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Individual and cumulative effects of agriculture, forestry and metal mining activities on the metal and phosphorus content of fluvial fine-grained sediment; Quesnel River Basin, British Columbia, Canada

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HIGHLIGHTS

- Individually, land use activities had an impact on sediment quality in sub-basins.
- Cumulative effects of these activities at the river-basin scale are not yet apparent.
- Sediment storage may be attenuating the disturbance signal to downstream locations.

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ABSTRACT

The impact of agriculture, forestry and metal mining on the quality of fine-grained sediment (<63 μm) was investigated in the Quesnel River Basin (QRB) (~11,500 km^2) in British Columbia, Canada. Samples of fine-grained sediment were collected monthly during the snow-free season in 2008 using time-integrated samplers at replicate sites representative of agriculture, forestry and mining activities in the basin (i.e. "impacted" sites). Samples were also collected from replicate reference sites and also from the main stem of the Quesnel River at the downstream confluence with the Fraser River. Generally, metal(loid) and phosphorus (P) concentrations for "impacted" sites were greater than for reference sites. Furthermore, concentrations of copper (forestry and mining sites), manganese (agriculture and forestry sites) and selenium (agriculture, forestry and mining sites) exceeded upper sediment quality guideline (SQG) thresholds. These results suggest that agriculture, forestry and metal mining activities are having an influence on the concentrations of sediment-associated metal(loid)s and P in the Quesnel basin.

Metal(loid) and P concentrations of sediment collected from the downstream site were not significantly greater than values for the reference sites, and were typically lower than the values for the impacted sites. This suggests that the cumulative effects of agriculture, forestry and mining activities in the QRB are presently not having a measureable effect at the river basin-scale. The lack of a cumulative effect at the basin-scale is thought to reflect: (i) the relatively recent occurrence of land use disturbances in this basin; (ii) the dominance of sediment contributions from natural forest and agriculture; and (iii) the potential for storage of contaminants on floodplains and other storage elements between the locations of disturbance activities and the downstream sampling site, which may be attenuating the disturbance signal.

1. Introduction

With a rapidly increasing world population, it is expected that there will be increasing pressures placed on terrestrial and aquatic systems due to expanding land and river use and associated environmental impacts such as land degradation, and soil and water pollution (Foley et al., 2005, 2011; Vörösmarty et al., 2010). In many parts of the world (e.g. Europe), such developments have been on-going for centuries. However, in many areas (e.g. central and northern Canada) such developments are fairly recent (i.e. years to decades) and there is concern associated with their impacts, particularly due to the scale and expected expansion of activities. Much of the work on the impacts of land and river development on river pollution has focused on individual activities – such as mining (i.e. point sources) and agriculture (i.e. diffuse sources) – in isolation from other activities that may be occurring in the same region (e.g. Lin and Wei, 2008; Moriarty et al., 2014; Palumbo-Roe et al., 2012; Walsh et al., 2007). Much less work considers

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multiple activities or stressors on particular landscapes or riverscapes (e.g. Bednarova et al., 2013; Zhang and Wei, 2012). In river basins, the cumulative effects of different activities are likely to be particularly relevant as downstream water quality is the result of the combined activities in the upstream basin due to the topographic confines of the basin and to hydrological and geomorphological processes that transport and focus material fluxes into a main channel. In recognition of this, cumulative effects assessment is now part of environmental policy and legislation in Canada, such as the Canadian Environmental Assessment Act (Dubé, 2003; Hegmann et al., 1999), and elsewhere, and is increasingly being seen as a useful approach for river basin and watershed management (Scherer, 2011). Despite the widespread recognition of the benefits of adopting a cumulative effects approach as a conceptual framework for river basin management, few studies have actually determined the effects of several land use activities on water quality in a particular river basin, especially in areas where resource extraction activities are relative new, and thus where the existing water quality is perceived to be relatively "pristine".

To address this need, we investigated the effects of several land use activities – both point and diffuse – on water quality in a medium-sized river basin (Quesnel) in central British Columbia (BC), Canada. This region has a low population density and considerable appeal for tourism and recreation given the landscape (e.g. forests, high mountains) and wildlife (e.g. moose, black and grizzly bears, mountain lions and wolves) attributes. Thus local communities have considerable concerns associated with recent, and planned, resource extraction developments in the basin, particularly on water quality and river flows. Recent research (Déry et al., 2012) has demonstrated marked increases in the occurrence of more extreme water flows (i.e. more extreme low and high flows) in the Quesnel basin and the larger Fraser basin into which it flows, and land use changes have been identified as one of the likely causes of this. We focused on one indicator of water quality, namely sediment quality, and focused on key metals (and metalloids) and particulate phosphorus (P). We selected P because of the many wetlands and lakes in the basin – including Quesnel Lake which is important for salmonids – and concerns over eutrophication. Specific objectives were: (i) to determine the effects of several individual land use activities on sediment quality; and (ii) to determine the cumulative effects of these activities on sediment quality at the downstream confluence with the Fraser River.

2. Materials and methods

2.1. The study site

The Quesnel River Basin (QRB; ~11,500 km^2) is located in south-central BC (Fig. 1). It 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 in the basin is 517 mm at the mouth of the river and 1072 mm near its headwaters (Burford et al., 2009). This variation is due partly to elevation change, from ~500 m above mean sea level (amsl) at the mouth to ~3000 m amsl in the headwaters, the Cariboo Mountains. Over half of the basin drains into Quesnel Lake. From the lake, the river flows ~100 km northwest to the town of Quesnel where it joins the Fraser River (drainage area is ~232,000 km^2).

