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ORIGINAL RESEARCH

Spatial Variability of Heavy Metal Contamination in Alluvial Soils in Relation to Flood Risk Zones in Southern Québec, Canada

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Abstract: The contamination of rivers and riparian soils is a growing problem for several catchments in southern Quebec due to agricultural pollutants and other sources of pollution. This study deals with the concentration of heavy metals in alluvial soils and their spatial variability following the various flood return periods (0–20 years and 20–100 years) and outside flood zones. The heavy metal concentration of some soils exceeds levels in government standards. The elements with the highest concentrations are mainly Ni, Pb and Zn. For instance, the levels of Zn and Pb can be as high as 310 and 490 mg kg^{-1}. In general, heavy metal concentrations are highest in active sedimentation zones (0–20 yrs). In this instance, the ANOVA test was conducted to determine whether the differences in heavy-metal concentrations in the soils could be significant between the three zones (Frequent Flood (FF), Moderate Flood (MF), and No Flood (NF)). With the increase in the flood return rate and current hydroclimatic changes, a downstream remobilization of contaminants can be expected, leading to a larger riparian area of contamination.

Keywords: contamination, alluvial soils, heavy metals, climate change, floods, contaminant remobilization

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Introduction

Despite the different government standards on environmental protection (air, water, and soil), several sites are affected to varying degrees by pollution, especially along rivers and streams in urban and agricultural areas. These sources of pollution are varied, and the precise origin of the contaminants is often difficult to determine due to the multiple discharge points (eg, discharge of urban effluent, fertilizers and pesticides, industrial effluent, mining excavated material)[1,2] With the progressive development of riverbanks in urban areas, on farmland and in industrial free zones, a marked increase of contamination problems can be expected in coming years.

In Quebec, the concern for the condition of the province's rivers and streams peaked after the 1970s and resulted in the adoption of more stringent legislation by the Quebec Environment Ministry on the purification of industrial wastewater. Examples include the adoption of regulations applicable to the pulp and paper and petroleum refining industries, the Quebec water purification program in 1978 and 1988, followed by the St. Lawrence Action Plan.[3] A recent report by the Quebec government on water quality[4] states that in general, the quality of the water in several rivers in southern Quebec is still a concern, especially in areas marked by intense agricultural activity. The waters of the Saint-François and Massawippi rivers, for instance, are qualified as poor or questionable, especially on farmland and in densely populated urban areas (eg, Sherbrooke and Drummondville). The degradation of the water results in bacteriological contamination and a concentration of nitrites and nitrates, particularly in the Massawippi River area. High levels of organic contaminants such as polybrominated diphenyl ethers (PBDEs) and perfluorinated compounds (PFCs) are also occasionally found. However, according to the latest report by the MDDEP,[4] analyses to detect the presence of certain heavy metals (Cd, Cu, Pb and Zn) along these two rivers do not show that the water quality criteria for aquatic life have been exceeded.[5] This differs from previous water quality analyses found in government reports,[6,7] which show rather poor water quality in relation to the concentration of some heavy metals (eg, Cu, Pb, Zn).

The Massawippi River, which crosses through former industrial and mining areas, was also subject to water quality monitoring and resulted in government reports.[6,7] Urban, agricultural and ancient mining activities have long been one of the main sources of pollutant discharge in watercourses in this area. In the Massawippi area, three copper mines (Eustis-Capelton-Albert Complex) were in operation at the turn of the century, the largest ones being Eustis-Capleton, with these two mines alone producing about 2 million tons of ore, including 54,400 tons of copper.[6,7] The study showed that the Eustis and Capel streams, which extend along former mine tailing sites, are highly acidified, and that the copper, iron, lead, and zinc levels far exceed the aquatic life criteria. The Eustis and Capel streams that receive the runoff from several mine tailing sites are thus contaminated and contribute probably to the concentration of metals discharged into the Massawippi and Saint-François.[6,7] Lastly, it is important to consider all the other polluting sources including agricultural waste and urban efluent, which are also potential sources of heavy-metal contamination.

With respect to the contamination of the Massawippi and Saint-François riverbanks, the results obtained during our previous studies[8–10] show that various heavy metals are found with concentrations exceeding the contamination limits established by government standards.[11] The contamination of alluvial soils is caused by layers of petroleum residue (C10-C50) and heavy metals, including Cu, Ni, Pb and Zn.[9,10,12] Such riparian soil contamination is generally found in surface horizons, although contaminants are found in deeper horizons ($>$60 cm), which is partly due to the heavy metals in the hydrocarbon-contaminated layers.[9,10] This vertical variability of contaminants in the soil profiles may also be caused by several factors, including the leaching of the most mobile metal elements such as Cd to deeper layers, river water levels during contamination events such as spills, or by contaminant remobilization during flood periods, which are frequent in the areas under study.

