

## Impact of land use activities on fine sediment-associated contaminants, Quesnel River Basin, British Columbia, Canada

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**Abstract** The impact of various land use activities (forestry, mining, and agriculture) on the quality of fine-grained sediment (<63  $\mu\text{m}$ ) was investigated in the Quesnel River Basin (approx. 12 000  $\text{km}^2$ ) in British Columbia, Canada. Samples of fine-grained sediment were collected monthly during the snow-free season in 2008 using time-integrated isokinetic samplers at sites representative of forestry, mining, and agricultural activities in the basin. Samples were also collected from replicate control sites that had undergone limited or no disturbance in recent years, and also from the main stem of the Quesnel River. Generally, metal and nutrient concentrations for “impacted” sites were greater than for control sites. Concentrations of As (mining sites), Cu (forestry sites) and Zn (forestry sites) were close to or exceeded upper Sediment Quality Guideline (SQG) thresholds, while Se concentrations for mining sites were elevated and within the range cited for contaminated environments. Phosphorus values were generally <1000  $\mu\text{g g}^{-1}$  for all land use activities and below available SQGs. Values for individual samples were, however, greater than upper SQG levels, such as 22.7  $\mu\text{g g}^{-1}$  (As), 801  $\mu\text{g g}^{-1}$  (Cu), 5.0  $\mu\text{g g}^{-1}$  (Se) and 2192  $\mu\text{g g}^{-1}$  (P). These preliminary results suggest that metal mining and forest harvesting are having a greater influence on the concentration of sediment-associated metals and nutrients in the Quesnel basin, than agricultural activities.

**Key words** sediment quality; land use; mining; contaminants; metals; aquatic ecosystems; cohesive sediment

### INTRODUCTION

In rivers, contaminants are transported in both dissolved and particulate forms. The majority of metals, phosphorus, radionuclides and organic contaminants have a strong affinity with particulates, especially fine sediments <63  $\mu\text{m}$  (Horowitz, 1991; Owens & Walling, 2002). Several studies report that roughly 90% of metals are transported in particulate form (Salomons & Förstner, 1984; Horowitz, 1991; Foster & Charlesworth, 1996). The partitioning of trace metals and nutrients is a function of the environmental conditions (i.e. redox, competitor ions, pH, temperature) and the nature of the contaminant source (Carter *et al.*, 2006; Luoma & Rainbow, 2008).

Land use activity is an important factor influencing both the source of cohesive sediment and its geochemical and contaminant transport properties. Horowitz & Stephens (2008) examined the influence of agricultural, forestry, rangeland, and urban land uses on contaminant and nutrient content in fine channel bed sediment collected from 51 river basins throughout the USA as part of the National Water Quality Assessment (NAWQA) program of the US Geological Survey (USGS). They found that urban land use had a significant influence on sediment-associated chemical concentrations, while all other land use categories had a lesser effect. Other studies have also demonstrated that land use activities enhance the concentration of sediment-associated contaminants in river systems (for a review see Taylor *et al.*, 2008).

While several contaminant source and transport studies have been conducted at the broad national scale (e.g. Horowitz & Stephens, 2008), this paper examines the effect of three land use activities (mining, agriculture and forest harvesting) on sediment-associated contaminant (metal and nutrients) concentrations in the Quesnel Basin, British Columbia. The study focuses on sampling high-energy events (high precipitation events and/or spring freshets) that typically provide the greatest yield of fine sediment and associated contaminant fluxes in river systems. The contaminant properties of the land use impacted sediment are compared to those collected at two reference sites. Specific objectives of the paper are to determine the contaminant concentrations of fine suspended sediments associated with different land use activities, and to examine if there are temporal and spatial differences between land uses.

