Erosion of the Alberta badlands produces highly variable and elevated heavy metal concentrations in the Red Deer River, Alberta

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HIGHLIGHTS

- Erosion of contaminated soil is a major cause of riverine heavy metal contamination.
- Examined riverine heavy metal dynamics in a highly erosive watershed.
- No evidence of widespread enrichment of suspended sediments with heavy metals.
- Elevated riverine heavy metal concentrations due to high instream sediment mass.
- Erosion of 'background' soils produced levels typical of heavily impacted rivers.

GRAPHICAL ABSTRACT
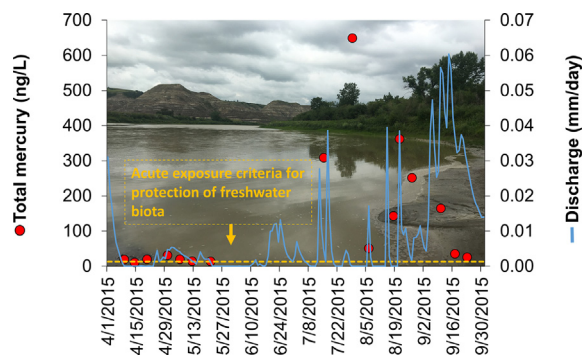
ABSTRACT

Erosion is important in the transport of heavy metals from terrestrial to fluvial environments. In this study, we investigated riverine heavy metal (Cd, Cu, Hg and Pb) dynamics in the Red Deer River (RDR) watershed at sites upstream ($n = 2$) and downstream ($n = 7$) of the Alberta badlands, an area of naturally high erosion. At sites draining the badlands, total water column Cd, Cu, Hg and Pb concentrations frequently exceeded guidelines for the protection of freshwater biota. Furthermore, peak concentrations of total Cd ($9.8\ \mu g\ L^{-1}$), Cu ($212\ \mu g\ L^{-1}$), Hg ($649\ ng\ L^{-1}$) and Pb ($361\ \mu g\ L^{-1}$) were higher than, or comparable to, values reported for rivers and streams heavily impacted by anthropogenic activities. Total suspended solids (TSS) explained a large proportion ($r^2 = 0.34$–0.83) of the variation in total metal concentrations in the RDR and tributaries and metal fluxes were dominated by the particulate fraction (60–98%). Suspended sediment concentrations (C_{sed}) and metal to aluminum ratios were generally not indicative of substantial sediment enrichment. Rather, the highly variable and elevated metal concentrations in the RDR watershed were a function of the high and variable suspended sediment fluxes which characterize the river system. While the impact of this on aquatic biota requires further investigation, we suggest erosion in the Alberta badlands may be contributing to Hg-based fish consumption advisories in the RDR. Importantly, this highlights a broader need for information on contaminant dynamics in watersheds subject to elevated rates of erosion.

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1. Introduction

The contamination of surface waters with heavy metals (elements with a specific density > 5 g cm^{-3}; Callender, 2003) is a major

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environmental concern (Driscoll et al., 2013; Sutherland, 2000). Heavy metals exhibit a range of toxic effects to aquatic and terrestrial biota (Driscoll et al., 2013; Flemming and Trevors, 1989; Mebane, 2010) in addition to impacts on human health (Lanphear et al., 2005; Tchounwou et al., 2012). Although natural sources exist (e.g., weathering and wildfires), anthropogenic activities (e.g., mining and smelting, urbanization and industrial processes) substantially increase heavy metal fluxes to rivers (Horowitz and Stephens, 2008; Horowitz et al., 2012; Macklin et al., 2006; Sutherland, 2000). Metals in aquatic environments are conventionally classified as particulate or dissolved with dissolved forms operationally defined as material passing through a 0.45 μm filter (Nystrand et al., 2012; Owens et al., 2005). While dissolved forms are considered immediately bioavailable, the extent to which particulate forms are bioavailable will depend on the lability of metal species in particulate phase and the physicochemical properties of the environment (Eggleton and Thomas, 2004). A large proportion of heavy metal transport to the world's lakes and oceans occurs via rivers (Callender, 2003) and due to the strong affinity of metals for soil/sediment surfaces (Horowitz, 1991) most of this is associated with the particulate phase (Horowitz et al., 2012; Martin and Meybeck, 1979; Viers et al., 2009). There is now strong evidence for anthropogenic contamination of suspended sediments in many of the world's rivers (Horowitz et al., 2012; Owens et al., 2005; Viers et al., 2009), and erosion events are a major vector for the transport of suspended sediments and associated contaminants from terrestrial to aquatic environments (Horowitz et al., 2012; Rickson, 2014; Sutherland, 2000; Walling, 2005). As such, understanding the role of erosion on heavy metal dynamics in river systems is an active and important area of research.

Two factors govern the flux of metals to fluvial systems during erosion events: (i) the concentration of sediment bound metals; and (ii) the mass of sediment transported during erosion events. Both of these factors can be increased by anthropogenic activities (Burton and Johnston, 2010). Atmospheric deposition, mining activities, solid and liquid wastes, urban road networks, phosphate fertilizers and legacy pesticides are potential sources of soil contamination (Cadwalader et al., 2011; Nicholson et al., 2003; Roberts, 2014; Taylor and Owens, 2009; Wuana and Okieimen, 2011), while land clearing activities, including road construction, agricultural practices, and forestry activities, are major drivers of accelerated erosion (Swank et al., 2001; Burton and Johnston, 2010; Culp et al., 2013; Rickson, 2014). In addition to soil contamination, suspended sediments may also be enriched due to the selective erosion and transport of fine particles during erosion and/or resuspension events. This preferential erosion of fines (i.e., clays and silts, <63 μm) is higher during low energy erosion/resuspension events. Selective erosion of fines also occurs during high energy events; however, a greater proportion of the sediment load is in the coarse fraction (i.e., fine and coarse sands, >63 μm) (Quinton et al., 2001). Importantly, due to the relatively high surface area of fine vs. coarse sediment particles, metals are often enriched in silts and clays (Horowitz, 1991; Owens et al., 2005; Taylor and Owens, 2009). Because silts and clays generally make up the bulk of the suspended sediment load (Owens et al., 2005), enrichment of metals in suspended sediments can be substantial. For example, Quinton and Catt (2007) reported sediment bound metal concentrations in agricultural runoff that were above thresholds for the protection of aquatic biota and on average ≈4 times higher than the soils from which they were derived. This suggests that erosion driven contamination of rivers may not be limited solely to systems that drain heavily contaminated soils.

Badlands are highly erosive environments formed in arid and semi-arid regions. They are typically characterized by sparse vegetation cover, lithologies which are dominated by active smectite clays, and the presence of steep slopes associated with well-defined rill systems (Kasanin-Grubin and Bryan, 2007; Liberti et al., 2009). Importantly, due to the high rates of erosion in these regions, rivers and streams that drain badlands are characterized by high concentrations of suspended sediment (Gallart et al., 2002); however, despite the potential for significant fluxes of sediment-bound metals in runoff from badlands, there is little information on riverine metal concentrations or fluxes in these systems. The Red Deer River (RDR) in western Canada drains the Alberta badlands and is characterized by high suspended sediment levels (Campbell, 1977). Importantly, the river is currently subject to fish consumption advisories due to elevated Hg concentrations in fish tissue (Alberta Health, 2009) and elevated metal concentrations in the water column have been reported downstream of the badlands (Anderson, 1996). However, the specific cause(s) of elevated Hg in fish tissue, or the role of sediments as a driver of elevated heavy metals in the RDR, have not been investigated. In this study, we examine the link between erosion in the Alberta badlands and the concentrations and fluxes of Cd, Cu, Hg and Pb in the RDR watershed. In addition to providing insights into heavy metal dynamics within the RDR itself, this study provides broader insights into the role of suspended sediment as a source of contaminants in highly erosional systems.

2. Methodology

2.1. Study area

The Red Deer River Watershed is located in southern Alberta and covers approximately 49,650 km^2. The headwaters of the RDR are in the Canadian Rockies where ≈70% of river discharge originates as snow melt (Tanzeeba and Gan, 2012). Peak flows in the RDR occur in the late spring/early summer months. The watershed transitions from alpine and foothills landscapes in the headwaters to prairie grasslands in the mid to lower reaches (Downing and Pettapiece, 2006). Average annual temperature is approximately 4 °C (taken at the city of Red Deer; http://climate.weather.gc.ca). Median annual precipitation across the watershed is 393 mm but varies from more 900 mm in the Rockies to approximately 270–400 mm in the grasslands (AMEC, 2009). Within the grasslands, the majority of annual precipitation occurs as rain during the May to September period (Downing and Pettapiece, 2006) with a smaller proportion (≈30% of annual precipitation) occurring as snow during colder months (Kasanin-Grubin and Bryan, 2007).

The underlying bedrock of the RDR watershed is formed predominately of Upper Cretaceous and Tertiary deposits (Campbell, 1977). Upper Cretaceous bedrock is dominated by shales, sandstones, thin ironstone bands, and coal seams while surficial Tertiary deposits consist of till, lacustrine deposits, and glacial outwash associated with Wisconsin glaciation (Campbell, 1977). In the mid to lower reaches of the watershed, the RDR is flanked by the Alberta badlands for approximately 300 km from the town of Nevis to Atlee near the Alberta-Saskatchewan border (Campbell, 1970; Bryan and Campbell, 1980) (Fig. 1). The Alberta badlands cover an area of approximately 800 km^2 (Campbell, 1977) and is formed from bedrock belonging predominately to the Horseshoe Canyon, Bearspaw and Dinosaur Park Formations (Price et al., 2013). Development of the Alberta badlands began approximately 15,000 years ago when meltwater incision exposed highly erodible bedrock during the retreat of Wisconsinan ice (Campbell, 1987).