Most of the QRB is frozen for 5–6 months of the year as minimum annual temperatures are typically below −30 °C. River flows are dominated by the annual freshet (flows associated with the spring thaw and the melting of snow and ice) and peak flows occur between late May and early July. Mean discharges for the Quesnel River at the Water Survey of Canada (WSC) gauging stations at Likely (52°37′N, 121°34′W; area is 5930 km^2) and Quesnel (52°50′N, 122°12′W; area

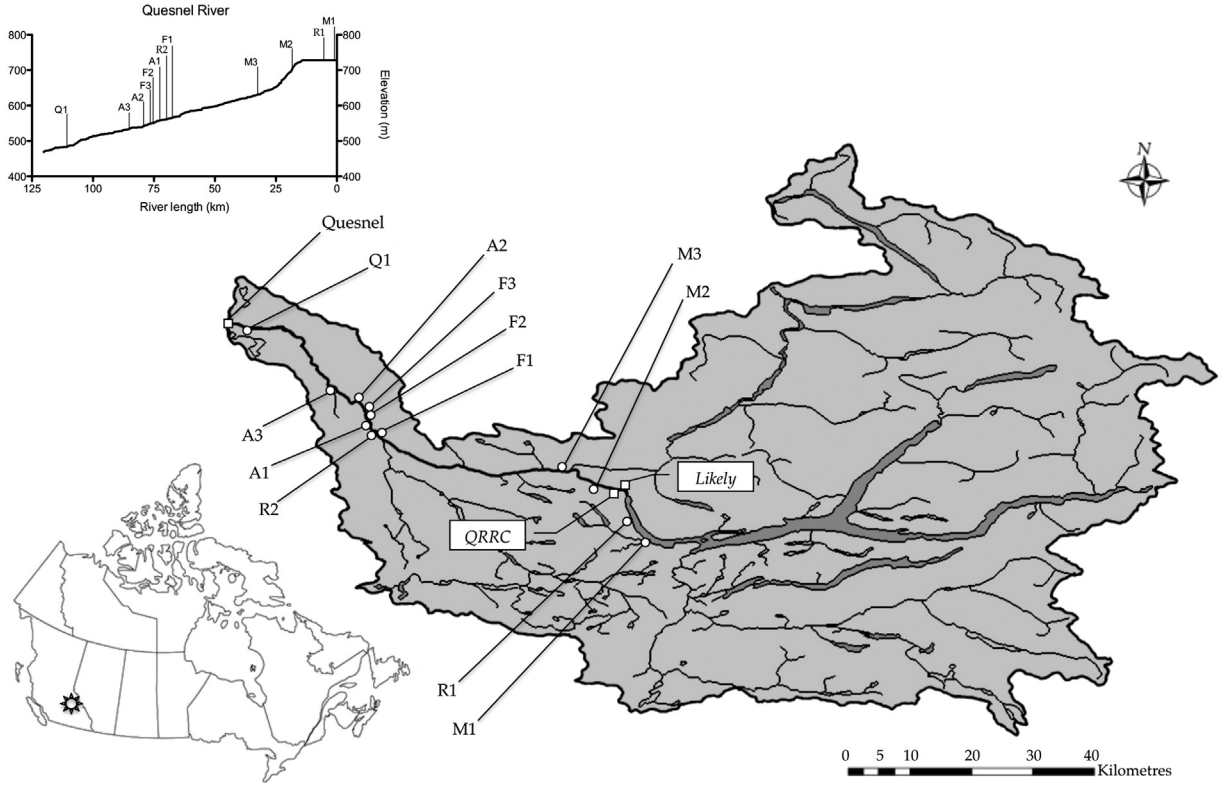

Fig. 1. Quesnel River Basin, British Columbia, and location of the sampling sites: F, forestry; A, agriculture; M, mining; R, reference; Q, Quesnel River (main channel). QRRC is the Quesnel River Research Centre, located near the community of Likely. The Quesnel River flows from the Cariboo Mountains in the east to the town of Quesnel in the west, where it joins the Fraser River. The main lakes (including Quesnel Lake in the middle) and rivers are also shown. Inset map (bottom left) shows location of the basin within Canada, and inset graph (top left) shows the gradient of the main stem of the Quesnel River and lower segment of Quesnel Lake downstream of site M1, and the relative locations of the tributary sample sites.