In this respect, the hydroclimatic changes noted over the last century in the Saint-François river basin are characterized by an increase in the annual and monthly rainfall as well as an increase in the flow rate of several rivers, including the Massawippi and Saint-François. These changes in hydroclimatic conditions have had a major impact on the number of flood events.[13,14] In fact, the increase in flood frequency since the early 20th century, and more specifically over the last 30 years, is a statistically significant change in flood recurrence. A greater number of spring floods have been noted along with more floods in the fall and winter.[13,14] In addition, an analysis of the hydrological series shows a greater number of peak discharges between 1970 and 1996. This increase corresponds to a period characterized by greater rainfall, especially between 1970 and 1990.[13] The increase in flooding over the last three decades in the study areas is a major concern if one considers that contaminant transport and remobilization are increasing and are resulting in a greater area of contamination in the downstream parts of the two rivers. The noted increase in the number of flood events results in alluvial plain aggradation and sediment remobilization.[14,15] To determine the geographic range and level of contamination of the alluvial soils of two major rivers in southern Quebec (the Massawippi and Saint-François), an extensive study of the upstream-downstream sections of the rivers was conducted in the summers of 2010 and 2011. The distribution of the sampling sites was done based on the various flood zones delimited by the flood-risk maps by municipalities and by federal and provincial environment departments.[16] The main objectives of the study were to (1) determine the total concentration of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in the riparian soils based on an upstream/downstream transect of the Massawippi and Saint-François rivers; (2) determine the spatial distribution of heavy metals based on the various flood recurrence zones (0–20 years and 20–100 years) as well as in the riparian zones not affected by flooding; and (3) determine the vertical distribution of the heavy metals in the soil profiles.

Materials and Methods

Sampling sites

Sampling sites were selected along the Massawippi and Saint-François rivers (Fig. 1) in southern Québec. The St. Lawrence Lowlands and the Appalachian Mountains are the two major physiographic divisions that characterize this large drainage basin. In the downstream part of the basin (Saint-François River), there are large flat surfaces mainly dominated by farmland, wooded and urban areas, and in the upstream part, the relief is dominated by hills and valleys with mixed forests and agricultural lands. The middle section of the Saint-François River (between Sherbrooke and Drummondville) is characterized by low floodplains (1–3 meters in height) covered mainly by fluvial deposits (silty and fine sand). The banks of the Richmond-Windsor section extend over 104.3 km, and the riverbanks predominantly consist of fluvial deposits (42%) and glaciolacustrine deposits (22.5%), as well as glaciofluvial outwash materials and rocky outcrops.[7] The regional geology of this area is characterized by complex tectonostratigraphic belts marked by multiple orogenic phases.[17] In the middle section of the Saint-François River, the tectonostratigraphic belts are composed principally from west to east by three distinct types of volcanogenic formations: ophiolite belt, polymetallic deposits and subalkaline volcanics interbedded. The section of the Saint-François River that crosses through these different rocky formations is fairly shallow in this area. Between Windsor and Richmond, for instance, the riverbed is about 5 m deep on average and rock outcrops can be seen all along the banks. This part of southern Québec is characterized by a cool and humid climate with an annual precipitation rate ranging from 61.7 to 130.0 mm and a total annual precipitation of 1144 mm (1970–2000), along with annual temperatures ranging from −11.9 °C to 18.1 °C, with a mean annuel temperature of 4.11 °C (Sherbrooke station no. 7028124).[18] The maximum discharge registered during 1925–2002 in the Saint-François River (middle section/station 030203) is 2719.1 $m^3 s^{-1}$ and the mean annual discharge is 189.7 $m^3 s^{-1}$.

The sampling period took place between 2010 and 2011 in the late summer and early fall (at low river water levels). Soil samples were collected to a depth of 0–20 cm (total of 56) and other soil samples (224) were collected at different depths (20–40, 40–60, 60–80, 80–100 cm), based on the depth of the soil profile (presence of bedrock). The aim of the double sampling (0–20 cm and 80–100 cm) was to determine the concentration of heavy metals in the sediments deposited on the surface by recent floods and to compare the results with the concentrations of heavy metals obtained in deeper horizons in the same soil profiles. In all, 280 soil samples were taken along the riverbanks in different areas (Eustis, Capelton, Windsor and Richmond), and 102 soil samples (surface and subsurface) were analyzed to determine the concentrations of heavy metals.