Due to its highly erosive nature, the Alberta badlands contribute >70% of the sediment load to the RDR despite making up only a small proportion (≈2%) of the overall watershed area (Campbell, 1977). Average annual erosion rates within the Alberta badlands have been estimated to be approximately 4 mm yr^{-1} (Campbell, 1987). Within the badlands, sediment fluxes to the RDR are initiated primarily by intense but short lived convective rainstorms (Bryan and Campbell, 1980). Surface crusts develop rapidly on shale slopes upon wetting. Surface sealing contributes to low infiltration rates which generate substantial overland runoff over the sparsely vegetated surface (Campbell, 1970). This in turn leads to significant erosion primarily via sheet-flow and rilling (Campbell, 1987). In addition, surface runoff may enter fissures or desiccation cracks to transport sediment via piping (Campbell, 1987; De Boer and Campbell, 1990).
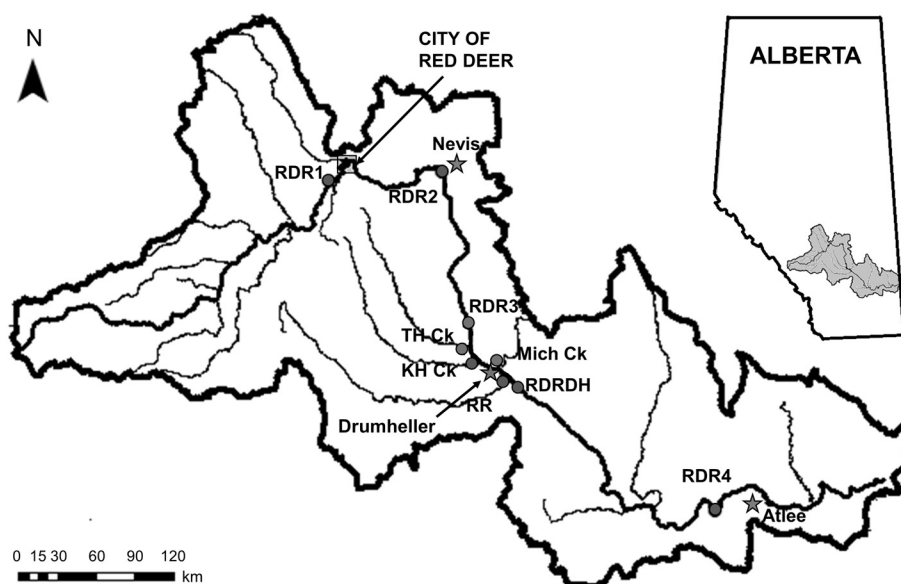
Fig. 1. Location of sampling stations in the Red Deer River Watershed

Land use in the watershed is predominately agricultural with crops and pastures covering approximately 44% of the total watershed area. The proportion of agricultural area in the RDR watershed increases downstream of Red Deer and is particularly prevalent in the Kneehills Creek (76%), Michichi Creek (64%), Threehills Creek (73%) and Rosebud River (77%) sub-watersheds. The remaining land area is mostly range-land in these four sub-watersheds ($\approx$23–34%) and across the RDR watershed as a whole ($\approx$34%). The RDR watershed has a population of approximately 270,000 people and only about 1% of the land area is classified as urban. The largest urban centre in the watershed is the city of Red Deer located along the RDR with a population of approximately 98,000 (Alberta Municipal Affairs, 2014). Oil and gas activities are common in the watershed and there are a number of abandoned coal mines in and around the town of Drumheller (Alberta Energy Regulator, www.mapviewer.aer.ca). Finally, recent estimates of Hg deposition have shown that wet deposition rates in the region (mean value at Esther, Alberta $\approx$0.2 µg m^{-2} month^{-1}) are relatively low (Cole et al., 2014).

2.2. Study sites and parameters

Two data sets were used to investigate riverine metal (Cd, Cu, Hg and Pb) dynamics in the southern Alberta badlands. The first comprises data collected from 2007 to 2015 at four stations in the RDR as part of Alberta Environment and Parks' (AEP) long-term river network (LTRN). Of the four stations, two are located upstream of the Alberta badlands (RDR1 and RDR2) and two stations within the badlands area (RDR3 and RDR4) (Fig. 1). Samples were collected monthly and ana-lyzed for a suite of water quality parameters. For the purpose of this study only total and dissolved Cd, Cu and Pb, total Hg, total suspended solids (TSS), total organic carbon (TOC), specific conductance, hardness and pH are analyzed. With the exception of total Hg, data for each pa-rameter cover 2007–2015. For total Hg, the period of record is 2010–2015. The second data set used in this study was derived from tributary sampling at Kneehills Creek (KH Ck), Threehills Creek (TH Ck), Michichi Creek (Mich Ck) and Rosebud River (RR) and a mainstem site down-stream of the town of Drumheller (RDRDH) (Fig. 1). All five stations are located within the badlands area and samples were collected once per week from April to September 2015. Samples were analyzed for the same suite of parameters described above for the LTRN stations in

addition to dissolved Hg. Additional information on the RDR watershed and the four sub-watersheds included in this study can be found in Aquality Environmental Consulting Ltd. (2009).

2.3. Laboratory analyses

Grab samples were collected in open containers from a point ap-proximate to the middle of the stream channel at each site just below the water surface. All Hg samples were collected using the "clean hands-dirty hands" Hg sampling protocol (Kirk and St. Louis, 2009). Samples for total Hg were analyzed using Cold Vapour Atomic Fluoresence Spectroscopy (CV-AFS). For total recoverable Cd, Cu and Pb, unfiltered samples were first digested with concentrated nitric acid at 180 °C in closed vessels by microwave heating. Solubilized sam-ples were then analyzed for metal concentrations by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). For analysis of dissolved Hg, Cd, Cu and Pb, samples were filtered through 0.45 µm acetate filters followed by determination using either CV-AFS or ICP-MS. Quality con-trol (QC) analysis of metal data included collection of field blanks during each sampling event ($n = 22$) and analysis of samples collected in trip-licate once per month ($n = 6$). QC data for field blanks did not indicate sample contamination. Precision, measured as percent relative standard deviation (%RSD) of triplicate samples, was <10% for totals and from 9 to 25% for dissolved samples (Supplementary Table 1). In addition to the QC described above, a certified reference material for trace metals (i.e., CRM TM-26.4; Environment and Climate Change Canada) was tested in 2015 as part of AEP's broader quality assurance program. Total recov-erable Cd, Cu and Pb were reported within the acceptance criteria of the CRM (unpublished data). Particulate metal concentrations for both data sets were calculated by subtraction of the dissolved from the total metal concentration (i.e., PMe = TMe − DMe). TSS was determined by filter-ing a known volume of water through a pre-weighed, 0.45 µm, glass fibre filter and drying to a constant weight at 105 ± 5 °C. Each filter was then reweighed to determine the weight of the retained residue (APHA, 1995). For TOC analysis, samples were first acidified and sparged with N_2 to remove inorganic carbon and then oxidized with a UV digestor in an acid-persulphate mixture to liberate CO_2. CO_2 was then determined using colourimetry following reaction with a phenol-phthalein reagent (Crowther and Evans, 1978).

Table 1
Percent of April to September samples exceeding Alberta surface water quality guidelines for the protection of freshwater biota in the RDR LTRN stations (2007–2015; n = 24 for Hg, n = 34 for Cd, Cu and Pb) and tributary and mainstem stations (2015; n = 16 Mich Ck, n = 24 all other stations).

	Hg (chronic)[a]	Hg (acute)[b]	Cd (chronic)[c]	Cd (acute)[d]	Pb (chronic)[e]	Cu (acute)[f]
RDR1	13	0	0	0	0	0
RDR2	25	0	0	0	0	0
RDR3	46	21	6	0	9	3
RDR4	79	42	26	0	26	9
TH Ck	54	29	21	4	25	21
KH Ck	54	33	17	4	17	13
Mich Ck	100	94	56	44	63	44
RR	79	46	21	4	33	8
RDRDH	63	50	13	0	21	13

[a] Chronic guideline = 5 ng L^{-1}.
[b] Acute guideline = 13 ng L^{-1}.
[c] Chronic guideline is hardness dependent = 0.04–0.37 µg L^{-1}.
[d] Acute guideline is hardness dependent = 0.20–7.7 µg L^{-1}.
[e] Chronic guideline is hardness dependent = 0.17–7.0 µg L^{-1}.
[f] Acute guideline is hardness dependent = 1.7–66.7 µg L^{-1}.

