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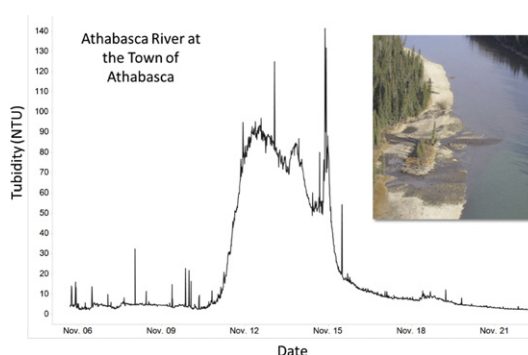
Initial environmental impacts of the Obed Mountain coal mine process water spill into the Athabasca River (Alberta, Canada)

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HIGHLIGHTS

- High inputs of suspended sediment, nutrients, metals, and PAHs due to a coal mine spill
- Dilution and elongation of the released plume decreased the threat to water quality
- Physical, biological, and chemical implications for the Athabasca River watershed

GRAPHICAL ABSTRACT



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ABSTRACT

On October 31, 2013, a catastrophic release of approximately 670,000 m³ of coal process water occurred as the result of the failure of the wall of a post-processing settling pond at the Obed Mountain Mine near Hinton, Alberta. A highly turbid plume entered the Athabasca River approximately 20 km from the mine, markedly altering the chemical composition of the Athabasca River as it flowed downstream. The released plume traveled approximately 1100 km downstream to the Peace-Athabasca Delta in approximately four weeks, and was tracked both visually and using real-time measures of river water turbidity within the Athabasca River. The plume initially contained high concentrations of nutrients (nitrogen and phosphorus), metals, and polycyclic aromatic hydrocarbons (PAHs); some Canadian Council of Ministers of the Environment (CCME) Guidelines were exceeded in the initial days after the spill. Subsequent characterization of the source material revealed elevated concentrations of both metals (arsenic, lead, mercury, selenium, and zinc) and PAHs (acenaphthene, fluorene, naphthalene, phenanthrene, and pyrene). While toxicity testing using the released material indicated a relatively low or short-lived acute risk to the aquatic environment, some of the water quality and sediment quality variables are known carcinogens and have the potential to exert negative long-term impacts.

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1. Introduction

The Athabasca River is a physically and ecologically diverse river that flows from its glaciated headwaters in Jasper National Park's Rocky Mountains to its terminus in the Peace-Athabasca Delta - a Ramsar Wetland of International Significance located within Wood Buffalo National Park - and Lake Athabasca, in the northeast corner of Alberta. Its basin (~159,000 km²) comprises almost one-fourth of Alberta's area, and it is the longest unregulated river in the Canadian Prairies. Water quality in the river ranges from ultra-oligotrophic in its mountainous headwaters to eutrophic at its lowland deltaic terminus. The river flows through a large number of ecozones, flowing from Alpine, Subalpine and Montane ecoregions, through the Boreal Foothills ecoregion, and entering the Boreal Mixedwood region, which comprises the lower ~75% of the basin (Bradford and Hanson, 1990). The Athabasca River is a source of water for many communities, businesses, agricultural, industrial, and private users, and supports a significant fishery in the region.

On the evening of October 31, 2013, a dyke failure of the Red/Green pit on the Obed Mountain Mine site in the Hinton region of Alberta, Canada (Fig. 1) released an estimated 670,000 m³ of coal slurry. Coal slurry, or process water, is the by-product of processing and cleaning coal that contains a mixture of water, sediment, and fine particulate coal (i.e., coal fines). Coal deposits and interbedded sediments can be enriched relative to background soils in a suite of organic and inorganic contaminants including hydrocarbons, heavy metals and coal-cleaning chemicals (e.g., acrylamide was used as a flocculant at the Obed mine) that may pose a threat to aquatic ecosystems (Gentzis and Goodarzi, 1997; Aken et al., 2014). The released slurry flowed downslope into the Main Tailings Pond, rapidly filling the pond to its capacity. The Main Tailings Pond then overflowed the coal slurry into a constructed spillway, after which it flowed downstream into Apetowun Creek, then Plante Creek and eventually into the Upper Athabasca River. The release caused substantial scouring of additional sediment and stream bank and was sufficiently powerful to break off or clear away mature pine trees and forests soils substantially beyond historical bank and riparian zone limits, in the upper ~5 km of the Apetowun Creek (Fig. S1). At the time of the spill, flows in the Athabasca River were near annual lows. Over the next two months, an elongating plume of noticeably turbid water, which eventually reached >100 km in length, flowed down to the length of the Athabasca River and made its way into the Peace-Athabasca Delta, ~1100 km downstream of the initial spill location.