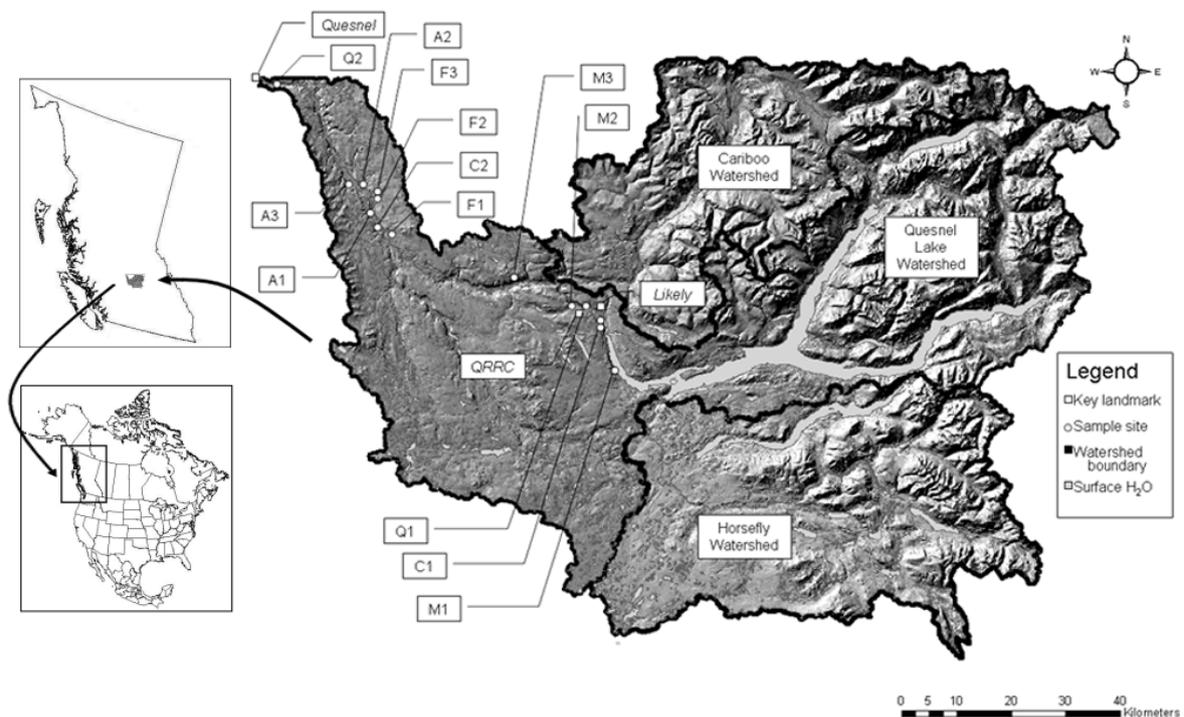
## THE STUDY CATCHMENT

The Quesnel River basin (Fig. 1) is prime habitat for anadromous salmonids such as sockeye, pink, chinook, and coho salmon and several other non-anadromous species that are important from an ecological and economic perspective. Average total annual precipitation to the basin is 517 mm at the mouth of the river and 1072 mm near its headwaters (Burford *et al.*, 2009). This variation is partially due to elevation change (from ~500 m at the mouth to ~3000 m a.m.s.l. in the headwaters). Over half of the basin drains into Quesnel Lake (maximum depth >600 m). Below the lake, the river flows ~100 km northwest to the town of Quesnel where it joins the Fraser River (drainage area is approx. 232 000 km<sup>2</sup>). Most of the Quesnel River basin is frozen for 5–6 months of the year (minimum annual temperatures are typically below –30°C) and river flows are dominated by the annual freshet. Peak flows occur during late May to early July. Mean discharge for the Water Survey of Canada (WSC) gauging stations at Likely (52°37'N, 121°34'W, area is 5930 km<sup>2</sup>) and Quesnel (52°50'N, 122°12'W, area is 11 500 km<sup>2</sup>) were 132 and 248 m<sup>3</sup> s<sup>-1</sup>, respectively, in 2007 (the last year of available data: WSC, 2009).

The Quesnel basin is influenced by four predominant land use activities: (1) forest harvesting; (2) agriculture (mainly livestock); (3) mining (mainly for copper and gold); and (4) urban, although these are very limited (the population upstream of Quesnel is only a few thousand people), and therefore ignored here. This project focuses mainly on the area of the basin below the output of the lake, which is located at the community of Likely.

## METHODOLOGY

Suspended sediment samples were collected using isokinetic samplers in stream reaches draining the following land use activities: forestry, agriculture, and mining (Fig. 1). Samplers were deployed at sites where the area upstream was dominated (>50%) by a particular land use (e.g. forestry or agriculture) or by an activity likely to influence the sediment in the stream (e.g. mining).