2.4. Statistical analyses and load calculations

To assess the potential toxicological impacts of trace metals in the RDR watershed, Cd, Cu, Hg and Pb concentrations were compared to the Alberta surface water quality guidelines (ASWQG) for the protection of freshwater aquatic life (AESRD, 2014). While the Canadian Council of Ministers of the Environment (CCME) and the ASWQG specify the use of total concentrations when comparing ambient surface water concentrations to guideline values (AESRD, 2014; CCME, 2003), the USEPA recommends using the dissolved fraction (USEPA, www.epa.gov/wqc). We therefore also compared dissolved metal concentrations to USEPA guidelines for Cd, Cu and Pb while for Hg we assessed dissolved concentrations against the ASWQG. We employed the Alberta guidelines for Hg because they provided more conservative thresholds for the protection of aquatic biota that could be more readily compared with results based on total Hg.

The role of sediments as a driver of metal variability across the watershed was investigated first by pooling data from the LTRN and tributary monitoring data sets and then by employing linear and multiple stepwise regressions to examine metal concentrations as a function of TSS and TOC. Variability in the concentration of trace metals in suspended sediments was also assessed using data from both the LTRN and tributary data sets. The concentration of each metal associated with suspended sediment (C_{sed}) was estimated from surface water data using the following equation:

$$C_{sed} \left(\mu g\ kg^{-1}\right) = \frac{PMe\ \left(\mu g\ L^{-1}\right)}{TSS\ \left(kg\ L^{-1}\right)} \tag{1}$$

In addition to C_{sed}, at each station, the particulate trace metal to aluminum ratio (PMe:PAl) was determined. An enrichment factor (EF) was then calculated by dividing measured ratios in the RDR watershed by values for the upper continental crust (Turekian and Wedepohl, 1961) to identify potential deviation from expected ratios. It is expected that EF will increase as sediments become more contaminated (Hotton and Sutherland, 2016; Viers et al., 2009). The partitioning of each metal between particulate and aqueous phases was quantified using the partitioning coefficient (K$_D$) to characterize and compare sediment binding properties among metals and among stations. K$_D$ was calculated using the following equation:

$$K_D \left(L\ kg^{-1}\right) = \frac{PMe\ \left(kg\ L^{-1}\right) \div TSS\ \left(kg\ L^{-1}\right)}{DMe\ \left(kg\ L^{-1}\right)} \tag{2}$$

Heavy metal and sediment fluxes were calculated for each of the five stations sampled during April–September 2015. Discharge data was obtained from Water Survey of Canada stations in each of the four tributaries and at the RDR site near Drumheller. At four of the five water quality sampling sites (KH Ck, TH Ck, RR and RDRDH), discharge stations were located upstream of sampling sites. Discharge at these water quality sites was therefore estimated by multiplying discharge from the upstream gauging station by the ratio of watershed area in the ungauged vs. gauged locations (Gianfagna et al., 2015). Watershed ratios in ungauged vs. gauged sites were generally close to 1 (i.e., 1.04–1.20 at KH Ck, RR and RDRDH; 2.06 at KH) indicating this method likely provided a good approximation of discharge at ungauged locations. Metal and TSS loads were calculated by multiplying the daily discharge by concentration. Because concentration data were collected at a weekly frequency, concentration values between measured data points were infilled using the mid-point interpolation method (Kerr et al., 2016). At each station, daily loads were summed for the April–September period. Per unit area fluxes were also calculated for each watershed based on effective drainage area. Effective drainage area is an estimate of the area which contributes to runoff during a median flow year (AMEC, 2009). Watershed areas (total and effective) and total stream discharge during the study period for each station are given in Supplementary Table 2.

3. Results and discussion

3.1. Spatial and seasonal variation in total metal concentrations

Trace metal concentrations at the four LTRN stations (RDR1-RDR4) exhibited distinct seasonality and spatial variability. Total Cd, Cu, Hg, Pb, TOC and TSS were higher during the open-water (April–October) season relative to the ice-covered season (November–March) and generally increased with distance downstream. Median metal and TSS concentrations at sites draining the badlands (RDR3 and RDR4) during the open-water season were frequently more than double those of stations upstream (RDR1 and RDR2) (Supplementary Table 3). A comparison of long-term data at the LTRN stations (April–September data only) with tributary and mainstem stations sampled in 2015 (April–September), shows that concentrations in the tributaries were comparable to, or

Table 2
Dissolved metal concentrations at RDR mainstem and tributary stations.

| Site		DCd (µg L^{-1})	DHg (ng L^{-1})	DCu (µg L^{-1})	DPb (µg L^{-1})
RDR1	Median	0.005		0.74	0.012
	Range	<0.002–0.027		0.27–3.06	<0.001–0.268
RDR2	Median	0.008		0.88	0.034
	Range	<0.002–0.051		0.42–3.34	<0.001–0.564
RDR3	Median	0.010		0.95	0.036
	Range	<0.002–0.135		0.05–5.20	<0.001–0.180
RDR4	Median	0.014		1.80	0.032
	Range	<0.002–1.290		0.05–16.60	<0.001–0.298
RR	Median	0.010	1.23	3.12	0.035
	Range	0.005–0.056	0.73–16.27	2.10–18.50	0.012–0.799
RDRDH	Median	0.012	0.96	1.80	0.030
	Range	0.008–0.031	0.49–4.90	1.15–4.07	0.014–0.105
TH Ck	Median	0.014	2.03	4.26	0.037
	Range	0.006–0.034	1.08–23.47	3.01–19.10	0.009–0.490
KH Ck	Median	0.011	1.48	3.20	0.030
	Range	0.007–0.029	0.84–27.33	2.53–13.10	0.014–1.170
Mich Ck	Median	0.022	8.48	7.65	0.131
	Range	0.007–0.120	1.40–135.20	3.61–52.10	0.022–1.950
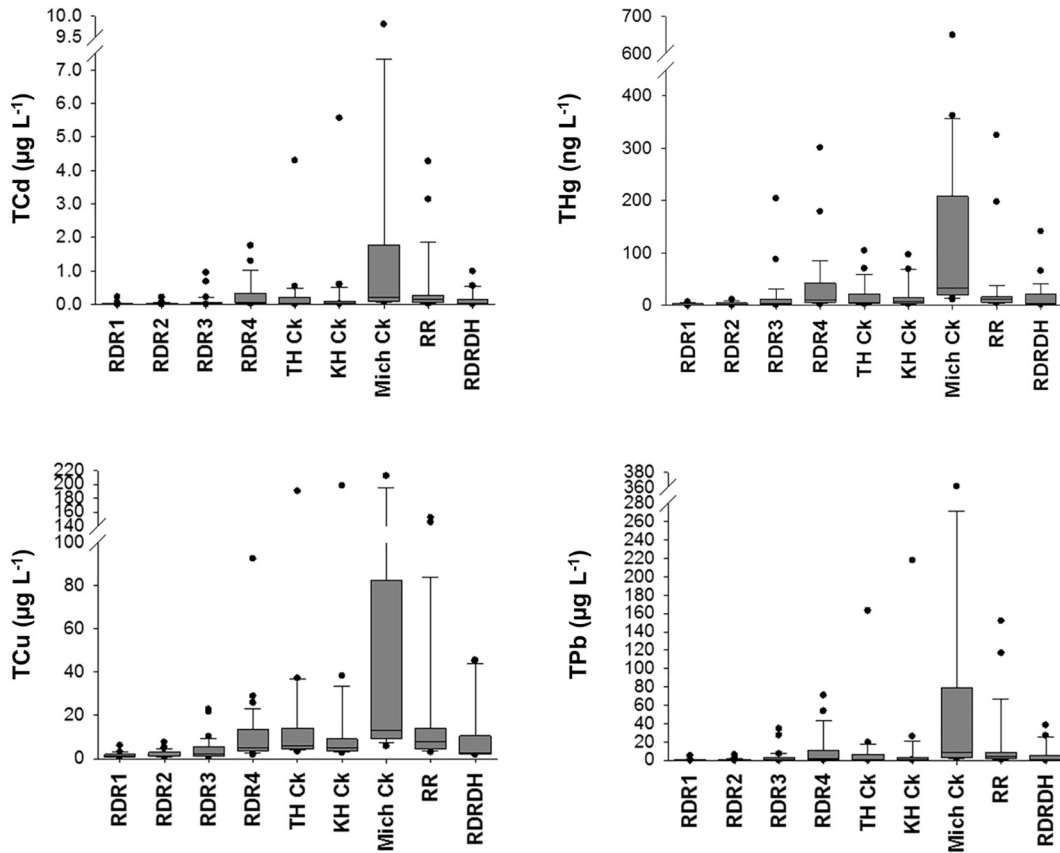
Fig. 2. Median and quartile ranges (25th and 75th) of Apr–Sep concentrations of total Cd, Hg, Cu and Pb from the RDR LTRN stations ($n = 24$ for Hg, $n = 34$ for Cd, Cu and Pb) and from tributary (TH Ck, KH Ck, Mich Ck and RR) and mainstem (RDR DH) stations ($n = 16$ Mich Ck, $n = 24$ all other stations) sampled during 2015. Whiskers represent the 10th and 90th percentiles.

higher than (i.e., Michichi Creek), the mainstem stations draining the badlands (RDR3 and RDR4) (Fig. 2).