The Obed mine release appears to have been the largest coal slurry spill in North American history, exceeding the magnitude of the 1972 Buffalo Creek flood in West Virginia (USA) that killed 125 people. A much larger spill of coal fly ash, a by-product of coal combustion, occurred in 2008 at the Tennessee Valley Authority's Kingston Fossil Plant in Roane County, Tennessee, USA when approximately 4,200,000 m³ of coal fly ash were released into the Emory River (Ruhl et al., 2009). Here we summarize the results of an emergency monitoring program implemented immediately after the Obed mine spill by the Government of Alberta's Department of Environment and Sustainable Resource Development (now Alberta Environment and Parks) and Coal Valley Resources Ltd., the owner of the Obed mine. The main objectives of this monitoring program were to both track and characterize the coal slurry as it flowed downstream and to perform an initial assessment of the potential environmental impacts resulting from the spill. Samples of water, sediment, soil, and spill material were collected from the Apetowun and Plante creeks, the Athabasca River, and from the mine itself, and were analyzed for a range of chemical parameters with special reference to compounds subject to regulatory limits or requirements. This initial assessment provides important context for understanding the long-term impacts of the spill on the receiving terrestrial and aquatic environments, and for informing the design of the long-term impacts assessment and monitoring program.

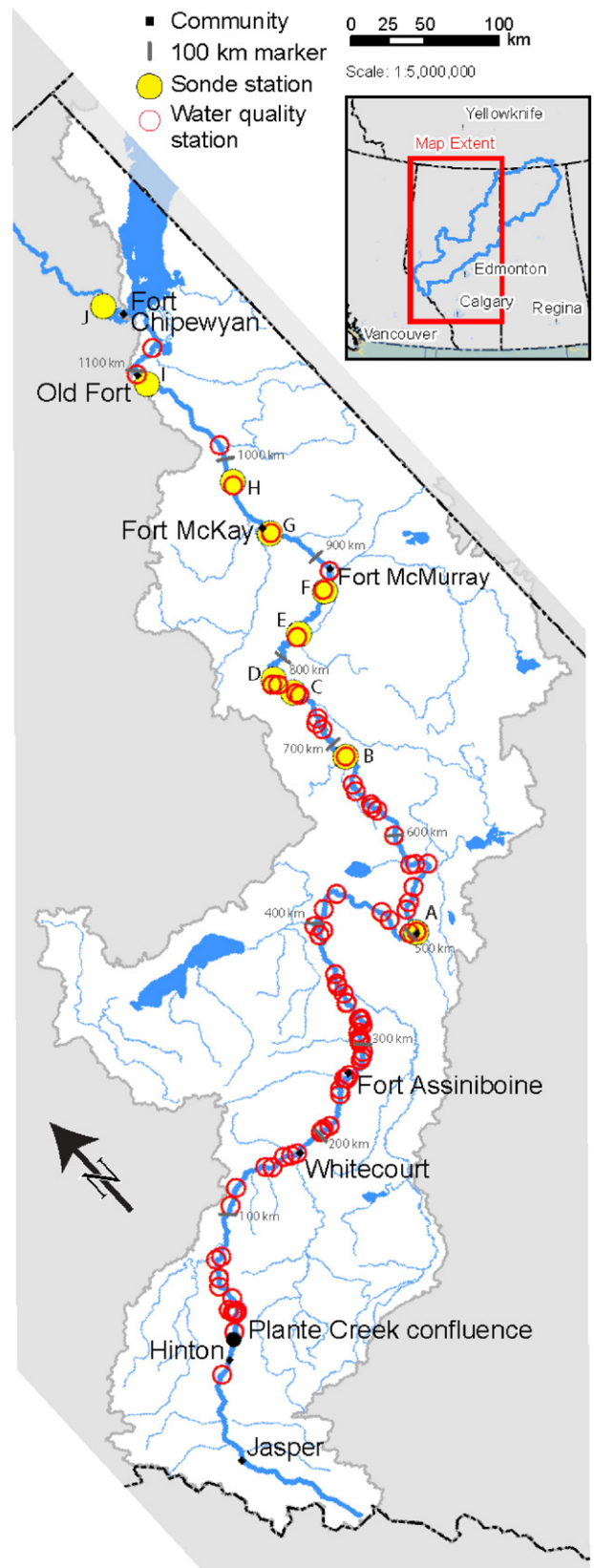


Fig. 1. Map of water quality sample collection locations and the sites where near real-time data sondes (labelled A–J) were deployed. Multi-probe sonde stations are indicated by filled yellow circles while water quality sample collection locations are indicated by open red circles.

2. Materials and methods

Real-time tracking of the released plume as it flowed down the length of the Athabasca River was of immediate concern after the spill. Initially, the plume was tracked visually from a helicopter; however, the formation of extensive river ice soon after the spill made visual tracking impossible after November 19, 2013. Therefore, automated measurements of water quality were collected using Hydrolab DS5 and YSI 6000 data sondes equipped with satellite or cellular-based telemetry systems. These were deployed at 10 stations located along the lower half of the Athabasca River (Fig. 1). Measurements of turbidity, conductivity, pH, and dissolved oxygen were collected and transmitted from these stations on 15-minute intervals.

A total of 107 water samples were collected from 76 locations between November 1 and December 18, 2013 (Fig. 1). Water samples were collected from both Plante Creek (<20 km from the mine) and the Athabasca River (>20 km from the mine). Measurements of turbidity, conductivity, pH, and dissolved oxygen were made during each sampling event using a hand-held Hydrolab DS5 data sonde, and on at least 85 other occasions (when water quality samples were not collected). The majority of water samples were collected from within the process-water plume itself ("in-plume" samples). Water quality samples were also collected from upstream of the plume's entry point into the Athabasca River ("upstream" samples), from locations downstream in advance of the plume's arrival ("pre-plume" samples), and after the passage of the plume ("post-plume" samples). Many stations, especially those located within the lower half of the Athabasca watershed, were sampled repeatedly to capture changes to water quality before (pre-plume), during (in-plume), and after (post-plume) the passage of the plume. Collectively, this sampling regime provides insight into the short-term impact of the spill on water quality within the Athabasca River.