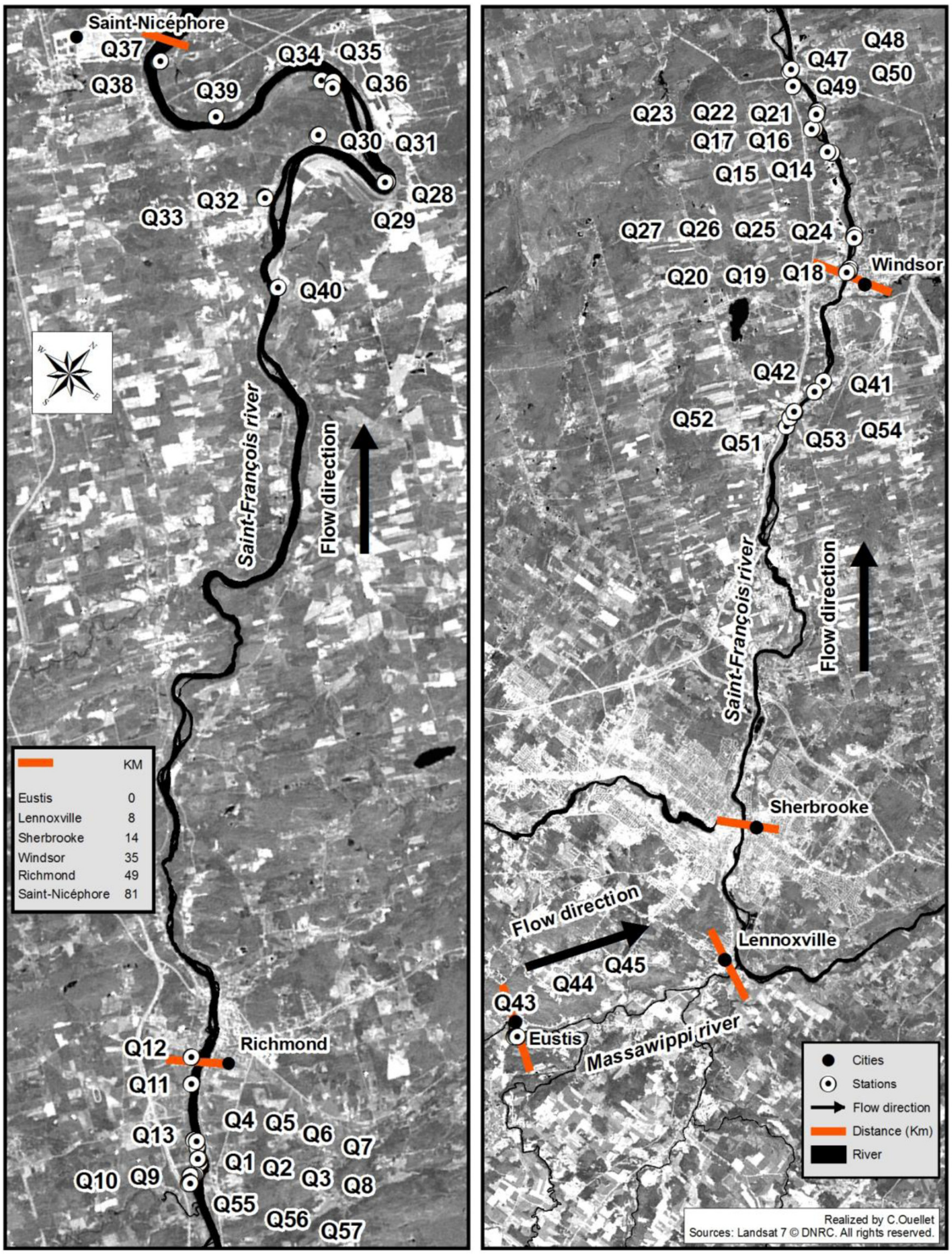

Figure 1. Location of sampling sites in all sectors (Massawippi, Windsor, Richmond and Drummondville areas).

Laboratory analysis

The samples were then stored in plastic bags and air-dried in our laboratories. Once dry, they were manually sieved through a 2-mm screen. They were analyzed in the laboratory to characterize the textural composition, pH and total organic carbon (TOC%). The cation exchange capacity (CEC) was determined with the method used by Carter and Gregorich.[19] For the grain size analysis, the dry sandy fraction was obtained by sieving, while the finer fractions were obtained using a Laser Particle Size Analyser (Fritsch/Analysette 22, Micro Tec plus) with a measurement range of 0.08 to 2,000 µm. The methods used for the chemical analyses consisted of determining the pH by using a 1:2 soil-solution ratio (CaCl2:0.01M) and the TOC (%) content methods.[19,20]

The metal elements (Cd, Cr, Cu, Ni, Pb and Zn) in the soil (106 samples selected) were analyzed by a government-accredited external laboratory (Maxxam Analytics Inc.). The protocol analysis conforms to the standard methods of Quebec's Ministry of Sustainable Development, Environment and Parks[11] and the

Canadian Council of Ministers of the Environment.[21] For the analysis of the concentration of metal elements, the laboratories followed the procedures established by the CEAEQ (specialized environmental analysis centre) described in government reports.[22,23]

For the analysis of heavy-metal concentrations, the soil samples are prepared as follows: (i) in a beaker, precisely 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%); (ii) cover the beaker with a watch glass, and then allow to heat at reflux for 30 min. 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, Agilent 7700x Model). The complete metals analysis procedures, including the duplicate analyses required to validate the laboratory tests, are described in detail in government documents.[22,23]

Soil contamination assessment

The level of contamination of the soil and land was determined based on the generic criteria in the MDDEP's policy,[11] which are defined in the government's "Policy on Soil Protection and Rehabilitation of Contaminated Sites." This report uses three generic criteria (A–C) to determine the degree of soil contamination. Contamination levels A to B are acceptable for residential uses; levels B to C are acceptable for industrial uses; and level > C is prohibited without treatment. Levels B and C indicate that contaminants are found in the soil, and these levels have certain usage constraints. Table 1 provides the contamination levels based on generic criteria (A–C) in the MDDEP's report (2007) for the main heavy metals found in soils and sediments.[11]

Table 1. Generic criteria (A–C) used by Quebec's Ministry of Sustainable Development, Environment and Parks (MDDEP) to determine the degree of soil contamination.