Total metal concentrations frequently exceeded guidelines for the protection of aquatic life at sites draining the badlands (Table 1). In addition, chronic and acute criteria were often exceeded by a large margin (see footnotes 1–6 in Table 1 vs. Fig. 2). For example, the acute guideline for Hg (13 ng L^{-1}) was exceeded by an order of magnitude on 12 occasions at Mich Ck, RR, RDRDH, RDR3 and RDR4. Furthermore, a comparison with values from the literature shows that total metal concentrations in the RDR watershed are generally at the upper range of values reported elsewhere (Supplementary Table 4). In fact, peak metal concentrations in the RDR and tributaries were often higher than those reported for various streams and rivers impacted by legacy mining (Blake et al., 2003; Domagalski, 2001; Domagalski et al., 2004; Nagorski et al., 2003; Nimick and Cleasby, 2004) or intensive urban and industrial activities (Baborowski et al., 2004; Hurley et al., 1998; Müller et al., 2008; Rozan and Benoit, 2001; Shanley and Chalmers, 2012; Tiefenthaler et al., 2008).

3.2. The role of suspended sediments in heavy metal dynamics

Total metal concentrations were significantly ($P < 0.05$) correlated with TSS (Fig. 3). While variation in metal concentrations was also related to TOC, the inclusion of TOC into a multiple linear regression model resulted in only minor (2–6%) improvements in the variation explained by the model (Supplementary Table 5). The exception was total Hg where the proportion of variation explained by both TSS and TOC (59%, Supplementary Table 5) was considerably higher than that explain by either TSS (34%) or TOC (36%) alone. However, the influence of TOC on THg dynamics was minimal when data from Michichi Creek were removed ($r^2 = 0.66$ for TSS only vs. 0.67 for TSS and TOC).
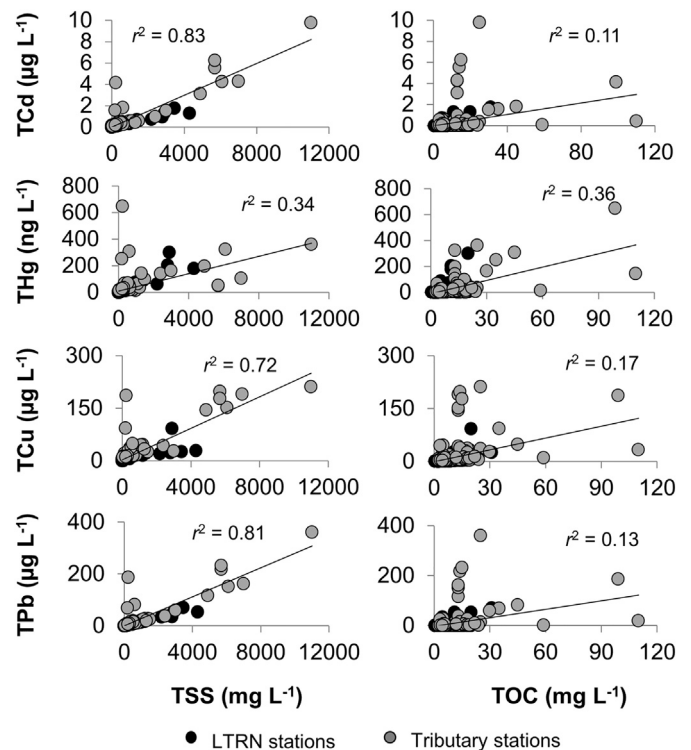

Fig. 3. Total Cd, Hg, Cu and Pb concentrations as a function of TSS and TOC.

Furthermore, when Michichi Creek was excluded, TSS alone was the best predictor of TCd, TCu and TPb and the overall proportion of variation explained by TSS increased to 90%, 84% and 90% respectively (Supplementary Table 6). Thus, while there is some evidence for TOC regulation of Hg in Michichi Creek, the positive relationship between total metals and TSS indicates episodic peaks in metal concentrations in the RDR and tributaries are driven primarily by sediment transport. This is further supported by analysis of metal partitioning which shows that as total metal concentrations increase, metal partitioning is increasingly dominated by the particulate fraction (Fig. 4).

3.3. Partitioning of heavy metals in the RDR and tributaries

3.3.1. Dissolved metal concentrations

Median DPb and DCd concentrations in the RDR and its tributaries (Table 2) were generally less than recent estimates of global riverine averages (0.079 µg L^{-1} and 0.08 µg L^{-1}, Gaillardet et al., 2003) and apart from Michichi Creek, there were few exceedances of freshwater thresholds (Table 3). For DCu, median concentrations at the main stem sites (Table 2) were less than, or slightly above, the global average (1.48 µg L^{-1}, Gaillardet et al., 2003). However, median values in the tributaries were up to 5 times higher than this value and the peak concentrations at each station (3.06–52.10 µg L^{-1}) were similar to values reported for streams and rivers impacted by mining or industrial/urban activities (Cheung et al., 2003; Rothwell et al., 2007). Furthermore, at Michichi Creek, 38% and 44% of dissolved Cu values exceeded short-term and long-term criteria (Table 3). The median DHg concentrations in the RDR and tributaries (Table 2) ranged from <1 to 8.5 ng L^{-1} with peak concentrations ranging from 4.9 to 135 ng L^{-1}. The maximum concentration at RDRDH (4.90 ng L^{-1}) exceeded the range of values recently summarized for North American rivers (0.50–3.41 ng L^{-1}) while tributary concentrations were in the upper range of DHg concentrations globally (Amos et al., 2014). All four tributaries exhibited exceedances with the highest frequency occurring at Michichi Creek (75% and 44% frequency for chronic and acute exposures respectively). At the remaining tributaries, acute exceedances were rare (4%) while exceedances of the chronic guideline ranged from 13 to 21% (Table 3).

3.3.2. Metal partitioning between aqueous and particulate phases

Partitioning coefficients (K_D) in the RDR watershed (Table 4) were generally within the range of values reported elsewhere (Babiarz et al., 2012; Benoit and Rozan, 1999; Brigham et al., 2009; Lawson et al., 2001; Warren and Zimmerman, 1994). However, the distribution of metals between particulate and aqueous phases differed among the

Table 3
Percent of April to September samples for dissolved metals which exceeded US EPA (Cd, Cu and Pb) and ASWQG guidelines (Hg) for the protection of freshwater aquatic life for short-term and long-term exposures. $n = 34$ for Cd, Cu and Pb at RDR1-RD4; $n = 16$ Mich Ck, $n = 24$ all other stations.

	Cd (CCC[a])	Cd (CMC[b])	Cu (CCC[a])	Cu (CMC[b])	Pb (CCC[a])	Pb (CMC[b])	Hg[c]	Hg[d]
RDR1	0	0	0	0	0	0		
RDR2	0	0	0	0	0	0		
RDR3	0	0	0	0	0	0		
RDR4	3	0	3	0	0	0		
TH Ck	0	0	8	4	0	0	4	21
KH Ck	0	0	0	0	0	0	4	21
Mich Ck	6	0	44	38	13	0	44	75
RR	0	0	0	0	0	0	4	13
RDR DH	0	0	0	0	0	0	0	0

Note: dissolved Hg concentrations not available for the RDR1-RDR4 stations.
[a] Criterion Continuous Concentration (hardness dependent).
[b] Criterion Maximum Concentration (hardness dependent).
[c] ASWG Hg acute freshwater aquatic life criteria (13 ng L^{-1}).
[d] ASWG Hg chronic freshwater aquatic life criteria (5 ng L^{-1}).

four metals. K_D values for Pb were higher than the other metals indicating a stronger affinity for sediment. Conversely, the relatively low K_D for Cu is indicative of weaker binding relative to Pb and to a lesser extent Cd and Hg. In terms of spatial variation within the RDR watershed, K_D values for Pb where generally similar among sites, while for Cu and to a lesser extent Cd, values were higher in the mainstem sites relative to the tributaries and were slighter higher upstream of the badlands (RDR1 and RDR2). Although these differences may reflect spatial variability in the binding properties of sediments in the RDR watershed, across all sites we observed a significant ($P < 0.05$) negative relationship between K_D and TSS for all four metals (Supplementary Table 7). A possible explanation for this is the 'particle concentration effect' whereby an increasing amount of colloidal material is included in the operationally defined dissolved fraction (i.e., <0.45 µm) as TSS increases, which in turn reduces K_D (Benoit and Rozan, 1999; Stordal et al., 1996). As such, the spatial patterns in dissolved metal concentrations observed in the RDR watershed (e.g., DCu, Table 2), together with recorded exceedances of aquatic criteria (Table 3), may be affected by colloidal species, and should therefore be interpreted with care.

