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Trace element chemistry of surficial fine-grained laminae in the South Saskatchewan River, Canada

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Abstract The role of surficial fine-grained laminae (SFGL) in the accumulation of heavy metals (Cu, Zn, Ni, Cd, Sn, Cs, Pb and U) in bottom sediments in a large prairie stream was investigated upstream and downstream of a large urban centre in the summer of 1999. Concentrations of dissolved trace metals in the South Saskatchewan River upstream and downstream of the city of Saskatoon did not show an effect of urban sources. The exception was U, which had consistently higher concentrations at the downstream site. Trace metal concentrations in SFGL downstream of the city of Saskatoon were significantly greater than those upstream on days experiencing low flow velocities. Further analysis of the data to determine the extent to which the higher trace metal concentrations can be explained by the higher percentage of silt and clay, and whether urban runoff from the city of Saskatoon affects trace metal concentrations in the South Saskatchewan River is in progress.

INTRODUCTION

Fine-grained sediment in fluvial systems is frequently transported as flocs (Droppo & Ongley, 1992). Flocculation and settling of the flocs on the riverbed result in the formation of surficial fine-grained laminae (SFGL). Field observations indicate that there is a continuous exchange of particles between sediment suspended in the water column and SFGL on the riverbed. During periods when flow velocity and bed shear stress are low, a net accumulation of SFGL occurs. During periods when flow velocity and bed shear stress are high, SFGL are eroded and may entirely disappear, thus exposing the underlying, coarser bed materials. The fine-grained and organic-rich nature of SFGL makes them a potentially significant short term sink for heavy metals within the channel (Droppo & Stone, 1994; Stone & Droppo, 1994; Symader *et al.*, 1994, 1995). Urban areas are a potential source of trace metals (e.g. Stone & Marsalek, 1996; Estèbe *et al.*, 1998). The objective of this study was to investigate the significance of SFGL as a short-term sink of heavy metals in a large stream on the Canadian prairies upstream and downstream of a large, urban centre. This paper presents an initial analysis of the available data collected during the summer season of 1999.

METHODOLOGY

Data collection

Sampling of water and SFGL was conducted biweekly during the summer of 1999 on the South Saskatchewan River upstream and downstream of the city of Saskatoon

(Fig. 1). The mean annual discharge of the South Saskatchewan River at Saskatoon is approximately 200 m^3 s^{-1}. Discharge is strongly regulated by the release of water from Lake Diefenbaker at the Gardiner Dam, 120 km upstream of Saskatoon. As a result, the discharge has a limited range of variation from approximately 100 to 300 m^3 s^{-1}, with peak discharges in January and a second peak flow period in June and July (Environment Canada, 1994). The downstream sampling site was located several kilometres downstream of the city of Saskatoon sewage treatment plant. Saskatoon has a separate storm sewer system that discharges runoff at various points into the South Saskatchewan River. At the sampling sites, the South Saskatchewan River is approximately 200 m wide.

At each site, sampling took place in the part of the cross-section where low flow velocities facilitated sediment deposition from the water column. At the upstream site, the South Saskatchewan River is a characteristic sandbed river, with many unstable bars. During high discharge events at this site, sand makes up a large proportion of the suspended load. Conversely, at the downstream site, the bed

