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Distribution of Contaminated Soils Along Transversal and Longitudinal Gradients in Dynamic Fluvial Environment (Southern Québec, Canada)

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ABSTRACT: This research combines a hydrological and pedological approach to better understand the spatial distribution of contaminated soils along the Massawippi River (southern Québec, Canada). This river crosses through former mines, which were some of the largest copper mining areas in North America from 1865 to 1939. To determine the spatial distribution and concentration of the metal elements, soil samples were taken in each flood recurrence zone appearing on official flood zone maps. The maximum values obtained for Cu and Pb are 380 and 200 mg kg⁻¹, respectively, for the soils in the frequent flood zones (FFzs), while the values for soils in the moderate flood zones (MFzs) range from 700 to 540 (Cu) and 580 to 460 mg kg⁻¹ (Pb). Contamination extends through several kilometers of the former mining sites (Eustis and Capleton), and concentration of metals in alluvial soils is slightly higher near the mine sites.

KEYWORDS: alluvial soils, contamination, dispersion of pollutants, floods, metal elements

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Introduction

The spatial distribution of pollutants along riverbanks may be complex as a result of hydrological and environmental variations in relation to the drainage basin. It often becomes necessary to consider different hydrological and pedological parameters that may provide additional data on the variability of the sites that run along the river corridor.^{1–3} Erosion and sedimentation are also crucial to understanding the spatial distribution of pollutants along riverbanks.^{4–7} During heavy floods, for instance, sediments (contaminated or not) may be transported downstream and redeposited further away on the riverbanks. It is known that floodplains can constitute temporary or permanent sedimentary reservoirs, thus potentially containing pollutants,^{8–10} and these can be remobilized by the current and successive floods.^{11,12} Sediment storage may depend significantly on river characteristics such as the configuration of the river channel, the depth of the river bed, flow velocity, microtopography, and flood frequency.^{13–15} The analysis of the hydrogeomorphological characteristics can enhance our understanding of sedimentation processes and the dynamics of river basin systems.^{1,2} Alluvial soils can also be sensitive indicators of change in the fluvial environment and provide relatively accurate information on the spatial distribution of nutrients, agricultural

pollution, or other contaminants.^{16–18} It is therefore important to consider both pedological and hydrological parameters in order to recognize phases of enhanced sediment accumulation in floodplain systems.^{19–21}

In floodplain soils contaminated by heavy metals, the solubility level can vary depending on the soil and sedimentary conditions of the sites, and several metals are not highly mobile in the mineral matrix.^{22,23} Contrary to organic compounds, metals are not biodegradable and can accumulate and persist in the river ecosystem.^{9,24} It is, therefore, not uncommon to find very high concentrations of metals in the riverbanks even several decades after the closure of industrial or mining sites.^{7,12} It is also known that sediment particles with a fine texture, such as clay, have a strong capacity to attach polluting particles and can play a key role in the storage of pollutants or micropollutants along the riverbanks.¹⁸ The presence of organic matter, often associated with clayey colloids, can also result in the retention and absorption of metals in the contaminated soils.^{25–28} These elements attach themselves firmly to the clay as well as to humic compounds and have little mobility, as a result of which they are not easily carried off by leaching. Remobilization is, therefore, required by the current and floods to dislodge the pollutants contained in the riverbanks. Frequent overflowing and

successive floods naturally have a direct impact on the transport and distribution of contaminants along the river corridor.

It is important to take into account the frequency of the floods involved in river system dynamics, particularly with respect to the distribution of contaminants along the riverbanks and in the soil profiles.^{25,29} It is also necessary to consider variations in flow (low or high) and flood frequency based on the new hydroclimatic conditions associated with climate change. The variations in the hydroclimatic characteristics associated with climate change^{30,31} may affect the hydrological patterns that impact sedimentological processes and soil properties. For instance, a certain sedimentary consistency in the soil profiles and low variability in soil properties can be indicators of high flood frequency.^{19,21,32}

The aim of this study is to measure the concentration of metal elements (eg, cadmium, copper, nickel, lead, and zinc) in the floodplain soils with their spatial distribution based on the various flood recurrence zones identified along the Massawippi River (southern Québec). This river passes

through old mining areas (Albert–Capleton–Eustis Complex) largely exploited during several decades (1865–1939) and were abandoned, leaving many mining debris along the riverbanks.³³ The former mining parks (Eustis site) cover a total surface area of 15 ha along the Massawippi River.³⁴ This river is also subject to frequent flooding, which favors a remobilization of contaminated sediment and their transport further downstream.

Regional Setting

The Massawippi River is a major tributary of the Saint-François River watershed (total area of 10,228 km²) located in southern Québec. The Massawippi River originates from Massawippi Lake, which covers an area of 608 km², and is part of a major physiographic region, ie, forming part of the Appalachian Mountains. The river flows southeast to northeast, ending in the downstream part of the Saint-François River at Lennoxville. In addition to the former Eustis and Capleton mining sites along the Massawippi River (Fig. 1), there are also

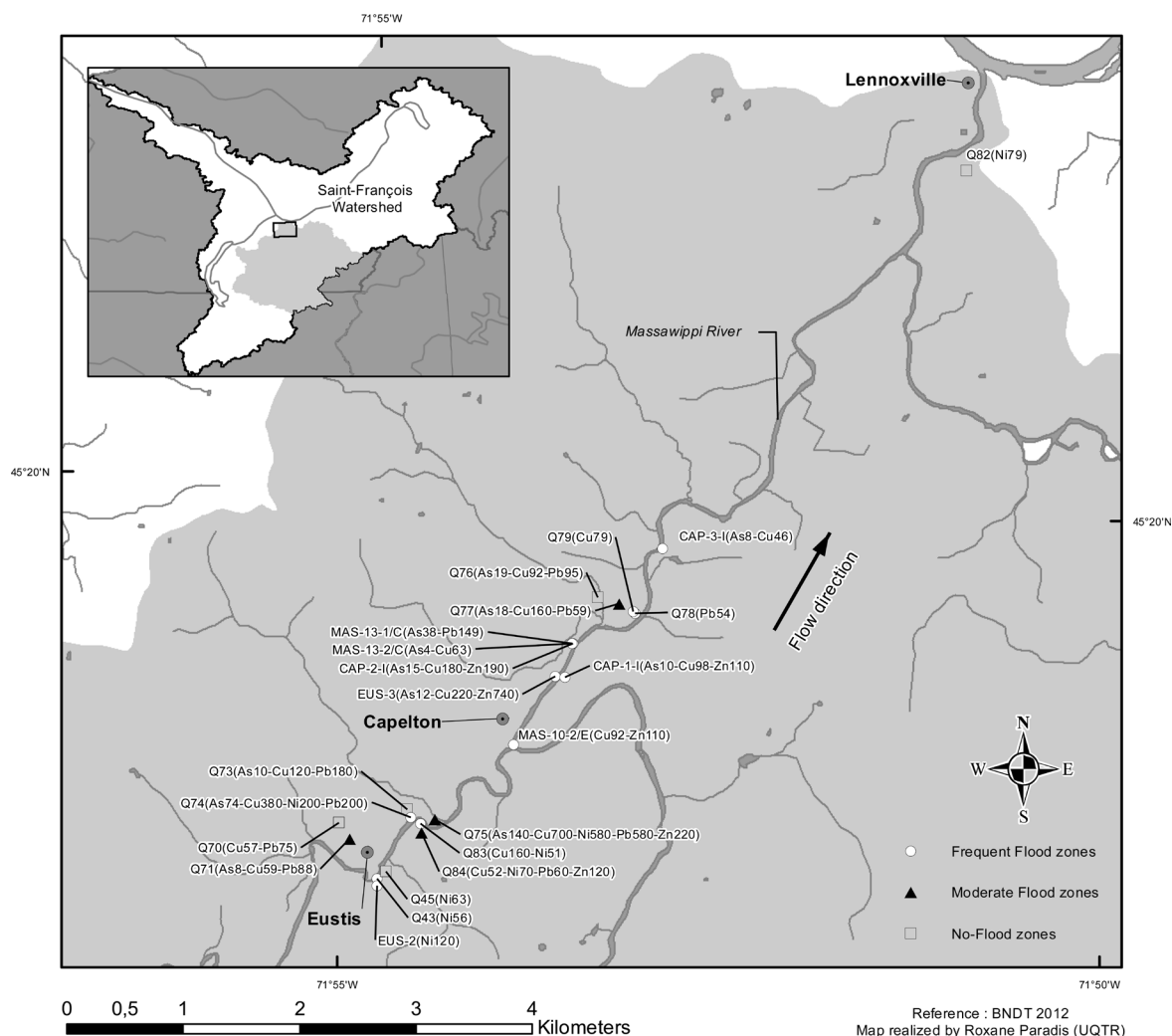


Figure 1. Location of the sampling sites with the highest concentrations of heavy metals (mg kg⁻¹) according to the different zones (FFz, MFz, and NFz) (Massawippi River, southern Québec). The former mining sites (Eustis and Capleton) are located in the middle section of the Massawippi River.

woodlands mainly consisting of ash stands (*Fraxinus pennsylvanica* Marsh. and *Fraxinus americana* L.), wildland and farmland mainly consisting of corn crops. The surficial deposits along the Massawippi River mainly consist of recent fluvial deposits (>1 m thick) or glacial and glaciolacustrine deposits.³³ Based on a compilation of digital data,^{35,36} the banks of the Massawippi River are calculated to extend over a total of 37 km (right and left banks), and fluvial deposits account for 66% of the channel banks in this area.³⁷ Upstream of the Eustis mine, the riverbanks are low and rocky, and downstream, they are characterized by low-relief alluvial floodplains (1–2 m in height) made up of fine sediments (Table 1).