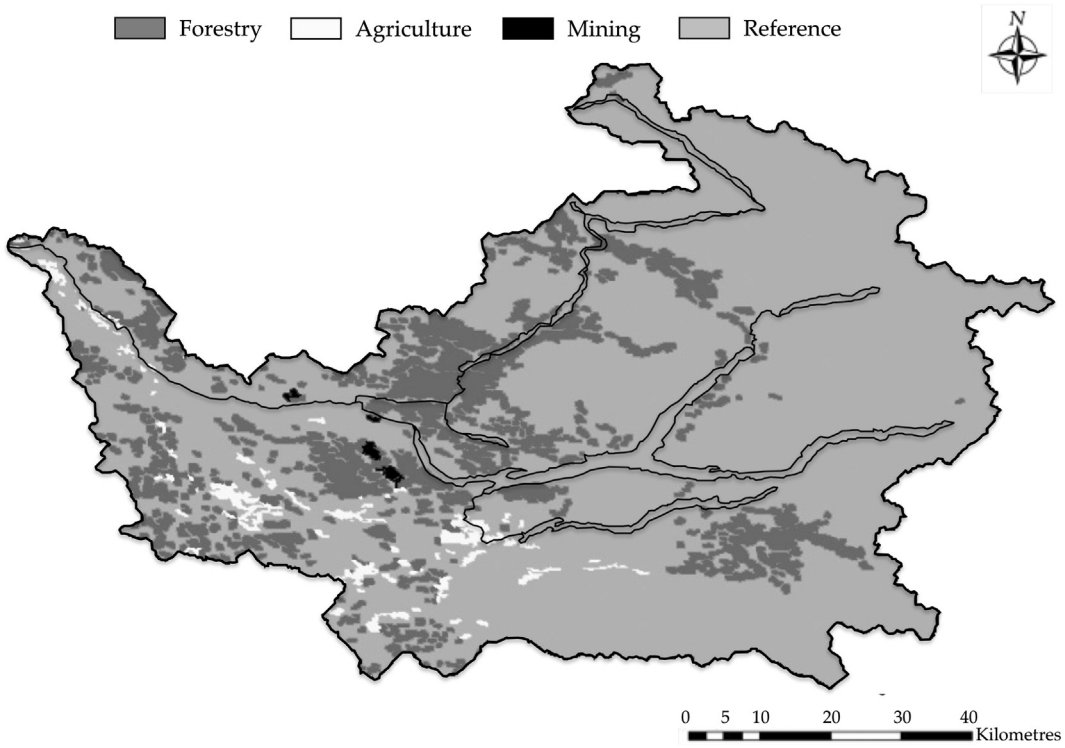

Fig. 2. Main land use distribution in the Quesnel River Basin, British Columbia. The main lakes (including Quesnel Lake in the middle) and the Quesnel River are also shown. Reference equates to "natural" forest.

is 11,500 km^2) were 132 and 248 m^3 s^{-1}, respectively, in 2007 (the last year of available corrected data prior to the field season: WSC, 2009).

The Quesnel basin is dominated by four main land uses (Fig. 2): (i) natural forest; (ii) forestry (i.e. forest harvesting); (iii) agriculture (mainly livestock); and (iv) mining (mainly for copper and gold). There are also some urban areas, although these are very limited – the population upstream of the town of Quesnel is only a few thousand people – and therefore ignored here; although we consider the implications of this in subsequent sections. We also ignored the effects of the town of Quesnel on sediment quality because the town is located at the confluence of the Quesnel and Fraser Rivers (Fig. 1) and downstream of our sampling sites. In 2008, the area distribution for each land use in the QRB was: natural forest = 62.8%; forestry = 31.9%; agriculture = 5%; and mining = 0.3%. This project focused mainly on the area of the basin below the output of Quesnel Lake (located at the community of Likely) as we assume that the lake – which is ~80 km long and >500 m deep – will trap most (>95%) of the inflowing sediment load from the upstream basin and therefore have minimal influence on sediment quality at the downstream sampling point (Q1, Fig. 1).

2.2. Field and laboratory methods

2.2.1. Suspended sediment collection

Suspended sediment samples were collected using time-integrated samplers (for details of the sampler see Phillips et al., 2000; Russell et al., 2000) in stream reaches draining: (i) forestry (n = 3; F1–F3); (ii) agriculture (n = 3; A1–A3); and (iii) mining (n = 3; M1–M3). The three forestry sites were generally similar (in terms of size, topography, climate, soils and land cover), as were the three agricultural sites, and thus are considered as field replicates. The mining sites differed as it was not possible to find three identical mine sites. Site M1 is an active copper mine. While this site discharges into Quesnel Lake, and is thus upstream of Likely, it was included here as it is the largest active mine within the watershed and its activities are of considerable local concern in terms of the delivery of contaminants to downstream aquatic systems, including the Quesnel River. Site M2 is the location of a gold placer mine that was in operation from 1892 to 1942. In 1935 it was the location of the largest hydraulic monitors installed in North America. Currently, the canyon of M2 measures 3 km long by 120 m deep. During operation, it displaced 9×10^6 m^3 of gravel. Site M3 is an active gold mine, which has both open pit and underground operations.

The sediment samplers were deployed at sites where the area upstream was dominated (>50%) by a particular land use (i.e. forestry or agriculture) or by a point-source activity likely to influence strongly the sediment in the stream (i.e. mining). Land use areas and relative proportions within each sub-basin were determined using Central Cariboo Forest District (Government of British Columbia, 2008a) and Quesnel Forest District (Government of British Columbia, 2008b) maps and remotely sensed data retrieved from the Hectares BC website (Biodiversity BC and the Nature Conservancy of Canada, 2012). Reference sites (n = 2; R1–R2) represented natural forest with a minimum of anthropogenic disturbance. However, at least one road is known to cross each reference sub-basin and much of the region has been previously deforested, and therefore it is not possible to claim with full certainty that reference sites represent pristine forests. In addition, one sampling site was located on the main stem of the Quesnel River; Q1 was located just upstream of the town of Quesnel, near its confluence with the Fraser River (Fig. 1), and is considered representative of the cumulative contributions from the entire upstream basin above the town of Quesnel, particularly those downstream of the lake (i.e. the downstream ~100 km of the main stem). It is important to note that site Q1 was not be influenced by discharges (e.g. sewage treatment works, industrial and urban sources) from the town.