Most water samples were analyzed for a broad suite of chemical parameters, including major ions, nutrients, metals, select species of polycyclic aromatic hydrocarbons (PAHs), and various other hydrocarbons and organic chemicals. Many parameters were measured in both filtered and unfiltered samples to yield dissolved and total concentrations. Samples were filtered in the laboratory within 24–48 h after collection for determination of dissolved parameters. Quality assurance/quality control (QA/QC) samples included trip and field blanks and duplicate samples collected at the same time and analyzed separately from field samples. Additional analytical details are available in the Supporting online material.

Composite sediment samples were collected after the spill from the source ponds (Red/Green Pit and Main Tailing Pond), depositional areas in the Athabasca River (MPS #4), upstream reference sites at Plante Creek (PLC-US) and the upper Athabasca River (ATR-US), and background soils. Sediment samples were analyzed for particle size, carbon content, total metals, and PAHs.

Here, we focus our discussion on those water and sediment quality variables that either have regulatory guidelines or that are known to be elevated in coal wash. Water chemistry data were screened against the most recent Canadian Council of Ministers of the Environmental (CCME) Water Quality Guidelines for the Protection of Aquatic Life (CCME, 1999). Sediment chemistry data were screened for CCME Interim Sediment Quality Guidelines for the Protection of Aquatic Life on the basis of acute toxicity (CCME, 2001). Chronic toxicity of PAHs in the released slurry that deposited in sediments along the river was also determined on the basis of equilibrium partitioning between sediments and sediment pore-water (Hansen et al., 2003). Standardized equilibrium partitioning sediment benchmark toxic units were calculated for sediments collected at a number of sites, and compared to values calculated for sediments previously collected at long-term monitoring sites along the Athabasca River. Finally, calculated PAH ratios provide semi-quantitative indicators of the nature or source of sediment PAH mixtures (Grimmer and Hildebrandt, 1975; Cretney et al., 1985; Wickstrom and Tolonen, 1987).

3. Results and discussion

3.1. Plume tracking and turbidity

Following the incident, the leading edge of the plume exhibited a general pattern of decreasing velocity as it traveled downstream (Fig. S2). Plume velocity was initially 3.1 km/h, decreased to approximately 1.5 km/h by the time it reached the Town of Athabasca, and further decreased to a plume velocity of <1 km/h between Fort McMurray and the river's terminus at the Athabasca Delta. This decrease in plume velocity is consistent with the generally decreasing gradient of the river as the watershed transitions from Rocky Mountain foothills to lowlands (Kellerhals et al., 1972) and is consistent with previous low flow (i.e., wintertime) time of travel estimates for the river (Van der Vinne and Andres, 1993).

The location of the plume was also tracked using a network of near real-time data sondes deployed at the Town of Athabasca and locations downstream (Fig. 1). At the Town of Athabasca (412 km downstream of the release point) the arrival of the plume increased turbidity within the Athabasca River from <5 to ~100 NTU in a 24-hour period (Fig. 2). However, the magnitude and rate of this increase in turbidity decreased as the plume traveled downstream. For example, at Boiler Rapids (807 km downstream) turbidity increased from <2 to ~8 NTU over a three-day period but it took nearly 6 days for turbidity to gradually decline to background levels. By the time the plume reached the Athabasca Delta on December 2 (1074 km downstream) an increase of only 2–3 NTU could be observed. Finally, a small (~1.5 NTU) increase in turbidity was noted in the Rivière des Rochers (~16 km downstream of Lake Athabasca's outflow) on December 7. This increase in turbidity within the Rivière des Rochers is imposed upon an otherwise steady decrease in turbidity within the river (Fig. S3). We therefore attribute this increase to the presence of the plume and evidence for it reaching and exiting Lake Athabasca.

The observed decrease in turbidity as the plume traveled downstream likely reflects three synergistic influences: (i) the settling of entrained particles along the river bed; (ii) the dilution of suspended sediment as additional tributaries flowed into the Athabasca River; and (iii) the lengthening of the plume itself as it moved downstream as the result of highly variable and turbulent river flow. In addition, the network of near real-time data sondes illustrates the difficulty in securing a representative grab sample for water quality chemical analysis (discussed further below). Finally, the timing of the spill (i.e., during low flow) carried important implications for the near real-time tracking of the released plume. Flow within the Athabasca River typically peaks between May and July as does suspended sediment load, which typically increases from ~5 to ~100 mg/L during the freshet at the town of Hinton (Fig. S4). If the Obed process water release were to have occurred during a period of elevated flow and sediment discharge, distinguishing the presence of the process water plume (either visually or using the sonde network) could have been difficult, if not impossible, in downstream reaches of the river.

The increase in turbidity described above resulted from the high suspended sediment load entrained within the plume. We estimate the solids content of the coal slurry released to be approximately 92,000 t of solid sediment (ref. 13 and see Supporting online material), which is <2% of the estimated total load of 6.4 million tonnes of sediment delivered to the Athabasca delta annually (Conly et al., 2002). The steady decrease in turbidity within the plume as it traveled downstream and the water quality results (summarized below) demonstrate that the immediate impacts related to this incident occurred in the areas nearest to and immediately downstream of the release point, rather than along the entire length of the river to Lake Athabasca.