Finally, in terms of climate, the entire catchment area is characterized by abundant rainfall during a good part of the year (total precipitation of 1107 mm/year), with annual temperatures ranging from –10.2° to 19.7°C (1981–2010), with a mean annual temperature of 6.3°C (station no. 7022160).³⁸ The mean annual discharge registered from 1952 to 2013 in the Massawippi River is 10.7 m³ s^{–1} (Table 1/gauging station no. 030220), and the peak discharge is 135.3 m³ s^{–1}. Gauging station (Fig. 2).³⁹ An increase in flooding was observed from 1970 to 2000 in the Massawippi River basin, including an increase in summer and fall floods.^{20,21} The increase in the flood rate over the last few decades is attributed to an increase in rainfall, thus leading to a marked increase in river water flow throughout the Massawippi and Saint-François watershed basins.

The government reports mentioned that the waters of the Massawippi River were contaminated by agricultural, industrial, or mining wastes, though the situation has improved since the 1990s.^{40,41} The government report by Berryman et al³³ indicates that the waters of the Massawippi River were contaminated by heavy metals over several kilometers as a result of the mine tailing sites at the Eustis site, which reduce water quality and hinder benthic fauna. The drainage water from the former mine tailings is highly acidic, which favors the leaching of heavy metals such as copper, iron, and zinc. The Eustis and Capel streams that also receive the runoff from several mine tailing sites are thus highly contaminated and contribute substantially to the concentration of metals discharged into the Massawippi River.^{33,42} Even several years after the closure of the Eustis mine, traces of metals are still found in contaminated layers along several kilometers of riverbanks, indicating the presence of persistent inorganic contaminants in the fluvial environment.^{43,44} The latest government report on the quality of the surface water of Québec's main rivers⁴¹ reveals that water quality has substantially improved since the last follow-up in 2002, although some areas still present a problem, especially with respect to the bacteriological contaminants originating from the contamination of urban and agricultural effluent. In the Massawippi River section, water quality is considered good to satisfactory based on the last report (pp. 14–15).⁴¹ It is only recently (2007–2009) that rehabilitation work was undertaken at the Eustis site by the Québec department of natural resources.³⁴

Table 1. Hydrogeomorphological characteristics of the Massawippi River (Southern Québec).

MEAN CHANNEL WIDTH (m) ^a	MEAN CHANNEL DEPTH (m)	MEAN CHANNEL HEIGHT (m)	MATERIALS OF BED RIVER	MATERIALS OF RIVERBANK	GAUGING STATION NUMBER	LOCATION	PERIOD RECORDED	MEAN ANNUAL DISCHARGE (m ³ /s)	MAXIMUM ANNUAL DISCHARGE (m ³ /s)	PEAK DISCHARGE (m ³ /s)	FLOOD EVENTS (1900–2013)
30	2.2	1.50–2.50	Sand and gravel (near Eustis, Capelton)	Sandy loam, silt loam	030220	45°17'04"N 71°57'46"W	1952–2013	10.7	74.5	135.3	30 ^b
36	2.8	1.50–2.50	Sand, silt and gravel (Downstream Capelton)	Fine sand, silt loam and sandy loam	030231	45°22'00"N 71°51'01"W	1964–1982	143.9	146.3	147.8	–

Notes: ^aTotal length of the Massawippi River: 17.6 km. ^bReturn period: 3.76 yrs.^{20,21,39}

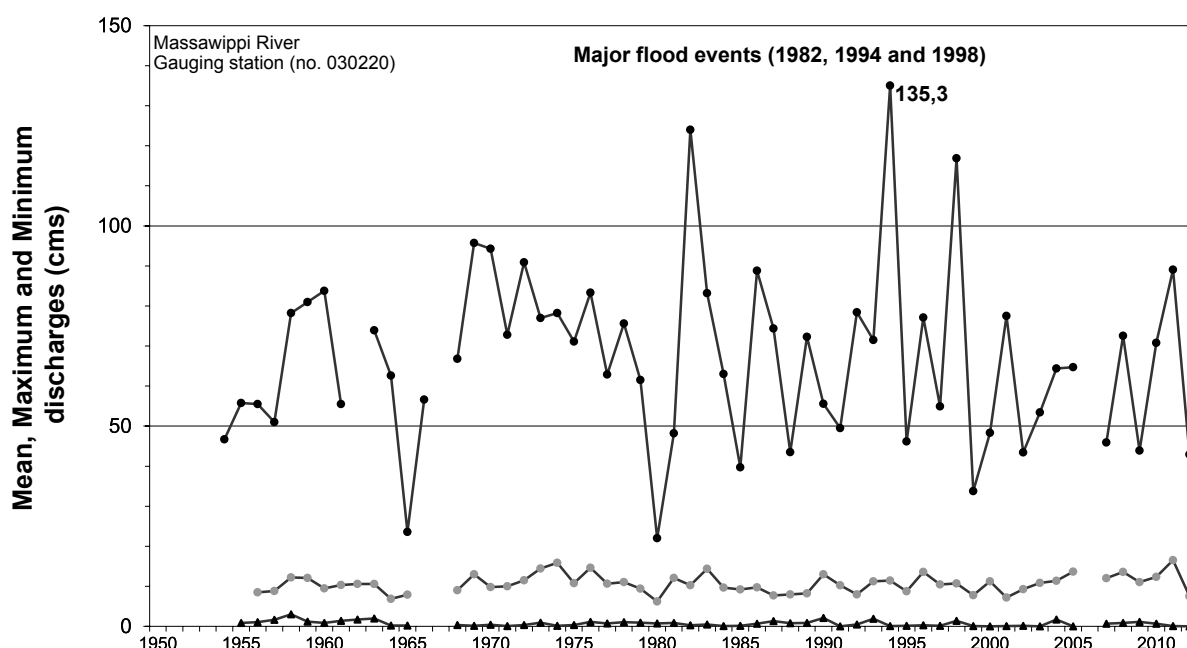


Figure 2. Mean, maximum, and minimum Massawippi River discharges (1954–2012) recorded at gauging station no. 030220 (source: CEHQ 2013). River overflowing was noted when discharge rates exceeded 30 m³/s. The years 1982, 1994, and 1998 are considered major flooding in the watershed of Massawippi and Saint-François rivers.

Materials and Methods

Sampling sites. The sampling sites selected were divided based on the location of the former mining sites (Eustis and Capleton) along the Massawippi River, while considering the flood-risk zones (recurrence interval of 0–20 years/(FFz) frequent flood zone; and interval of 20–100 years/(MFz) moderate flood zone), with adjacent zones located outside the floodplains (no-flood zone (NFz)). We used the flood-risk maps from the land-use plans developed by the Ministry of Municipal Affairs and Regions⁴⁵ as well as official maps from the federal and provincial governments.⁴⁶ On some of the maps, the flood zones appear with a delineation showing strong current (interval of 0–20 years) and low current (interval of 20–100 years). The sampling sites are all located in wooded areas and are divided based on their upstream and downstream location from the mining sites along the Massawippi River. For each sampling site, soil samples were collected at depths of 0–20, 20–40, 40–60, 60–80, and 80–100 cm, and sampling was conducted during the summers of 2011 and 2012. Soil sampling was done based on the guidelines drawn up by the environment ministry for contaminated soils.⁴⁷ A total of 31 sampling sites were selected, including 14 sites in FFzs, 7 sites in MFzs, and 10 sites in NFzs, for a total of 95 soil samples for all the sites. Other soil samples collected from 2003 to 2010 (10 profiles) and located near the Eustis and Capleton sites were also included in databases. In addition, a control site located outside the Massawippi River area was considered in comparing the content of metal elements in recent fluvial sediment (Saint-François River sector). A Global Positioning System (GPS/Garmin 60CSx model) was used to

precisely locate the sampling sites, and these data were retranscribed into an Excel table and then used to position the sites on digital maps using ArcGIS® mapping software. For each site that was sampled, additional measurements were done such as drainage, the overall slope, and the microtopography.

