70%	24.14%
Site2 (S2)	1.49%	61.98%	5.61%	21.97%	12.00%	49.23%	37.37%	22.07%	63.90%	24.19%
Site3 (S3)	1.37%	53.61%	1.52%	22.04%	11.36%	37.22%	24.96%	22.37%	56.06%	15.00%
Site4 (S4)	1.21%	54.36%	3.38%	18.67%	9.34%	55.92%	29.56%	14.75%	49.99%	25.03%
Site5 (S5)	1.08%	62.46%	3.45%	22.28%	12.04%	43.58%	32.32%	16.79%	61.49%	26.53%
Site6 (S6)	1.38%	55.31%	5.02%	20.79%	11.61%	43.70%	35.80%	12.07%	62.34%	26.12%
Site7 (S7)	1.11%	48.55%	3.46%	18.59%	8.09%	53.22%	28.19%	5.37%	48.04%	23.20%
Site8 (S8)	1.27%	55.49%	4.16%	17.78%	8.49%	39.36%	28.61%	10.87%	46.94%	23.66%
Maximum	1.80%	62.46%	5.61%	22.28%	12.04%	57.71%	37.37%	22.37%	63.90%	26.53%
Minimum	1.08%	48.55%	1.52%	17.78%	8.09%	37.22%	24.96%	5.37%	46.94%	15.00%
Median	1.32%	55.40%	3.81%	20.13%	10.37%	46.46%	30.94%	13.41%	58.38%	24.16%
Average	1.34%	56.10%	3.85%	20.20%	10.29%	47.49%	31.14%	14.46%	56.18%	23.48%
Standard deviation	0.23%	4.52%	1.23%	1.79%	1.63%	7.68%	4.13%	5.82%	6.93%	3.62%

3.3 Conclusions

The mineralogical analyses (XRD and LOI) show that suspended sediment contains more clay minerals (smectite), carbonates (dolomite and calcite) and organic carbon, while bedload sediment contains more quartz and feldspars (albite). The textural composition analysis shows that solid particle smaller than 250 µm accounts for the largest portion of bedload sediment collected from the surface down to a depth of 30 cm. For the <63µm fraction, suspended sediment contains more clay-sized (<2µm) particles than bedload sediment.

The trace elemental speciation data indicate that compared with other metals, Sr, Cd, and Mo were largely in the exchangeable fraction, which can easily enter the water column and pose adverse impacts on aquatic biota. Substantial amounts of Cu, Sr, Cd, Mn, Co, and Pb in sediments were associated with carbonate fraction. Fe-Mn oxides and residual fraction were predominant scavengers for Co, Pb, Ni, Fe, and Cr. Copper and Mo had special affinity towards organics and represented relatively high proportions in oxidizable fraction. For most heavy metals except for Cu and Mo, larger parts of non-residual fractions can be observed in suspended sediments than in bedload sediments.

WQGs reveal that dissolved toxic metals and nutrients showed no harm to aquatic system of the NSR. SQGs suggest that the total concentrations of Mn, Ni and Cr in all sediment samples, Cu in bedload samples and Cd in suspended samples were of environmental concern in the present study and can occasionally be associated with adverse biological effects. According to RAC, for all sediments, Cr, Fe fell in the low-risk category, Co and Pb showed medium risk to the environment and Mn fell in the very high-risk category. Other metals such as Ni, Mo, Cu, Sr and Cd showed different levels of toxicity to the environment at different sampling sites.

Overall, the enrichment of heavy metals in river sediments and their fractionation patterns indicate that the NSR was influenced by anthropogenic inputs. Rapid urbanization and reclamation processes along the river generate industrial effluents, municipal waste, and agrochemical runoff which can cause environmental threats to the aquatic system.

Chapter 4: Limitations and future directions

Study limitations

In this study, although some trace metals showed different concentrations and distribution patterns between suspended and bedload sediments, little variation was observed spatially along the river (from S1 to S8). This is because sampling activities and pre-treatment processes are highly labour intensive as they must be done in a short time to avoid sampling errors. Thus, a simple, time-integrated, in situ suspended sampler designed by Phillips et al. (2000) can be used in the future to obtain representative and sufficient suspended samples.

Sequential extraction methods have been applied to a variety of substrates such as river sediments, agricultural soils, road particulates (urban soils), airborne particulate matters, etc. (Alvarez et al., 2006; Fujiwara et al., 2006; Moćko and Wacławek, 2004; Robertson et al., 2003; Yang et al., 2006). This approach helps to better understand the behaviour of toxic elements in the natural environment and provides additional information to assess sediment quality (Bacon and Davidson, 2008). However, there are a lot of problems regarding the non-selectivity of the reagents, as they may alter surface chemical characteristics of sediments tested and lead to incomplete extraction and redistribution of metals among the remaining fractions during extraction processes (Zimmerman and Weindorf, 2010) (Qiang et al., 1994; Shan and Chen, 1993). For example, a study conducted on soils indicated that metal concentrations determined by sequential extraction for the fractions of exchangeable, carbonates, and Fe-Mn oxides were less than the actual concentrations (Shan and Chen, 1993). Parat et al. (2003) compared three different procedures and found that sodium acetate could remove considerable amounts of metals in forms other than exchangeable ones. Independent studies of mining waste (Lacal et al., 2003) and anoxic sediments (Burton et al., 2006; Peltier et al., 2005) indicated that hydroxylamine hydrochloride can mistakenly increase the metal concentration bound to Fe-Mn fraction by dissolving sulfide minerals. To solve this problem, Tlustoš et al. (2005) suggested that at least two independent procedures should be applied to minimise the influences of different extractants. However, Kalembkiewicz and Sočo (2005) still obtained unreliable Cr distribution pattern after using 11 different schemes. In addition, before adding extractants, metal re-distributions could possibly happen in processes of sample drying (room temperature or freeze drying) and grinding (Bacon and Davidson, 2008). Thus, to precisely assess the sediment quality, other techniques such as X-ray-based analysis can be conducted in the future research (Calmano et al., 2001; Tipping et al., 1985).

Future directions

Generally, bulk suspended sediments are collected during high flow events. Although the peak flow of the NSR is usually in June and July, the spring flow cannot be neglected. Factors that may cause the early peak flow include; (1) overland flow and erosion caused by the snowmelt in the drainage basin in late winter or early spring, (2) water contributions from tributaries along the lower reaches of the river in late March to early May, and (3) wastewater discharge from industrial and municipal effluents in snowmelt season (Laceby et al., 2019). This is important because all those factors will increase suspended sediment content and human-derived contaminants in the river.