3.2. Impacts on water quality

Upstream of the release, both Plante Creek and the Athabasca River were characterized by low concentrations of most organic and inorganic

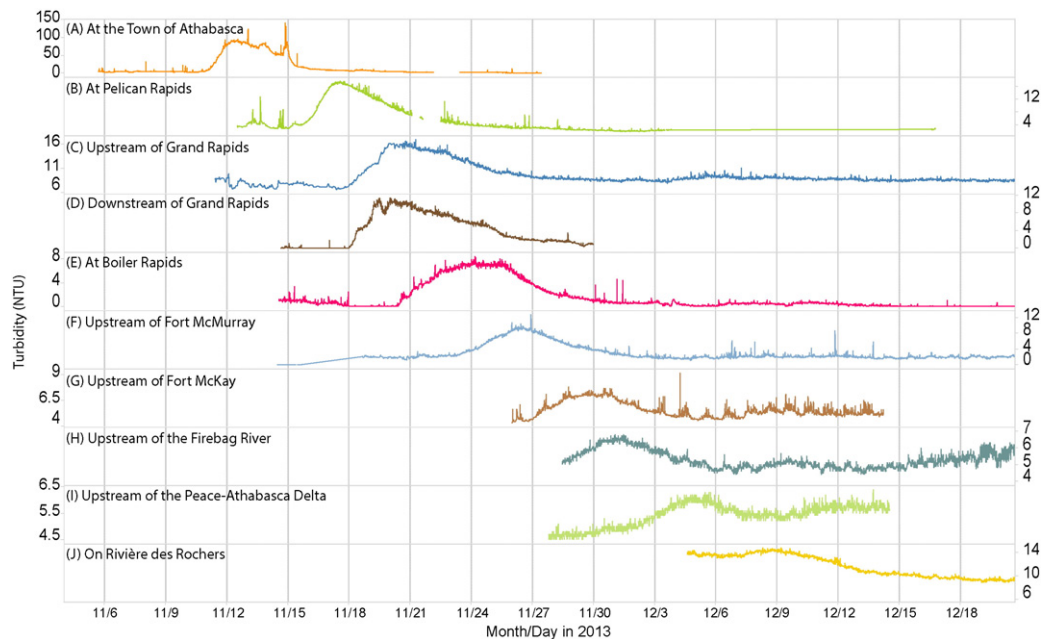


Fig. 2. Turbidity within the Athabasca River between early-November and mid-December 2013 as measured by the network of near real-time data sondes (note the different y-axis scales for each panel). Measurements were taken at 15-minute intervals.

constituents (Fig. 3). In contrast, within Plante Creek, total suspended solids (TSS) reached as high as 83,000 mg/L immediately after the spill. After flowing into the Athabasca River, TSS within the plume decreased to 9300 mg/L (49 km downstream). TSS concentrations within the plume continued to decline as the plume flowed downstream, reaching 760 mg/L near Fort Assiniboine (258 km downstream) and 76 mg/L at the town of Athabasca (546 km downstream) (Fig. 3). After ~850 km (immediately upstream of the City of Fort McMurray), TSS concentrations within the plume were indistinguishable from water samples collected pre- and post-plume (i.e., <5 mg/L). This is in contrast to turbidity results from the sonde network, which allowed for clear identification of the plume.

With the exception of a single sample from Plante Creek, both dissolved and total organic carbon (DOC and TOC) concentrations within the plume were similar to upstream waters (Fig. 3); however, the plume was enriched in both total nitrogen (TN; Plante Creek_{max}: 150 mg/L, Athabasca River_{max}: 15 mg/L) and total phosphorus (TP; Plante Creek_{max}: 13 mg/L, Athabasca River_{max}: 0.6 mg/L). In-plume concentrations of both TN and TP remained elevated until below the confluence with the Pembina River (326 km downstream), after which point within plume concentrations closely matched both pre- and post-plume. In contrast, nitrate and nitrite ($\text{NO}_3^- + \text{NO}_2^-$) concentrations in post-plume river water remained elevated relative to pre-plume samples, which were below the method detection limit. While the cause of this remains unclear, an increase in total dissolved phosphorus (TDP) is noted between 500 and 550 km (Fig. 3), which bracket the point-source effluent discharge from the Alberta-Pacific (ALPac) Forest Industries Inc. bleached kraft pulp mill. We therefore attribute this increase in TDP to the point source discharge of effluent from the mill, which is an important ecosystem stressor on the Athabasca River (Wrona et al., 1996; Scrimgeour and Chambers, 2000; Dubé et al., 2006).