Physical and chemical analysis. To determine soil texture, particle sizes from the Canadian System of Soil Classification were used.⁴⁸ These textural classes are comparable to those used by international classification systems.⁴⁹ The samples were air-dried in the laboratory on aluminum plates with all organic debris and roots removed. Once dried, the soil samples were sieved (<2 mm) using a shaker for 20–30 minutes. To precisely determine the proportion of each particle size (sand, silt, and clay), a Laser Particle Sizer was used (Fritsch/Analysette 22, Micro Tec plus). The method developed by Yeomans and Bremner⁵⁰ was used to determine the soil organic content. The sample was placed in a glass jar, and an acid solution was added (dichromate solution—K₂Cr₂O₇—H₂SO₄) as reagent for 30 minutes. The last stage consisted in using the titration technique with ammonium ferrous sulfate (0.05 mol L⁻¹) to determine the organic content in the remaining solution. Finally, to measure soil acidity, a glass electrode (pH-meter) was plunged into a beaker containing the soil sample, which was dissolved (30 minutes) with CaCl₂ (0.01 M) for a ratio of 1:2 of soil.⁵¹ The procedures used to determine the concentration of metal elements in the soils are based on the analytical standards determined by the Quebec Center of Expertise in Environmental Analysis. All the analyses were performed by outside laboratories (Maxxam Analytics Inc. and Biolab Inc.) that followed governmental procedures.^{52,53}

The method includes the following steps: in a beaker, weigh 1.00 g of homogenized and dried soil, add 4 mL of nitric acid (50%) (V/V) and 10 mL of hydrochloric acid (20%); cover the beaker with a watch glass, and allow to heat at reflux for 30 minutes without stirring. Allow to cool and rinse the watch glass with water. Filter into a 100-mL volumetric flask; rinse the beaker and filter with water, and then transfer to a plastic bottle. The sample is then analyzed using inductively coupled plasma mass spectrometry (ICP-MS). For details on the analytical procedures used for metals analysis, it can also refer to documents elaborated by government laboratories.^{47,52,53}

Statistical analysis. In order to compare the different zones (FFz, MFz, and NFz), Duncan's test and Tukey's test were conducted at each stage and for each metal with the highest contamination (eg, Pb and Zn). To determine the degree of correlation among the various metal elements (eg, Cu, Ni, Pb, and Zn) and soil properties (eg, pH, percentage of organic content), a Pearson analysis was done on the most highly contaminated soils in the floodplain areas. The statistical analyses were done with R statistical computing software (version 3.0.2), and a 95% confidence interval was used for all the statistical analyses.

Results and Discussion

Soil properties. The physical and chemical properties (pH, soil organic carbon% (SOC%), grain size%) of the alluvial soils in floodplain zones (frequent and moderate zones) show limited variability. Most of the soil profiles examined in the riverbanks are made up of fine sandy loam or silt loam (Table 2). The alluvial sediments in the soil profile show weak structure (ie, granular form with low cohesion), with relatively uniform horizontal layers that indicate a regular flow at the time of deposition. This textural similarity is also linked to weak pedogenic development, indicating that these soils developed in recent fluvial sediments. The constant material input from successive floods results in a superimposition of fine layers with little differentiation and development. The soil texture of soils in the NFzs has a comparable proportion of silt and sand particles and low clay minerals compared to floodplain soils, but with a coarser mineral matrix (eg, medium or coarse sand). Nonalluvial soils are made up of materials from various origins (eg, glacial materials), giving them a generally more varied and coarser texture. Gravel layers and stones are also found in some soil profiles located outside the floodplain zones. In the NFzs, the mean silt and sand values range from 62.3 to 32.4%, and the mean values obtained from the FFz and MFz range from 63.4 to 67.5% for silt, and from 31.8 to 27.7% for sand, respectively. In all the profiles analyzed, the clay fraction rarely exceeds 5% (mean and median values between 4.87 and 4.04%). Several soil profiles indicate a very low percentage of clay through the pedon (0–100 cm depth). Soils with a high content of clay and fine silt have greater retention and absorption properties than sandy or silty textures.^{54,55} Soils with coarser textures (dominance of sand and silt) do not have the

same retention capacity to keep fine particles (eg, organic matter) or metal elements (eg, heavy metals).^{56–58} Regarding the percentage of organic carbon in the soils under study, marked differences were noted between the various study areas. The mean values are 1.74% in the FFzs compared to 1.92% in the MFzs and 2.32% in the NFzs (Table 2). The mean SOC values in the NFzs are significantly higher than those observed in the flooding zones. The results obtained with tests reveal a statistical difference with a $P < 0.000$ (between NFzs and FFzs) and $P < 0.011$ (between NFz and MFz). Most of the soils in the NFzs generally have a higher organic matter content. For instance, the maximum SOC content (9.72%) is collected in the NFzs at the subsurface (0–20 cm) soil layer (Q58/right bank). The soils in the NFzs also have a more irregular pattern of SOC distribution, with a higher concentration in the surface layers and a decrease at the base of the profile (eg, Q82: top 2.51 vs 0.26%), while the soils in the flood zones have a lower SOC content in the surface at the base of the soil profile. The SOC mean values obtained in the soils of the two flood zones range from 1.86% (FFz) to 1.75% (MFz) at the top, and from 0.73% (FFz) to 1.48% (MFz) at the base of the soil profile. Despite these differences between the SOC% in soil profiles for each zone, the values obtained by statistical tests are not significant ($P \geq 0.05$). With respect to soil acidity, most of the soils have lower pH values (between 3.18 and 5.84). The high levels of acidity found in several soils are likely because of the proximity of waste rock piles, which contribute to the acidification of the environment through storm water runoff or floods. This water that flows through mine tailings is in fact often known as acid mine drainage (AMD) because of the dissolution of metals, in particular pyrite (mineral found in abundance in mine tailings), which acidifies drainage water.⁵⁹ In the Eustis mine area, one of the government reports³³ indicates an acidity level of 2.5 (pH) in the water of streams (Eustis and Capel) crossing through mine tailings and flowing into the Massawippi River, which has a major adverse impact on living organisms such as benthic communities. The sediment and soils around the former mining sites are understandably also highly acidic.

Our results also show that the soils not affected by flooding have lower pH values, especially in the subsurface horizons (0–20 cm). For instance, the pH values obtained for soil profile Q82 (NFz) are 4.3 at the top and 4.9 at the base of the profile. In the two flood zones, the mean values range from 4.65 (FFz) to 4.27 (MFz), respectively (Table 2). However, the values obtained by statistical tests indicate no significant difference between the soil profiles in each zone ($P > 0.05$ for all values). The soils in the NFzs show a mean value of 4.02, with maximum and minimum values ranging from 3.18 to 5.19, while the soils in the two flood zones have maximum and minimum values ranging from 3.20 to 5.84 (FFz) and 3.47 to 5.56 (MFz), respectively.

Concentration of metal elements. Table 2 shows the data on the metals that were analyzed for the soils in different areas under study (FFz, MFz, and NFz) as well as the generic

Table 2. Soil properties and concentration of metal elements along the riverbanks of Mississippi River in different flood zones (FFz and MFz) and outside of inundated zones (NFz).

ZONES	pH ^a	SOC (%)	SAND (%)	SILT (%)	Al (mg kg ⁻¹)	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Se	Pb	Zn
Frequent flood zone (interval 0–20 yrs) ^x (min-max)	4.65 3.20–5.84	1.74 0.22–5.13	31.8	63.4	11600	21	90	0.51	12	26	41	32000	930	33	1.8	25	53
Moderate flood zone (interval 20–100 yrs) ^y (min-max)	4.27 3.47–5.56	1.92 0.38–5.21	27.7	67.5	9900	37	70	0.62	6	21	95	28700	338	23	<1 ^d	71	62
No flood zone ^z (min-max)	4.02 3.18–5.19	2.32 0.25–9.72	32.4	62.3	10300	8	39	0.58	8	23	27	20500	313	31	<1	29	44
Control site	6.07	1.11	61.6	36.4	–	–	–	<0.5 ^d	–	15	12	–	–	29	–	9	54
Min.	3.18	0.22	0.49	27.7	4700	5	5	<0.5	2	2	5	6500	70	1	<1	5	10
Max. (sample depth in cm)	5.84	9.72	70.7	88.0	22000	140^y (0–20)	330^y (0–20)	2.3^y (0–20)	38^x (60–80)	53	700^y (0–20)	75000	4100^x (60–80)	79^z (20–40)	13^x (0–20)	580^y (0–20)	220^y (0–20)
Natural background ^b	–	–	–	–	–	15	265	1.3	20	75	50	–	1000	55	1	40	130
Criterion A ^c	–	–	–	–	–	6	200	1.5	15	85	40	–	770	50	1	50	110
Criterion B	–	–	–	–	–	30	500	5	50	250	100	–	1000	100	3	500	500
Criterion C	–	–	–	–	–	50	2000	20	300	800	500	–	2200	500	10	1000	1500

Notes: ^aThe data show the mean values in soil profiles (0–100 cm depth) for each zones and control site ($n = 100$). ^bGeochemical background of soil in Appalachian Region and the level of soil contamination (A, B and C criteria) establish by Environment Ministry.⁶⁰ Bold values exceed the criterion A of the level of soil contamination.⁶⁰ The letters ^{x,y} and ^z refer to different zones (FFz, MFz and NFz). ^cA, B and C criteria definitions: Level A: For soils with constituents at or less than this level, the soils are considered uncontaminated; Level B: This level is an intermediate value, approximately 5 to 10 times above level A. For residential and recreational land use this level is the remediation standard, while for exclusive commercial or industrial land use it is the investigation standard. Level C: At this level, contamination of soil is significant. For exclusive commercial or industrial land use, level C is the remediation standard. ^dThese values (<0.5 and <1) corresponding to the detection limit provided by the laboratories.