Metal elements (mg/kg)	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Level						
Criterion A[a]						
Low	1.5	85	40	50	50	110
Criterion B						
Moderate	5	250	100	100	500	500
Criterion C						
Heavy	20	800	500	500	1500	1500

Notes: [a]The level of soil contamination (A, B or C criteria) for metal elements determined by the MDDEP[11]; Contamination levels A to B, residential uses; levels B to C, industrial used; levels > C, use is prohibited without treatment.

Statistical analysis

Standard statistical analyses were conducted on all the soil samples in order to determine the maximum and minimum concentrations of heavy metals found in the soils at different depths. Also, correlation tests (Pearson and Spearman) and variance tests (ANOVA) were conducted to determine the degree of correlation between the total heavy metal concentrations (eg, Ni, Pb and Zn) and certain soil properties (pH, total organic carbon) as well as compare inter-site variability (ie, Frequent Flood Zone/FF = 0–20 yrs recurrence; Moderate Flood Zone/MF = 20–100 yr recurrence; and No Flood Zone/NF) of the various flood recurrence zones, and thus obtain the significant values. The total concentration of heavy metals and soil properties (pH and TOC%) were tested for correlations between them using Pearson's correlation coefficient based on the assumption that the data (pH, TOC and heavy metals) were normally distributed. However, normality tests showed that the variables are not normally distributed and that no joint distribution is possible between them. To counter this problem, we therefore preferred using Spearman coefficient R_S, which is based on data ranks and not on the actual data. In this case, the values obtained are considered significant with a threshold of $P < 0.05$ and 0.01 (P-value). For the pH and heavy metals variables, correlation analyses (Spearman coefficient) were done by separating the pH values into two groups, ie, one with all the pH data and another with only <5.0 pH data.

A variance analysis (ANOVA test) was done to compare the differences among the two flood zone recurrences (FF and MF), including the zone not affected by floods (NF). We tried to determine whether the three chosen flood zones (FF, MF and NF) had an impact or not on the concentration of heavy metals (Pb and Zn) found in the surface horizons (0–20 cm). Data distribution and normality were first checked before conducting the ANOVA test. Preliminary tests showed that there was no normality and equality with the variables, which is why statistical transformations had to be used to standardize the data. Based on the different tests used, mathematical transformation $T(y) = \ln(y)$ appeared to be the most adequate before performing the variance test (ANOVA). The latter was done based on the initial ranks of initial data to confirm the results. This procedure is also known as the Friedman test. By conducting the ANOVA test, it could be said that the different flood zones (FF, MF and NF) had a significantly different impact on the concentration of the chosen heavy metals (Ni, Pb and Zn). Since the ranks are used and not the actual data, the Duncan test was applied. The ANOVA analysis was done by considering the pairs of the different flood recurrence zones (FF-MF, FF- NF and MF-NF). In this instance, to validate the results, the retained threshold (P-value) is 0.05. Lastly, all the statistical analyses and tests were conducted using the SAS®/STAT software program (version 9.2).

Results and Discussion

Classification and soil properties

The soil profiles (±1 m in depth) in the flood zones have been classified in the Regosolic and Brunisolic order of the Canadian System of Soil Classification.[24] The Orthic Regosol (O.R), Cumulic Regosol (CU.R), Gleyed Regosol (GL.R) and Gleyed Cumulic Regosol (GLCU.R) make up most of the alluvial soil in the floodplains being studied. These soils generally show little development and are characterized by the absence of Ah and B horizons, or weak development of B horizon characterized by little chemical alteration. For soils located outside of flood zones (NF), Orthic Dystric Brunisol (O.DYB) and Gleyed Dystric Brunisol (GL.DYB) are predominant. There are also podzolic soils such as Orthic Humic Podzol (O.HP) and Orthic Ferro-Humic Podzol (O.FHP).

The various properties of the soils that were analyzed consist of pH, total organic carbon content (TOC%), cation exchange capacity (CEC), and texture. Table 2 shows a summary of these chemical and physical properties of the soil samples (depth of 0–20 cm) based on the flood recurrence zones (FF and MF) and the zone not affected by flooding (NF). Note that soil acidity (pH) is relatively comparable for the soils in the FF and MF zones, whereas surface soils are more acidic in the zones not affected by flooding (NF). For the flood zones, the mean values are 5.13 ± 0.75 (FF) and 4.49 ± 0.46 (MF), while the NF zone shows an average of 3.89 ± 0.89, with maximum and minimal values ranging from 5.78 to 2.79. This higher acidity of the "non-flood" soils could be attributed to the higher levels of organic matter, which contains acidifying compounds. It is known that humified organic compounds contain various acids (fulvic and humic) that lead to soil acidification.[25] Note, furthermore, that the NF zone generally has a higher total organic carbon content (TOC%) which mainly comes from the accumulation of plant litter, such as leaves

Table 2. Properties of soil samples (0–20 cm deep) along the Massawippi and Saint-François river banks in different flood zones (FF and MF) and no flood areas (NF).