In addition to suspended sediment and nutrients, the plume was also characterized by many total metal concentrations that were much higher than upstream waters (Figs. 3 and S5). For example, total Al reached as high as 29,300 mg/L within Plante Creek and 43,300 mg/L within the Athabasca River (suggesting concentrations in Plante Creek were already declining when it was initially sampled, post-spill). In contrast, upstream total Al concentrations were <10 mg/L and <3000 mg/L

in Plante Creek and the Athabasca River, respectively. However, the plume was not uniformly enriched in all metals analyzed. Concentrations of Mg, Ca, Sr, Mo, and Se were similar to upstream waters, with the exception of a single sample collected from Plante Creek immediately after the spill. The remaining metals measured were highest closest to the point of release, often an order-of-magnitude or more greater than upstream conditions. Total metal concentrations subsequently decreased rapidly as the plume flowed downstream. Yet some metals (e.g., Al, V) remained clearly elevated (relative to pre- and post-plume samples) for almost 1000 km downstream. For example, total V within the plume remained ~50% higher than in pre- and post-plume water samples for ~800 km. After travelling this distance (i.e., downstream of the City of Fort McMurray), the total concentration of many elements within the plume matched closely with samples collected before and after its passage. Thus, despite the clear presence of the plume as revealed by the near real-time measurements of turbidity (Fig. 2), total metal concentrations within the plume were roughly similar to ambient conditions downstream of the City of Fort McMurray.

The high total Al, As, Ba, Fe, Pb, Mn, Se, Ag, Th, U, and Zn concentrations observed closest to the mine also equalled or exceeded various CCME guidelines, including both the Maximum Acceptable Concentrations from the Canadian Drinking Water Guidelines and Protection of Aquatic Life Guidelines (Table S1). Almost all guideline exceedances were observed within 60 km of the release point and during first two weeks following the release.

In contrast to most total metals, most water samples collected from within the plume – with the exception of a first few initial samples – were characterized by dissolved metals concentrations that matched closely with upstream and pre-plume samples (Figs. 3 and S6). In addition, the concentration of many dissolved metals (other than selenium and uranium) tended to increase (albeit subtly) rather than decrease with distance downstream. For example, dissolved arsenic in the Athabasca River increased from ~0.1 µg/L to ~0.7 µg/L by ~1000 km downstream. For most dissolved metals, this downstream increase is relatively gradual; however, notable increases in dissolved potassium and copper occur after the confluence with the Pembina River (317 km), while increases in dissolved cadmium and nickel occurred downstream of the confluence of the Lesser Slave River with the Athabasca River (386 km). The Lesser Slave River receives effluent discharge