criteria for the contamination thresholds (A, B, and C criteria; see legend in Table 2) established by Québec's environment ministry.⁶⁰ Table 2 also provides the values for the natural geochemical background for the soils and sediment originating from the Appalachian region provided by the government.⁶⁰ In some cases, the concentration of metals (natural background) in the soil and sediment from the Appalachian region have values above or below Criterion A established by the Environment Policy. This is the case, for instance, for metals such as cadmium, chromium, and lead that have values below Criterion A. Based on the results, certain soil samples have relatively high concentrations of metal elements (eg, As, Cu, Ni, Pb, Zn) that exceed the guideline contamination thresholds.⁶⁰ Arsenic (140 mg kg^{-1}) and copper (700 mg kg^{-1}) levels are especially high and exceed Criterion C, which indicates major soil contamination. Manganese (4100 mg kg^{-1}) also exceeds the soil contamination threshold of Criterion C. These values are generally higher than those obtained for the geochemical background and the control site (Table 2). Also, note that the mean values obtained for certain elements show slightly higher concentrations for soils in the FFzs (interval of 0–20 years), while certain other metals (eg, As, Co, Cu, Pb, and Zn) have higher values for the areas characterized by less frequent flooding (interval of 20–100 years). The maximum concentrations obtained for all the samples that were analyzed are mainly found in areas with less flooding. This explained by the fact that lower flood frequency reduces sediment remobilization and leaching. Also, the highest organic matter content in these floodplain soils (surface layers) can help increase metal retention.^{26,61–63}

Figure 3 presents the mean, median, maximum, and minimum values for the metals (Cu, Pb, and Zn) with high values in the soil profiles for the three zones under study (FFz, MFz, and NFz). It was noted that for certain soil samples, copper, lead, and zinc have significantly higher concentrations in the MFzs than in the other zones, with maximum values of 700, 580, and 220 mg kg^{-1} . The mean and median values obtained in alluvial soils for the MFz are 95 and 28 mg kg^{-1} (Cu), 71 and 19 mg kg^{-1} (Pb), and 62 and 52 mg kg^{-1} (Zn), respectively. The soils in the NFzs show non-negligible concentrations of metals, in particular of copper (79 mg kg^{-1}). Table 3 lists the concentrations of metals obtained in the surface layers (0–20 cm depth) of alluvial soils in the FFzs. Certain soil profiles (Q74 and Q83) also have high concentrations of Cu (380 mg kg^{-1}) and Pb (200 mg kg^{-1}), with values exceeding soil contamination thresholds of Criterion A.⁶⁰ However, most of the surface samples (0–20 cm) that were analyzed have values corresponding to the natural background. Finally, Table 2 provides the maximum values of the main metals that were analyzed while taking into account the depths and their distribution based on the study areas (FFz, MFz, and NFz). Once again, the surface (0–20 cm) or subsurface (20–40 cm) layers are the most affected by contamination, and in several cases, they originate from soils in the MFzs. The statistical analyses conducted with Duncan's and Tukey's tests for the three study areas (FFz, MFz, and NFz) do not reveal any significant differences among the zones in the concentration of the metals that were analyzed (Cd, Cr, Cu, Ni, Pb, and Zn), except for nickel ($P < 0.0428$), which shows significant differences between the FFzs and MFzs, given that Ni concentrations are generally higher in the alluvial soils of the MFzs.

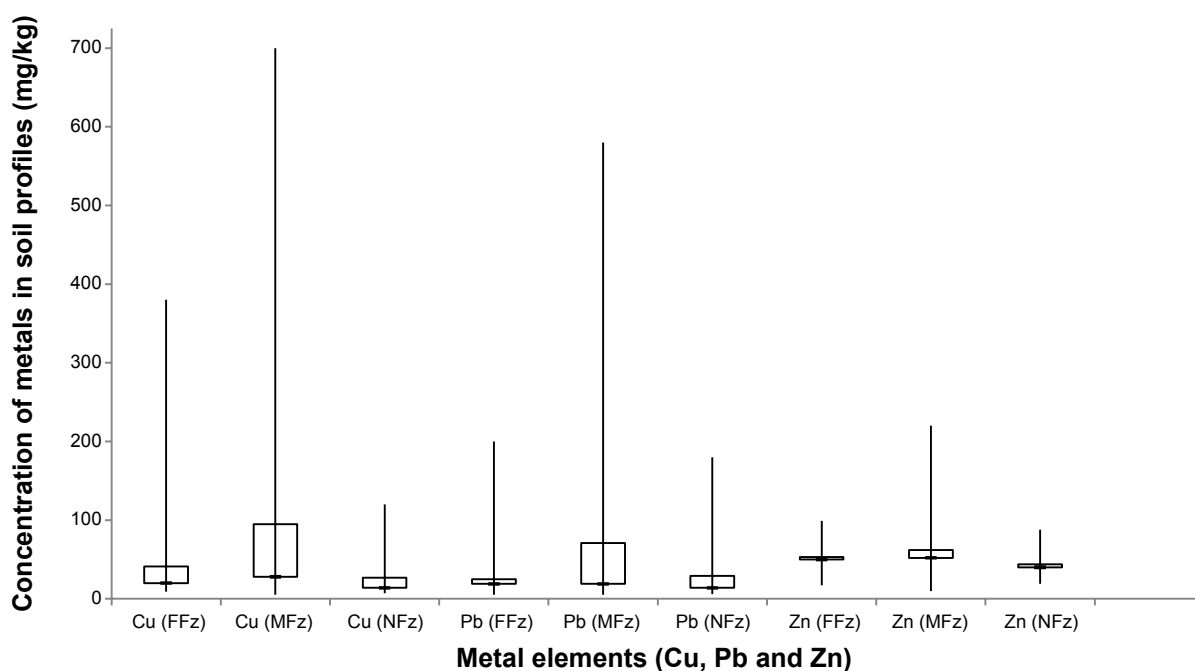


Figure 3. Metal concentrations (mg kg^{-1}) for Cu, Pb, and Zn in soils in different flood zones and outside the floodplains (graph shows the average, median, maximum, and minimum values).

Table 3. Concentrations of metal elements in subsurface horizons (0–20 cm depth) of alluvial soils in Frequent Flood zones along the Massawippi River.

SITES	pH	SOC ^a	Cd	Cr	Cu	Ni	Pb	Zn
Q43	5.34	4.49	<0.5	24	17	41	22	73
Q44	5.35	5.13	<0.5	24	24	32	29	73
Q60	4.80	3.63	<0.5	19	11	30	18	17
Q60B	3.89	4.52	<0.5	21	14	29	20	54
Q62	4.37	2.49	0.6	24	11	25	21	69
Q63	4.52	2.15	<0.5	25	12	27	15	34
Q66	4.32	2.59	<0.5	30	20	23	20	49
Q69	4.78	3.03	<0.5	42	26	49	23	74
Q72	5.04	1.94	<0.5	21	28	36	18	58
Q74	3.69	3.03	<0.5	16	380^b	16	200	79
Q78	4.68	1.26	<0.5	13	25	15	20	39
Q79	4.55	1.08	<0.5	14	54	17	37	61
Q80	5.68	1.86	<0.5	17	25	25	22	50
Q83	4.37	2.07	0.7	29	160	35	66	99
Min.	3.69	1.08	<0.5	13	11	15	15	17
Max.	5.68	5.13	0.7	42	380	49	200	99
Mean	4.67	2.81	0.5	23	58	29	37	59
SD	0.55	1.24	0.5	8	100	10	48	21

Notes: ^aSoil organic carbon in percent (dry weight). ^bBold values exceed A or B criteria of the level of soil contamination.⁶⁰ Metal concentration is expressed in mg kg⁻¹.

Table 4 presents the comparative values between the soils analyzed in the various study zones (FFz, MFz, and NFz) and those located along (1–3 m) the Massawippi River, near the former Eustis and Capleton mines. For the sites on the riverbanks, soil sampling was done from 2006 to 2010,^{43,44} which is prior to the rehabilitation work at the former Eustis mine site, which was completed in 2009.³⁴ The concentrations of the main metals analyzed on the riverbanks (eg, EUS-3-I, CAP-2-I) showed generally higher values than at the other sites in the FFzs and MFzs (Table 4). Besides cadmium and chromium, all the other metals exceed the contamination thresholds of Criteria A and B⁶⁰ (ie, As, Cu, Ni, and Zn). However, when comparing all the sites, the maximum recorded values may be found either on the riverbanks (eg, 740 mg kg⁻¹ Zn) or several meters to a dozen meters from the bank (eg, 700 mg kg⁻¹ Cu and 580 mg kg⁻¹ Pb; see Fig. 1). The riverbank soils contain, in addition to heavy metals, traces or layers contaminated with hydrocarbons (C₁₀–C₅₀) that are easily visible in the profiles. This hydrocarbon contamination appears to originate from illegal or accidental spills, with the source being the former Eustis mine.^{43,44}

Level of contamination in soil profiles. For the soil profiles being presented that are representative of other profiles, it was noted that the highest concentrations of metals (Cu, Ni, Pb, and Zn) are generally found in the alluvial soils, for both the FFz and MFz (Table 2 and Fig. 4), and that the highest concentrations are generally found in the surface layers (0–20 and

20–40 cm depth), except for profile Q79, which has higher Ni and Zn concentrations in the deeper layers (60–80 cm). Copper and lead frequently exceed the contamination threshold of Criterion A and occasionally the threshold of Criterion B.⁶⁰ Concentrations of the other two metals (Ni and Zn) are generally lower in all the profiles, although nickel occasionally exceeds the Criterion A threshold. It was also noted that profile Q82, located outside the floodplains (NFz), also had high nickel concentrations (63 and 79 mg kg⁻¹) that exceed the contamination threshold of Criterion A.