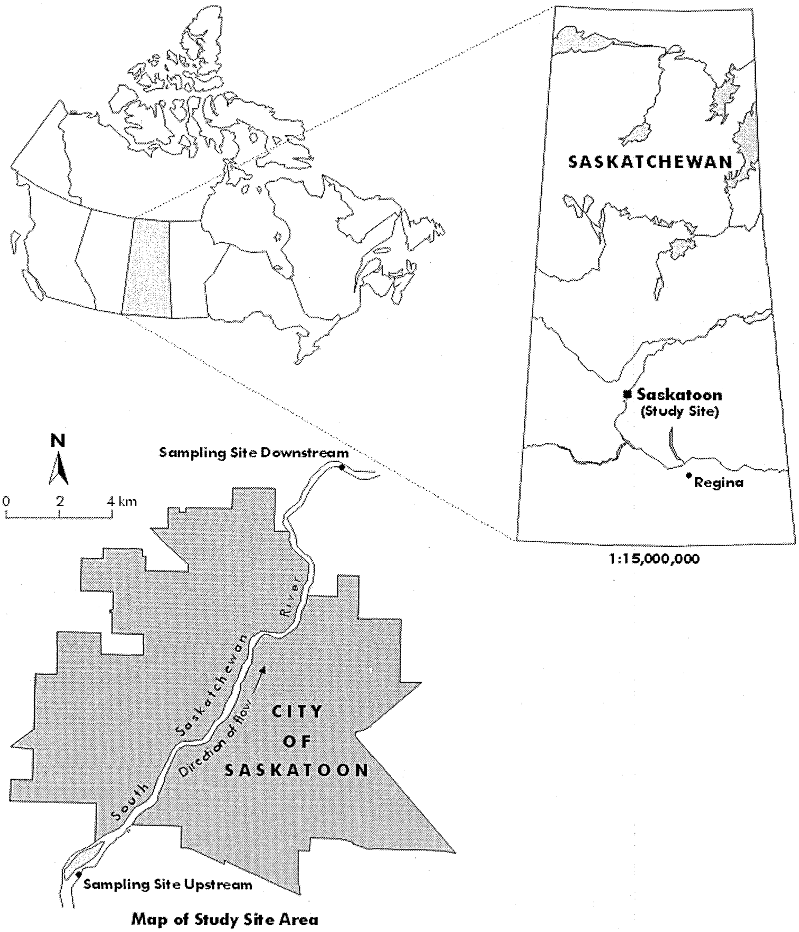

Fig. 1 Location of sampling sites on South Saskatchewan River.

consists predominantly of gravel, with isolated sand bars in low velocity areas of the river.

During sampling, flow conditions were characterized in part by measuring flow velocity at one third and two thirds of the depth with an American Sigma PVM current meter. Water samples were filtered in the field using 0.45 μm Nuclepore SFCA syringe filters for determination of total dissolved solids concentrations and trace element analysis. Samples for suspended sediment concentration were collected with a DH-48 sampler. Surficial fine-grained laminae samples were collected in sediment traps consisting of a series of petri dishes fixed to a frame made of PVC tubes. At each site, three frames were placed on the river bed for approximately 24 h. Three petri dishes from each frame were collected for analyses of particle morphology and size distribution. The petri dishes were closed under water and placed in containers for transport to the lab. Separate samples of SFGL for trace element analysis were collected in a similar manner. Bulk samples of SFGL for determining particle size distributions and accumulation rates were collected on rubber mats. Sediment accumulated on the mats was wet-sieved using a metal 63 μm sieve to separate the silt and clay from the sand fraction. All samples were collected in triplicate and analysed separately. All trace element analyses (Cu, Ni, Sn, Pb, Zn, Cd, Cs and U) were carried out at the ICP-MS facility of the Department of Geological Sciences of the University of Saskatchewan. Samples of SFGL for trace metal analysis were not sieved. The accuracy of trace metal analysis was evaluated by analysing duplicate samples, blanks and reference materials (BHVO-1, USGS; SLRS-4, National Research Council).

RESULTS AND DISCUSSION

Flow conditions and sediment characteristics

Mean flow velocity, used here as a proxy for discharge, was slightly higher at the upstream site than at the downstream site. The mean flow velocity at both sites was greater on 23 June and 6 August than on other sampling dates because of the release of water from Lake Diefenbaker (Fig. 2(a)). A similar temporal pattern was shown by the suspended sediment concentration at the upstream site, which peaked on 23 June and 6 August. On 23 July, suspended sediment concentration at the upstream site was in excess of 40 mg l^{-1}, even though flow velocities were relatively low. High suspended sediment concentrations measured on this day coincided with a particle size distribution with 24% silt and clay, which is substantially greater than on any other day of the study period at this site. At the downstream site, suspended sediment concentrations did not vary directly with mean flow velocity. The lowest suspended sediment concentrations were measured on the dates with the lowest mean flow velocities, but, unlike at the upstream site, peak values of the mean flow velocity did not correspond to peaks in suspended sediment concentration. Suspended sediment concentrations were lower at the downstream site than at the upstream site, except on 9 June and 19 August. Concentrations of total dissolved solids were similar and ranged from 260 to 340 mg l^{-1} at both sites.