Soil samples (0–20 cm depth)	pH ($CaCl_2$)	% TOC	CEC[a] ($cmol_{(+)}\ kg^{-1}$)	% sand	% silt	% clay	Texture[b]
Frequent Floods (FF) (n = 30)							
Mean	5.13	1.99	10.10	48.08	49.97	2.05	Silt loam
Maximum	6.07	5.13	33.03	76.84	67.29	3.72	
Minimum	3.53	0.63	0.48	29.43	21.85	1.05	
Standard deviation	0.75	1.12	7.24	12.97	12.44	0.52	
Moderate floods (MF) (n = 9)							
Mean	4.49	3.17	6.99	52.74	45.42	1.83	Sandy loam
Maximum	5.36	5.13	9.79	72.80	65.39	2.70	
Minimum	3.95	1.54	1.99	32.19	26.0	1.10	
Standard deviation	0.56	1.43	2.62	13.06	12.66	0.52	
No floods (NF) (n = 17)							
Mean	3.89	5.59	6.37	56.76	41.68	1.56	Sandy loam
Maximum	5.78	30.67	31.15	81.07	67.28	2.70	
Minimum	2.79	0.84	0.32	30.47	18.29	0.63	
Standard deviation	0.89	6.76	7.92	15.44	14.83	0.65	

Notes: [a]CEC included the cations Ca, Mg, K, Na; [b]textural class determined by the Canadian System of Soil Classification.[23]

and organic debris. For the NF zone, the ground biomass accumulates over the year, while for the zones subjected to flooding, biomass is often transported downstream with the river current, leaving the soil partially or totally stripped.[26,27] Lastly, it is important to bear in mind the buffer capacity of the soils which could in turn affect pH variability. The buffer capacity depends on the total ionic charge, and especially the organic content amount, and, to a lesser extent, the content of clays and oxides or iron and aluminum in the soils.[28] For the cation exchange capacity (CEC), the main values obtained for each zone are of the order of 10.10 $\text{cmol}_{(+)}\ \text{kg}^{-1}$ (SD 7.24) (FF), 6.99 $\text{cmol}_{(+)}\ \text{kg}^{-1}$ (SD 2.62) (MF), and 6.37 $\text{cmol}_{(+)}\ \text{kg}^{-1}$ (SD 7.92) (NF), respectively. These values are relatively low and can be explained by the low clay content and the low levels of organic matter found in most of the soils that were analyzed. In terms of texture, most of the soil samples analyzed in the flood zones are made up of fine material, mainly fine sandy loam, loamy fine sand and loam (Table 2). These fine textures are in fact a common feature of flood deposits.[15,29] The percentages obtained range from 29% to 81% for the sands and 1% to 3% for the clays. The low clay fraction in the alluvial soils is partly due to the origin of the parent materials, which are mainly made up of fluvial (66.2%) and glaciolacustrine (27.8%) deposits (shallow-water facies) containing a high proportion of loam, sandy loam, or loamy sand materials.[15] Finally, greater textural variability was noted for the soils outside the flood zones, ranging from coarse sand to finer sediment (sand, sandy loam and loamy sand). This variability is explained by the diversity of the superficial deposits found on higher terrain (eg, fluvial terraces, moraines and meltwater features) along the rivers and streams in the study areas.[15]

These various soil properties (pH, TOC, CEC, and texture) come into play in several pedogenetic processes, including the retention or absorption of metal elements, in particular via organic matter and fine particulate matter (clay sheets or fine loam) in the mineral matrix.[30–32] Also, metal elements (including the most mobile ones such as Cd and Zn) can be leached toward the deeper horizons in the profile,[33–35] especially in acidic soils.[36–38] The study by Remon et al,[37] for instance, shows that the solubility of several heavy metals substantially increases with pH levels under 4.5, including metals such as Pb, Ni and Cr. Furthermore, the work by Shu et al,[38] shows a depletion of heavy metals at the base of the profile due to acidification. Like the pH level, the organic carbon content and grain size are involved to different degrees in the retention or remobilization of the metal elements contained in the soils and partly explain the pattern of distribution of the contaminants in the profile.[31,33,36,37]

Statistically, the correlation analyses (Spearman coefficient) performed on the different variables (pH, organic carbon and metal concentration) show no correlation or a weak positive (or negative) correlation, except for the pH and Zn variables (Table 3). The values obtained for these two variables show correlation coefficients of 0.577 and 0.810 based on the two groups retained (group with all pH data and group with only <5.0 pH data, respectively) (Fig. 2). The results obtained with the Spearman coefficient (0.810) in fact show that the more acidic soils (<5.0) are more strongly correlated with Zn. However, outside of these two variables (pH and Zn), correlations appear to be rather weak and even non-existent for the variables analyzed.

Metal concentrations in alluvial soils

The metal concentrations (Cd, Cr, Cu, Ni, Pb and Zn) in the soil profiles of the Massawippi and Saint-François rivers are shown in Table 4 and Figure 3. Metal concentrations (Pb and Zn) are generally higher in the surface horizons (0–20 cm) than in the deeper horizons of the profiles (60–80 or 80–100 cm), though they show relatively high concentrations in deeper layers (>80 cm) of soil profiles (Table 4). The higher concentration of Pb measured on the surface of some soils may depend on the metal's low mobility in penetrating the deeper soil horizons. This metal is not easily solubilized, especially at pH levels higher

Table 3. Spearman correlation coefficients[a] between soil properties (pH and TOC%) and three metal elements (Ni, Pb and Zn) in surface soils (0–20 cm) (n = 56).