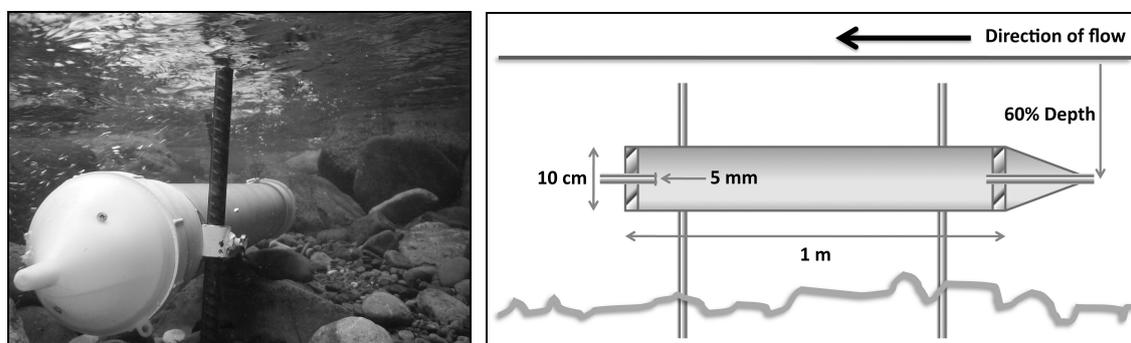


**Fig. 1** Quesnel River basin, British Columbia, and the location of the sampling sites: F, forestry; A, agriculture; M, mining; C, control; Q, Quesnel River (main stem); QRRC, Quesnel River Research Centre.

Given that 63% of the area of the Quesnel River basin is forested (Burford *et al.*, 2009) and significant historical and contemporary forest harvesting has taken place over a large portion of the total area, the impact of forest harvesting practices on suspended sediment-associated contaminants was of particular interest due to the scale of such operations. All forestry sites (F1, F2 and F3) are in a similar reach of the Quesnel River and are subject to similar weather, climate and lithology. All three agricultural sites (A1, A2 and A3) represent pasture land uses with cattle being the predominant livestock and are within the slower flowing lowland section of the Quesnel River (Fig. 1) characterized by flood plains and steep exposed cutbanks. At all three locations there are no barriers between the tributaries and the cattle pastures. Sites M1, M2 and M3 represent catchments containing an open pit copper mine, an inactive hydraulic gold mine, and a combined open pit and underground gold mining operation, respectively.

The control sites, C1 and C2, were chosen due to a lack of evidence of recent disturbance within both catchments, suggesting that suspended sediment should be indicative of inputs from natural coniferous forest. However, much of the region has been previously deforested and it is unlikely to represent pristine forests. Two sampling sites were located on the main stem of the Quesnel River. Site Q1 is located at the UNBC Quesnel River Research Centre (QRRC) and is representative of the outflow of Quesnel Lake. Site Q2 is located at the town of Quesnel and thus is considered representative of contributions from the upstream basin, particularly those downstream of the lake.

Suspended sediment was collected using the Phillips sampler (Phillips *et al.*, 2000) (Fig. 2). Flow velocity within the main chamber of the sampler is reduced by a factor greater than 600 that causes sediment to settle (for further details see Phillips *et al.*, 2000; Russell *et al.*, 2000). Russell *et al.* (2000) evaluated the sampler and demonstrated that it was suitable for collecting fine fluvial sediment for analysis of most sediment-associated contaminants and nutrients.



**Fig. 2** Sediment sampler deployed in the field (left) and in cross-section (right).

Sediment samples were collected from each of the 13 sites at monthly intervals over the snow-free period of May 2008 to October 2008. This allows an assessment of the spatial (i.e. within and between land use type) and temporal (i.e. during the course of the sampling campaign) variations in sediment-associated contaminants.

Sediment samples collected from sites in the Quesnel River basin were sieved to  $<63 \mu\text{m}$  and freeze-dried for preservation. In the laboratory, samples underwent acid and microwave digestion using nitric and hydrochloric acids, and then were analysed using ICP mass spectrometry for metals and nutrients. Here we focus on preliminary results for arsenic (As), cadmium (Cd), copper (Cu), phosphorus (P), selenium (Se) and zinc (Zn). To facilitate comparison between sites, samples were corrected for differences in particle size by adjusting element concentrations based on the ratio of the specific surface area (SSA) of each sediment sample relative to the average SSA of the samples collected from the two control sites. The SSA of each sample was calculated from its particle size distribution, which was determined using a Mastersizer 2000 laser diffractometry