3.3.3. Metal concentrations in suspended sediment

Unlike total metals in the water column, the concentration of each metal associated with suspended sediment (C_{sed}) did not increase downstream of the badlands (Table 4). This indicates that the increased riverine metal concentrations observed downstream of the badlands are
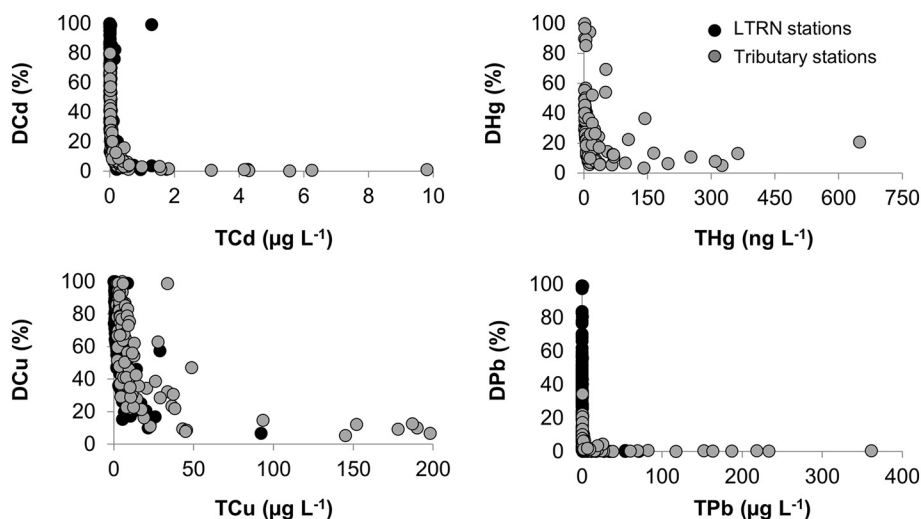

Fig. 4. Percent dissolved Cd, Hg, Cu and Pb as a function of total metal concentration.

Table 4
Median sediment concentrations (C_{sed}) and partition coefficients ($\log K_D$) for Hg, Cd, Cu and Pb at RDR mainstem and tributary stations[a]. Values in parentheses are the interquartile ranges (IQR).

	Hg		Cd		Cu		Pb	
	Sediment (µg kg^{-1})	$\log K_D$	Sediment (µg kg^{-1})	$\log K_D$	Sediment(mg kg^{-1})	$\log K_D$	Sediment (mg kg^{-1})	$\log K_D$
RDR1			832 (640)	5.1 (0.5)	13 (27)	4.1 (0.9)	17 (11)	5.7 (0.9)
RDR2			696 (467)	4.9 (0.4)	25 (24)	4.3 (0.7)	19 (13)	5.8 (0.7)
RDR3			561 (448)	4.8 (0.6)	23 (25)	4.2 (0.9)	17 (6)	5.8 (0.7)
RDR4			519 (169)	4.6 (0.3)	18 (14)	3.8 (0.7)	16 (5)	5.7 (0.6)
TH Ck	70 (58)	4.5 (0.5)	634 (328)	4.7 (0.4)	25 (23)	3.8 (0.3)	19 (8)	5.7 (0.6)
KH Ck	86 (36)	4.7 (0.5)	662 (245)	4.7 (0.3)	23 (20)	3.8 (0.6)	20 (5)	5.8 (0.5)
Mich Ck[b]	121 (186)	4.2 (0.7)	1089 (918)	4.7 (0.6)	26 (28)	3.5 (0.8)	39 (24)	5.5 (0.9)
RR	45 (21)	4.5 (0.6)	544 (71)	4.7 (0.3)	21 (6)	3.8 (0.3)	15 (3)	5.6 (0.5)
RDRDH	66 (25)	4.8 (0.8)	466 (249)	4.6 (0.3)	31 (18)	4.2 (0.5)	17 (4)	5.7 (0.3)

[a] Median C_{sed} and K_D at LTRN stations (RDR1-RDR4) calculated from Apr-Sep data only.
[b] Single outlier removed due to very high TOC in sample. Values with outlier included = Hg: 122 (204); Cd: 1163 (919); Cu: 27 (31); Pb: 39 (24).

driven primarily by increases in sediment mass and not by an increase in sediment concentration. Similarly, the relatively high total metal concentrations in the water column of the RDR and tributaries compared to other rivers (Supplementary Table 4) do not appear to be related to C_{sed}. Median C_{sed} for Cd, Cu and Pb in the RDR watershed (Table 4) were similar to values for relatively un-impacted rivers in North America (Cu = 34 mg kg^{-1} and Pb = 22 mg kg^{-1}), less than estimates of global riverine averages (Cd = 1550 µg kg^{-1}, Cu = 76 mg kg^{-1} and Pb = 61 mg kg^{-1}) (Viers et al., 2009), and well below values reported in watersheds impacted by urban and/or industrial activities (Audry et al., 2004; Meybeck et al., 2007; Müller et al., 2008). For Hg, median concentrations in suspended sediment (Table 4) were generally higher than the baseline median for fine (<63 µm) streambed sediments across the USA (40 µg kg^{-1}) (Horowitz and Stephens, 2008), similar to the estimated average for streambed sediments in Canada (75 µg kg^{-1}) (CCME, 1999a), and well below values reported for suspended sediments in rivers impacted by intensive urban and/or industrial activities (Hurley et al., 1998; Meybeck et al., 2007; Müller et al., 2008).

Apart from Cd, metal to Al ratios of suspended sediments in the RDR watershed (Table 5) indicate negligible (<2) to moderate (2–5) anthropogenic enrichment (Sutherland, 2000). However, it should be noted that because our ratios are based on concentrations of total recoverable metals (rather than total metals), it is likely that these numbers are biased high. Digestion procedures such as those employed in this study (i.e., based on digestion with HNO_3 or HNO_3/HCl) do not include hydrofluoric acid and as such do not completely liberate metals associated with aluminosilicates (Wilson et al., 2006; da Silva et al., 2014). Importantly, this has been shown to result in almost complete recovery of elements such as Cd, Pb, Cu and Hg but only partial recovery of Al (Sutherland et al., 2004). For example, Chen and Ma (1998) used a digestion procedure similar to ours (USEPA 3051) and found that Cd recovery from a reference sediment (NIST SRM 2704) was 90%, while Al recovery was only 25%. Based on this ratio, our EF values for Cd (Table 5) would be substantially reduced (i.e., 1.9–5.5), and as such, would be more indicative of moderate enrichment.

Table 5
Median enrichment factors for particulate[a] trace metal to aluminum ratios at tributary and mainstem stations in the RDR. Values in parentheses are the interquartile ranges (IQR).

	Cd:Al	Hg:Al[a]	Cu:Al	Pb:Al
RDR1	19.7 (34.5)	9.7 (10.7)	2.3 (4.6)	2.4 (1.7)
RDR2	14.0 (31.6)	7.3 (11.9)	3.7 (6.1)	2.5 (2.6)
RDR3	10.5 (17.9)	4.1 (7.6)	3.7 (4.2)	2.0 (1.1)
RDR4	8.9 (8.6)	2.7 (1.7)	3.1 (2.1)	1.9 (1.8)
RR	10.7 (3.1)	1.5 (0.6)	2.9 (1.4)	1.9 (0.7)
RDRDH	6.6 (2.8)	1.6 (1.0)	3.0 (1.4)	1.5 (0.5)
TH Ck	8.0 (3.3)	1.6 (1.1)	2.3 (1.4)	1.4 (0.5)
KH Ck	8.4 (4.4)	2.2 (0.7)	2.3 (1.0)	1.7 (0.5)
Mich Ck	9.5 (3.9)	2.1 (1.3)	1.6 (1.6)	2.0 (1.0)

[a] For the RDR1-RDR4 stations the ratio of total Hg to total Al was used.

Although aquatic life criteria for suspended sediments are not currently available, median C_{sed} values for Cd were well below probable effects levels (PELs) (3500 µg kg^{-1}) at all stations, but exceeded interim sediment quality guidelines (ISQGs) (600 µg kg^{-1}) for bed sediments at several sites (CCME, 1999b). Apart from Pb at Michichi Creek, median C_{sed} values were below ISQGs at all sites for Hg, Cu and Pb (CCME, 1999a; CCME, 1999c; CCME, 1999d). It should be noted that while C_{sed} may reflect near surface concentrations in the fine fraction of bed sediments (Horowitz et al., 2012), values for the bulk bed sediment will likely be lower. As such, our comparison with guidelines for bed sediments are likely overly protective and do not necessarily reflect the real risk to benthic biota. When considered collectively, the comparison with sediment guidelines, the EF values, the comparison of C_{sed} with literature values, and the absence of any increases in C_{sed} downstream of the badlands, strongly suggest that the high total metal concentrations observed in the water column of the RDR and tributaries do not result from sediment contamination. Rather, the RDR has one of the highest flow weighted suspended sediment concentrations in Canada (den Hartog and Ferguson, 1978) and variability in sediment flux in the RDR is among the highest of rivers globally (Meybeck et al., 2003). These two factors (high sediment concentrations and highly variable sediment fluxes) are the principle drivers of the regular guideline exceedances and the high degree of variability in total riverine metal concentrations which characterize the RDR watershed.

3.4. Trace metal fluxes in the RDR and tributaries

It should be noted that load estimates from fixed frequency sampling regimes will produce errors which increase as a function of decreasing sampling frequency (Kronvang and Bruhn, 1996). Given the sporadic nature of sediment delivery from the Alberta badlands (Bryan and Campbell, 1980), it is likely that even at a weekly sampling frequency, episodic peaks in sediment and associated metal concentrations will be missed. Having said this, several important findings can still be derived from our load estimates. Contributions to metal loading from upstream of the badlands (RDR2) were low (2–8%) despite contributing most of the flow to RDRDH ($\approx$70%). In contrast, the four tributaries contributed a substantial proportion of the metal load at RDRDH (Hg: 22%; Cd: 40%; Cu: 25%; Pb: 36%) while providing only $\approx$9% of the flow (Table 6). Heavy metal loads in the RDR and tributaries were dominated by the particulate fraction (Fig. 5; Supplementary Fig. 1–4). The proportion of total loads in particulate form ranged from 60% for Cu at Michichi Creek to >98% for Pb at all stations. Particulate fluxes were highly episodic with a substantial proportion of the total load occurring over a short period. For example, 67% and 69% of particulate Pb load occurred over 5 days at KH Ck and TH Ck, respectively. This reflects the highly episodic nature of sediment delivery that characterizes the Alberta badlands (Campbell, 1977; De Boer and Campbell, 1990; Meybeck et al., 2003).