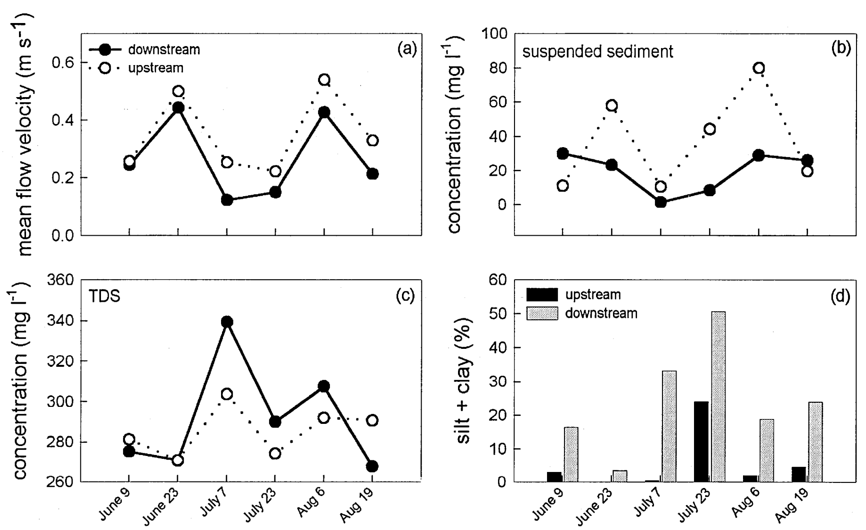

Fig. 2 Temporal plots of (a) mean flow velocity, (b) mean suspended sediment concentration, (c) mean dissolved solids concentration, and (d) mean % silt and clay in sediment traps, at the upstream and downstream sites.

The percentage of silt and clay of the sediment collected on the rubber mats at the upstream site was consistently lower than at the downstream site. This reflects the localized input to the river of sand from dune fields south of Saskatoon. At the downstream site, the percentage of silt and clay was greatest on 7 and 23 July (Fig. 2(d)) which coincides with the period of low mean flow velocities after the peak mean flow velocity of 23 June. Overall, decreases in the percentage of silt and clay from one sampling time to the next are associated with periods of high mean flow velocities (Fig. 2(a) and (b)). Nevertheless, no simple, direct relationship between the percentage of silt and clay and mean flow velocity is apparent.

Temporal variation in dissolved and particulate trace element concentrations

Analysis of dissolved trace element concentrations upstream and downstream reveals that dissolved concentrations did not vary in a straightforward manner with mean flow velocity and discharge over the course of the field season. Dissolved concentrations of Cu, Ni and Sn showed little variation from 9 June to 23 July (Fig. 3). On 6 August, concentrations for these elements stayed relatively constant at the upstream site, but showed an increase at the downstream site. Conversely, on 19 August, concentrations for Cu, Ni and Sn showed an increase at the upstream site and a decrease at the downstream site. On this date, dissolved concentrations for these three elements at the upstream site were the highest for the entire field season. Analysis of precipitation records is currently in progress to determine the magnitude of the contribution of urban runoff to the discharge. Variations in the concentrations of dissolved Pb were largely similar to those of Cu, Ni and Sn. Concentrations of dissolved Zn and Cd at both sites showed no readily discernible temporal pattern.