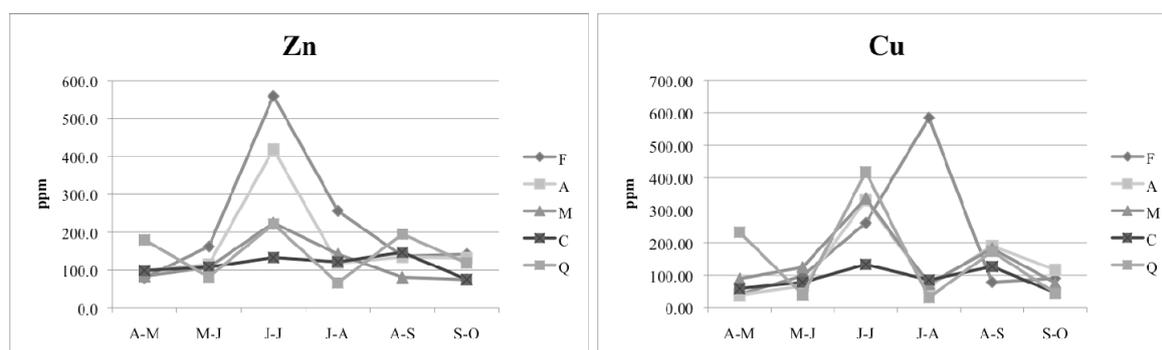
analyser at Simon Fraser University, British Columbia. Samples were pretreated with hydrogen peroxide and sodium hexametaphosphate prior to analysis.

## RESULTS AND DISCUSSION

### Temporal variability

An analysis of element concentrations over time reveals that elements for some land use activities exhibit considerable variation, while others exhibit limited variation. To illustrate this, Fig. 3 shows variations in Zn and Cu over the May to October 2008 sampling period. Values of Zn and Cu for the control sites are fairly constant over the sampling period. However, for streams influenced by forestry, agricultural and mining activities, over time values varied by factors of 4–6. For Zn, values for these three land use activities are greatest for samples representing the June–July period, while for Cu maximum values occur throughout the summer months depending on land use, although the samples representing the June–July period are again typically elevated. For the sites on the main stem of the Quesnel River, not surprisingly, Zn and Cu values tend to vary more than the control streams but less than streams draining forestry, agriculture or mining, although it is difficult to identify any obvious trends over time. The more muted temporal variation for the Quesnel River are likely to reflect variations in the timing of contributions from streams draining different land use activities, which differ in Zn and Cu concentrations (and thus sediment and chemical delivery) over time. Further analysis is, however, required to confirm this.

The temporal trends shown in sediment chemistry (Fig. 3) are broadly similar for most of the other elements measured (i.e. As, Cd, P and Se), where values for the control sites were fairly uniform over time whereas streams impacted by forestry, agricultural and mining land uses were more variable over time. For those elements where there is noticeable variation (e.g. Cd, Cu, P and Zn), maximum values typically occur in the summer months (i.e. within the period June to September). This likely corresponds to increased suspended sediment and associated contaminant fluxes during the spring freshet (typically late May to July for the Quesnel River) and intense summer storms, in addition to land management activities such as application of fertilizers and manures to agricultural land, and increased harvesting and tree planting of forested land (Christie & Fletcher, 1999; Taylor *et al.*, 2008).