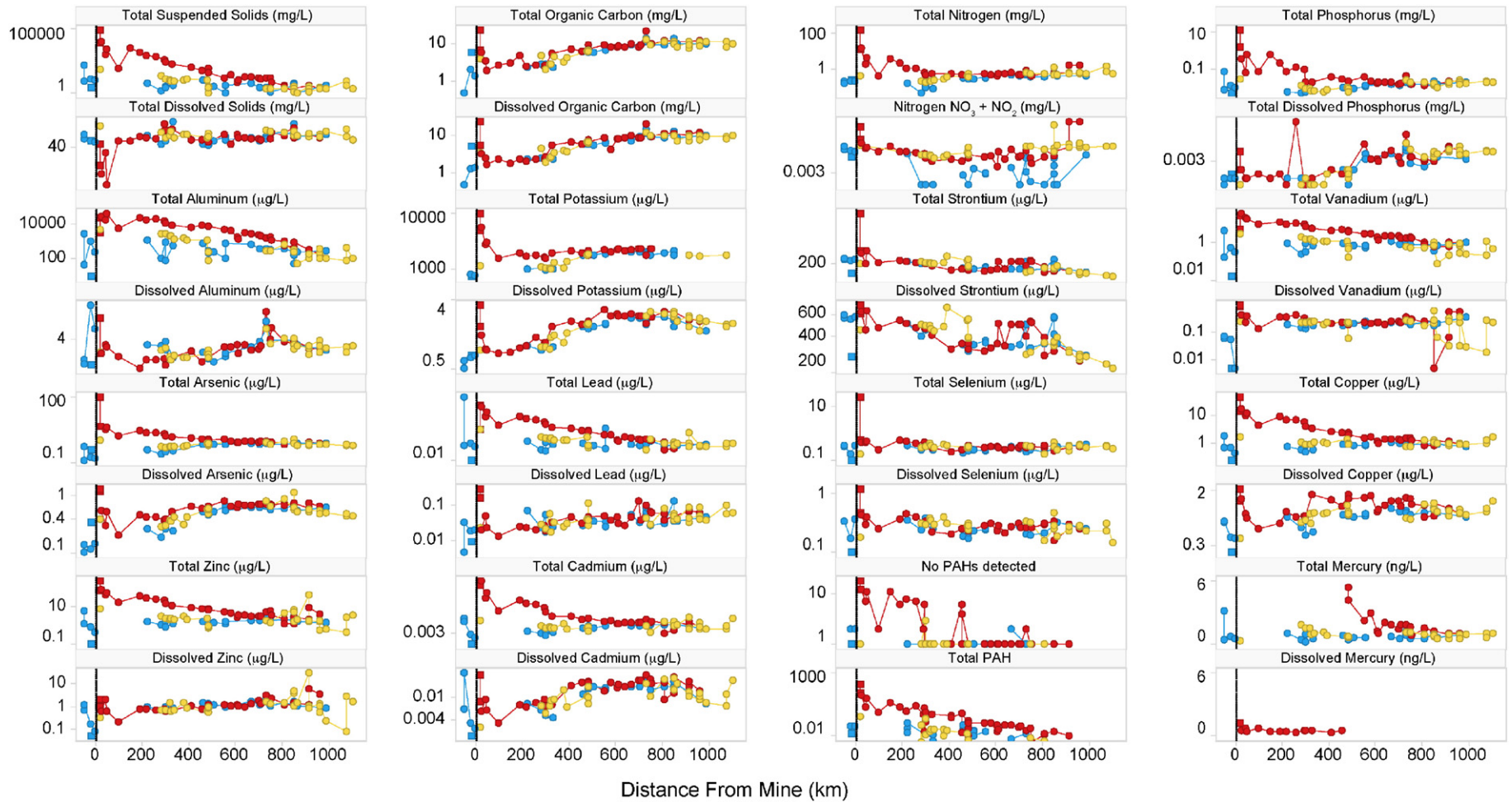


Fig. 3. Downstream profiles of various water quality parameters within Plante Creek (squares) and the Athabasca River (circles) plotted versus distance from the release point (0 km mark). Samples collected upstream of the release or downstream of the plume (pre-plume) are shown in blue, samples from within-plume samples in red, and samples from after the passage of the plume (post-plume) in yellow.

from a pulp mill operated by Slave Lake Pulp that is a known source of dissolved ions, nutrients, and metals (Stantec Consulting, 2013). Another increase in the dissolved concentration of many lithogenic (e.g., Li, B, Al) and siderophile (e.g., Co, B) elements occurred at ~730 km from the mine, where the Athabasca River and regional tributaries begin to incise lower Cretaceous-aged marine rocks downstream of the Grand Rapids (Fig. 1), again indicating local dissolved metal sources distinct from the plume. Collectively, these observations suggest that the spill exerted little influence over dissolved element concentrations within the Athabasca River.

Unfiltered (i.e., total) Hg concentrations were <1 ng/L in upstream water, which is typical for this region of the Athabasca River during periods of low flow (C.A. Cooke, unpublished data). Unfortunately, Hg samples collected from within the released plume were filtered at the analytical laboratory (Alberta Innovates - Technology Futures in Vegreville, AB) prior to analysis and without our knowledge. Thus only dissolved Hg data are available for samples collected in the initial days after the spill (i.e., samples collected within ~450 km of the mine). Dissolved Hg concentrations were similar to upstream water (<1 ng/L), suggesting the plume contained little dissolved Hg. In contrast to samples collected in upstream reaches, in-plume samples collected at the Town of Athabasca (and locations downstream) were not filtered. Total Hg concentrations in these unfiltered water samples were higher (~5 ng/L) than pre- and post-plume samples (<1 ng/L). Total Hg concentrations then decreased to pre- and post-plume concentrations by ~800 km downstream of the spill. While incomplete, these data suggest that the plume was enriched in particulate (but not dissolved) Hg, as observed for many of the other metals measured.

It is important to note that despite elevated total metal concentrations within the plume, river waters quickly returned to pre-plume concentrations. Post-plume samples were collected from locations along the length of the river and typically returned to pre-plume condition within a few days after the passage of the plume. This suggests that any short-term or acute impacts from the spill was transient; however, longer-term or chronic impacts will depend upon the fate of sediment deposited along the riverbed, especially in reaches immediately downstream of Plante Creek.

In addition to particulate-bound metals, the released plume was enriched in PAHs. The number of PAHs detected in upstream waters was low ($n \leq 2$ of 53 parent and alkylated species monitored), and total PAH concentrations (the sum of all analyzed PAHs within a sample; \sum PAH) were <0.1 $\mu\text{g/L}$ (Fig. 3). In contrast, 18 PAH species were detected and \sum PAH reached 120 $\mu\text{g/L}$ within Plante Creek immediately after the spill. The number and total concentration of PAH species detected in samples decreased to 13 and 17 $\mu\text{g/L}$, respectively, after the plume merged with the Athabasca River, with retene, a diagenic compound associated with biogenic precursors like plant terpenes (Meyers and Ishiwatari, 1993), exhibiting the highest concentration of all the PAHs detected. The number of PAHs detected was higher than upstream (i.e., $n \geq 9$ of 53) in all but two samples collected within 350 km of the release point. Total PAH concentrations decreased more rapidly, reaching <3 $\mu\text{g/L}$ by 250 km downstream, and essentially background concentrations (as defined by pre- and post-plume samples) by ~550 km downstream. Retene continued to be detected in all but three samples collected within the plume, in contrast to most pre- and post-plume samples within which all PAHs quantified (including retene) were below the method detection limit (0.01 $\mu\text{g/L}$). \sum PAH declined near-exponentially with river distance, reaching the method detection limit by ~800 km.

As with the total metals results, several PAH species in water exceeded CCME guidelines (Table S1). Anthracene, benzo(a)anthracene, benzo(a)pyrene, fluoranthene, and pyrene all exceeded CCME Protection of Aquatic Life guidelines in the initial days after the spill. Some of these PAHs are known to be carcinogenic, making their presence, concentrations, and fate in aquatic ecosystems of public concern (Atwater and Mavinic, 1985; Chung and King, 1999).