Table 6
Total metal loads and per unit area fluxes[a] from the Red Deer River and tributaries for April to September 2015.

	Total Cd		Total Hg		Total Cu		Total Pb		TSS		TOC	
	kg	mg km^{-2}	kg	mg km^{-2}	kg	g km^{-2}	kg	g km^{-2}	Mg	kg km^{-2}	Mg	kg km^{-2}
RDR2[b]	5	350	0.6	44	532	38	64	5	2416	173	2060	135
RDRDH	95	4145	11.9	520	6480	284	3571	156	200348	8780	3983	123
RR	31	11,580	2.1	776	1311	496	1037	392	48479	18324	522	44
Mich Ck	2	5517	0.2	553	66	152	94	218	2698	6233	51	46
KH Ck	2	1066	0.1	71	103	51	80	40	2795	1400	112	75
TH Ck	2	1315	0.1	83	130	76	80	47	3877	2267	165	136

[a] Based on effective drainage area (Supplementary Table 2).
[b] Calculated from monthly data collected as part of the LTRN.

Among the tributaries, total metal loadings and per unit area fluxes of the four metals were highest at Rosebud River (Table 6). Higher total metal loads from Rosebud River were related to the greater proportion of flow coming from this river (i.e., ≈80% of discharge from the four tributaries came from the RR). In terms of per unit area metal fluxes, spatial patterns among the four tributaries closely reflected those of TSS. As such, variation in metal fluxes among the four sub-watersheds appears to be a function of sediment quantity rather than any differences in sediment quality. Metal fluxes in the RDR and tributaries are generally lower than those reported for urban (Huber and Helmreich, 2016), agricultural (Miller et al., 2003), mixed land use (Brigham et al., 2009; Babiarz et al., 2012; Shanley and Chalmers, 2012) and suburban watersheds (Naik and Hammerschmidt, 2011). Furthermore, TSS fluxes in the RDR and tributaries were at the low to medium range of rivers globally (Meybeck et al., 2003). The relatively low fluxes from the RDR and tributaries are likely a reflection of the low amounts of precipitation and runoff which characterize the semi-arid climate of the region. It is also important to note that most of the sediment flux to the RDR comes from the badlands (Campbell, 1977), and as such, per unit area fluxes from the badlands portion of each sub-watershed will likely be considerably higher than the values reported in Table 6. Finally, the variability in sediment fluxes in the RDR is among the highest of rivers globally (Meybeck et al., 2003). Therefore, while the overall fluxes in the region are relatively low, the system will be characterized by substantial deviations from these values.

4. Conclusions

Our study provides important insights into riverine metal dynamics in high erosion regions such as badlands. While elevated heavy metal concentrations in rivers are often associated with contamination, we found little evidence of widespread metal enrichment of suspended sediments in the RDR watershed. Instead, erosion of relatively unenriched soils from the Alberta badlands generated total metal concentrations in the water column typical of heavily impacted rivers and streams. Although C_{sed} and dissolved metal data were generally not indicative of widespread toxicological effects on aquatic biota, if, and to what extent, elevated total metal concentrations are impacting biota in the RDR watershed remains an important question. In terms of human health, we know that the RDR is currently under a fish consumption advisory due to elevated Hg in fish tissue. Given that our results show the primary source of Hg to the river is soil erosion, it is reasonable to suggest that this has played a key role. As such, further work is needed in the RDR watershed to understand the link between Cd, Cu, Hg and Pb inputs from the badlands, instream transformation processes, and uptake and assimilation by aquatic biota. More broadly, our results highlight the need for more information on contaminant dynamics in watersheds subject to naturally and/or anthropogenically elevated rates of erosion. We show that substantially elevated riverine metal concentrations can occur in watersheds where sediment bound metal concentrations are not enriched. If heavy metal inputs from highly
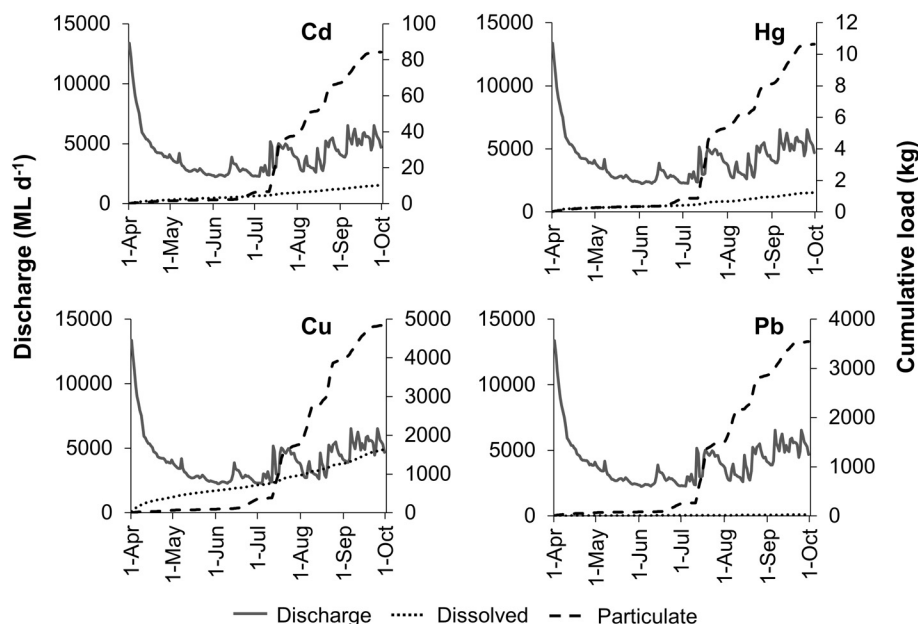

Fig. 5. Discharge and cumulative trace metal loads at the RDRDH station Apr–Sep 2015

erodible watersheds such as the RDR are assimilated into the aquatic food web, this may have implications for aquatic biota and human health. Importantly, this could go undetected in watersheds such as the RDR if assessments of potential risk are based solely on C_{sed} and/or dissolved metal data. Therefore, a greater focus on contaminant fluxes, transformations and impacts in highly erodible watersheds such as the RDR is warranted.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.04.037.

References

Alberta Environment and Sustainable Resource Development (AESRD), 2014. Environmental Quality Guidelines for Alberta Surface Waters. Water Policy Branch, Policy Division, Edmonton, p. 48.
Alberta Health, 2009. Mercury in Fish Rivers and Lakes, southern Alberta. Alberta Health, Edmonton, Alberta, Canada.
Alberta Municipal Affairs, 2014. Municipal Affairs 2014 Population List. Government of Alberta, Edmonton, Alberta, Canada.
AMEC, 2009. South Saskatchewan River Basin in Alberta: Water Supply Study, Alberta Agriculture and Rural Development. Lethbridge, Alberta, Canada.
American Public Health Association (APHA), 1995. Standard methods for the examination of water and wastewater. Total Suspended Solids. 2540 D.
Amos, H.M., et al., 2014. Global biogeochemical implications of mercury discharges from rivers and sediment burial. Environ. Sci. Technol. 48 (16):9514–9522. http://dx.doi.org/10.1021/es502134t.
Anderson, A.-M., 1996. An Analysis of Non-compliance Patterns to Prairie Provinces Water Board Objectives in the Red Deer River at the Alberta/Saskatchewan Boundary. Alberta Environment, Edmonton, Alberta, Canada.
Audry, S., Blanc, G., Schäfer, J., 2004. Cadmium transport in the Lot–Garonne River system (France) – temporal variability and a model for flux estimation. Sci. Total Environ. 319 (1–3):197–213. http://dx.doi.org/10.1016/S0048-9697(03)00405-4.
Aquality Environmental Consulting Ltd, 2009. Red Deer River State of the Watershed Report. Report Prepared for the Red Deer River Watershed Alliance. Red Deer, Alberta, Canada ISBN 978-0-9812391-0-1. http://www.rdrwa.ca/node/59.
Babiarz, C., et al., 2012. Watershed and discharge influences on the phase distribution and tributary loading of total mercury and methylmercury into Lake Superior. Environ. Pollut. 161:299–310. http://dx.doi.org/10.1016/j.envpol.2011.09.026.
Baborowski, M., von Tümpling, j.W., Friese, K., 2004. Behaviour of suspended particulate matter (SPM) and selected trace metals during the 2002 summer flood in the River Elbe (Germany) at Magdeburg monitoring station. Hydrol. Earth Syst. Sci. 8 (2):135–150. http://dx.doi.org/10.5194/hess-8-135-2004.
Benoit, G., Rozan, T.F., 1999. The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers. Geochim. Cosmochim. Acta 63 (1):113–127. http://dx.doi.org/10.1016/S0016-7037(98)00276-2.
Blake, W.H., et al., 2003. Heavy metal concentrations during storm events in a rehabilitated industrialized catchment. Hydrol. Process. 17 (10):1923–1939. http://dx.doi.org/10.1002/hyp.1218.
Brigham, M.E., Wentz, D.A., Aiken, G.R., Krabbenhoft, D.P., 2009. Mercury cycling in stream ecosystems. 1. Water column chemistry and transport. Environ. Sci. Technol. 43 (8):2720–2725. http://dx.doi.org/10.1021/es802694n.
Bryan, R.B., Campbell, I.A., 1980. Sediment entrainment and transport during local rainstorms in the Steveville Badlands, Alberta. Catena 7 (1):51–65. http://dx.doi.org/10.1016/S0341-8162(80)80003-8.
Burton, G.A., Johnston, E.L., 2010. Assessing contaminated sediments in the context of multiple stressors. Environ. Toxicol. Chem. 29 (12):2625–2643. http://dx.doi.org/10.1002/etc.332.
Cadwalader, G.O., et al., 2011. Erosion and physical transport via overland flow of arsenic and lead bound to silt-sized particles. Geomorphology (Amsterdam, Netherlands) 128 (1–2):85–91. http://dx.doi.org/10.1016/j.geomorph.2010.12.025.