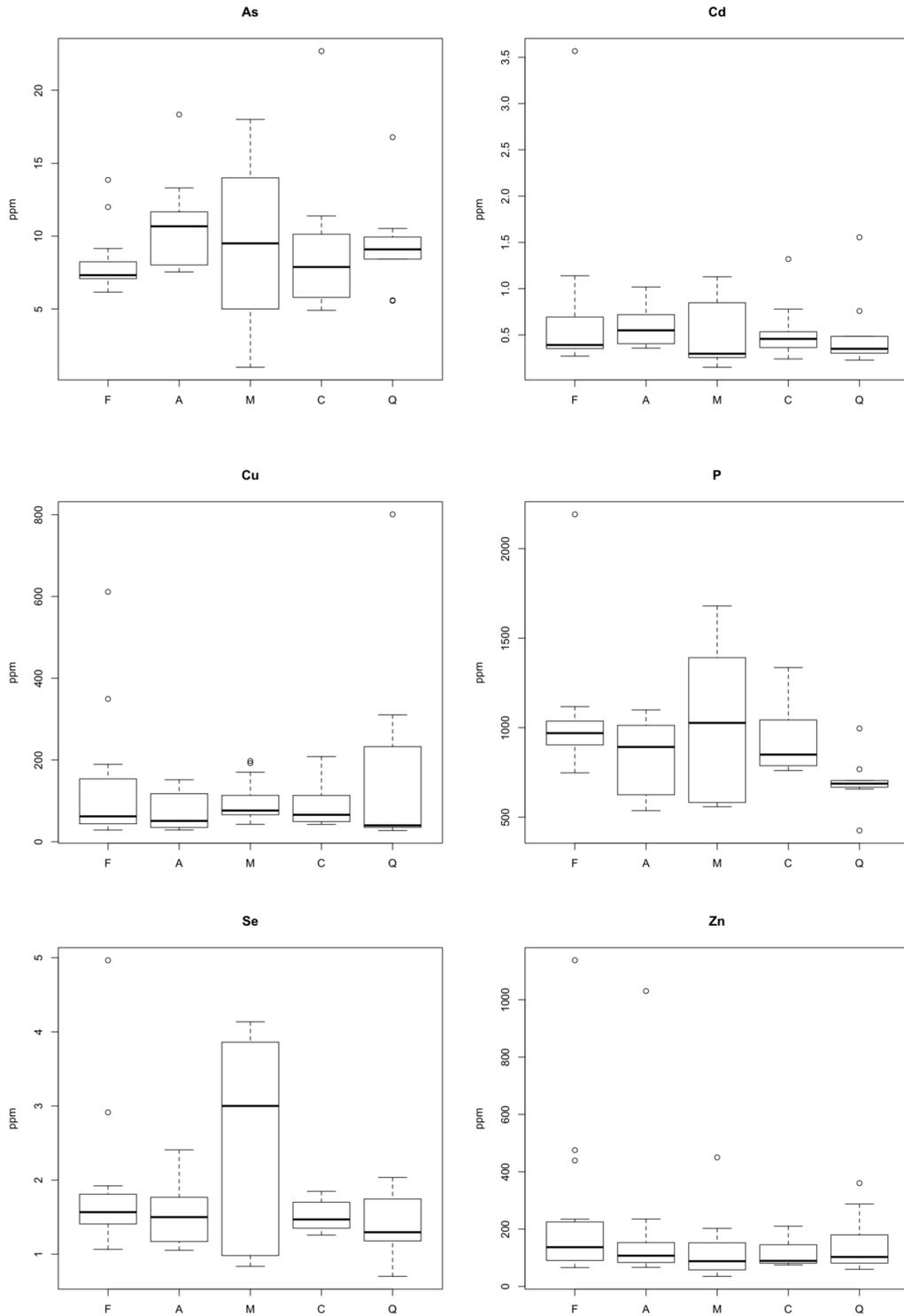


**Fig. 3** Temporal variation of average Zn and Cu concentrations for streams draining different land use activities: forestry (F), agriculture (A), mining (M), control (C), and Quesnel River (Q). X-axis titles correspond to sample periods: April–May (A–M), May–June (M–J), June–July (J–J), July–August (J–A), August–September (A–S), and September–October (S–O).

### Spatial variability

The sediment-associated As, Cd, Cu, P, Se and Zn levels for streams draining mining (M), forestry (F), agriculture (A), control (C) and for the main stem of the Quesnel River (Q) are presented as box-and-whisker plots in Fig. 4. For Cu, there appears to be little variation between land use

activities (e.g. forestry, agriculture and mining) and Cu levels are similar to those for the control sites. One of the largest mean Cu values for an individual site is 186.5  $\mu\text{g g}^{-1}$  for site M3, which drains a combined open pit and underground gold (Au) mining operation. The mean value for site M2, which drains an inactive Au mine, is 60.7  $\mu\text{g g}^{-1}$  and this site clearly reduces the overall average value for the mine sites.



**Fig. 4** Box-plots of As, Cd, Cu, P, Se and Zn for streams draining forestry (F), agriculture (A), mining (M), control (C), and for the main stem of the Quesnel River (Q).

Values for Zn also show limited variation between sites, although mean values for sites impacted by forestry and agriculture activities are slightly greater than the mean value for control sites. Christie & Fletcher (1999) also found elevated levels of Zn for sediment downstream of forested sites, reflecting abrasion of Zn from galvanized culverts. The situation for Cd and P is broadly similar to Cu and Zn, although the mean P concentration for the mining sites and the mean Cd value for the agricultural sites are noticeably larger than the other land use categories. Interestingly, the P values for the sediment collected from the agricultural sites were not noticeably different than the control sites, although the values are consistent with the range of values presented by Owens & Walling (2002) for pasture land. The implication of the generally low to medium values of P (i.e. typically  $<1000 \mu\text{g g}^{-1}$ ) is that the risk of eutrophication is probably not high under current conditions, although further work is needed to substantiate this claim.