No real vertical pattern of contamination was noted in the soil profiles, although the surface layers (0–20 and 20–40 cm) generally showed higher metal concentrations (eg, Q74, Q77, and Q83; Fig. 4). There is a definite risk that the remobilization of sediment contaminated during flooding will affect these surface layers to a greater extent. In the NFzs, the concentrations of metal elements are generally lower and correspond to the natural geochemical background, except for some metals such as copper and lead, which can exceed the Criterion A threshold in the surface layers (eg, 120 Cu and 180 Pb mg kg⁻¹). Low concentrations of arsenic (10 and 19 mg kg⁻¹) were also found in soil profiles located in NFz. The presence of contaminants in these soils is difficult to explain since they are found several dozens of meters from the alluvial plains and mine tailings. The plausible explanation that would account for their presence in these soils would be the transport of local airborne inputs that may originate from former

Table 4. Comparison of metals element concentrations between soil profiles and horizons contained hydrocarbons-contaminated layers in riverbanks of Massawippi River.

SITES	As ^a	Cd	Cr	Cu	Ni	Pb	Zn	HYDROCARBONS (mg kg ⁻¹)
Massawippi River								
Frequent flood zone (FFz)	18	0.5	26	41	33	295	53	–
Moderate flood zone (MFz)	30	0.6	21	95	23	71	61	–
No-flood zone (NFz)	8	0.6	23	27	31	29	41	–
Soil profiles with hydrocarbons layers								
MAS-10-1	nd	<0.5 ^c	14	9	24	7	38	<100
MAS-10-2	nd	0.6	15	93	23	38	110	<100
EUS-1-I	7	<0.5	19	17	35	11	67	<100
EUS-2-I	5	<0.5	64	14	120	11	61	<100
EUS-3-I	12	<0.5	15	220	31	35	740	<100
MAS-13-I	38	0.8	nd	nd	nd	149	nd	<60
MAS-13-2	4.5	0.2	20	63	31	16	93	nd
CAP-1-I	10	<0.5	15	98	26	23	110	<100
CAP-2-I	15	<0.5	15	180	25	36	190	<100
CAP-3-I	8	<0.5	12	46	21	10	75	<100
Criterion A ^b	6	1.5	85	40	50	50	110	300
Criterion B	30	5	250	100	100	500	500	700
Criterion C	50	20	800	500	500	1500	1500	3500

Notes: ^aMetal concentration (mean value) is expressed in mg kg⁻¹ (nd = no data). ^bThe level of soil contamination (A, B or C criteria) for metal elements established by the Environment Ministry.⁶⁰

waste rock piles left uncovered for several decades. Besides this, there is no other source of industrial waste around the mining sites.

Of all the profiles that were analyzed, copper had the highest concentrations, which is easily explained by the presence of mine tailings from the mining of copper ore at the former Eustis and Capleton mines. Mine tailings also contain high concentrations of iron sulfide and pyrite, which contribute to the acidification of the environment.³³ Mining operations took place from 1865 to 1939,^{33,34} and thereafter, the former mines long remained abandoned and unmonitored. More recently, the Eustis mine tailing sites (about 15 ha) underwent rehabilitation, with the last phase being completed in 2009.³⁴

Correlation of soil properties and metal elements.

Significant positive correlations were noted between Cu and Pb ($r = 0.948$), Fe and Pb ($r = 0.951$), Fe and Cu ($r = 0.946$), and Fe and Zn ($r = 0.955$) (Table 5). Also, high correlations were observed between Cu and Zn ($r = 0.758$) and Pb and Zn ($r = 0.753$). Al and Cu elements are highly correlated but negative. Figure 5 also shows the high correlation between Cu, Pb, and Zn for the MFzs, with the highest concentrations of all the values obtained. It is not infrequent to find combinations of metals such as Cu, Pb, and Zn in the contaminated soils, particularly in the waste rock piles.^{56,57} In fact, these same metals (Cu, Pb, and Zn) have the highest concentrations

in the soils that were analyzed. Copper is in fact the metal with the highest level (eg, 700 mg kg⁻¹).

With respect to different soil properties (eg, pH, SOC, particle size) and the various metals analyzed, no strong positive correlation was noted between these variables, and the coefficients that were obtained were mainly negative (Table 5). For instance, the correlation between pH and different metal variables remains mainly negative. It is known that soil acidity can contribute to increasing the solubility of certain metals, such as cadmium and chromium, which become more soluble with $\text{pH} < 5.5$.^{56,57} It is therefore likely that the low concentration of certain metals (eg, cadmium) is partly because of the high soil acidity, which favors the solubility of this metal. Several studies show that the drop in soil pH could lead to desorption of metallic elements into soil profiles.^{5,8,26} In addition, no strong relationship was found between SOC and the various metals. The high concentration of the organic particles of a soil is usually considered as a key parameter in the adsorption of the metal elements in the soil.^{56,57} The electropositive charge of several metallic elements (eg, Cu, Pb, Zn) promotes the ionic linkages with the fine organic particles, which are characterized by opposite charges (ie, electronegative charges). This can promote the formation of microaggregates and macroaggregates, which reduce metal mobility in soil profiles.^{8,25,26} Note that SOC(%) concentrations measured in the alluvial soils are rather low (mean value = 1.99), which reduces

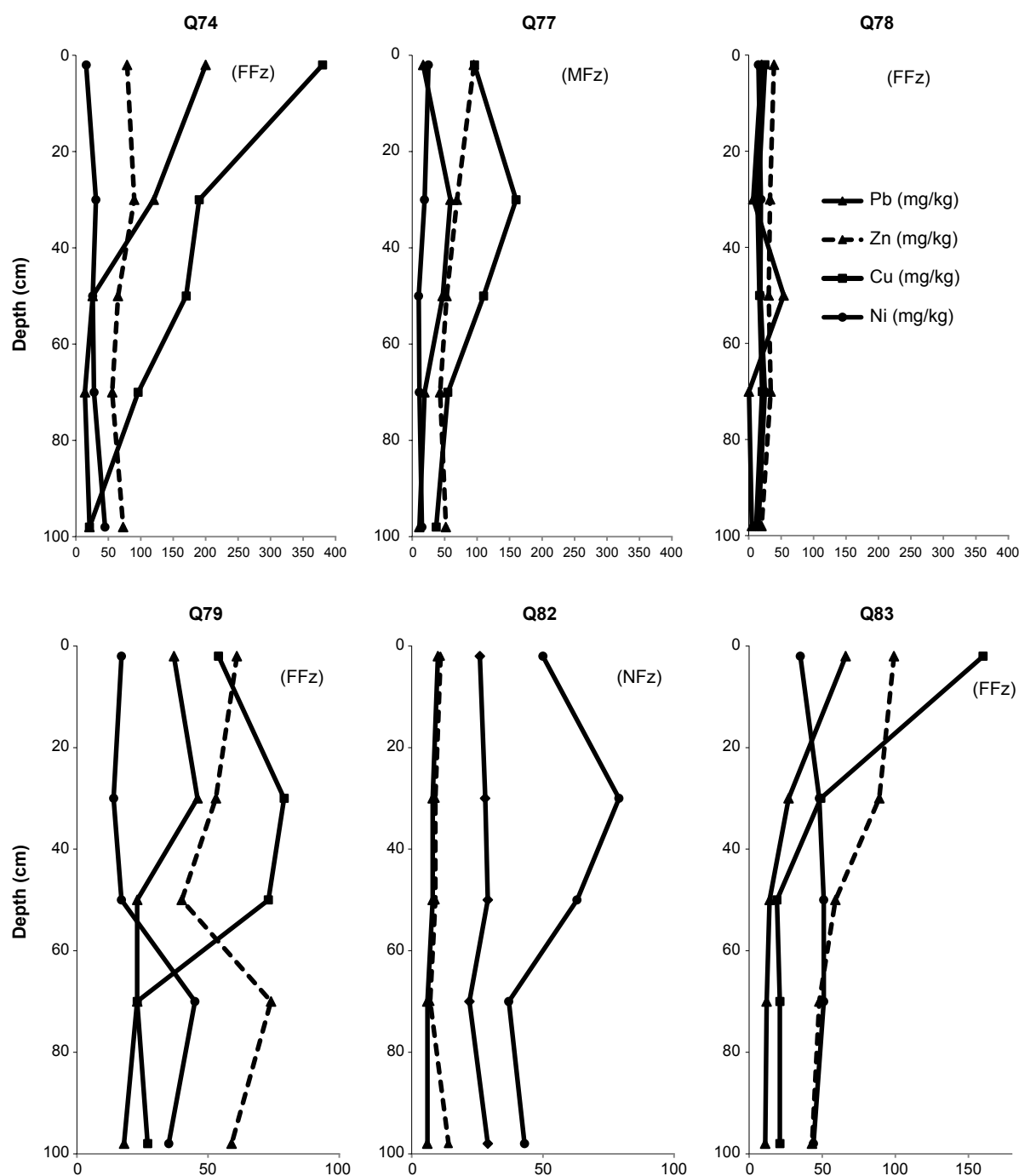


Figure 4. Graph of soil profiles (0–100 cm depth) with heavy metal (Cu, Ni, Pb, and Zn) concentrations (mg kg^{-1}).

the possibility of retention or adsorption of the metals found in the mineral soil. This undoubtedly accounts for the low correlation coefficients obtained among these variables (SOC% vs metal elements). This could also apply to the Clay(%) variable and the other metals with very low correlation coefficients. Most of the soils that were analyzed contain low quantities of clay, rarely reaching 5% (mean and median values of 4.9 and 4.4%), which substantially reduces the metal retention potential of the clay particles. It is known that soils with a fine matrix (texture mainly characterized by clay) generally have a

higher heavy metal retention potential,^{56,57} and the presence of carbonates or ligands, such as humic colloids, can strongly influence the retention of cations and metal elements in soils. A strong negative correlation was also noted between some variables such as Sand and Silt, Sand and Al, and Cu and Al (Table 5).