Sediment samples were collected from each of the 12 sites (Fig. 1) at monthly intervals; in other words, the samplers collected sediment over a ca. 30 day period, were emptied and then reset for the subsequent 30 day sampling period (see below). Samples were collected over the snow-free period from May 2008 to October 2008; outside of this period, river flows are minimal and the hydrological connectivity between the land and the river system is considerably reduced as the landscape

is essentially frozen. Collecting integrated sediment samples over a month enabled a sufficient amount of sediment to be retained by each sampler to allow laboratory analysis (~1 g minimum). The initial deployment and final removal of samplers over the six-month field season was dictated by spring thaw (i.e. freshet) and late-fall drought and/or freeze timing.

At the end of each month-long sample period the contents of each sampler were washed out on-site using either ambient clean water or distilled water, and collected in a sealable 20 L plastic bucket. The buckets were pre-cleaned using P-free cleaning agents (i.e. to avoid contamination). Samplers were then returned to their rebar moorings and depth was adjusted for any monthly stage changes to maintain the sampler at ~60% water depth, as recommended by Phillips et al. (2000).

Despite precautions taken during the site planning process some samples were lost, leaving gaps in the data set. Specifically, one sampler was lost due to insufficient mooring during freshet (i.e. site A1), and some channels, although promising during April reconnaissance, proved ephemeral and dried-up during fall sampling periods (i.e. sites F1, F3 and M3). However, samples from all land use types were collected during all sample periods.

2.2.2. Channel bed sediment collection

It is well recognized that a portion of the fine-grained sediment transported in a river is deposited and retained on/in the channel bed (Horowitz and Stephens, 2008), before remobilization into the water column during subsequent high flows. In order to characterize stored fine-grained sediment geochemically, samples of upper 5–10 cm of the channel bed sediment were collected adjacent to each time-integrated sampler during the second half of the 2008 field season (July–October), thus enabling a comparison between suspended and bed sediment samples. Channel bed sediment samples were collected using a re-suspension method (for details see Lambert and Walling, 1988; Owens et al., 1999; Walsh et al., 2007). Due to the late season sampling, fewer bed sediment samples than suspended sediment samples were collected. In all, 21 channel bed samples were collected. It was not possible to collect bed sediment at sites F1 and F3, leaving site F2 as the only representative of the forestry sites with two samples. Replicate analysis was possible for all other land use types with two samples for each of sites A1, A2, M1, M2 and M3 and three samples for each of sites A3, R1 and R2. No channel bed samples were collected from Q1 due to the high depth of water at this site; often >3 m in the thalweg.

2.2.3. Laboratory analysis

After collection, suspended and bed sediment samples were allowed to settle for 24 h prior to the removal of the supernatant by siphoning. To facilitate analysis of the fine-grained fraction, samples were wet sieved to <63 μm (Horowitz and Stephens, 2008; Walling and Woodward, 1992), secured in Nasco Whirl-paks®, and frozen. In order to best preserve chemical integrity, all samples were processed and frozen within 72 h of collection. Finally, sediment samples were freeze-dried for preservation and subsequent chemical analysis.

A range of base cations, trace metal(loid)s, and a nutrient (P), totaling 32 geochemical properties, were selected for analysis. Samples underwent acid (nitric and hydrochloric) and microwave digestion (Milestone MLS 1200 Mega digestion system, Milestone Inc., Shelton, CT, USA) following US EPA Method 3051A (USEPA, 2007). Pseudo-total element concentrations (in mg kg^{-1} of dry sediment) were then determined using inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500cx, Agilent Technologies, Santa Clara, CA, USA). Geochemical properties were chosen to represent a range of identified aquatic contaminants (Luoma and Rainbow, 2008) and we focused on arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se), zinc (Zn) and P, in correspondence with those elements with available sediment quality guideline (SQG) values (described further below) and for which there is concern from local communities. We also analyzed all samples for aluminum (Al) to determine if there were differences between sites, as Al is often used to standardize sediment-associated properties like metals and P for differences in particle size composition. As per Allen (1989), multiple blanks, standards (e.g. certified reference material; Till 3, NRC, 1995) and replicate samples were included in ICP-MS testing to ensure quality control of the sample analysis.

2.2.4. Un-mixing model

In order to determine the relative contributions of the four land uses to the suspended sediment collect at the downstream site (Q1), as part of the assessment of cumulative effects, we used a multivariate un-mixing model approach that has been used extensively to determine the sources of sediment at a sampling site in a range of environments, including agricultural, forested and urban (e.g. Carter et al., 2003; Collins et al., 1997; Koiter et al., 2013a; Mckinley et al., 2013; Owens et al., 2012; Walling et al., 1999). We used the suspended sediment samples collected from the different land use activities (agriculture, A1–A3; forestry, F1–F3; mining, M1–M3; and reference, R1–R2) to characterize the geochemical signal (or "fingerprint") from these land uses, and then compared these signals to the suspended sediment samples collected at the downstream sampling location at Q1. Given the large number of geochemical properties analyzed (i.e. 32), for the un-mixing model it was necessary to reduce these properties down to those that were able to distinguish best between the different land uses. This was achieved using a standard two-stage statistical process (Carter et al., 2003; Collins et al., 1997; Owens et al., 2012; Walling et al., 1999) whereby the Kruskal–Wallis H test and discriminant function analysis (DFA) were used to identify those properties that can best distinguish the four land uses (A, F, M and R). The best suite of properties that were statistically able to distinguish the sediment collected from the four land use categories then formed the "composite fingerprint" (Walling et al., 1999). This composite fingerprint was then used in an un-mixing model to determine the relative contributions of the four land uses to the sediment samples collected at Q1 using:

$$\sum_{i-1}^{n}\left\{\left(C_i-\left(\sum_{s=1}^{m}P_sS_{si}\right)\right)/C_i\right\}^2 \quad (1)$$

where n = number of geochemical properties comprising the optimum composite fingerprint (i.e. those properties that can statistically differentiate the four land uses); C_i = concentration of property (i) in sediment collected from each land use; m = number of land use categories (i.e. n = 4; A, F, M and R); P_s = the optimized percentage contribution from land use category (s); and S_{si} = mean concentration of geochemical property (i) in land use category (s).

It was assumed that the sum of all source contributions was equal to 100% and that the contribution from each source varied between 0% and 100%. We did not include correction factors for variations in organic matter content and particle size differences between samples from different source groups and between source materials and sediment samples, in keeping with recent thinking on this (Koiter et al., 2013b; Martínez-Carreras et al., 2010a; Smith and Blake, 2014). Multivariate un-mixing model analysis was undertaken using the Solver add-in with Microsoft Excel for Mac version 12.2.9. The model was given a maximum run time of 600 s in which to conduct 5000 iterations at a precision of 0.000001 and tolerance at 5%.

3. Results and discussion

3.1. Aluminum concentrations

There were no significant differences ($p > 0.05$) in the Al contents of the suspended sediment samples collected from agricultural, forestry, mining and reference sites; the average values for each of these land use types were ~23,900, 24,400, 21,900 and 26,200 mg kg^{-1},

Table 1
Comparison of mean suspended and bed sediment metal(loid) and P concentrations (mg kg^{-1} dry weight) for impacted land use activities (i.e. agriculture, forestry and mining) in the Quesnel River Basin (QRB) to: (i) reference sites in the QRB; (ii) regional background values; (iii) sediment quality guidelines (SQG) for Canada (LEL, lowest effect level; SEL, severe effect level); and (iv) values for the suspended sediment samples collected at the downstream site (Q1) which represents the cumulative effects from the QRB downstream of Quesnel Lake. Values in bold represent potentially toxic concentrations (i.e. >SEL). Standard error values are presented in parentheses. Values for the QRB are raw data uncorrected for particle size differences.

Element	Land use				Regional background level[a]	SQG[b]		Site Q1
	Forestry	Agriculture	Mining	Reference		LEL	SEL	
	Suspended sediment/bed sediment							
As	9 (±0.7)/8 (±0.3)	11 (±0.6)/12 (±1.1)	15 (±2.1)/18 (±3.8)	9 (±1.5)/7 (±1)	7 (±1.4)	6	33	11
Cd	0.8 (±0.26)/0.4 (±0.03)	0.7 (±0.06)/1 (±0.09)	0.6 (±0.09)/0.8 ± 0.12	0.5 (±0.09)/1 ± 0.12		0.6	10	0.4
Cr	67 (±4)/52 (±1.3)	61 (±2.2)/53 (±2.3)	48 (±3.1)/47 (±3.5)	63 (±4.3)/42 (±5.5)		26	110	55
Cu	**147 (±49)**/46 (±3.9)	78 (±9.2)/55 (±3.9)	**116 (±11)**/101 (±16)	92 (±17)/88 (±20)	35 (±4.9)	16	110	44
Hg	0.22 (±0.09)/0.09 (±0.01)	0.1 (±0.02)/0.08 (±0.01)	0.16 (±0.03)/0.14 (±0.03)	0.08 (±0.01)/0.08 (±0.01)		0.2	2	0.05
Mn	740 (±48)/671 (±66)	**3584 (±1737)**/**1106 (±184)**	**1570 (±195)**/806 (±112)	**1886 (±424)**/**1636 (±533)**	524 (±97)	460	1100	608
Ni	41 (±2.6)/42 (±2.4)	43 (±1.8)/48 (±2.7)	39 (±7.5)/39 (±3.3)	39 (±2.5)/40 (±1.1)	30 (±8.0)	16[c]	75[c]	39
Pb	22 (±6.8)/6 (±0.2)	14 (±1.5)/10 (±0.8)	10 (±0.7)/9 (±0.8)	10 (±0.9)/8 (±1.2)	2 (±0.4)	31	250	12
Se	2.0 (±0.32)/**3.4 (±0.30)**	1.7 (±0.07)/**4 (±0.24)**	**3.1 (±0.35)**/**4.3 (±0.38)**	1.5 (±0.07)/**3.5 (±0.17)**		–	2[d]	1.5
Zn	262 (±88)/81 (±4.9)	180 (±54)/97 (±5.5)	144 (±25)/93 (±6.7)	117 (±15)/96 (±15)	53 (±6.3)	120	820	106
P	1077 (±114)/1114 (±11)	896 (±18.5)/1038 (±15)	1217 (±89.3)/1137 (±82)	950 (±65)/1068 (±58)		600	2000	795
n	14/2	16/7	15/6	11/6				5