3.3. Impacts on sediment quality

The plume contained material from the mine's water storage pond (the Red/Green Pit) and the Main Tailings Pond (MTP). The ponds were used to store process and surface waters, soils and coal fines liberated during the coal washing process, and trace amounts of coal ash from the coal-fired finishing dryers. As the release material flowed down Apetowun Creek and into Plante Creek and the Athabasca River, it eroded and entrained natural sediments within the watershed in the plume. Nearly all of this material eventually deposited along the bed of the Athabasca River. Surveys of the Athabasca riverbed conducted in May 2014 (i.e., prior to the following year's freshet; see Electronic supplement) indicated that the bulk of the release material deposited in the Athabasca River was restricted to areas of laminar flow (i.e., "run" and "pool" habitats, in contrast to "riffle" habitats) between the creek mouth and ~7 km downstream. Downstream of this point, river gradient and water velocities increase, resulting in predominantly riffle/rapid river meso-habitats.

A summary comparison of the physical properties and chemical composition of source material, local sediments in the Apetowun watershed, upstream Athabasca River bed sediment, and deposited spill material is provided in Table 1. Source ponds and spill materials were generally finer than background soils and upstream river sediments, while total carbon content was higher in source ponds (19%) and spill materials (10%) than in reference sediments from Plante Creek (2%) and the Athabasca River (6%). The source and spill materials also contained elevated concentrations of Al, As, Ba, Be, Cu, Pb, Hg, Se, U, and Zn relative to background and reference sediments. Of these metals, only As (in source ponds, spill material, and background sediments) was present at concentrations that exceeded the CCME interim sediment quality guideline of 5.9 mg/kg, and no metals exceeded their probable effects level (PEL). Source and spill materials also contained elevated concentrations of a number of PAHs, compared to background and reference sediments. Of these elevated PAHs, concentrations of anthracene, acenaphthene, fluorene (spill material only), naphthalene (source material only), phenanthrene, 2-methylnaphthalene, fluoranthene, benzo(a)anthracene, and pyrene were measured at a concentration that exceeded the CCME interim sediment quality guidelines (Table S1); however, no PAHs exceeded their PEL. Several parent and alkylated PAHs – including anthracene, fluorene, naphthalene, pyrene and benzo(a)anthracene – are known to occur naturally in Canadian coal deposits and are often exposed to the environment through mining operations (NRCC, 1983; Atwater and Mavinic, 1985).

3.4. Potential effects on aquatic life

The water quality results summarized above demonstrate the potential for both direct and indirect effects to aquatic life, including exceedances to published guidelines for the protection of aquatic life. The most notable pathway was the physical smothering and scouring effects of the released material on periphyton, benthic invertebrates and local fish communities. These impacts were the most acute within the upper reaches of the Apetowun and Plante Creeks, where the physical impact of the release was the most pronounced (Fig. S1). The release of plume contained sufficient energy to scour the entire channel bed and riparian areas of the upper 5 km of Apetowun Creek. At approximately 5 km downstream, Apetowun Creek makes an abrupt westerly turn, which caused the initial release of material to crest its stream banks and dissipate much of its energy into the surrounding forest. The most frequently reported potential effects of large scale spills on periphyton include the reduction in available stable substrate for organisms to adhere due to smothering, abrasion of exposed periphyton by high levels of suspended solids, and eventually dislodgement by increased flows (Biggs, 1996; Azim et al., 2005). These effects, along with effects of elevated concentrations of toxic metals and organics,

Table 1
Summary statistics for sediment samples collected from the source (Red-Green Pit and Main Tailings Pond), unimpacted (background) soils, deposited spill material (Athabasca River), and reference sediments (Plante Creek and the Athabasca River). Parameters with varying degrees of detection limits (DL) were changed to the highest reported DL, while values below the DL were changed to the DL for the calculation of summary statistics. Concentrations are expressed on a dry weight basis.

Sediment quality parameter	Source material			Background soils			Spill material			Reference sediments		
	Avg (mg/kg)	STD	n	Avg (mg/kg)	STD	n	Avg (mg/kg)	STD	n	Avg (mg/kg)	STD	n
Aluminium	9453	2434	8	10,322	5188	9	11,170	2932	4	5583	1999	4
Arsenic	8	2	8	5	4	9	6	1	4	5	2	5
Cadmium	0.24	0.04	8	0.80	1.11	9	0.27	0.05	4	0.2	0.2	5
Chromium	10	8	8	17	7	9	11	2	4	9	3	5
Copper	13	7	8	13	7	9	14	3	4	6	3	5
Lead	14	2	8	8	4	9	14	4	4	5	1	5
Mercury	0.071	0.014	9	0.055	0.061	9	0.069	0.004	3	0.020	0.003	4
Selenium	0.49	0.09	8	0.27	0.23	9	0.50	0.11	4	0.25	0.10	4
Zinc	58	13	8	54	31	9	59	10	4	32	9	5
2-Methylnaphthalene	–	–	0	0.007	0.004	9	0.071	0.040	3	0.021	0.002	4
Acenaphthene	0.03	0.01	8	<0.009	0.01	9	0.02	0.01	3	<0.01	0.01	5
Acenaphthylene	<0.005	0.000	8	<0.009	0.002	9	<0.01	0.00	3	<0.01	0.00	5
Anthracene	0.038	0.017	8	<0.009	0.002	9	0.060	0.026	3	0.010	0.004	5
Benzo(a)anthracene	<0.005	0.000	8	<0.009	0.002	9	0.031	0.019	3	<0.01	0.00	5
Benzo(a)pyrene	<0.005	0.000	8	<0.018	0.004	9	0.012	0.002	3	<0.01	0.00	5
Chrysene	<0.005	0.000	8	<0.009	0.002	9	0.013	0.0023	3	<0.01	0.00	5
Dibenz(a,h)anthracene	<0.005	0.000	8	<0.009	0.002	9	<0.01	0.00	3	<0.01	0.00	5
Fluoranthene	0.066	0.052	8	<0.009	0.002	9	0.087	0.055	3	<0.01	0.00	5
Fluorene	0.059	0.049	8	<0.009	0.002	9	0.041	0.026	3	<0.01	0.00	5
Naphthalene	0.094	0.054	8	0.007	0.003	9	<0.05	0.00	3	<0.05	0.02	5
Phenanthrene	0.142	0.069	8	0.009	0.005	9	0.08	0.04	3	0.01	0.01	5
Pyrene	0.095	0.039	8	<0.009	0.002	9	0.09	0.06	3	<0.01	0.00	5