Callender, E., 2003. 9.03 - heavy metals in the environment—Historical trends A2 - Holland, Heinrich D. In: Turekian, K.K. (Ed.), Treatise on Geochemistry. Pergamon, Oxford:pp. 67–105 http://dx.doi.org/10.1016/B0-08-043751-6/09161-1.
Campbell, I.A., 1970. Erosion rates in the Steveville Badlands, Alberta. Canadian Geographer/Le Géographe canadien 14 (3):202–216. http://dx.doi.org/10.1111/j.1541-0064.1970.tb01568.x.
Campbell, I.A., 1977. Stream discharge, suspended sediment and erosion rates in the Red Deer River basin, Alberta, Canada. International Association of Hydrological Sciences Publication 122, 244–259.
Campbell, I.A., 1987. Badlands of Dinosaur Provincial Park, Alberta. Canadian Geographer/Le Géographe canadien 31 (1):82–87. http://dx.doi.org/10.1111/j.1541-0064.1987.tb01592.x.
Canadian Council of Ministers of the Environment (CCME), 1999a. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Mercury. Canadian Council of Ministers of the Environment, Winnipeg.
Canadian Council of Ministers of the Environment (CCME), 1999b. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Cadmium. Canadian Council of Ministers of the Environment, Winnipeg.
Canadian Council of Ministers of the Environment (CCME), 1999c. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Copper. Canadian Council of Ministers of the Environment, Winnipeg.
Canadian Council of Ministers of the Environment (CCME), 1999d. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Lead. Canadian Council of Ministers of the Environment, Winnipeg.
Canadian Council of Ministers of the Environment (CCME), 2003. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives. Canadian Council of Ministers of the Environment, Winnipeg.
Chen, M., Ma, L.Q., 1998. Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. J. Environ. Qual. 27 (6):1294–1300. http://dx.doi.org/10.2134/jeq1998.00472425002700060004x.
Cheung, K.C., Poon, B.H.T., Lan, C.Y., Wong, M.H., 2003. Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China. Chemosphere 52 (9):1431–1440. http://dx.doi.org/10.1016/S0045-6535(03)00479-X.
Cole, A., et al., 2014. A survey of mercury in air and precipitation across Canada: patterns and trends. Atmosphere 5 (3), 635.
Crowther, J., Evans, J., 1978. Dual Channel for the Determinations of Dissolved Organic and Inorganic Carbon. Ontario Ministry of the Environment, Laboratory Services Division, Toronto, Ontario, Canada.
Culp, J.M., Brua, R.B., Benoy, G.A., Chambers, P.A., 2013. Development of reference conditions for suspended solids in streams. Canadian Water Resources Journal/Revue canadienne des ressources hydriques 38 (2):85–98. http://dx.doi.org/10.1080/07011784.2013.780794.
De Boer, D.H., Campbell, I.A., 1990. Runoff chemistry as an indicator of runoff sources and routing in semi-arid, badland drainage basins. J. Hydrol. 121 (1):379–394. http://dx.doi.org/10.1016/0022-1694(90)90242-P.
Domagalski, J., 2001. Mercury and methylmercury in water and sediment of the Sacramento River Basin, California. Appl. Geochem. 16 (15):1677–1691. http://dx.doi.org/10.1016/S0883-2927(01)00068-3.
Domagalski, J.L., Alpers, C.N., Slotton, D.G., Suchanek, T.H., Ayers, S.M., 2004. Mercury and methylmercury concentrations and loads in the Cache Creek watershed, California. Sci. Total Environ. 327 (1–3):215–237. http://dx.doi.org/10.1016/j.scitotenv.2004.01.013.
Downing, D.J., Pettapiece, W.W., 2006. Natural regions and subregions of Alberta. T/852, Government of Alberta. Canada, Edmonton, Alberta.
Driscoll, C.T., Mason, R.P., Chan, H.M., Jacob, D.J., Pirrone, N., 2013. Mercury as a global pollutant: sources, pathways, and effects. Environ. Sci. Technol. 47 (10):4967–4983. http://dx.doi.org/10.1021/es305071v.
Eggleton, J., Thomas, K.V., 2004. A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. Environ. Int. 30 (7):973–980. http://dx.doi.org/10.1016/j.envint.2004.03.001.
Flemming, C.A., Trevors, J.T., 1989. Copper toxicity and chemistry in the environment: a review. Water Air Soil Pollut. 44 (1):143–158. http://dx.doi.org/10.1007/bf00228784.
Gaillardet, J., Viers, J., Dupré, B., 2003. 5.09 - trace elements in river waters A2 - Holland, Heinrich D. In: Turekian, K.K. (Ed.), Treatise on Geochemistry. Pergamon, Oxford:pp. 225–272 http://dx.doi.org/10.1016/B0-08-043751-6/05165-3.
Gallart, F., Llorens, P., Latron, J., Regüés, D., 2002. Hydrological processes and their seasonal controls in a small Mediterranean mountain catchment in the Pyrenees. Hydrol. Earth Syst. Sci. 6 (3):527–537. http://dx.doi.org/10.5194/hess-6-527-2002.
Gianfagna, C.C., Johnson, C.E., Chandler, D.G., Hofmann, C., 2015. Watershed area ratio accurately predicts daily streamflow in nested catchments in the Catskills, New York. Journal of Hydrology: Regional Studies 4:583–594 Part B. 10.1016/j.ejrh.2015.09.002.
den Hartog, G., Ferguson, H.L., 1978. Hydrologic Atlas of Canada, Plate 25: Suspended Sediment Concentrations. Fisheries and Environment Canada, Ottawa, Ontario, Canada.
Horowitz, A.J., 1991. A Primer on Sediment-Trace Element Chemistry, United States Geological Survey. Lewis Publishers, Michigan, USA.
Horowitz, A.J., Stephens, V.C., 2008. The effects of land use on fluvial sediment chemistry for the conterminous U.S. — results from the first cycle of the NAWQA program: trace and major elements, phosphorus, carbon, and sulfur. Sci. Total Environ. 400 (1–3):290–314. http://dx.doi.org/10.1016/j.scitotenv.2008.04.027.
Horowitz, A.J., Stephens, V.C., Elrick, K.A., Smith, J.J., 2012. Concentrations and annual fluxes of sediment-associated chemical constituents from conterminous US coastal rivers using bed sediment data. Hydrol. Process. 26 (7):1090–1114. http://dx.doi.org/10.1002/hyp.8437.

Hotton, V.K., Sutherland, R.A., 2016. The legacy of lead (Pb) in fluvial bed sediments of an urban drainage basin, Oahu, Hawaii. Environ. Sci. Pollut. Res. 23 (6):5495–5506. http://dx.doi.org/10.1007/s11356-015-5777-8.

Huber, M., Helmreich, B., 2016. Stormwater management: calculation of traffic area runoff loads and traffic related emissions. Water 8 (7), 294.

Hurley, J.P., Cowell, S.E., Shafer, M.M., Hughes, P.E., 1998. Tributary loading of mercury to Lake Michigan: importance of seasonal events and phase partitioning. Sci. Total Environ. 213 (1–3):129–137. http://dx.doi.org/10.1016/S0048-9697(98)00084-9.

Kasanin-Grubin, M., Bryan, R., 2007. Lithological properties and weathering response on badland hillslopes. Catena 70 (1):68–78. http://dx.doi.org/10.1016/j.catena.2006.08.001.

Kerr, J.G., Eimers, M.C., Yao, H., 2016. Estimating stream solute loads from fixed frequency sampling regimes: the importance of considering multiple solutes and seasonal fluxes in the design of long-term stream monitoring networks. Hydrol. Process. 30 (10):1521–1535. http://dx.doi.org/10.1002/hyp.10733.

Kirk, J.L., St. Louis, V.L., 2009. Multiyear total and methyl mercury exports from two major sub-Arctic Rivers draining into Hudson Bay, Canada. Environ. Sci. Technol. 43 (7): 2254–2261. http://dx.doi.org/10.1021/es803138z.

Kronvang, B., Bruhn, A.J., 1996. Choice of sampling strategy and estimation method for calculating nitrogen and phosphorus transport in small lowland streams. Hydrol. Process. 10 (11):1483–1501. http://dx.doi.org/10.1002/(SICI)1099-1085(199611)10:11<1483::AID-HYP386>3.0.CO;2-Y.