[a] Average values for sites in the QRB based on data in British Columbia Drainage Geochemical Atlas (Lett et al., 2008).
[b] SQG values developed for Ontario, Canada (Persaud et al., 1993) which are typically used (in full or slightly revised) in Canada (CCME, 1999) and BC (Nagpal et al., 2006).
[c] Jaagumagi (1992): LEL and SEL for Ni based on screening level concentration (SLC).
[d] Nagpal (2001).

respectively. Given the similarity in Al values between the different land use types, we did not correct the metal(loid) and P contents of the sediment samples for differences in Al and thus particle size composition, so as to avoid manipulation of raw data. This is particularly relevant when comparing to "background" and SQG values from other studies, as these are also provided as raw, uncorrected, values. Other workers (e.g. Koiter et al., 2013b; Martínez-Carreras et al., 2010a,b; Smith and Blake, 2014) have also suggested that caution needs to be taken when correcting sediment-associated element values for differences in particle size (and by inference Al contents) unless precise site-specific relations between particle size and/or Al and each element have been established; i.e. unnecessary manipulation of raw data should be avoided.

3.2. Comparisons to background and reference levels

It is important to compare the concentrations of sediment-associated metal(loid)s and nutrients measured in this study to those for background and reference levels so as to determine if, and to what degree, concentrations are elevated relative to what might be found naturally. Reference levels were based on the two QRB reference sites (R1 and R2), while background levels were based on comparisons to the BC drainage geochemical atlas database (Lett et al., 2008). For the study area, the sediment data in the geochemical atlas are based on stream sediment samples collected since 1976 from predominantly undisturbed locations, of which the <180 μm fraction was analyzed for elements using similar procedures to this study (i.e. hydrochloric and nitric acid digestion, and ICP-MS) (Lett et al., 2008), and thus the values are comparable. For the relevant elements in the geochemical atlas (i.e. As, Cu, Mn, Ni, Pb and Zn), the "background" values for the QRB are lower than those for the sediment samples collected from the study sites (Table 1). This may reflect differences in the way the samples were collected, as well as differences in sample locations, in addition to differences in the size fraction analyzed (63 μm vs 180 μm). The effect of the latter is likely to be increased concentrations associated with the finer sediment analyzed in this study. Once these effects are taken into account, the data in Table 1 suggest that the sediment samples collected in this study are elevated compared to background values, especially for the agricultural, forestry and mining sites.

Table 1 also compares metal(loid) and P values of suspended sediment for impacted sites (agriculture, forestry and mining) with reference sites for the QRB collected as part of this study. In most cases, average values for impacted sites are greater (or similar) than average values for the reference sites. In some cases, average values for impacted sites are significantly ($p < 0.05$) greater than reference sites, for example: (i) Mn for agricultural sites; (ii) As, Hg, P and Se for mining sites; and (iii) Cu, Hg, Pb and Zn for forestry sites. Both As and Se are by-products of the Cu and Ag mining processes (Azcue et al., 1995; Korte and Coulston, 1998; Luoma and Rainbow, 2008), which likely explains their elevated levels. In the case of forestry practices, Cu-rich local geology may have been disturbed and transported during forestry practices resulting in elevated levels for that land use (Hassan et al., 2005). There is also a link between elevated Zn in sediments in harvested watersheds due to Zn contributions from culverts used in logging road construction and from tire/break wear from heavy machinery and trucks (Christie and Fletcher, 1999), which may explain the elevated concentrations recorded in this study. The elevated levels of Mn associated with agriculture may reflect the addition of Mn-based fertilizers (Schulte and Kelling, 1999). There are also elevated levels of Hg at the forestry and mining sites, although values are still relatively low (see below). While Hg is not part of present mining operations in Canada, it is sometimes naturally present in ores and can be a by-product of mining activities or other land disturbance activities, such as forestry (Luoma and Rainbow, 2008).

3.3. Comparisons to national and provincial sediment quality guidelines (SQGs)

It is common practice to compare sediment-associated contaminant concentration data to recognized SQGs (CCME, 1999; Long and Morgan, 1991; Luoma and Rainbow, 2008; Persaud et al., 1993; Smith et al., 1996). Of the 32 geochemical elements analyzed through ICP-MS, only 11 were found in SQGs for Canada. Therefore, a condensed field of elements with consensus-based levels of toxicity was available. Values for As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Zn and P, for both suspended and bed sediment, were compared to these SQGs (Table 1).

In the case of suspended sediment samples (Table 1), generally, values are below upper threshold levels (e.g. severe effect level; SEL) for SQGs. Values of Cu for forestry and mining sites, Mn for agriculture, mining and reference sites, and Se for mining sites exceed SEL thresholds (in bold, Table 1) and are thus of concern. Furthermore, the Se levels for sites impacted by mining are within the range cited in the literature for contaminated environments (Luoma and Rainbow, 2008; Nagpal, 2001). It is important to emphasize that the values for the QRB presented in Table 1 represent mean values for each land use activity and that some individual samples were significantly greater than SEL levels, such as 801 mg kg^{-1} for Cu, 5.7 mg kg^{-1} for Se and 2509 mg kg^{-1} for P.