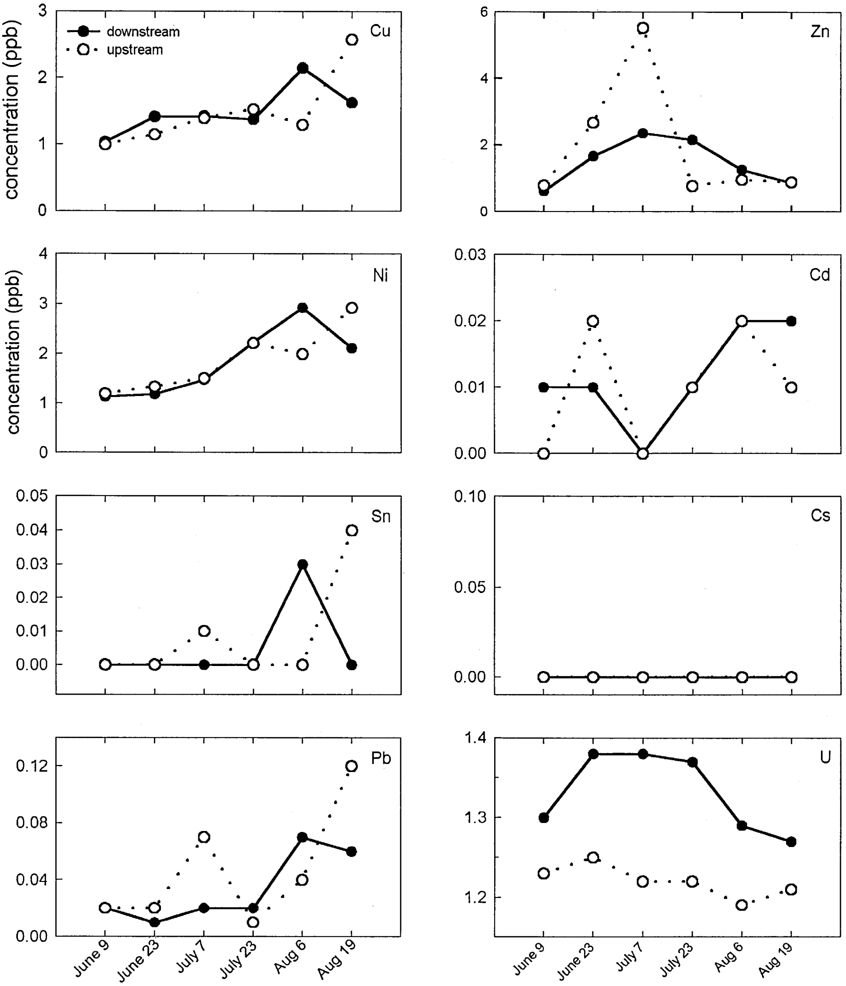

Fig. 3 Mean dissolved trace element concentrations (ppb) at downstream and upstream sites.

Concentrations of dissolved U at the upstream site showed little variations through time, but at the downstream site concentrations reached the highest values on 23 June, 7 and 23 July and decreased thereafter. Concentrations of Cd, Sn and Cs frequently were below the detection limit.

At the downstream site, trace metal concentrations in SFGL varied directly with percentage of silt and clay and inversely with mean flow velocity (Figs 2 and 4). On 23 June and 6 August, for example, high flow velocities resulted in a low percentage of silt and clay and, as a result, trace element concentrations in SFGL were lower than on the other days. At the upstream site, trace metal concentrations in SFGL remained relatively stable over the field season. The limited range of concentrations likely reflects the generally coarser nature of the SFGL, which on all days contained a substantial percentage of fine sand. Changes in the generally low percentage of silt and clay at this site did not result in significant changes in trace metal concentrations.

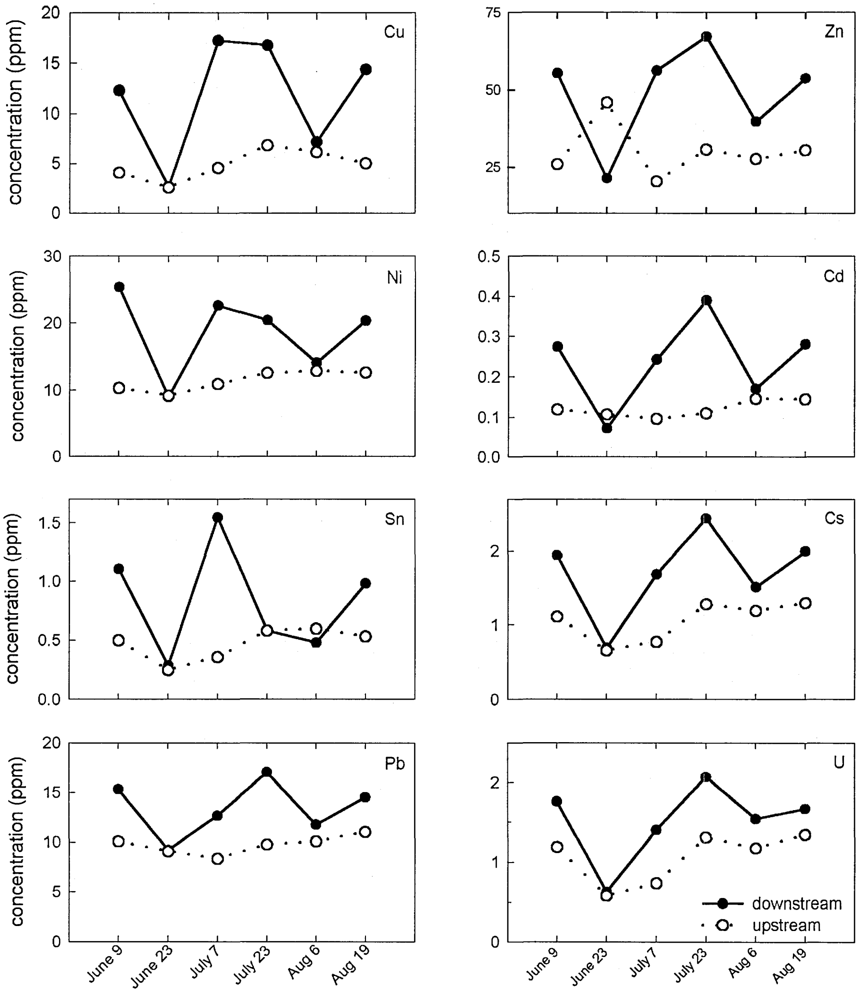

Fig. 4 Mean trace element concentrations (ppm) in SFGL at downstream and upstream sites.