Sediment source fingerprinting is a link between geochemical properties of suspended sediments and those of their sources (Stone et al., 2022). By comparing the properties with those of the individual potential sources, the fingerprinting approach is considered to be a reliable way of assembling the information required (Stone and Collins, 2010). To document sediment sources, representative samples are needed (Stone and Collins, 2010). For example, in a large-scale river drainage basin, the sub-catchments from an individual tributary or discrete geological zones can help to investigate the spatial provenance of suspended sediment (Bottrill et al.; Owens et al.; Walling, 1999). In small catchments, to appropriately characterise sediment provenance, different sources such as topsoil of the woodland, road dust, pasture and cultivation, solids from sewage should be considered as "fingerprints" (Carter et al., 2003; Motha et al., 2004; Walling and Collins, 2005; Walling and Woodward, 1995). In the future research, a sediment source fingerprinting approach can be included to elucidate the contributions of different types of sources (such as channel banks, forests, agricultural land and urban areas) or even major tributaries which contribute sediments to the main stream (Stone et al., 2022).

References

AEP, 2018. Environmental quality guidelines for Alberta surface waters.

AESRD, 2014. North Saskachewan River : Water Quality and Related studies (2007-2012).

Ahdy, H.H.H. and Youssef, D.H., 2011. Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt. Chemistry and Ecology, 27(5): 427-443.

Al-Mamun, A. and Zainuddin, Z., 2013. Sustainable river water quality management in Malaysia. IIUM Engineering Journal, 14(1).

Alliance, N.S.W., 2012. Atlas of the North Saskatchewan River Watershed in Alberta.

Alvarez, J.M., Lopez-Valdivia, L.M., Novillo, J., Obrador, A. and Rico, M.I., 2006. Comparison of EDTA and sequential extraction tests for phytoavailability prediction of manganese and zinc in agricultural alkaline soils. Geoderma, 132(3-4): 450-463.

Anderson, A.M., 2011. SYNTHESIS OF RECENT KNOWLEDGE ON WATER QUALITY, SEDIMENT QUALITY AND NON-FISH BIOTA IN THE NORTH SASKATCHEWAN RIVER. Synthesis.

Anderson, A.M., 2012. Investigations of Trends in Select Water Quality Variables at Long-Term Monitoring Sites on the North Saskatchewan River. Prepared for Alberta Environment and Sustainable Resource Development.

Ankley, G.T., Di Toro, D.M., Hansen, D.J. and Berry, W.J., 1996. Technical basis and proposal for deriving sediment quality criteria for metals. Environmental Toxicology and Chemistry: An International Journal, 15(12): 2056-2066.

Ashmore, P.E. and Day, T.J., 1988. Spatial and temporal patterns of suspended-sediment yield in the Saskatchewan River basin. Canadian Journal of Earth Sciences, 25(9): 1450-1463.

Atkinson, N., Utting, D.J. and Pawley, S.M., 2018. An update to the glacial landforms map of Alberta. Alberta Geological Survey, 735(10.13140).

áVan Rees, K.C.J., 1995. Speciation of particulate-bound cadmium of soils and its bioavailability. Analyst, 120(3): 659-665.

Bacon, J.R. and Davidson, C.M., 2008. Is there a future for sequential chemical extraction? Analyst, 133(1): 25-46.

Bell, B., 2015. Water quality of the North Saskatchewan River and its four tributaries in Alberta's Industrial Heartland.

Bengtsson, L. and Enell, M., 1986. Chemical analysis.[in:] Berglund BE,(ed.) Handbook of Holocene Palaeoecology and Palaeohydrology. Wiley & Sons, Chichester.

Bish, D.L., William Carey, J., Vaniman, D.T. and Chipera, S.J., 2003. Stability of hydrous minerals on the martian surface. Icarus, 164(1): 96-103.

Bjorge, R.R., 1983. Mortality of cattle on two types of grazing areas in northwestern Alberta Canada, woodland pastures, intensively managed pastures. Rangeland Ecology & Management/Journal of Range Management Archives, 36(1): 20-21.

Black, K.S., Tolhurst, T.J., Paterson, D.M. and Hagerthey, S.E., 2002. Working with natural cohesive sediments. Journal of hydraulic engineering, 128(1): 2-8.

Borovec, Z., 1993. Partitioning of silver, beryllium and molybdenum among chemical fractions in the sediments from the Labe (Elbe) river in Central Bohemia, Czech Rep. GeoJournal, 29(4): 359-364.

Bottrill, L.J., Walling, D.E. and Leeks, G.L., Using recent overbank deposits to investigate contemporary sediment sources in larger river basins, pp. 369-387.

Boughriet, A., Proix, N., Billon, G., Recourt, P. and Ouddane, B., 2007. Environmental impacts of heavy metal discharges from a smelter in Deûle-canal sediments (Northern France): concentration levels and chemical fractionation. Water, Air, and Soil Pollution, 180(1): 83-95.

Bouzidi, A., Ararem, A., Imessaoudene, D. and Yabrir, B., 2015. Sequential extraction of Cs and Sr from Ain Oussera soils around Es-Salam research reactor facility. Journal of Environmental Sciences, 36: 163-172.

Burton, E.D., Phillips, I.R. and Hawker, D.W., 2006. Factors controlling the geochemical partitioning of trace metals in estuarine sediments. Soil and Sediment Contamination: An International Journal, 15(3): 253-276.

Caine, N., 2014. Mechanical and chemical denudation in mountain systems, Mountain geomorphology. Routledge, pp. 138-158.

Calmano, W., Mangold, S. and Welter, E., 2001. An XAFS investigation of the artefacts caused by sequential extraction analyses of Pb-contaminated soils. Fresenius' Journal of Analytical Chemistry, 371(6): 823-830.

Canada, S., 2022. Statistics Canada. 2022. (table) Census Profile. 2021 Census. Statistic Canada Catalogue no.98-316-X2021001 Ottawa.

Carter, J., Owens, P.N., Walling, D.E. and Leeks, G.J.L., 2003. Fingerprinting suspended sediment sources in a large urban river system. Science of the total environment, 314: 513-534.

Chatterjee, S.K., Bhattacharjee, I. and Chandra, G., 2010. Water quality assessment near an industrial site of Damodar River, India. Environmental monitoring and Assessment, 161(1): 177-189.

Clearwater, 2010. An assessment of sediment quality, benthic invertebrates and epolithic algae in the North Saskatchewan River.

Clesceri, L.S., Greenberg, A.E. and Trussell, R.R., 1989. Standard methods for the estimation of water and wastewater. American Public Health Association, Washington.

Collins, A.L., Walling, D.E. and Leeks, G.J.L., 1997. Fingerprinting the origin of fluvial suspended sediment in larger river basins: combining assessment of spatial provenance and source type. Geografiska Annaler: Series A, Physical Geography, 79(4): 239-254.

Dade, W.B., Davis, J.D., Nichols, P.D., Nowell, A.R.M., Thistle, D., Trexler, M.B. and White, D.C., 1990. Effects of bacterial exopolymer adhesion on the entrainment of sand. Geomicrobiology Journal, 8(1): 1-16.

Dagg, M., Benner, R., Lohrenz, S. and Lawrence, D., 2004. Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: plume processes. Continental shelf research, 24(7-8): 833-858.

Davis, A.P., Shokouhian, M. and Ni, S., 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. Chemosphere, 44(5): 997-1009.

de Andrade Passos, E., Alves, J.C., dos Santos, I.S., Jose do Patrocínio, H.A., Garcia, C.A.B. and Costa, A.C.S., 2010. Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. Microchemical Journal, 96(1): 50-57.