Mean bed sediment-associated contaminant concentrations, comparable to the suspended sediment values for each land use, are also presented in Table 1. As with the suspended sediment, most land use values are equal to or exceed reference site values. Of greatest interest are values which exceed upper SQG thresholds and in the case of SEL values, these include: Mn for reference (the average value for agriculture is essentially equal to the SEL value); and Se for agriculture, forestry, mining and reference (in bold, Table 1), with values being greatest for mining sites. The differences between the suspended sediment and channel bed sediment from the same site, may reflect differences in particle size between the two types of sediment, and differences in the nature of the sediment; the suspended sediment were integrated samples collected over periods of 1 month, whereas the channel bed sediment were instantaneous samples of resuspended sediment that were resident on the channel bed for unknown periods.

Although some values listed in Table 1 are relatively high and identified here as “of concern”, because they exceeded SQG upper thresholds, it should be recognized that such elevated values do not necessarily mean that these metal(loid)s and nutrient are toxic to aquatic ecosystems and detrimental to human health. The values presented represent pseudo-totals and studies (e.g. Carter et al., 2006; Stone and Droppo, 1996) have shown that a significant portion may not be bioavailable (i.e. not easily available for uptake or use by organisms). Thus, comparison of pseudo-total metal(loid)s and nutrient concentrations with SQGs should be treated with some caution.

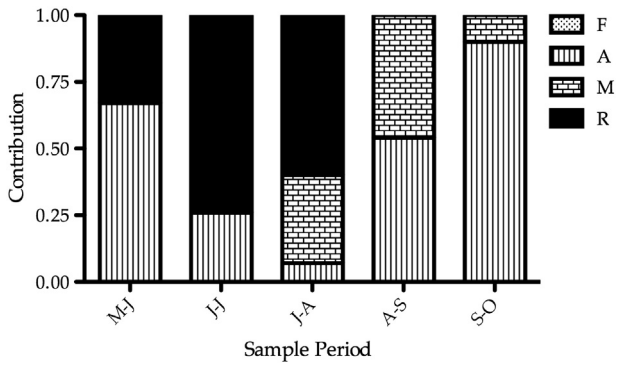

Fig. 3. Relative contributions (expressed as decimal fractions) to the Quesnel River Basin outlet (site Q1) from different land use types (i.e. F = forestry, A = agriculture, M = mining, and R = reference), estimated using a multivariate unmixing model-based approach. Sample periods are represented from May to October, 2008 (May–June (M–J), June–July (J–J), July–August (J–A), August–September (A–S), September–October (S–O)). Note: a suspended sediment sample was not collected from site Q1 during the April–May 2008 period.

3.4. Cumulative effects

Based on the above assessment for individual sub-basins, the following metal(loid)s and nutrient were influenced by the three “disturbance” land use activities (by comparison to the reference sites): (i) Mn by agriculture; (ii) Cu, Hg, Pb and Zn by forestry; and (iii) As, Hg, P and Se by mining. Similarly, SQGs (i.e. SEL) were exceeded for the suspended sediment samples in the case of: (i) Mn for agriculture; (ii) Cu for forestry; and (iii) Cu, Mn and Se for mining. It is therefore reasonable to assume that these three land use activities have influenced the metal(loid) and P content of fine-grained sediment (i.e. suspended and bed) in the QRB.

In order to determine if these land use activities had a cumulative effect on the sediment quality at the larger basin-scale, we compared the values for the land use activities based on representative sub-basins to those for sediment samples collected at the downstream sampling point which receives sediment from the entire QRB downstream of the lake (Table 1). Although the values for the "disturbance" land uses (i.e. agriculture, forestry and mining) are often greater than those for Q1, for all elements values for Q1 are not statistically ($p > 0.05$) greater than equivalent values for the reference sites (R1 and R2); although mean values were slightly greater than reference values for As and Pb. In some cases (e.g. Hg, Mn) values are significantly ($p < 0.05$) lower that the references sites. This suggests that although the disturbed land use activities influenced the metal(loid)s and P content of the streams which drain them, that at the basin scale their influence is not detectable at present. The reasons for this are probably due to the relative importance of the different land use activities in delivering sediment to the downstream sampling site.

To determine the relative contributions of the four land use activities (agriculture, forestry, mining and reference) to the sediment collected at Q1, we used an un-mixing model (Eq. (1)). Fig. 3 shows the relative contributions from the four main land use activities to the monthly time-integrated samples collected at Q1 determined using the unmixing model. From Fig. 3 it is clear that the main contributions are from reference (i.e. “natural” forest) and agricultural land uses. The former represents the land use with the least disturbance in the QRB, while agriculture is typically associated with the lowest levels of metal(loid) and P concentrations of the three disturbance land uses (Table 1). Consequently, the element values measured at Q1 reflect these two dominant land uses. The increased relative sediment contributions from mining in the later sampling periods (Fig. 3) are likely to reflect site-specific mining operations, such as excavation and discharges from tailings ponds. The relatively low contribution of forestry activities (i.e. harvesting and road construction) to the samples collected at site Q1 contrasts to the relatively high surface area that this land use occupies in the QRB (Fig. 2). However, erosion rates from land under forest harvesting can often be relatively low due to the implementation of riparian buffers strips, and improved forest harvesting practices and road maintenance in recent decades in response to better codes of practice and environmental legislation; for example, the construction of riparian buffer strips reduces the connectivity between hillslopes and river channels (Pike et al., 2010).