Spatial distribution of metal contamination. The spatial distribution of the contamination of alluvial soils and nonalluvial soils by different heavy metals (As, Cu, Ni, Pb, and Zn) is illustrated in Figure 1. In the Eustis mine area and

Table 5. Correlations between soil properties and metal elements in Moderate flood zone (interval 20-100 yrs) of the riverbanks of Massawippi River ($n = 95$).

SOIL VARIABLES	SOIL pH	SOC (%)	SAND	SILT	CLAY	Al (mg kg ⁻¹)	Fe	Cu	Ni	Pb	Zn
Soil pH	1										
SOC	-0.064	1									
Sand	0.106	0.361	1								
Silt	-0.095	-0.319	-0.993	1							
Clay	-0.144	-0.498	-0.761	0.683*	1						
Al	-0.010	-0.367	-0.869	0.835*	0.665*	1					
Fe	-0.397	0.457	-0.040	0.085	-0.180	0.273	1				
Cu	-0.025	0.019	-0.131	0.149	-0.017	-0.869	0.946*	1			
Ni	0.329	-0.047	0.125	-0.154	0.080	0.102	-0.052	-0.128	1		
Pb	-0.242	0.069	-0.100	0.120	-0.043	0.200	0.951*	0.948*	-0.122	1	
Zn	-0.061	0.093	-0.320	0.336	0.135	0.397	0.955*	0.758*	0.079	0.753*	1

Notes: *Correlation is significant at the 0.5 level.

a few kilometers downstream of the site, a higher contamination was noted in the alluvial soils in the FFzs, especially for As, Cu, Ni, Pb, and Zn. Concentrations are significantly higher and exceed the Criterion A and, on a few occasions, the contamination thresholds of Criterion B.⁶⁰ This is the case for sites Q74, Q83; EUS-2, EUS-3; MAS-10-2/Eustis. In the sites located in the MFzs and NFzs, soils contaminated with As, Cu, Ni, Pb, and Zn were also found. The soils from the MFzs are the ones with the highest metal concentrations, in particular arsenic (140 mg kg⁻¹), copper (700 mg kg⁻¹), lead (580 mg kg⁻¹), and nickel (580 mg kg⁻¹). Outside the floodplains, some sites present high values, in particular for copper (120 mg kg⁻¹) and lead (180 mg kg⁻¹). There are also soils contaminated with As, Cu, and Pb upstream of the former Eustis mine in the MFzs and NFzs, with respective values of 8 mg kg⁻¹ (As), 59 mg kg⁻¹ (Cu), and 88 mg kg⁻¹ (Pb). For the sites near the former Capleton mine, a few kilometers downstream, several contaminated sites are also found, including MAS-13-I/Capleton, CAP-1-I/Capleton, and CAP-2-I/Capleton, where the contamination thresholds of Criteria A and B are exceeded. For instance, arsenic, copper, lead, and zinc concentrations are, respectively, around 8–38 mg kg⁻¹, 63–220 mg kg⁻¹, 149 mg kg⁻¹, and 110–740 mg kg⁻¹ (Table 4). The soils located in the MFzs and NFzs were also found to exceed the contamination thresholds of Criteria A and B on a number of occasions for arsenic, copper, and lead, with values of 18–19 mg kg⁻¹ (As), 92–160 mg kg⁻¹ (Cu), and 59–95 mg kg⁻¹ (Pb). Finally, in the area upstream of Lennoxville, less than a dozen kilometers from the Capleton site, the analyzed soils did not reach the contamination threshold of Criterion A, except in the case of profile Q82 located outside the floodplains (Fig. 4). For example, nickel concentrations were 79 mg kg⁻¹ (20–40 cm in depth) and 50 mg kg⁻¹ (0–20 cm) and 63 mg kg⁻¹ (40–60 cm) in the other soil layers.

Finally, for the soils located near the former Eustis waste rock piles (eg, Q43, Q74, Q83; see Fig. 1) that were sampled after the site was rehabilitated,³⁴ relatively high contamination levels were detected that exceed the contamination thresholds of Criteria A and B. For instance, the soils at sites Q74 and Q83 show high levels of As, Cu, Ni, and Pb (eg, 200 mg kg⁻¹ for both Ni and Pb). These sites are located less than 2 km from the Eustis mine, and the contaminants found in the riverbank sediment most likely originate from the former waste rock piles. Note that rehabilitation work was done at the former Eustis mining site from 2007 to 2009³⁴ and consisted of covering the mine tailings with a waterproof barrier to prevent oxidation, rainwater infiltration, and subsequent AMD. Despite the rehabilitation work, some riverbank near the site still contain heavy metals, which are likely to be resuspended with the sediments during successive floods and carried downstream. This reflects the problems inherent in remobilization, and the persistence of environmental contaminants several decades after mining operations ended in this area.^{33,34}

Furthermore, in a number of studies on the transport of contaminants by rivers and streams, several authors^{3,4,18} discussed the problem of the persistence of contaminants in the river environment. In addition, strong currents or successive floods can carry contaminants over very long distances, several kilometers from the point source. Riverbank soils often present the highest concentration of pollutants. With respect to current findings and those from previous studies,^{43,44} it was noted that contaminants can be transported over long distances. However, the remobilization and transport of pollutants along riverbanks appear more complex than the previously anticipated means of dispersion. In fact, higher contamination levels were expected in FFzs than in MFzs. However, it was noted that the latter had values often higher than those recorded in the FFzs (interval of 0–20 years). This means

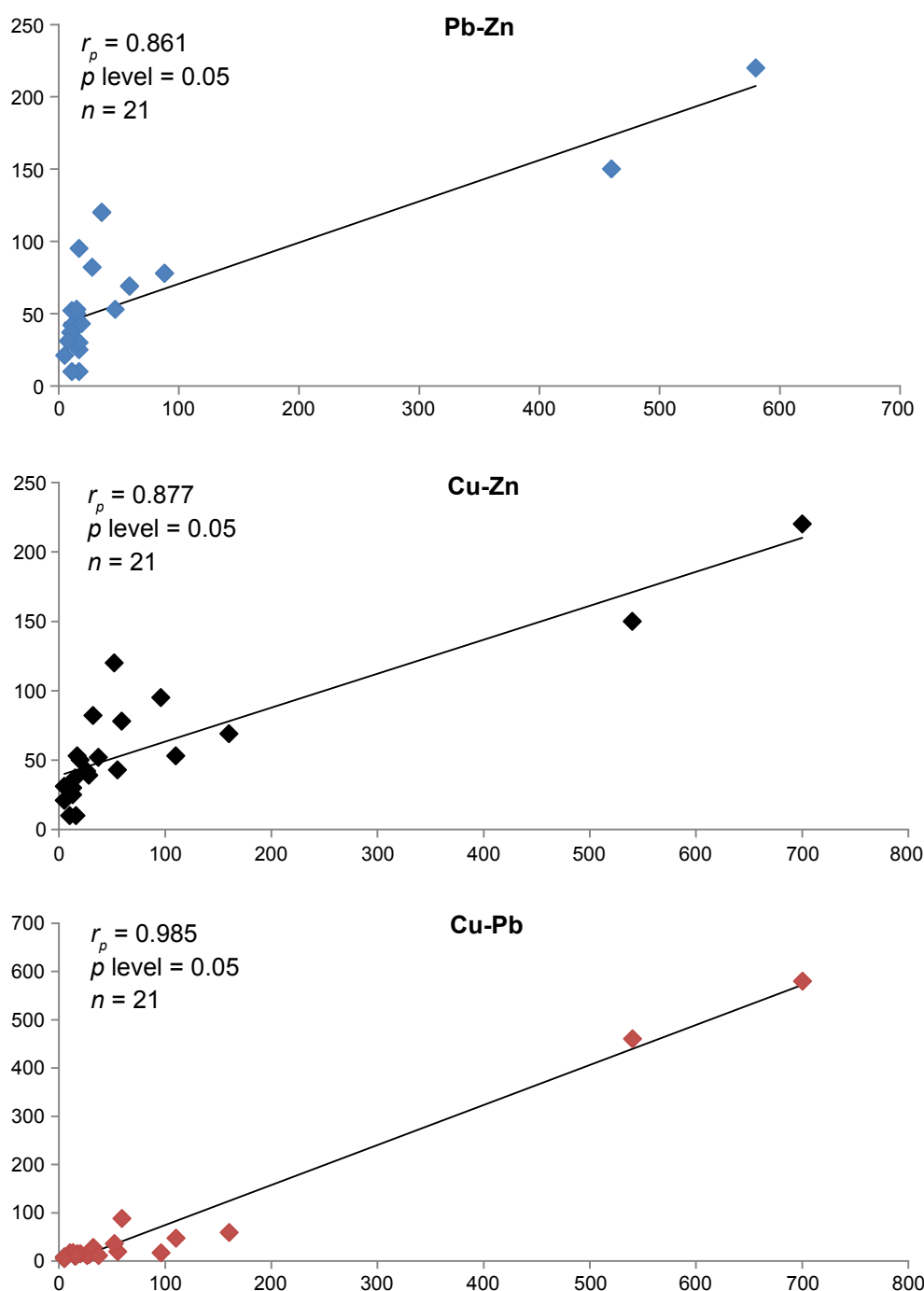


Figure 5. Correlation (Pearson coefficient) between the main metal element (Cu, Pb, and Zn) found in the MFzs (interval 20–100 years). The results show a strong positive correlation between each variable.

that the remobilization of pollutants and their sedimentation can occur at micro-scales sometimes equivalent only to a few meters or dozens of meters, in keeping with the respective flood recurrence zone boundaries. Furthermore, in the zones less affected by flooding (recurrence of 20–100 years), pollutants may remain in place longer and constitute to some extent quasi-permanent storage areas.