Dean, W.E., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition; comparison with other methods. Journal of Sedimentary Research, 44(1): 242-248.

Del Rio-Salas, R., Ruiz, J., De la O-Villanueva, M., Valencia-Moreno, M., Moreno-Rodríguez, V., Gómez-Alvarez, A., Grijalva, T., Mendivil, H., Paz-Moreno, F. and Meza-Figueroa, D., 2012. Tracing geogenic and anthropogenic sources in urban dusts: Insights from lead isotopes. Atmospheric Environment, 60: 202-210.

Dhanakumar, S., Murthy, K.R., Solaraj, G. and Mohanraj, R., 2013. Heavy-metal fractionation in surface sediments of the Cauvery River Estuarine Region, Southeastern Coast of India. Archives of environmental contamination and toxicology, 65(1): 14-23.

Dickson, A.G., 1992. The development of the alkalinity concept in marine chemistry. Marine chemistry, 40(1-2): 49-63.

Dudas, M.J. and Pawluk, S., 1969. Chernozem soils of the Alberta Parklands. Geoderma, 3(1): 19-36.

Dumanski, S., Pomeroy, J.W. and Westbrook, C.J., 2015. Hydrological regime changes in a Canadian Prairie basin. Hydrological Processes, 29(18): 3893-3904.

Enguix González, A., Ternero Rodríguez, M., Jiménez Sá, J.C., Fernández Espinosa, A.J. and Barragán De La Rosa, F.J., 2000. Assessment of metals in sediments in a tributary of Guadalquiver River (Spain). Heavy metal partitioning and relation between the water and sediment system. Water, Air, and Soil Pollution, 121(1): 11-29.

Fantle, M.S. and DePaolo, D.J., 2004. Iron isotopic fractionation during continental weathering. Earth and Planetary Science Letters, 228(3-4): 547-562.

Förstner, U., 2004a. Sediment dynamics and pollutant mobility in rivers: an interdisciplinary approach. Lakes & Reservoirs: Research & Management, 9(1): 25-40.

Förstner, U., 2004b. Traceability of sediment analysis. TrAC Trends in Analytical Chemistry, 23(3): 217-236.

Forstner, U. and Salomons, W., 1980. Trace metal analysis on polluted sediments. Part 2 Evaluation of Environmental Impact. Environmental Technology Letters, 1: 506-517.

Forstner, U. and Wittmann, G.T.W., 1979. Metal pollution in the aquatic environment. Springer-Verlag.

Förstner, U. and Wittmann, G.T.W., 1981. Heavy metals in the aquatic environment. Berlin: Springer Verlag.

Förstner, U. and Wittmann, G.T.W., 2012. Metal pollution in the aquatic environment. Springer Science & Business Media.

Foster, I.D.L. and Charlesworth, S.M., 1996. Heavy metals in the hydrological cycle: trends and explanation. Hydrological processes, 10(2): 227-261.

Fujiwara, F., Dos Santos, M., Marrero, J., Polla, G., Gómez, D., Dawidowski, L. and Smichowski, P., 2006. Fractionation of eleven elements by chemical bonding from airborne particulate matter collected in an industrial city in Argentina. Journal of Environmental Monitoring, 8(9): 913-922.

Gaillardet, J., Viers, J. and Dupré, B., 2003. 5.09 - Trace Elements in River Waters. In: H.D. Holland and K.K. Turekian (Editors), Treatise on Geochemistry. Pergamon, Oxford, pp. 225-272.

Gao, X., Chen, C.-T.A., Wang, G., Xue, Q., Tang, C. and Chen, S., 2010. Environmental status of Daya Bay surface sediments inferred from a sequential extraction technique. Estuarine, coastal and shelf science, 86(3): 369-378.

Ghrefat, H.A., Yusuf, N., Jamarh, A. and Nazzal, J., 2012. Fractionation and risk assessment of heavy metals in soil samples collected along Zerqa River, Jordan. Environmental Earth Sciences, 66(1): 199-208.

Gibbs, R.J., 1973. Mechanisms of trace metal transport in rivers. Science, 180(4081): 71-73.

Golder, 2013a. City of Edmonton 2012 Intensive River Intake Sampling Program., City of Edmonton Drainage Services.

Golder, 2013b. City of Edmonton 2012 North Saskatchewan River Water quality sampling program, City of Edmonton Drainage Services.

Golder, 2013c. Final 2012 Environmental Monitoring Program. Results of the storm sewer, combined sanitary and sewer and storm water management lake and wetland sampling programs, and estimated loading rates to the North Saskatchewan River.

Golder, A., 2014. Evaluation of auatic plants and controlling factors in the North Saskatchewan River.

Green, 1972. Sampling design and statistic methods for environmental biologists. Geological map of Alberta. Research Council of Alberta.

Grizzetti, B., Bouraoui, F., Billen, G., van Grinsven, H., Cardoso, A.C., Thieu, V., Garnier, J., Curtis, C., Howarth, R.W. and Johnes, P., 2011. Nitrogen as a threat to European water quality.

Gu, X. and Evans, L.J., 2007. Modelling the adsorption of Cd (II), Cu (II), Ni (II), Pb (II), and Zn (II) onto fithian illite. Journal of colloid and interface science, 307(2): 317-325.

Gu, X. and Evans, L.J., 2008. Surface complexation modelling of Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II) adsorption onto kaolinite. Geochimica et Cosmochimica Acta, 72(2): 267-276.

Gu, X., Evans, L.J. and Barabash, S.J., 2010. Modeling the adsorption of Cd (II), Cu (II), Ni (II), Pb (II) and Zn (II) onto montmorillonite. Geochimica et Cosmochimica Acta, 74(20): 5718-5728.

Halliday, R., 2009. From the mountains to the sea: The state of the Saskatchewan River Basin. Saskatoon, SK: Partners FOR the Saskatchewan River Basin.

Hao, W., Kashiwabara, T., Jin, R., Takahashi, Y., Gingras, M., Alessi, D.S. and Konhauser, K.O., 2020. Clay minerals as a source of cadmium to estuaries. Scientific Reports, 10(1).

Harrison, R.M., Laxen, D.P.H. and Wilson, S.J., 1981. Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. Environmental Science & Technology, 15(11): 1378-1383.

Health, C., 2018. Strontium in Drinking Water—Guideline Technical Document for Public Consultation. Health Canada Ottawa, ON, Canada.

Heiri, O., Lotter, A.F. and Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. Journal of paleolimnology, 25(1): 101-110.

Horowitz, A.J., 1991. A primer on sediment-trace element chemistry, 2. Lewis Publishers Chelsea.

Horowitz, A.J., 2008. Determining annual suspended sediment and sediment-associated trace element and nutrient fluxes. Science of The Total Environment, 400(1): 315-343.

Horowitz, A.J. and Elrick, K.A., 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Applied geochemistry, 2(4): 437-451.