Although the data in Table 1 suggest that, at present, the cumulative effects of agriculture, forestry and mining activities are not detectable at the downstream Q1 site, there are some important caveats to consider. First is the fairly limited time period over which samples were collected; six months in 2008. Given the known temporal variability in suspended sediment quality (e.g. Carter et al., 2006), samples collected over additional years are required to provide a more comprehensive assessment. That said, given the replicate samples sites and multiple samples collected (both suspended and channel bed), the data

presented in Table 1 provide a good indication of present conditions. Second, while replicate samples were collected for each site and for each land use, ideally more representative sub-basins should be sampled; especially for reference sites. Third, some of the differences between metal(loid) and P values measured at Q1 compared to those for the agriculture, forestry and mining sites (i.e. Hg and Mn) suggest that there may be other sources that contribute sediment to Q1, such as bank erosion of material with low metal(loid) values. For the sub-basins, the sediment samples reflect the combined contribution of all upstream sources, including that derived from hillslope and channel bank erosion. However, erosion of channel banks along the main stem of the Quesnel River may have lower metal(loid) and P values and represent an unsampled source, and there may be other similar unsampled sources of sediment that we are unaware of. For example, we did not collect sediment samples to characterize inputs from small urban sources. This was because of the low population density and the small size of the communities in the basin, although the combined effect of lots of septic tanks, for example, could impact sediment quality, particularly in the case of P concentrations. However, the low metal(loid) and P concentrations measured at Q1 imply that such unsampled sources are not causing a detriment to sediment quality at Q1. Further work is required to check this.

In addition, it is important to recognize that there may be important sediment storage elements, such as floodplains, wetlands and small lakes, between the sub-basins and Q1 which may be buffering the chemical signal which need to be assessed. Thus it could be that the pulse of contaminated sediment derived from the disturbance activities in the basin have yet to reach the basin outlet. Several other studies (e. g. Kronvang et al., 2013; Lecce and Pavlowsky, 1997; Walling and Owens, 2003; Walling et al., 2003) have document that floodplains, for example, can store considerable amounts of sediment and associated chemicals, including metals and P. In such situations there can be a disconnection between upstream land use activities and the signals measured at downstream locations. If true, then an implication of this is that downstream monitoring sites may not always be suitable indicators of the level of upstream disturbance.

An important point to raise is that the information presented above relates to metal(loid) and P concentrations for sediment. We did not sample and analyze for the dissolved or colloidal fractions of the elements considered. It is possible that some elements may have undergone chemical transformations between: (i) sources and sub-basin sediment collection locations; and/or (ii) sub-basin sites (i.e. agriculture, forestry, mining and reference) and Q1 (cf. Koiter et al., 2013b). It is also possible that there may have been chemical transformations of the sediment while it was retained in the samplers. Further work is on-going to assess these issues more fully. To obtain a complete understanding of land use activities on water quality in a basin requires sampling of both water and sediment, and the determination of water–sediment–chemical interactions.

4. Conclusions

Fine-grained suspended and bed sediment samples were collected from streams draining different land use activities in the Quesnel River Basin (QRB). Metal(loid) and P contents for sediment collected from all land uses typically exceed geological background values. In addition, metal(loid) and P concentrations for impacted sites (i. e. agriculture, forestry and mining) were greater than for reference sites. This suggests that agriculture, forestry and mining are individually affecting the metal(loid) and P content of sediment in the rivers and streams that drain them. For several metal(loid)s, concentrations in suspended and channel bed sediment were greater than upper sediment quality guideline thresholds – such as Cu, Mn and Se for mining sites, Cu and Se for forestry sites, and Mn and Se for agriculture sites – and may be of concern in terms of water quality and effects on aquatic life. Selenium levels were greatest for sites impacted by mining.

Metal(loid) and P concentrations of sediment collected from the downstream site (Q1), where the Quesnel River is confluent with the Fraser River, were not significantly greater than values for the reference sites, and were typically lower than the values for the impacted sites. This suggests that the cumulative effects of agriculture, forestry and mining activities in the QRB are presently not having a measureable effect at the basin-scale; at least in terms of the determinands measured (i.e. select metal(loid)s and P). The lack of a cumulative effect at the basin-scale is thought to reflect: (i) the relatively recent occurrence of land use disturbances in this basin; (ii) the dominance of sediment contributions from natural forest (as determined from an un-mixing model); and (iii) the potential for storage of contaminants on floodplains and other storage elements between the locations of disturbance activities and the downstream sampling site.

The lack of a downstream signal of cumulative effects due to land use activities in this large basin could be interpreted in a variety of ways. It could suggest that the basin is resilient to such disturbance activities and could even accommodate an expansion of existing activities (e.g. more mines, agricultural intensification and urban growth) or additional new activities (e.g. oil and gas exploration). However, the lack of a signal could be misleading for several reasons, including intermediate storage effects. Studies have demonstrated that while storage elements like floodplains tend to be net sinks of sediments and associated chemicals, they can also become net sources given certain conditions, such as changes in hydro-meteorological conditions (e.g. increased streamflows, bank erosion, changing groundwater levels, hyporheic exchanges) and changes in redox conditions in the floodplain sediment. Further monitoring and sampling are required in the QRB, and other similar river basins and watersheds, to determine: (i) the extent of sediment and contaminant storage; and (ii) how the sources, stores and fluxes of sediments and contaminants may change in the future given anticipated changes in climate and the expected growth of land use activities in the basin.

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