In addition, several of these metal elements, including lead and zinc, are considered low-soluble metals,⁵⁶ which allows them to remain in the soil over a long period of time.

It is known that zinc and more specifically lead can last a long time in soils.^{3,5,14} However, increased soil acidity ($\text{pH} < 4.5$) may favor the solubility of these metals. For the soils analyzed in the MFzs, pH levels are relatively comparable to those observed in the FFzs, along with the organic carbon content and variations in texture (Table 2). These various soil properties do not appear before the factors that can explain the higher concentration of heavy metals observed in certain soils in the MFzs. It is possible that other factors come into play such as internal leaching, fluctuations in groundwater, and flood

recurrence, which, although less frequent, may favor slightly lower leaching of heavy metals in alluvial sediments.^{10,12,18} In short, all these elements (distance from the riverbank, flood recurrence, metal mobilization) must be taken into account to better understand the mode of dispersion and accumulation of pollutants in the river environment. Furthermore, it is also important to consider the effects of the transport of local airborne inputs, in particular in the context of mine tailings left uncovered and abandoned, which can be a major source of contamination for surrounding areas.

Conclusions

Even several decades after the end of mining operations at the Albert–Eustis–Capleton Complex, heavy metals are still present in the alluvial soils along the banks of the Massawippi River. The main metals consist of arsenic, copper, nickel, lead, and zinc, which have the highest concentrations that sometimes exceed the soil contamination criteria established by the Québec's environment ministry. The highest concentrations occur downstream of the Eustis and Capleton sites with values between 220 and 380 mg kg⁻¹ for copper and 190 and 740 mg kg⁻¹ for zinc, respectively. High copper levels in some alluvial soils (700 mg kg⁻¹) can be explained by the presence of old tailings coming from copper mining along the Massawippi river.

The soils in the MFzs also contain high concentrations of various heavy metals, including copper, zinc, and lead. Metal concentrations are generally higher in the surface layers, but there are also high levels of contaminants in the lower layers of the profile (>60 cm). Relatively high traces of metal are also found in the soils outside the floodplains, even if these are located several dozen or hundreds of meters away, which indicates the possibility of the transport of local airborne inputs originating from waste rock piles left uncovered for several years after mining operations ended. No particular spatial pattern was detected in the distribution of contaminants in the upstream–downstream river axis. High concentrations of metals are equally found at the sites adjacent to the former mines as in those further away. Finally, no significant decrease in metals in the alluvial soils was detected even after the rehabilitation of the Eustis mining site, which began in 2007 and ended in 2009.

Finally, the continuing presence of high levels of certain heavy metals (eg, Cu, Pb, and Zn) in soils even after the Eustis mine closed in 1939 shows the problem of the persistence of contaminants in the river environment and the negative effects of their remobilization during the occurrence of floods. In the current context where there is potential for an increase in flood frequency in the coming decades, there is a possibility that the contamination along the riverbanks could extend over several dozen kilometers from the source point.

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Author Contributions

Wrote the first draft of the manuscript: DSL and FB. Contributed to the writing of the manuscript: DSL, FB, and IB. Analyzed the data: DSL, VGB, and IB. Agreed with manuscript results and conclusions: DSL, FB, IB, VGB, and CC. All the authors reviewed and approved the final manuscript.

REFERENCES

1. Miller JR, Lechler PJ, Desilets M. The role of geomorphic processes in the transport and fate of mercury in the Carson River basin, West-Central Nevada. *Environ Geol*. 1998;33:249–262.
2. Diodato N, Gericke A, Bellocchi G. Modelling the inter-annual variability of sediment yields: a case study for the upper Lech River. *Catena*. 2012;97:12–19.
3. Grygar TM, Sedláček J, Bábek O, Nováková T, Strnad L, Mihaljevič M. Regional contamination of Moravia (South-Eastern Czech Republic): temporal shift of Pb and Zn loading in fluvial sediments. *Water Air Soil Pollut*. 2012;223:739–753.
4. Ciszewski D. Flood-related changes in heavy metal concentrations within sediments of the Biała Przemsza River. *Geomorphology*. 2001;40:205–218.
5. Ciszewski D. Heavy metals in vertical profiles of the middle Odra River overbank sediments: evidence for pollution change. *Water Air Soil Pollut*. 2003;143:81–98.
6. Majerová L, Grygar MT, Elznicová J, Strnad L. The differentiation between point and diffuse industrial pollution of the floodplain of the Ploucnice River, Czech Republic. *Water Air Soil Pollut*. 2013;224:1688.
7. Lecce SA, Pavlowsky RT. Floodplain storage of sediment contaminated by mercury and copper from historic gold mining at Gold Hill, North Carolina, USA. *Geomorphology*. 2014;206:122–132.
8. Rinklebe J, Franke C, Neue HU. Aggregation of floodplain soils as an instrument for predicting concentrations of nutrients and pollutants. *Geoderma*. 2007;141:210–223.
9. Martin CW. Recent changes in heavy metal contamination at near-channel positions of the Lahn River, Central Germany. *Geomorphology*. 2012;13(9–140):452–459.
10. Gonzalez-Fernandez O, Queralt I, Carvalho ML, Garcia G. Lead, zinc, arsenic and copper pollution in the alluvial plain of a mining Wadi: the Beal case (Cartagena-La Union Mining District, SE Spain). *Water Air Soil Pollut*. 2013;220:279–291.
11. Schipper AM, Lotterman K, Leuven RS, Ragas MJ, de Kroom H, Hendricks AJ. Plant communities in relation to flooding and soil contamination in lowland Rhine River floodplain. *Environ Pollut*. 2010;159:182–189.
12. Wang S, Yan Y, Li Y. Spatial and temporal variations of suspended sediment deposition in the alluvial reach of the upper Yellow River from 1952 to 2007. *Catena*. 2012;92:30–37.
13. Anderson MG, Walling DE, Bates PD, eds. *Flood-Plain Processes*. Chichester, UK: John Wiley & Sons; 1996:658.
14. Walling DE, Owens PN, Carter J, et al. Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. *Appl Geoch*. 2003;18:195–220.
15. Wyżga B, Ciszewski D. Hydraulic controls on the entrapment of heavy metal-polluted sediments on a floodplain of variable width, the upper Vistula River, Southern Poland. *Geomorphology*. 2010;117:272–286.
16. Swennen R, Van Kerr I, De Vos W. Heavy metal contamination in overbank sediments of the Geul River (East Belgium): its relation to former Pb–Zn mining activities. *Environ Geol*. 1994;24:12–21.
17. Lehto J, Lusa M, Virkanen J, et al. Metal distribution in lakes surrounding the Kostomuksha iron mine and ore dressing mill in Northwestern Russia. *Air Soil Water Res*. 2010;3:67–77.
18. Martínez-Carreras N, Andreas Krein A, Gallart F, et al. The influence of sediment sources and hydrologic events on the nutrient and metal content of fine-grained sediments (Attert River Basin, Luxembourg). *Water Air Soil Pollut*. 2012;223:5685–5705.
19. Drouin A, Saint-Laurent D, Lavoie L, Ouellet C. High-precision digital elevation model to evaluate the spatial distribution of soil organic carbon in active floodplains. *Wetlands*. 2011;31:1151–1164.