Horowitz, A.J. and Elrick, K.A., 2017. The use of bed sediments in water quality studies and monitoring programs. Proc. IAHS, 375: 11-17.

Huang, B., Kuo, S. and Bembenek, R., 2004. Availability of cadmium in some phosphorus fertilizers to field-grown lettuce. Water, air, and soil pollution, 158(1): 37-51.

Huang, J.-H. and Kretzschmar, R., 2010. Sequential extraction method for speciation of arsenate and arsenite in mineral soils. Analytical chemistry, 82(13): 5534-5540.

Ianni, C., Magi, E., Rivaro, P. and Ruggieri, N., 2000. Trace metals in Adriatic coastal sediments: distribution and speciation pattern. Toxicological & Environmental Chemistry, 78(1-2): 73-92.

Ip, C.C.M., Li, X.-D., Zhang, G., Wai, O.W.H. and Li, Y.-S., 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. Environmental Pollution, 147(2): 311-323.

Iwegbue, C.M.A., Nwajei, G.E., Eguavoen, O. and Ogala, J.E., 2009. Chemical fractionation of some heavy metals in soil profiles in vicinity of scrap dumps in Warri, Nigeria. Chemical Speciation & Bioavailability, 21(2): 99-110.

Jain, C.K., 2004. Metal fractionation study on bed sediments of River Yamuna, India. Water research, 38(3): 569-578.

Jain, C.K., Gupta, H. and Chakrapani, G.J., 2008. Enrichment and fractionation of heavy metals in bed sediments of River Narmada, India. Environmental monitoring and assessment, 141(1): 35-47.

Jain, C.K. and Sharma, M.K., 2001. Distribution of trace metals in the Hindon River system, India. Journal of hydrology, 253(1-4): 81-90.

James, S.C., Shrestha, P.L. and Roberts, J.D., 2006. Modeling noncohesive sediment transport using multiple sediment size classes. Journal of Coastal Research, 22(5): 1125-1132.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. ACS Publications.

Jenne, E.A., Kennedy, V.C., Burchard, J.M. and Ball, J.W., 1980. Sediment collection and processing for selective extraction and for total trace element analysis. Contaminants and sediments, 2: 169-191.

Jones, B.F. and Bowser, C.J., 1978. The mineralogy and related chemistry of lake sediments, Lakes. Springer, pp. 179-235.

Kalembkiewicz, J. and Sočo, E., 2005. Investigations of Chemical Fraction of Cr in Soil. Polish Journal of Environmental Studies, 14(5).

Ke, X., Gui, S., Huang, H., Zhang, H., Wang, C. and Guo, W., 2017. Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe River protected area, China. Chemosphere, 175: 473-481.

Kessler, 2010. NSR Industrial Heartland Substance Loading Calculation 2000-2008, Alberta Environment.

Kienzle, S.W., 2012. Water Yield and Streamflow Trend Analysis for Alberta Watersheds. Alberta Innovates, Energy and Environment Solutions.

Kilincarslan Kaygun, A., Eral, M. and Akyil Erenturk, S., 2017. Removal of cesium and strontium using natural attapulgite: evaluation of adsorption isotherm and thermodynamic data. Journal of Radioanalytical and Nuclear Chemistry, 311(2): 1459-1464.

Kolter, S., 2018. Ubiquity of Microplastic Pollution in Canada. Student Research Proceedings, 3(1).

Korfali, S.I. and Davies, B.E., 2004. Speciation of metals in sediment and water in a river underlain by limestone: role of carbonate species for purification capacity of rivers. Advances in Environmental Research, 8(3-4): 599-612.

Kumar, V., Sharma, A., Chawla, A., Bhardwaj, R. and Thukral, A.K., 2016. Water quality assessment of river Beas, India, using multivariate and remote sensing techniques. Environmental monitoring and assessment, 188(3): 1-10.

Lacal, J., da Silva, M.P., García, R., Sevilla, M.T., Procopio, J.R. and Hernandez, L., 2003. Study of fractionation and potential mobility of metal in sludge from pyrite mining and affected river sediments: changes in mobility over time and use of artificial ageing as a tool in environmental impact assessment. Environmental Pollution, 124(2): 291-305.

Laceby, J.P., Kerr, J.G., Zhu, D., Chung, C., Situ, Q., Abbasi, S. and Orwin, J.F., 2019. Chloride inputs to the North Saskatchewan River watershed: the role of road salts as a potential driver of salinization downstream of North America's northern most major city (Edmonton, Canada). Science of The Total Environment, 688: 1056-1068.

Langmuir, D., 1997. Aqueous environmental geochemistry.

Li, J., He, M., Han, W. and Gu, Y., 2009. Availability and mobility of heavy metal fractions related to the characteristics of the coastal soils developed from alluvial deposits. Environmental monitoring and assessment, 158(1): 459-469.

Li, P., Qian, H., Howard, K.W.F., Wu, J. and Lyu, X., 2014. Anthropogenic pollution and variability of manganese in alluvial sediments of the Yellow River, Ningxia, northwest China. Environmental Monitoring and Assessment, 186(3): 1385-1398.

Li, X., Coles, B.J., Ramsey, M.H. and Thornton, I., 1995. Sequential extraction of soils for multielement analysis by ICP-AES. Chemical Geology, 124(1-2): 109-123.

Liang, B., Han, G., Liu, M., Yang, K., Li, X. and Liu, J., 2018. Distribution, sources, and water quality assessment of dissolved heavy metals in the Jiulongjiang River water, Southeast China. International journal of environmental research and public health, 15(12): 2752.

Liebens, J., 2001. Heavy metal contamination of sediments in stormwater management systems: the effect of land use, particle size, and age. Environmental Geology, 41(3): 341-351.

Linder, M.C., Wooten, L., Cerveza, P., Cotton, S., Shulze, R. and Lomeli, N., 1998. Copper transport. The American journal of clinical nutrition, 67(5): 965S-971S.

Liss, S.N., Droppo, I.G., Leppard, G.G. and Milligan, T.G., 2004. Flocculation in natural and engineered environmental systems. CRC press.

Liu, H., Li, L., Yin, C. and Shan, B., 2008. Fraction distribution and risk assessment of heavy metals in sediments of Moshui Lake. Journal of Environmental Sciences, 20(4): 390-397.

Lu, F.-H., Ni, H.-G., Liu, F. and Zeng, E.Y., 2009. Occurrence of nutrients in riverine runoff of the Pearl River Delta, South China. Journal of Hydrology, 376(1): 107-115.

Lu, X.Q., Werner, I. and Young, T.M., 2005. Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay. Environment International, 31(4): 593-602.

Lu, X.X., Ran, L.S., Liu, S., Jiang, T., Zhang, S.R. and Wang, J.J., 2013. Sediment loads response to climate change: A preliminary study of eight large Chinese rivers. International Journal of Sediment Research, 28(1): 1-14.

Ma, T., Sheng, Y., Meng, Y. and Sun, J., 2019. Multistage remediation of heavy metal contaminated river sediments in a mining region based on particle size. Chemosphere, 225: 83-92.