can result in reduced biomass and species richness and changes in community composition (Resh, 2008; Walsh and Wepener, 2009).

To assess the potential for impairment to the benthic environment, we calculated the chronic sum equilibrium-partitioning sediment benchmark toxic unit (Σ ESBTU) (Hansen et al., 2003) for sediments collected in November 2013 from both Plante Creek and the Athabasca River (see Electronic supplement). We also calculated the Σ ESBTU of sediments collected during the fall of 2004 from the Athabasca River as part of Alberta Environment and Sustainable Resource Development's long-term river monitoring program. A Σ ESBTU of ≤ 1.0 is considered acceptable for the protection of benthic invertebrates. The Σ ESBTU values for all sediment samples were very low (< 0.02) for all sites sampled during both periods (Table S2). These Σ ESBTUs do not consider the antagonistic, additive, or synergistic effects of other sediment contaminants in combination with PAHs, or the potential for bioaccumulation and trophic transfer of PAHs or other contaminants to aquatic life, wildlife or humans. They also do not take into effect the potential increase in toxicity of PAH body burdens in aquatic invertebrates in shallow waters with high UV radiation transparency, such as may be present in the Upper Athabasca River during mid- to late-summer. It also should be noted that, despite the clear presence of high coal content in Plante Creek and the Athabasca River immediately downstream of their confluence, based on total organic carbon contents of $> 17\%$, Σ ESBTUs are still very low at these two sites, and indistinguishable from other sites upstream and downstream on the Athabasca River. The United States Environmental Protection Agency has also highlighted the likely effect of high sediment coal content in reducing PAH partitioning, and the values calculated here seem to at least confirm relatively low PAH partitioning, if not reductions in it (Hansen et al., 2003).

The ratios of PAHs used to qualify the nature of PAH mixtures indicate a stronger coal signal in Plante Creek and immediately downstream of its confluence with the Athabasca River, as expected. For example, Indeno[1,2,3-cd]pyrene:[Indeno[1,2,3-cd]pyrene + Benzo(g,h,i)pyrene] ratios of 0.52 at both sites (Table S2) are much closer to the signal for coal soot (0.56) than for gasoline emissions (0.18) (Cretney et al., 1985). However, the Fluoranthene:(Fluoranthene + Pyrene) ratios at most sites are intermediate to those of hard coal emissions (0.58) and automobile emissions (0.43), or perhaps closer to a signal expected of automobile emissions (Grimmer and Hildebrandt, 1975). Concentrations of perylene, a

biogenic compound indicative of natural sources, were very low in Plante Creek and the Upper Athabasca River, as would be expected in sediments dominated by coal tailings (Wickstrom and Tolonen, 1987), and the signature for biogenic sources increased in prevalence at the town of Athabasca and further downstream, consistent with the conclusion that most suspended sediments in the slurry were deposited in the upper reaches of the river.

Although source and spill materials contained elevated concentrations of several metals and PAHs, some of which exceeded applicable guidelines, concentrations were below levels likely to cause short-term adverse toxicological effects to aquatic organisms. These results were supported by initial toxicity tests conducted on spill material samples. Rainbow trout exposed to waters collected on November 2, 2013 from the Main Tailings Pond, lower Plante Creek and Athabasca River downstream of Plante Creek exhibited 100%, 80%, and 100% survival, respectively (i.e., 96-h LC50 $> 100\%$) (CVRI, 2014). Therefore, undiluted effluent taken from the main tailings pond appears to have had little or no acute toxicity to rainbow trout, including relative to water from Plante Creek and Athabasca River. However, these short-term acute toxicity tests would not account for the likely immediate and toxic impacts of high concentrations of suspended sediments on fish or invertebrate health, or chronic effects of habitat disruption or contaminant deposition.

The on-going long-term monitoring program currently includes assessing trends and patterns in water and sediment quality, benthic algae and invertebrates, fish and fish habitat and fish tissue chemistry, and examining a number of potential pathways of effects. Descriptions of monitoring results and potential impacts in different components in the aquatic ecosystem will be presented in subsequent papers.

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Appendix A. Supplementary data

Supporting information includes: additional methods and materials; Tables S1–S4; and Figs. S1–S6. Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2016.03.058>.

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