For Se, mean values for the mining sites are noticeably higher than the forestry and agricultural sites and for the control sites. For As, values are high for both the mining and the agricultural sites, relative to the control sites. Perhaps more importantly in the case of the mining sites, the maximum values of As and Se are considerably higher than the other land use activities. Se is often enriched in some of the pyrite ores from which Au and Cu are mined, and As is often a constituent of waste products of Cu and Au mining. Both metals are of particular concern because they are amongst the most hazardous and toxic of trace metals (Luoma & Rainbow, 2008).

### Comparison to sediment quality guidelines

Table 1 presents mean metals and nutrient levels for impacted (forestry, agriculture and mining) and control sites. In most cases, average values for “impacted” sites are greater than mean values for the control sites. In some cases, mean values are noticeably greater, for example, As and Se for mining sites and Cu and Zn for forestry sites. Table 1 also compares mean values for land use activities with sediment quality guidelines (SQGs). Generally, values for the streams in the Quesnel River basin are below upper threshold levels (e.g. SEL and PEL) for SQGs. Values of As for mining sites, and Cu and Zn for forestry sites are, however, close to or exceed upper SQG thresholds and are thus of concern. In addition, Se values for mining sites are elevated (undisturbed soil =  $0.2 \mu\text{g g}^{-1}$ ) and within the range cited for contaminated environments (Luoma & Rainbow, 2008). It is important to emphasize that the values for the Quesnel River basin presented in Table 1 represent mean values for each land use activity and that some individual samples were significantly greater than upper SQG levels, such as  $22.7 \mu\text{g g}^{-1}$  (As),  $801 \mu\text{g g}^{-1}$  (Cu),  $5.0 \mu\text{g g}^{-1}$  (Se) and  $2192 \mu\text{g g}^{-1}$  (P).

Although some of the mean values listed in Table 1 are relatively high, and identified here as “of concern”, it should be recognized that such high values do not necessarily mean that these metals and nutrients are toxic to aquatic ecosystems and detrimental to human health. The values presented are total concentrations, and research (e.g. Stone & Droppo, 1996; Carter *et al.*, 2006)

**Table 1** Comparison of mean contaminant concentrations ( $\mu\text{g g}^{-1}$ ) for land use activities to sediment quality guidelines (SQG): LEL, lowest effect level; SEL, severe effect level; ISQG, interim SQGs; PEL, probable effect level; FAC, freshwater ambient criteria (above which environmental degradation is expected).

	Land use				Persaud <i>et al.</i> (1993)		CCME (2002)		Luoma & Rainbow (2008)
	F	A	M	C	LEL	SEL	ISQG	PEL	FAC
<b>Metals</b>									
As	8	11	12	9	6	33	6	17	–
Cd	0.7	0.6	0.5	0.5	0.6	10	0.6	3.5	–
Cu	133	75	96	92	16	110	36	197	–
Se	1.8	1.5	2.5	1.5	–	–	–	–	2–4
Zn	235	171	120	120	120	820	120	320	–
<b>Nutrients</b>									
P	1037	854	994	950	600	2000	–	–	–

Note: means are based on the particle-size corrected concentration values. Outliers (see Fig. 4) were not removed from the data set.

has shown that a significant portion may not be bioavailable (i.e. not easily available for uptake or use by organisms). Thus, comparison of total values of metals and nutrients with SQGs should be treated with some caution, and information on metal and nutrient speciation would be more informative for identifying risk to aquatic organisms and human health.

## CONCLUSION

Fine-grained suspended sediment was collected from streams draining different land use activities in the Quesnel River basin, British Columbia. While mean metals and nutrient values for the control sites exhibited little variation over the sampling period (May–October 2008), there were more pronounced temporal variations for streams draining catchments impacted by forestry, agricultural and mining activities. Generally, metal and nutrient concentrations for impacted sites were greater than for control sites. Furthermore, values of As for mining sites, and Cu and Zn for forestry sites were close to or exceeded upper SQG thresholds and may be of concern. The Se levels for sites impacted by mining are elevated and within the range cited in the literature for contaminated environments. These preliminary results suggest that metal mining and forest harvesting are having a greater influence on the concentration of sediment-associated metals and nutrients in the Quesnel basin, than agricultural activities. This finding is not inconsistent with that of Horowitz & Stephens (2008), described earlier. Additional work is ongoing to confirm this finding, and to assess the wider significance of the results.

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