Metal element	Ni	Pb	Zn
Soil properties			
pH (all data)	0.643*	–0.370**	0.577**
pH (<5)	0.711*	0.142**	0.810*
TOC (%)	–0.117**	0.458*	–0.267**

Notes: [a]Correlation is significant at the 0.01 level; *significant values; **not significant values.

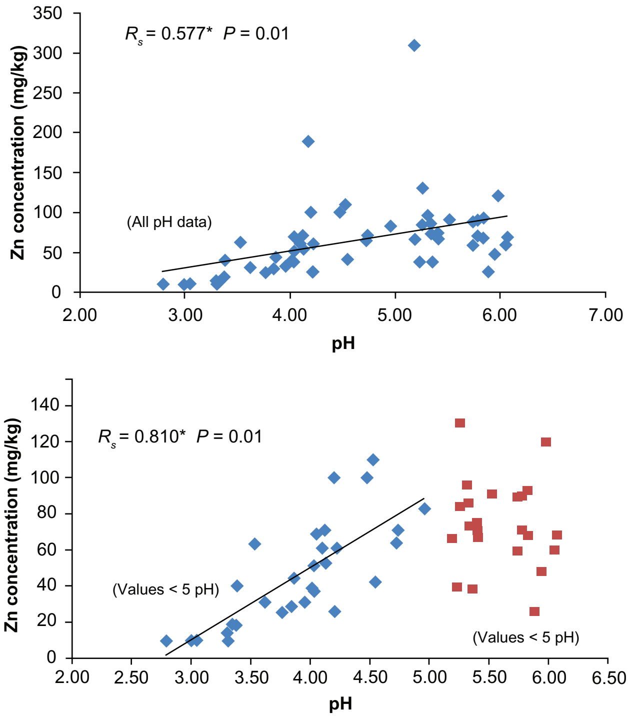

Figure 2. Results of correlation analysis between Zn concentration (mg/kg) and pH of soil samples at upper layer (0–20 cm).

than 5.5.[38,39] For certain profiles, the concentration of heavy metals (Pb, Zn) exceeds Level B in the Quebec Government's generic standards.[11] Furthermore, in the zones affected by flooding (FF and MF zones), heavy-metal concentrations generally appear to be higher than at the sites not affected by flooding (NF) (Fig. 3). The elements with the highest concentrations are generally Ni, Pb and Zn. In frequently flooded zones (FF), Ni and Zn concentrations in the surface horizons (0–20 cm) can range from <1 to 120 mg kg^{-1} (Ni) and 38 to 310 mg kg^{-1} (Zn), compared to 5 to 490 mg kg^{-1} for Pb. The maximum concentration of Pb (490 mg kg^{-1}) in alluvial soils is 30 times higher than the average Pb concentration found in a natural state evaluated at 15.3 mg kg^{-1} (SD 17.5).[40] Pb is known to be a stable and persistent element in soils[38,39] along with other heavy metals, including Cu and Ni,[30,32,33] while Cd is much more mobile and can be easily leached outside the soil profile.[31,33] In this respect, Cd, Cr and Cu show relatively low levels in the samples that were collected, ie, values below the contamination limits in the established standards.[11] Metals such as Cd, Pb and Cr are known to be toxic at high concentrations for living organisms and for human health.[36,43–45] The surface samples (0–20 cm) are those that are most often contaminated, although high concentrations are found in deeper horizons (60–80 and 80–100 cm). Soil in the FF zone is more often contaminated, although contaminated soil is also found outside the flood zones (Drummondville sector), where Pb and zinc concentrations are relatively high (160 and 110 mg kg^{-1}, respectively). In the present case, local pollution that originates from potentially contaminated backfill deposited on the soil surface is suspected as the cause.

The concentration of metal elements from our results of soil samples (Table 4) repeatedly showed

Table 4. Concentration of metal elements in soil samples along the Massawippi and Saint-François rivers including flood (FF, MF) and no flood zones (NF).

Metal concentrations (mg/kg)	Cd	Cr	Cu	Ni	Pb	Zn
(0–20 cm depth) (n = 56)						
Minimum value	<0.5	<2	<2	<1	5	38
Maximum value	0.9	55	**46**[a]	**120**	**490**	**310**
Mean	<0.5	19	17	31	28	66
Standard deviation	0.2	9.3	11.5	22.4	66.1	47.6
Median	0.7	18	15	29	15	63.5
Kurtosis	–	3.67	0.12	5.8	45.3	12.1
(80–100 cm depth) (n = 34)						
Minimum value	<0.5	11	3	17	<0.5	22
Maximum value	0.6	56	**95**	**170**	45	**240**
Mean	<0.5	20	23	35	12	56
Standard deviation	<0.5	8.85	27.2	26.9	10.0	46.7
Median	<0.5	18	9	29	8	37.5
Kurtosis	–	10.4	1.16	20.5	2.82	6.35