Martin, J.-M. and Meybeck, M., 1979. Elemental mass-balance of material carried by major world rivers. Marine Chemistry, 7(3): 173-206.

McBride, M.B., 1994. Environna ental Chemistry Of So|| LS, 141580. Obtenido de Recuperado de: https://d1wqtxts1xzle7. cloudfront. net/35536696 ….

McDonald, D., 2013. Pilot Water Quality Objectives and Allowable Contaminant Loads for the North Saskatchewan River.

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci, 282(4): 401-450.

Miller, W.P., Martens, D.C. and Zelazny, L.W., 1986. Effect of sequence in extraction of trace metals from soils. Soil Science Society of America Journal, 50(3): 598-601.

Milliman, J.D. and Syvitski, J.P.M., 1992. Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers. The journal of Geology, 100(5): 525-544.

Moćko, A. and Wacławek, W., 2004. Three-step extraction procedure for determination of heavy metals availability to vegetables. Analytical and Bioanalytical Chemistry, 380(5): 813-817.

Modak, D.P., Singh, K.P., Chandra, H. and Ray, P.K., 1992. Mobile and bound forms of trace metals in sediments of the lower Ganges. Water Research, 26(11): 1541-1548.

Mohiuddin, K.M., Zakir, H.M., Otomo, K., Sharmin, S. and Shikazono, N., 2010. Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. International Journal of Environmental Science & Technology, 7(1): 17-28.

Mondal, P., Schintu, M., Marras, B., Bettoschi, A., Marrucci, A., Sarkar, S.K., Chowdhury, R., Jonathan, M.P. and Biswas, J.K., 2020. Geochemical fractionation and risk assessment of trace elements in sediments from tide-dominated Hooghly (Ganges) River Estuary, India. Chemical Geology, 532: 119373.

Morley, N.H., Statham, P.J. and Burton, J.D., 1993. Dissolved trace metals in the southwestern Indian Ocean. Deep Sea Research Part I: Oceanographic Research Papers, 40(5): 1043-1062.

Motha, J.A., Wallbrink, P.J., Hairsine, P.B. and Grayson, R.B., 2003. Determining the sources of suspended sediment in a forested catchment in southeastern Australia. Water resources research, 39(3).

Motha, J.A., Wallbrink, P.J., Hairsine, P.B. and Grayson, R.B., 2004. Unsealed roads as suspended sediment sources in an agricultural catchment in south-eastern Australia. Journal of Hydrology, 286(1-4): 1-18.

Müller, D.B., Wang, T., Duval, B. and Graedel, T.E., 2006. Exploring the engine of anthropogenic iron cycles. Proceedings of the National Academy of Sciences, 103(44): 16111-16116.

Nemati, K., Bakar, N.K.A., Abas, M.R. and Sobhanzadeh, E., 2011. Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. Journal of hazardous materials, 192(1): 402-410.

Neufeld, S., 2010. North Saskatchewan River Water Quality. The Edmonton Sustainability.

Novotny, J.A. and Peterson, C.A., 2018. Molybdenum. Advances in Nutrition, 9(3): 272-273.

Nriagu, J.O., 1979. Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. Nature, 279(5712): 409-411.

NSWA, 2010. State of the North Saskatchewan River Watershed Report.

Okbah, M.A., Shata, M.A. and Shridah, M.A., 2005. Geochemical forms of trace metals in mangrove sediments—Red Sea (Egypt). Chemistry and Ecology, 21(1): 23-36.

Owens, P., Batalla, R.J., Collins, A.J., Gomez, B., Hicks, D.M., Horowitz, A.J., Kondolf, G.M., Marden, M., Page, M.J. and Peacock, D.H., 2005. Fine-grained sediment in river systems: environmental significance and management issues. River research and applications, 21(7): 693-717.

Owens, P.N., Walling, D.E. and Leeks, G.L., Tracing fluvial suspended sediment sources in the catchment of the River Tweed, Scotland, using composite fingerprints and a numerical mixing model, pp. 291-308.

Pagnanelli, F., Moscardini, E., Giuliano, V. and Toro, L., 2004. Sequential extraction of heavy metals in river sediments of an abandoned pyrite mining area: pollution detection and affinity series. Environmental Pollution, 132(2): 189-201.

Palleiro, L., Patinha, C., Rodríguez-Blanco, M.L., Taboada-Castro, M.M. and Taboada-Castro, M.T., 2016. Metal fractionation in topsoils and bed sediments in the Mero River rural basin: bioavailability and relationship with soil and sediment properties. Catena, 144: 34-44.

Panchuk, K., 2019. Physical Geology; First University of Saskatchewan Edition.

Parat, C., Lévêque, J., Dousset, S., Chaussod, R. and Andreux, F., 2003. Comparison of three sequential extraction procedures used to study trace metal distribution in an acidic sandy soil. Analytical and Bioanalytical Chemistry, 376(2): 243-247.

Parks, A.E.a., 2015. The water management framwork-8years of implementation.

Paterson, C.G. and Nursall, J.R., 1975. The effects of domestic and industrial effluents on a large turbulent river. Water Research, 9(4): 425-435.

Peijnenburg, W.J.G.M., Zablotskaja, M. and Vijver, M.G., 2007. Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. Ecotoxicology and environmental safety, 67(2): 163-179.

Peltier, E., Dahl, A.L. and Gaillard, J.-F., 2005. Metal speciation in anoxic sediments: When sulfides can be construed as oxides. Environmental science & technology, 39(1): 311-316.

Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanette, M.L. and Orio, A.A., 1985. Heavy metal speciation in the sediments of northern Adriatic Sea. A new approach for environmental toxicity determination. Heavy metals in the environment, 2(1): 454-456.

Persaud, D., Jaagumagi, R. and Hayton, A., 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario.

Phillips, J.M., Russell, M.A. and Walling, D.E., 2000. Time-integrated sampling of fluvial suspended sediment: a simple methodology for small catchments. Hydrological Processes, 14(14): 2589-2602.

Pilechi, A., Rennie, C.D., Mohammadian, M., Zhu, D. and Delatolla, R., 2012. Physical mixing patterns of water and contaminants in the North Saskatchewan River. Prepared for AESRD.

Plan, C., Hub, K., Atlas, M.W., Water, S.A., Stuff, K., Guide, C., Water, F.E.T., Roadmap, W.R.D.I. and Water, G.E.P., 1997. Determination and partitioning of heavy metals in sediments of the Vaal Dam System by sequential extraction. SA Waterbulletin.

Pomeroy, J.W., de Boer, D. and Martz, L.W., 2005. Hydrology and water resources of Saskatchewan. Citeseer.

Prartono, T., Sanusi, H.S. and Nurjaya, I.W., 2016. Seasonal distribution and geochemical fractionation of heavy metals from surface sediment in a tropical estuary of Jeneberang River, Indonesia. Marine pollution bulletin, 111(1-2): 456-462.

Pratap, A., Mani, F.S. and Prasad, S., 2020. Heavy metals contamination and risk assessment in sediments of Laucala Bay, Suva, Fiji. Marine Pollution Bulletin, 156: 111238.