Even though there is a large body of data on trace metal concentrations in bed sediments, little information is available about trace metal concentrations in SFGL from other studies. For SFGL collected in three southern Ontario streams, Stone & Droppo (1994) reported Zn concentrations ranging from 32.6 to 56.5 ppm, Pb concentrations ranging from 13 to 20.6 ppm, and Cu concentrations ranging from 9.3 to 12.7 ppm. Concentrations for these three metals are of a similar magnitude as those found in SFGL in the South Saskatchewan River in the present study. Comparison with the Provincial Sediment Quality Guidelines (PSQG) for Ontario (Persaud *et al.*, 1993) shows that concentrations in SFGL at the downstream site exceeded the Lowest Effect Level (LEL) for Ni (LEL = 16 mg kg^{-1}) on all sample dates but 6 August. In addition, on 7 and 23 July, Cu exceeded the LEL of 16 mg kg^{-1}. The LEL is the level of contamination that can be tolerated by the majority of benthic organisms. Metal concentrations in excess of the LEL indicate the possibility of adverse effects on some benthic organisms so that further testing and a management plan for remediation may be required. Metal concentrations in SFGL, however, did not exceed at any time the PSQG Severe Effect Levels indicative of severe pollution.

Spatial variation in dissolved and particulate trace element concentrations

Analysis of dissolved trace element concentrations upstream and downstream over the course of the field season reveals that water samples from the two sampling sites did not vary consistently for the majority of elements (Fig. 3). The exception was U with concentrations ranging from 1.20 to 1.25 ppb at the upstream site and from 1.27 to 1.38 ppb at the downstream site. Testing for significant differences in mean dissolved elemental concentrations at the upstream and downstream sites using the Mann-Whitney U test (Hammond & McCullagh, 1978) confirmed that few elements, with the exception of uranium, had downstream concentrations significantly greater than those upstream (Table 1).

Statistical analysis for significant differences between sample means for trace metal concentrations in SFGL collected upstream and downstream of the city indicates that concentrations were significantly higher downstream than upstream on days characterized by low flow velocities (Table 2). On the days of high flow velocity, 23 June and 6 August, mean concentrations at the downstream site were substantially lower than on the other dates and similar to those at the upstream site.

Table 1 Mann-Whitney U test for dissolved trace metal concentrations.

	9 June 1999	23 June 1999	7 July 1999	23 July 1999	6 August 1999	19 August 1999
Cu		×			×	
Zn				×	×	
Ni					×	
Cd	×					
Sn					×	
Cs						
Pb						
U	×	×	×	×	×	×

Table 2 Mann-Whitney U test for trace metal concentrations in SFGL.

	9 June 1999	23 June 1999	7 July 1999	23 July 1999	6 August 1999	19 August 1999
Cu	×		×	×		×
Zn	×		×	×		×
Ni	×		×	×		×
Cd	×		×	×		×
Sn	×		×			×
Cs	×		×	×		×
Pb	×		×	×		×
U	×		×	×	×	

The low trace metal concentrations on these two dates can be explained by the low percentage of silt and clay of the SFGL on these two dates. The results suggest that SFGL is more effective than filtered water for detecting changes in trace element concentrations upstream and downstream of an urban centre. However, the utility of SFGL to detect changes in water quality varies with flow conditions which influence the nature and extent of the deposits.

CONCLUSIONS

A comparison of trace metal concentrations in the South Saskatchewan River upstream and downstream of the City of Saskatoon indicates that concentrations of most trace metals in the dissolved phase do not show an effect of urban sources. The exception was U, which showed consistently higher concentrations downstream. Concentrations of Cu, Zn, Ni, Cd, Sn, Cs, Pb and U in SFGL samples downstream of the city of Saskatoon were significantly greater than those upstream on days experiencing low flow velocities. Further analysis of the data to determine the extent to which the higher trace metal concentrations can be explained by the higher percentage of silt and clay, and whether urban runoff from the city of Saskatoon affects trace metal concentrations in the South Saskatchewan River is in progress.

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