Note: [a]Bold values exceed the contamination levels of A criterion determined by the MDDEP.[12]

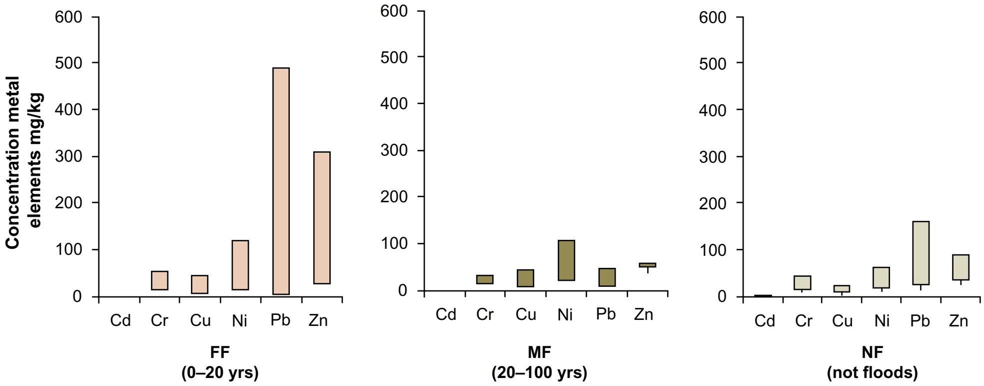

Figure 3. Concentration of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in soil samples (0–20 cm depth) in different flood-recurrence zones (FF, MF) and no flood zone (NF).

values exceeding Criterion A of the MDDEP contamination limit,[11] especially for Ni, Pb and Zn. Furthermore, when our values are compared to those obtained by Choinière and Beaumier[40] for soils and sediments (natural background) in the Appalachian geological region (A4) where our area is located, heavy-metal concentrations in our soils are significantly higher than those obtained by the above authors[40] in the Appalachian region. For instance, Ni, Pb and Zn have values 10 to 30 times higher than those obtained for soils and sediments at natural sites.[40] As a comparison, the mean level obtained for zinc is about 67.3 mg kg^{-1} (SD 82.3), and 15.3 mg kg^{-1} for Pb (SD 17.5), respectively, whereas the levels are 120, 130 and 310 mg kg^{-1} for Zn and 160 and 490 mg kg^{-1} for Pb for different soil profiles (Q5-1, Q24-1 and Q49-1).

The study by Garrett et al,[46] which includes the Appalachian region in the eastern United States (Area 9), shows that the median values of the metals and metalloids obtained in the surface horizons (A-horizon) are 6 (As), 34 (Cr), 16 (Cu), 26 (Pb), and 63 (Zn) mg kg^{-1}, respectively. These values are comparable to those obtained in the soils and sediments (natural background) of the Appalachian geological region in southern Québec,[40] but lower than our measured values. Although these values are representative of the natural backgrounds of the surrounding soils, it could be easily said that the contamination rates in our soil profiles are linked to anthropogenic contamination, which in some cases exceeds the Criterion B contamination levels.[11] Such contamination may come from various sources since the rivers in question pass through urban areas (Sherbrooke, Windsor), farmland and former mining sites (Eustis-Capelton) for the upstream portion of the Massawippi River. Pb, Zn and Ni may also come from industrial discharge,[7,47] and urban effluent may contain all kinds of contaminants, including heavy metals. The mine tailings from the Eustis-Capelton complex, located along the Massawippi River, are probably a major source of heavy-metal contamination,[7,10,47] with the metals being transported over several kilometres and now found in the alluvial soils of the Massawippi and Saint-François rivers. In addition to this major spatial distribution (over 100 km) of contaminants, the frequently flooded zones (FF) are those that are the most contaminated, which indicates that floods are a major carrier in the transport and remobilization of contaminants along the riverbanks. In this instance, the ANOVA test was conducted to determine whether the differences in heavy-metal concentrations in the soils could be significant between the three zones (FF, MF and NF). The level used for the analysis of variance is $\alpha = 0.05$ probability. The analysis results

Table 5. Results of the ANOVA test between three zones (FF, MF and NF) with a threshold at $P = 0.05$.

Comparison between the three zones[a]	Difference between means		Confidence interval (95%)
FF-MF	31.50	24.11	38.88*
FF-NF	19.50	13.60	25.40*
MF-NF	–12.00	–20.01	–3.98*
MF-FF	–31.00	–38.88	–24.11*
NF-FF	–19.00	–25.40	–13.60*
NF-MF	12.00	3.98	20.01*

Notes: [a]Soil samples in upper layer (0–20 cm); *significant at 0.05 level.