Lanphear, B.P., et al., 2005. Low-level environmental lead exposure and children's intellectual function: an international pooled analysis. Environ. Health Perspect. 113 (7):894–899. http://dx.doi.org/10.1289/ehp.7688.

Lawson, N.M., Mason, R.P., Laporte, J.M., 2001. The fate and transport of mercury, methylmercury, and other trace metals in Chesapeake Bay tributaries. Water Res. 35 (2), 501–515.

Liberti, M., et al., 2009. Mapping badland areas using LANDSAT TM/ETM satellite imagery and morphological data. Geomorphology 106 (3–4):333–343. http://dx.doi.org/10.1016/j.geomorph.2008.11.012.

Macklin, M.G., et al., 2006. A geomorphological approach to the management of rivers contaminated by metal mining. Geomorphology 79 (3–4):423–447. http://dx.doi.org/10.1016/j.geomorph.2006.06.024.

Martin, J.-M., Meybeck, M., 1979. Elemental mass-balance of material carried by major world rivers. Mar. Chem. 7 (3):173–206. http://dx.doi.org/10.1016/0304-4203(79)90039-2.

Mebane, C.A., 2010. Cadmium Risks to Freshwater life: Derivation and Validation of Low-effect Criteria Values Using Laboratory and Field Studies (Version 1.2). U.S. Geological Survey, Reston, Virginia.

Meybeck, M., Laroche, L., Dürr, H.H., Syvitski, J.P.M., 2003. Global variability of daily total suspended solids and their fluxes in rivers. Global Planet. Change 39 (1–2):65–93. http://dx.doi.org/10.1016/S0921-8181(03)00018-3.

Meybeck, M., et al., 2007. Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950–2005). Sci. Total Environ. 375 (1–3):204–231. http://dx.doi.org/10.1016/j.scitotenv.2006.12.017.

Miller, C.V., Foster, G.D., Majedi, B.F., 2003. Baseflow and stormflow metal fluxes from two small agricultural catchments in the Coastal Plain of the Chesapeake Bay Basin, United States. Appl. Geochem. 18 (4):483–501. http://dx.doi.org/10.1016/S0883-2927(02)00103-8.

Müller, B., et al., 2008. How polluted is the Yangtze river? Water quality downstream from the three gorges dam. Sci. Total Environ. 402 (2–3):232–247. http://dx.doi.org/10.1016/j.scitotenv.2008.04.049.

Nagorski, S.A., Moore, J.N., McKinnon, T.E., Smith, D.B., 2003. Geochemical response to variable streamflow conditions in contaminated and uncontaminated streams. Water Resour. Res. 39 (2) n/a-n/a. 10.1029/2001WR001247.

Naik, A.P., Hammerschmidt, C.R., 2011. Mercury and trace metal partitioning and fluxes in suburban Southwest Ohio watersheds. Water Res. 45 (16):5151–5160. http://dx.doi.org/10.1016/j.Watres.2011.07.023.

Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. Sci. Total Environ. 311 (1–3):205–219. http://dx.doi.org/10.1016/S0048-9697(03)00139-6.

Nimick, D.A., Cleasby, T.E., 2004. Chapter D5: Trace elements in water in streams affected by historical mining. U.S. Department of Interior and U.S, Geological Survey, Reston, Virginia.

Nystrand, M.I., Österholm, P., Nyberg, M.E., Gustafsson, J.P., 2012. Metal speciation in rivers affected by enhanced soil erosion and acidity. Appl. Geochem. 27 (4): 906–916. http://dx.doi.org/10.1016/j.apgeochem.2012.01.009.

Owens, P.N., et al., 2005. Fine-grained sediment in river systems: environmental significance and management issues. River Res. Appl. 21 (7):693–717. http://dx.doi.org/10.1002/rra.878.

Price, G.J., et al., 2013. Bedrock geology of Alberta; Alberta energy regulator, AER/AGS map 600, scale 1:1 000 000.

Quinton, J.N., Catt, J.A., 2007. Enrichment of heavy metals in sediment resulting from soil erosion on agricultural fields. Environ. Sci. Technol. 41 (10):3495–3500. http://dx.doi.org/10.1021/es062147h.

Quinton, J.N., Catt, J.A., Hess, T.M., 2001. The selective removal of phosphorus from soil. J. Environ. Qual. 30 (2):538–545. http://dx.doi.org/10.2134/jeq2001.302538x.

Rickson, R.J., 2014. Can control of soil erosion mitigate water pollution by sediments? Sci. Total Environ. 468–469:1187–1197. http://dx.doi.org/10.1016/j.scitotenv.2013.05.057.

Roberts, T.L., 2014. Cadmium and phosphorous fertilizers: the issues and the science. Procedia Engineering 83:52–59. http://dx.doi.org/10.1016/j.proeng.2014.09.012.

Rothwell, J.J., Evans, M.G., Daniels, S.M., Allott, T.E.H., 2007. Baseflow and stormflow metal concentrations in streams draining contaminated peat moorlands in the Peak District National Park (UK). J. Hydrol. 341 (1–2):90–104. http://dx.doi.org/10.1016/j.jhydrol.2007.05.004.

Rozan, T.F., Benoit, G., 2001. Mass balance of heavy metals in new Haven Harbor, Connecticut: predominance of nonpoint sources. Limnol. Oceanogr. 46 (8):2032–2049. http://dx.doi.org/10.4319/lo.2001.46.8.2032.

Shanley, J.B., Chalmers, A.T., 2012. Streamwater fluxes of total mercury and methylmercury into and out of Lake Champlain. Environ. Pollut. 161:311–320. http://dx.doi.org/10.1016/j.envpol.2011.07.006.

da Silva, Y.J.A.B., do Nascimento, C.W.A., Biondi, C.M., 2014. Comparison of USEPA digestion methods to heavy metals in soil samples. Environ. Monit. Assess. 186 (1): 47–53. http://dx.doi.org/10.1007/s10661-013-3354-5.

Stordal, M.C., Gill, G.A., Wen, L.S., Santschi, P.H., 1996. Mercury phase speciation in the surface waters of three Texas estuaries: importance of colloidal forms. Limnol. Oceanogr. 41 (1):52–61. http://dx.doi.org/10.4319/lo.1996.41.1.0052.

Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream, Oahu. Hawaii. Environ. Geol. 39 (6):611–627. http://dx.doi.org/10.1007/s002540050473.

Sutherland, R.A., Tack, F.M.G., Ziegler, A.D., Bussen, J.O., 2004. Metal extraction from road-deposited sediments using nine partial decomposition procedures. Appl. Geochem. 19 (6):947–955. http://dx.doi.org/10.1016/j.apgeochem.2003.11.002.

Swank, W.T., Voce, J.M., Elliott, K.J., 2001. Long-term hydrologic and water quality responses following commercial clearcutting of mixed hardwoods on a southern Appalachian catchment. Forest Ecol. and Management 143:163–178. http://dx.doi.org/10.1016/S0378-1127(00)00515-6.

Tanzeeba, S., Gan, T.Y., 2012. Potential impact of climate change on the water availability of South Saskatchewan River basin. Clim. Chang. 112 (2):355–386. http://dx.doi.org/10.1007/s10584-011-0221-7.

Taylor, K.G., Owens, P.N., 2009. Sediments in urban river basins: a review of sediment–contaminant dynamics in an environmental system conditioned by human activities. J. Soils Sediments 9 (4):281–303. http://dx.doi.org/10.1007/s11368-009-0103-z.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy metals toxicity and the environment. EXS 101:133–164. http://dx.doi.org/10.1007/978-3-7643-8340-4_6.

Tiefenthaler, L.L., Stein, E.D., Schiff, K.C., 2008. Watershed and land use-based sources of trace metals in urban storm water. Environ. Toxicol. Chem. 27 (2):277–287. http://dx.doi.org/10.1897/07-126r.1.

Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the Earth's crust. Geol. Soc. Am. Bull. 72 (2):175–192. http://dx.doi.org/10.1130/0016-7606(1961)72[175:doteis]2.0.co;2.

Viers, J., Dupré, B., Gaillardet, J., 2009. Chemical composition of suspended sediments in world rivers: new insights from a new database. Sci. Total Environ. 407 (2): 853–868. http://dx.doi.org/10.1016/j.scitotenv.2008.09.053.

Walling, D.E., 2005. Tracing suspended sediment sources in catchments and river systems. Sci. Total Environ. 344 (1–3):159–184. http://dx.doi.org/10.1016/j.scitotenv.2005.02.011.

Warren, L.A., Zimmerman, A.P., 1994. The influence of temperature and NaCl on cadmium, copper and zinc partitioning among suspended particulate and dissolved phases in an urban river. Water Res. 28 (9):1921–1931. http://dx.doi.org/10.1016/0043-1354(94)90167-8.

Wilson, M.A., Burt, R., Lee, C.W., 2006. Improved elemental recoveries in soils with heating boric acid following microwave Total digestion. Commun. Soil Sci. Plant Anal. 37 (3–4):513–524. http://dx.doi.org/10.1080/00103620500449377.

Wuana, R.A., Okieimen, F.E., 2011. Heavy metals in contaminated soils: areview of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology 2011:20. http://dx.doi.org/10.5402/2011/402647.