Priju, C.P. and Narayana, A.C., 2007. Heavy and trace metals in Vembanad Lake sediments.

Qiang, T., Xiao-Quan, S., Jin, Q. and Zhe-Ming, N., 1994. Trace metal redistribution during extraction of model soils by acetic acid/sodium acetate. Analytical chemistry, 66(21): 3562-3568.

Rao, C.R.M., Sahuquillo, A. and Lopez-Sanchez, J.F., 2010. Comparison of single and sequential extraction procedures for the study of rare earth elements remobilisation in different types of soils. Analytica Chimica Acta, 662(2): 128-136.

Rath, P., Panda, U.C., Bhatta, D. and Sahu, K.C., 2009. Use of sequential leaching, mineralogy, morphology and multivariate statistical technique for quantifying metal pollution in highly polluted aquatic sediments—A case study: Brahmani and Nandira Rivers, India. Journal of Hazardous materials, 163(2-3): 632-644.

Robertson, D.J., Taylor, K.G. and Hoon, S.R., 2003. Geochemical and mineral magnetic characterisation of urban sediment particulates, Manchester, UK. Applied geochemistry, 18(2): 269-282.

Rodrigues, M.L.K. and Formoso, M.L.L., 2006. Geochemical distribution of selected heavy metals in stream sediments affected by tannery activities. Water, Air, and Soil Pollution, 169(1): 167-184.

Ryan, P.C., Hillier, S. and Wall, A.J., 2008. Stepwise effects of the BCR sequential chemical extraction procedure on dissolution and metal release from common ferromagnesian clay minerals: a combined solution chemistry and X-ray powder diffraction study. Science of the Total Environment, 407(1): 603-614.

Saeedi, M., Li, L.Y., Karbassi, A.R. and Zanjani, A.J., 2013. Sorbed metals fractionation and risk assessment of release in river sediment and particulate matter. Environmental monitoring and assessment, 185(2): 1737-1754.

Sakai, H., Kojima, Y. and Saito, K., 1986. Distribution of heavy metals in water and sieved sediments in the Toyohira river. Water Research, 20(5): 559-567.

Sattarova, V., Aksentov, K., Alatortsev, A., Shakirov, R., Ivanov, M. and Legkodimov, A., 2021. Distribution and contamination assessment of trace metals in surface sediments of the South China Sea, Vietnam. Marine Pollution Bulletin, 173: 113045.

Schindler, D.W. and Donahue, W.F., 2006. An impending water crisis in Canada's western prairie provinces. Proceedings of the National Academy of Sciences, 103(19): 7210-7216.

Shan, X. and Chen, B., 1993. Evaluation of sequential extraction for speciation of trace metals in model soil containing natural minerals and humic acid. Analytical Chemistry, 65(6): 802-807.

Sharma, V.K., Rhudy, K.B., Koening, R. and Vazquez, F.G., 1999. Metals in sediments of the Upper Laguna Madre. Marine Pollution Bulletin, 38(12): 1221-1226.

Shaw, R.D., Mitchell, P. and Anderson, A.M., 1994. Water quality of the North Saskatchewan River in Alberta. Surface Water Assessment Branch, Technical Services and Monitoring Division ….

Sims, J.T. and Kline, J.S., 1991. Chemical fractionation and plant uptake of heavy metals in soils amended with co-composted sewage sludge. 0047-2425, Wiley Online Library.

Singh, A.K., Hasnain, S.I. and Banerjee, D.K., 1999. Grain size and geochemical partitioning of heavy metals in sediments of the Damodar River – a tributary of the lower Ganga, India. Environmental Geology, 39(1): 90-98.

Singh, K.P., Mohan, D., Singh, V.K. and Malik, A., 2005. Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India. Journal of Hydrology, 312(1): 14-27.

Sousa, J.C.G., Ribeiro, A.R., Barbosa, M.O., Pereira, M.F.R. and Silva, A.M.T., 2018. A review on environmental monitoring of water organic pollutants identified by EU guidelines. Journal of hazardous materials, 344: 146-162.

Srivastava, S.K., Gupta, V.K. and Mohan, D., 1994. Status of some toxic heavy metal ions in the upper reaches of river Ganges. Journal of the Indian Chemical Society, 71(1): 29-34.

Stone, M., 2012a. Assessment of Sediment Quality and Sources in the North Saskatchewan River and Its Tributaries.

Stone, M., 2012b. Assessment of sediment quality and sources in the North Saskatchewan River and its tuibutaries.

Stone, M. and Collins, A., 2010. A Review of Literature on Cohesive Sediment Transport Processes, Methodological Frameworks and Management Strategies in Relation to the North Saskatchewan and other Alberta Rivers. Prepared for Alberta Environment.

Stone, M., Collins, A.L. and Laceby, J.P., 2022. Natural and anthropogenic impacts on the geochemical composition and metal speciation of fine sediment in a glacier-fed Canadian river basin. Journal of Soils and Sediments, 22(1): 365-380.

Stone, M. and Saunderson, H., 1992. Particle size characteristics of suspended sediment in southern Ontario rivers tributary to the Great Lakes. Hydrological processes, 6(2): 189-198.

Sundaray, S.K., 2007. Water quality assessment of Mahanadi river Orissa India using multivariate statistical approach.

Sundaray, S.K., Nayak, B.B., Lin, S. and Bhatta, D., 2011. Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments—A case study: Mahanadi basin, India. Journal of Hazardous Materials, 186(2): 1837-1846.

Tessier, A., Campbell, P.G.C. and Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical chemistry, 51(7): 844-851.

TetraTech, 2012. North Saskatchewan Intergrated Water Quality Model Enhancement for Scenarios Analysis, Alberta Environment.

Thodsen, H., Hasholt, B. and Kjærsgaard, J.H., 2008. The influence of climate change on suspended sediment transport in Danish rivers. Hydrological Processes: An International Journal, 22(6): 764-774.

Thorne, L.T. and Nickless, G., 1981. The relation between heavy metals and particle size fractions within the severn estuary (U.K.) inter-tidal sediments. Science of The Total Environment, 19(3): 207-213.

Tipping, E., Hetherington, N.B., Hilton, J., Thompson, D.W., Bowles, E. and Hamilton-Taylor, J., 1985. Artifacts in the use of selective chemical extraction to determine distributions of metals between oxides of manganese and iron. Analytical Chemistry, 57(9): 1944-1946.

Tlustoš, P., Száková, J., Stárková, A. and Pavlíková, D., 2005. A comparison of sequential extraction procedures for fractionation of arsenic, cadmium, lead, and zinc in soil. Open Chemistry, 3(4): 830-851.

Tokarsky, O., 1971. Hydrogeology of the Grimshaw-Chinook valley area. Alberta.

Toomey, M., 1988. The Alberta digital elevation model. International Archives of Photogrammetry and Remote Sensing, 27(B3): 775-783.

Turner, R.E., Rabalais, N.N., Justic, D. and Dortch, Q., 2003. Global patterns of dissolved N, P and Si in large rivers. Biogeochemistry, 64(3): 297-317.