20. Saint-Laurent D, Mesfioui M, Evin G. Hydroclimatic variability and relation with flood events (southern Québec, Canada). *Water Res.* 2009;36:43–56.
21. Saint-Laurent D, Lavoie L, Drouin A, St-Laurent J, Ghaleb B. Estimation of floodplain sedimentation rates using flood events, soil properties and recent flood history. *Glob Planet Change.* 2010;70:76–91.
22. Zglobicki W, Lata L, Plak A, Reszka M. Geochemical and statistical approach to evaluate background concentrations of Cd, Cu, Pb, and Zn (case study: Eastern Poland). *Environ Earth Sci.* 2011;62:347–355.
23. de Klerk LP, Klerk AR, Wepener V. An assessment of mercury contamination and the relationship between environmental variables and mercury concentrations in a seasonal wetland. *Water Air Soil Pollut.* 2013;224:1547–1562.
24. Louhi A, Hammadi A, Achouri M. Determination of some heavy metal pollutants in sediments of the Seybouse River in Annaba, Algeria. *Air Soil Water Res.* 2012;5:91–101.
25. Ruiz-Sinoga JD, Pariente S, Diaz AR, Martinez-Murillo JF. Variability of relationships between soil organic carbon and some soil properties in Mediterranean rangelands under different climatic conditions (South of Spain). *Catena.* 2012;94:17–25.
26. Du Laing G, Rinklebe J, Vandecasteele B, Meers E, Tack FMG. Trace metal behavior in estuarine and riverine floodplain soils and sediments: a review. *Sci Total Environ.* 2009;407:3972–3985.
27. Frohne T, Rinklebe J, Diaz-Bone RA. Contamination of floodplain soils along the Wupper River, Germany, with As, Co, Cu, Ni, Sb, and Zn and the impact of pre-definite redox variations on the mobility of these elements. *Soil Sediment Contam.* 2014;23:779–799.
28. Overesch M, Rinklebe J, Broll G, Neue HU. Metals and arsenic in soils and corresponding vegetation at Elbe river floodplains (Germany). *Environ Pollut.* 2007;145(3):800–812.
29. Li MS, Yang SX. Heavy metal contamination in soils and phytoaccumulation in a manganese mine wasteland, South China. *Air Soil Water Res.* 2008;1:31–41.
30. Whitfield PH, Bodtker K, Cannon AJ. Recent variation in seasonality of temperature and precipitation in Canada, 1976–95. *Int J Climatol.* 2002;22:1617–1644.
31. Yagouti A, Boulet G, Vincent L, Mekis E. Observed changes in daily temperature and precipitation indices for southern Québec, 1960–2005. *Atmos Ocean.* 2008;46:243–256.
32. Daniels JM. Floodplain aggradation and pedogenesis in a semiarid environment. *Geomorphology.* 2003;56:225–242.
33. Berryman D, St-Onge J, Gendron A, Brochu C. L'impact d'anciens parcs à résidus miniers sur la qualité de l'eau et les communautés benthiques de la rivière Massawippi et des ruisseaux Eustis et Capel, Québec. 2003. Direction du suivi de l'état de l'environnement, envirodoq no ENV/2003/0043. Ministère de l'Environnement, Québec, 47.
34. Ministère des Ressources naturelles et de la Faune (MRNF). Restauration du Complexe minier Eustis. Gouvernement du Québec. 2013. Available at: <https://www.mern.gouv.qc.ca/english/mines/quebec-mines/index.asp>. Accessed January 6, 2014.
35. Ministère des Forêts (MFQ). Carte des dépôts meubles (1:50 000). Service des inventaires forestiers, Gouvernement du Québec, Québec. 1993.
36. Avramtechev L. Geological Map of Québec, (scale 1:500 000). Ministry of Energy and Resources, Government of Québec, Québec. 1985.
37. Lavoie L, Saint-Laurent D, St-Laurent J. Pedological and sedimentological analyses of alluvial soils and paleosols on floodplain terraces. *Can J Soil Sci.* 2006;86:813–826.
38. Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs (MDDEFP). Normales climatiques du Québec, 1981–2010. Gouvernement du Québec. 2013. Available at: <http://www.mddep.gouv.qc.ca/climat/normales/index.asp>. Accessed February 9, 2014.
39. Centre d'expertise hydrique du Québec (CEHQ). Water level and flow rates. Government of Québec. 2013. Available at: <http://www.cehq.gouv.qc.ca/hydrometrie/index-en.htm>. Accessed April 12, 2013.
40. Ministère du Développement durable, de l'Environnement et des Parcs (MDDEFP). Portrait global de la qualité de l'eau des principales rivières du Québec. Gouvernement du Québec. 2004. Available at: <http://www.mddep.gouv.qc.ca/eau/bassinversant/global-2004/index.htm>. Accessed January 21, 2014.
41. Ministère du Développement durable, de l'Environnement et des Parcs (MDDEFP). Portrait global de la qualité de l'eau des principales rivières du Québec. Gouvernement du Québec. 2012. Available at: <http://www.mddefp.gouv.qc.ca/eau/portrait/eaux-surface1999-2008/index.htm>. Accessed February 14, 2014.
42. Painchaud J. État de l'écosystème aquatique du bassin versant de la rivière Saint-François: faits saillants 2001–2003, Québec. Ministère du Développement durable, de l'Environnement et des Parcs, Direction du suivi de l'état de l'environnement. 2007:19. Available at: <http://www.mddep.gouv.qc.ca/eau/bassinversant/bassins/stfrancois/FS-St-Francois.pdf>. Accessed May 26, 2014. [ISBN 978-2-550-49727-1 (PDF)].
43. Saint-Laurent D, St-Laurent D, Duplessis P, Lavoie L. Isotopic record of lead contamination in alluvial soils and tree rings on recent floodplains (southern Québec, Canada). *Water Air Soil Pollut.* 2010;209:451–466.
44. Saint-Laurent D, Baril F, Hähni M, Paré MC. Hydrocarbons, Pb-concentrations, and Pb-isotope ratios in contaminated alluvial soils, southern Québec, Canada. *Soil Sediment Contam.* 2014;23:76–93.
45. Ministère des Affaires municipales et des Régions (MAMR). Cartes des zones inondables (1:20 000) de la MRC de Coaticook. Service de l'aménagement et de l'urbanisme, Gouvernement du Québec, Québec. 2007.
46. Centre d'expertise hydrique du Québec (CEHQ). Flood risk-areas, Government of Québec. 2003. Available at: http://www.cehq.gouv.qc.ca/index_en.asp. Accessed November 6, 2013.
47. Centre d'expertise en analyse environnementale du Québec (CEAEQ). Sampling Guide for Environmental Analysis. Ministry of Environment of Québec, Canada. 2010. Available at: <http://www.ceaeq.gouv.qc.ca/documents/publications/echantillonnage/solsC5.pdf>. Accessed November 8, 2013.
48. Canadian Soil Classification Working Group (CSCW). *Canadian System of Soil Classification. Agriculture and Agri-Food Canada*, 3rd ed Ottawa. National Research Canada Press Editor; 1998:187. [Publication 1646].
49. IUSS-ISRIC-FAO. World reference base for soil resources. A framework for international classification, correlation and communication. World Soil Resources Reports, 2007:103. Available at: http://www.fao.org/fileadmin/templates/nr/images/resources/pdf_documents/wrb2007_red.pdf. Accessed March 9, 2014.
50. Yeomans JC, Bremner JM. A rapid and precise method for routine determination of organic carbon in soil. *Commun Soil Sci Plant Anal.* 1988;19:1467–1476.
51. Carter MR, Gregory EG. *Soil Sampling and Methods of Analysis. Canadian Society of Soil Science.* Boca Raton, FL: Lewis Publishers; 2008:823.
52. Centre d'expertise en analyse environnementale du Québec (CEAEQ). Analytical method—determination of assimilated metals: inductively coupled plasma mass spectrometry. MA. 200, Met 1.2. Ministry of Environment of Québec, Canada. 2010. Available at: www.ceaeq.gouv.qc.ca/methodes/pdf/MA200Met12.pdf. Accessed June 4, 2013.
53. Centre d'expertise en analyse environnementale du Québec (CEAEQ). Guidelines for Analytical Chemistry, DR-12-SCA-0, Ministry of Environment of Québec, Canada. 2011. Available at: www.ceaeq.gouv.qc.ca/accreditation/pala/DR12SCA01_lignes_dir_chimie.pdf. Accessed June 4, 2014.
54. Choppala G, Bolan N, Lamb D, Kunhikrishnan A. Comparative sorption and mobility of Cr(III) and Cr(VI) species in a range of soils: implications to bio-availability. *Water Air Soil Pollut.* 2013;224:1699–1710.
55. Lai TM, Lee W, Hur J, et al. Influence of sediment grain size and land use on the distributions of heavy metals in sediments of the Han River Basin in Korea and the assessment of anthropogenic pollution. *Water Air Soil Pollut.* 2013;224:1609–1621.
56. Alloway BJ. Heavy Metals in Soils. Blackie and Academic Professional. 2nd ed. London, UK: Springer; 1995.
57. Baize D, Tercé M. Les éléments traces dans les sols. Approches fonctionnelles et spatiales. Paris, France: INRA; 2002.
58. Brady NC, Weil RR. *The Nature and Properties of Soils.* 4th ed. Columbus, OH, USA: Pearson; 2008.
59. Bryson LJ, Crundwell FK. The anodic dissolution of pyrite (FeS₂) in hydrochloric acid solutions. *Hydrometallurgy.* 2014;143:42–53.
60. Ministère du Développement durable, de l'Environnement et de la Faune (MDDEFP). Politique de protection des sols et de réhabilitation des terrains contaminés. Annexe 2: Les critères génériques pour les sols et pour les eaux souterraines. Gouvernement du Québec. 2002. Available at: http://www.mddep.gouv.qc.ca/sol/terrains/politique/annexe_2.htm. Accessed April 9, 2012.
61. Foulds SA, Brewer PA, Macklin MG, Haresign W, Betson RE, Rassner SM. Flood-related contamination in catchments affected by historical metal mining: an unexpected and emerging hazard of climate change. *Sci Total Environ.* 2014;47(6–477):165–180.
62. Bai J, Xiao R, Cui B, et al. Assessment of heavy metal pollution in wetland soils from the young and old reclaimed regions in the Pearl River Estuary, South China. *Environ Pollut.* 2011;159:817–824.
63. Bellucci LG, Frignani M, Paolucci D, Ravanelli M. Distribution of heavy metals in sediments of the Venice lagoon: the role of the industrial area. *Sci Total Environ.* 2002;295:35–49.