Table 6. Metal concentrations of soil samples (n = 56) between the Eustis (Massawippi River) and Drummondville areas (Saint-François River).[a]

Mean concentration of metals (mg/kg) in upper layer (0–20 cm)	Distance from Eustis mine (0 km)	Windsor (39 km)	Richmond (56 km)	Drummondville[b] (100 km)
Cd	<0.5	<0.7	<0.5	<0.6
Cr	30	18	17	14
Cu	18	17	19	12
Ni	46	27	27	19
Pb	21	56	16	29
Zn	62	86	65	48

Notes: [a]Only sites located in frequent flood zones (FF/recurrence of 0–20 yrs) are represented in this Table; [b]Saint-Nicéphore is part of the Drummondville area.

indeed confirm that there is a significant difference among the three zones being compared. The zone with a 0–20 year recurrence (FF) is the one most affected by contamination in surface soils (upper layer of 0–20 cm), while the 20–100 year zone (MF) is lightly or moderately affected, and the non-flood zone (NF) is not affected or only slightly. The comparative results for the three zones can be found in Table 5.

The heavy metals found in the alluvial soils in the Drummondville area, more than 100 km from the Eustis-Capelton sites (Fig. 1), may come from the upstream-contaminated former mining sites. During successive floods, the contaminated sediments may be remobilized, transported and redeposited further downstream along the riverbanks. This flooding and deflooding process was in fact the subject of various studies that showed a redistribution of contaminants along the banks of rivers and streams.[48–50] At some sites, it was noted that contaminants could be transported over several kilometres.[51,52] In our case, no longitudinal gradient (downstream vs. upstream) could be detected that showed a marked reduction in heavy-metal concentrations from the point source (Eustis mine) to the downstream areas (Windsor, Richmond and Drummondville). However, higher concentrations were noted for certain heavy metals (Pb and Zn) at the sites several dozen kilometres away, in particular for the Richmond and Drummondville areas (Table 6).

These results appear to indicate that the contaminants can be transported over long distances and that they are then redeposited along the riverbanks during flood events. In a scenario where floods could increase because of current climate change, as can already be seen in our study areas,[13,14] it could be assumed that the contamination will extend to other riverside areas located downstream, which would have the effect of increasing the spatial range of the contamination to areas that have been or impacted only slightly or not at all. This is all the more worrisome since the downstream riverside areas mostly consist of farmland. These results also present the problem of the continued presence of heavy metals in rivers and streams. If the main source of the contaminants is the former mining site at the Eustis-Capelton-Albert Complex, more than 70 years have elapsed since the mines were closed in 1939, which means that the alluvial plains constitute long-term contaminant-deposition sedimentary areas. Based on these results, government authorities will have to consider implementing efficient measures to mitigate the adverse effects of the transport of contaminants along riverbanks, to ensure a healthy environment for the community and future generations.

Conclusions

This study, conducted along the banks of the Massawippi and Saint-François rivers, reveals that the alluvial soils in the flood zone with a recurrence of 0–20 years (FF) are more contaminated than the soils located in the flood zone with a recurrence of 20–100 years (MF). Moreover, the soils located near the riverbanks but outside the flood zones (NF) are not contaminated (with the exception of two soil samples). Generally speaking, the level of soil contamination is relatively low but several sites exceed the Criteria B and C contamination levels established by Quebec's environment ministry.[11] In some cases, these limits attain contamination levels that are 10 to 30 times higher than those measured in the study area's soils and sediment (natural background). With respect to contaminant transport, no longitudinal gradient (downstream vs. upstream) could be detected that showed a marked reduction in heavy-metal concentrations from the point source (Eustis mine) to the downstream areas (Windsor, Richmond and Drummondville). However, higher concentrations were noted for certain heavy metals (Pb and Zn) at the sites several dozen kilometres away, in particular for the Richmond and Drummondville areas. This contamination may originate from sources other than mine tailings from the former Eustis-Capelton-Albert complex, such as urban or agricultural effluent. Regardless of the potential sources of pollution, it can be noted that the transport of contaminants can occur over very long distances, thus contributing to significantly increasing the contamination of new riverside areas. Therefore, it becomes crucial to better control the various sources of pollution along waterways and ensure that current regulations (municipal, provincial and federal) are efficient and applied stringently to limit sources of pollution.

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Author Contributions

Conceived and designed the experiments: DSTL. Analysed the data: DSTL, CM. Wrote the first draft of the manuscript: DSTL. Contributed to the writing of the manuscript: DSTL, VGB. Agree with manuscript results and conclusions: DSTL, VGB, FB, CM, JSB. Jointly developed the structure and arguments for the paper: DSTL Made critical revisions and approved final version: DSTL, VGB, FB, CM, JSB. All authors reviewed and approved of the final manuscript.

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Competing Interests

Author(s) disclose no potential conflicts of interest.

Disclosures

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Appendix

Table A1. Location of sampling sites in the Massawippi and Saint-François areas, including the different flood zones (FF, MF) and no flood zone (NF).

Location of sampling sites	Flood zone (0–20 yrs recurrence/FF)	Flood zone (20–100 yrs recurrence/MF)	Outside of flood zones (NF)
Drummondville	Q34 to Q36		Q28 to Q33, Q37 to Q40
Richmond	Q1, Q2, Q4 to Q8, Q11 to Q13	Q55 to Q57	Q3, Q9, Q10
Windsor	Q14, Q20, Q23 to Q27, Q41, Q42, Q48 to Q53	Q18, Q19, Q21, Q22, Q47, Q54	Q15 to Q17
Massawippi	Q43, Q44		Q45
Number of sampling sites	30	9	17