Turowski, J.M., Rickenmann, D. and Dadson, S.J., 2010. The partitioning of the total sediment load of a river into suspended load and bedload: a review of empirical data. Sedimentology, 57(4): 1126-1146.

Ullman, D.J., Carlson, A.E., Hostetler, S.W., Clark, P.U., Cuzzone, J., Milne, G.A., Winsor, K. and Caffee, M., 2016. Final Laurentide ice-sheet deglaciation and Holocene climate-sea level change. Quaternary Science Reviews, 152: 49-59.

Ure, A.M., Quevauviller, P.H., Muntau, H. and Griepink, B., 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. International journal of environmental analytical chemistry, 51(1-4): 135-151.

Venkateswaran, P., Vellaichamy, S. and Palanivelu, K., 2007. Speciation of heavy metals in electroplating industry sludge and wastewater residue using inductively coupled plasma. International Journal of Environmental Science & Technology, 4(4): 497-504.

Vieira, J.S., Pires, J., Martins, F.G., Vilar, V.J.P., Boaventura, R.A.R. and Botelho, C., 2012. Surface water quality assessment of Lis river using multivariate statistical methods. Water, Air, & Soil Pollution, 223(9): 5549-5561.

von Gunten, K., Alam, M.S., Hubmann, M., Ok, Y.S., Konhauser, K.O. and Alessi, D.S., 2017. Modified sequential extraction for biochar and petroleum coke: Metal release potential and its environmental implications. Bioresource Technology, 236: 106-110.

Walling, D.E., 1999. Linking land use, erosion and sediment yields in river basins, Man and river systems. Springer, pp. 223-240.

Walling, D.E., 2009. The impact of global change on erosion and sediment transport by rivers: current progress and future challenges.

Walling, D.E. and Collins, A.L., 2005. Suspended sediment sources in British rivers. Sediment budgets, 1(291): 2005123-33.

Walling, D.E. and Fang, D., 2003. Recent trends in the suspended sediment loads of the world's rivers. Global and Planetary Change, 39(1): 111-126.

Walling, D.E., He, Q. and Blake, W., 1999. Use of 7Be and 137Cs measurements to document short-and medium-term rates of water-induced soil erosion on agricultural land. Water Resources Research, 35(12): 3865-3874.

Walling, D.E. and Woodward, J.C., 1995. Tracing sources of suspended sediment in river basins: a case study of the River Culm, Devon, UK. Marine and Freshwater Research, 46(1): 327-336.

Wang, J., Liu, G., Liu, H. and Lam, P.K.S., 2017. Multivariate statistical evaluation of dissolved trace elements and a water quality assessment in the middle reaches of Huaihe River, Anhui, China. Science of the total environment, 583: 421-431.

Wang, Q., Li, Y. and Wang, Y., 2011. Optimizing the weight loss-on-ignition methodology to quantify organic and carbonate carbon of sediments from diverse sources. Environmental Monitoring and Assessment, 174(1-4): 241-257.

Wilson, M.A., Burt, R. and Lee, C.W., 2006. Improved Elemental Recoveries in Soils with Heating Boric Acid Following Microwave Total Digestion. Communications in Soil Science and Plant Analysis, 37(3-4): 513-524.

Wisner, P.E., Clarke, W.G. and Roake, A.F., 1981. Studies for abatement of pollution from combined sewer overflows in Canada. Journal of Hydrology, 51(1-4): 329-338.

Xiao, R., Bai, J., Lu, Q., Zhao, Q., Gao, Z., Wen, X. and Liu, X., 2015. Fractionation, transfer, and ecological risks of heavy metals in riparian and ditch wetlands across a 100-year chronosequence of reclamation in an estuary of China. Science of the Total Environment, 517: 66-75.

Yang, Y., Campbell, C.D., Clark, L., Cameron, C.M. and Paterson, E., 2006. Microbial indicators of heavy metal contamination in urban and rural soils. Chemosphere, 63(11): 1942-1952.

Yao, Q., Wang, X., Jian, H., Chen, H. and Yu, Z., 2015. Characterization of the particle size fraction associated with heavy metals in suspended sediments of the Yellow River. International journal of environmental research and public health, 12(6): 6725-6744.

Yu, K.-C., Tsai, L.-J., Chen, S.-H. and Ho, S.-T., 2001. Correlation analyses on binding behavior of heavy metals with sediment matrices. Water Research, 35(10): 2417-2428.

Yuan, C.-g., Shi, J.-b., He, B., Liu, J.-f., Liang, L.-n. and Jiang, G.-b., 2004. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environment International, 30(6): 769-783.

Zaremehrjardy, M., 2020. Modelling snow dynamics and groundwater-surface water interactions in mountainous, foothill and plain regions in North Saskatchewan River Basin, Canada.

Zhang, G., Bai, J., Xiao, R., Zhao, Q., Jia, J., Cui, B. and Liu, X., 2017. Heavy metal fractions and ecological risk assessment in sediments from urban, rural and reclamation-affected rivers of the Pearl River Estuary, China. Chemosphere, 184: 278-288.

Zhang, G.-H., Wang, L.-L., Tang, K.-M., Luo, R.-T. and Zhang, X.C., 2011. Effects of sediment size on transport capacity of overland flow on steep slopes. Hydrological sciences journal, 56(7): 1289-1299.

Zhang, J., Huang, W.W. and Martin, J.M., 1988. Trace metals distribution in Huanghe (Yellow River) estuarine sediments. Estuarine, Coastal and Shelf Science, 26(5): 499-516.

Zhu, W., Bian, B. and Li, L., 2008. Heavy metal contamination of road-deposited sediments in a medium size city of China. Environmental monitoring and assessment, 147(1): 171-181.

Zimmerman, A.J. and Weindorf, D.C., 2010. Heavy Metal and Trace Metal Analysis in Soil by Sequential Extraction: A Review of Procedures. International Journal of Analytical Chemistry, 2010: 387803.

Appendix

Figure S1 Sampling site1

Figure S2 Bedload sediment sieving

Figure S3 Filtered suspended sediments

Table S1 Metal distribution in different fractions of NSR sediments

		Step1 (F1) Ratio (%)	Step2 (F2) Ratio (%)	Step3 (F3) Ratio (%)	Step4 (F4) Ratio (%)	Step5 (F5) Ratio (%)
	Suspended sediment					
Cu	Max	0.67%	21.75%	11.83%	38.08%	59.49%
	Min	0.35%	7.86%	2.80%	24.19%	27.74%
	Median	0.52%	9.46%	6.71%	28.98%	54.77%
	Standard deviation	0.12%	5.39%	2.51%	3.98%	10.85%
	Average	0.49%	12.22%	6.86%	29.73%	50.69%
Ni	Max	0.88%	12.24%	31.55%	14.26%	62.26%
	Min	0.16%	6.88%	18.99%	10.28%	41.43%
	Median	0.57%	8.25%	25.52%	12.20%	53.26%
	Standard deviation	0.27%	1.57%	3.96%	1.23%	6.13%
	Average	0.53%	8.69%	25.17%	12.00%	53.61%
Cd	Max	9.28%	64.07%	26.43%	6.65%	21.96%
	Min	4.59%	44.54%	19.25%	4.96%	0.00%
	Median	7.48%	55.40%	24.26%	5.38%	9.63%
	Standard deviation	1.52%	7.11%	2.50%	0.58%	8.52%
	Average	7.14%	54.11%	23.72%	5.55%	9.47%
Mn	Max	2.42%	66.21%	36.76%	2.92%	20.76%
	Min	0.97%	53.65%	19.95%	1.97%	2.56%
	Median	1.61%	56.95%	28.90%	2.70%	7.82%
	Standard deviation	0.43%	5.08%	6.33%	0.31%	5.83%
	Average	1.61%	58.61%	28.59%	2.63%	8.56%
Cr	Max	0.47%	1.55%	5.48%	5.58%	91.55%
	Min	0.35%	1.03%	3.85%	3.04%	86.98%

	Median	0.39%	1.11%	4.22%	3.81%	90.42%
	Standard deviation	0.05%	0.16%	0.54%	0.77%	1.37%
	Average	0.40%	1.17%	4.32%	3.94%	90.17%
Pb	Max	0.13%	20.98%	46.08%	15.13%	44.82%
	Min	0.01%	13.63%	32.88%	8.42%	18.74%
	Median	0.02%	17.03%	35.77%	10.59%	34.74%
	Standard deviation	0.04%	2.66%	4.21%	2.27%	8.40%
	Average	0.04%	16.99%	36.70%	10.78%	35.49%
Fe	Max	0.02%	2.11%	27.35%	8.99%	71.34%
	Min	0.00%	1.26%	20.62%	6.32%	61.52%
	Median	0.01%	1.74%	22.77%	7.91%	67.71%
	Standard deviation	0.01%	0.24%	1.91%	0.88%	2.72%
	Average	0.01%	1.73%	23.11%	7.80%	67.36%
Sr	Max	25.39%	44.80%	8.42%	3.14%	52.12%
	Min	14.90%	25.42%	5.82%	1.59%	18.25%
	Median	17.72%	32.40%	6.77%	2.22%	40.85%
	Standard deviation	3.37%	7.63%	0.77%	0.47%	10.29%
	Average	18.56%	33.79%	6.85%	2.21%	38.58%
Mo	Max	10.42%	2.36%	15.30%	29.01%	74.90%
	Min	2.01%	0.59%	6.51%	11.78%	48.57%
	Median	4.46%	1.83%	12.39%	20.54%	60.44%
	Standard deviation	2.73%	0.61%	2.92%	5.90%	8.16%
	Average	4.87%	1.73%	11.82%	21.06%	60.52%
Co	Max	0.26%	21.80%	51.16%	12.87%	43.87%
	Min	0.13%	9.90%	26.94%	9.35%	25.47%
	Median	0.18%	16.66%	32.02%	10.85%	39.84%
	Standard deviation	0.04%	4.69%	8.02%	1.19%	5.58%
	Average	0.18%	16.55%	34.07%	10.70%	38.51%

	Bedload sediment					
Cu	Max	2.77%	55.32%	13.45%	39.66%	24.49%
	Min	1.10%	36.13%	6.17%	20.18%	6.78%
	Median	1.77%	44.91%	9.48%	25.78%	15.29%
	Standard deviation	0.54%	7.27%	2.90%	5.58%	5.88%
	Average	1.85%	45.64%	9.97%	26.86%	15.67%
Ni	Max	2.14%	11.04%	29.41%	14.01%	56.16%
	Min	1.00%	7.03%	22.93%	10.89%	46.80%
	Median	1.28%	8.88%	25.91%	12.34%	51.36%
	Standard deviation	0.38%	1.53%	2.33%	1.04%	2.79%
	Average	1.37%	8.92%	26.07%	12.22%	51.42%
Cd	Max	22.07%	44.74%	25.93%	12.64%	26.75%

	Min	15.26%	28.70%	12.70%	5.31%	4.68%
	Median	19.86%	38.17%	17.34%	9.63%	15.16%
	Standard deviation	2.46%	6.26%	4.42%	2.32%	9.93%
	Average	19.30%	36.88%	18.47%	9.28%	16.06%
Mn	Max	9.11%	55.41%	28.77%	3.78%	20.80%
	Min	3.94%	42.41%	18.91%	2.99%	11.58%
	Median	6.52%	49.69%	22.92%	3.31%	17.79%
	Standard deviation	1.61%	4.39%	2.82%	0.25%	2.75%
	Average	6.55%	49.55%	23.27%	3.31%	17.32%
Cr	Max	0.64%	1.19%	4.29%	5.51%	92.78%
	Min	0.30%	0.75%	2.89%	3.02%	90.11%
	Median	0.34%	0.90%	3.37%	3.36%	91.39%
	Standard deviation	0.13%	0.18%	0.46%	0.90%	0.98%
	Average	0.40%	0.94%	3.47%	3.74%	91.45%
Pb	Max	0.34%	26.41%	32.39%	10.84%	49.73%
	Min	0.04%	14.80%	19.26%	6.82%	36.21%
	Median	0.11%	24.09%	26.69%	8.37%	41.13%
	Standard deviation	0.10%	3.66%	3.76%	1.18%	4.03%
	Average	0.13%	23.35%	26.39%	8.41%	41.72%
Fe	Max	0.02%	5.59%	22.06%	7.64%	70.63%
	Min	0.01%	1.50%	20.01%	5.79%	65.91%
	Median	0.01%	3.79%	20.86%	6.62%	69.14%
	Standard deviation	0.00%	1.23%	0.76%	0.55%	1.73%
	Average	0.01%	3.83%	20.94%	6.63%	68.59%
Sr	Max	14.57%	22.80%	6.93%	2.77%	67.71%
	Min	10.11%	11.86%	4.98%	2.34%	53.08%
	Median	12.40%	18.77%	6.68%	2.64%	59.67%
	Standard deviation	1.44%	3.50%	0.64%	0.14%	4.64%
	Average	12.27%	18.87%	6.47%	2.62%	59.77%
Mo	Max	19.01%	9.32%	28.82%	32.37%	76.76%
	Min	3.69%	1.67%	7.99%	9.89%	27.94%
	Median	9.11%	3.55%	17.88%	22.31%	46.39%
	Standard deviation	4.63%	2.33%	6.07%	6.80%	16.18%
	Average	10.28%	4.18%	18.44%	21.19%	45.91%
Co	Max	2.00%	20.96%	31.09%	11.40%	42.38%
	Min	0.86%	16.92%	28.03%	10.35%	36.42%
	Median	1.44%	18.58%	28.42%	10.70%	39.96%
	Standard deviation	0.34%	1.57%	1.16%	0.37%	2.05%
	Average	1.43%	18.77%	29.03%	10.77%	40.00%

F1, exchangeable bound; F2, carbonate bound. F3, Fe-Mn oxides bound; F4, organic bound; F5, residual bound.