# Mechanisms Triggering Metal Release From Floodplain Soils and Sediments, Three Nations Creek, Ontario, Canada

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## ABSTRACT
Three Nations Creek (TNC) is an intermittent tributary that runs roughly 6 km past the Xstrata Copper–Kidd Metallurgical Site to the Porcupine River. The creek historically received surface runoff, and drainage that contributed to elevated concentrations of metals including Zn and Cu, in the floodplain soils and sediments of the creek. Containment measures for surface water installed in the late 1990's and early 2000 have been successful in reducing concentrations of metals in the creek water with no toxicity issues; however, concentrations in the creek can increase with occasional toxicity events, during spring freshet and autumn periods. The severity and duration of these events differs with the season and varies with extremes in climatic events. Kidd Metallurgical Site initiated development of a Remedial Action Plan for TNC with reference to the occasional high concentration events in the creek. The objectives of this study were to identify the fundamental mechanisms that trigger seasonal metal release from the TNC floodplain and to identify measures to reduce or eliminate, to the extent practicable, conditions within TNC that result in occurrences of high concentrations of metals in the creek water. Testing results and monitoring in development of the remedial strategy are presented.

Key Words: metals, zinc, organic soils, organic sediments, contaminant loading

## INTRODUCTION
The Xstrata Copper–Kidd Metallurgical Site (Kidd Metsite) is located within the City of Timmins about 24 km east of the city centre along Highway 101. Three Nations Creek (TNC) runs roughly 6 km along the south edge of the Kidd Metsite originating to the north of the Pamour Mine site and west of the Kidd Metsite flowing east to the Porcupine River (Figure 1). The original creek channel was the outlet for Three Nations Lake; however, the headwater area was realigned to drain approximately 40% of flow to the southeast through a realigned branch to accommodate open pit development at the Pamour Mine. Three Nations Creek historically received surface runoff, and drainage from Kidd Metsite's Jarosite Pond Area that contributed to elevated concentrations of metals including Zn and Cu, in the floodplain soils and sediments of the creek.

Containment measures for surface water conducted by Kidd Metsite were installed in the late 1990's and early 2000 that successfully reduced concentrations of metals in the creek water with no toxicity issues; however, in 2005 a severe summer drought in the Timmins area resulted in diminished intermitted flow in TNC and caused the floodplain to dry out. With the onset of annual fall rains and resumption of saturated and flowing conditions, an apparent flushing of zinc from the previously dry areas occurred within a limited time window, where elevated concentrations of zinc in several reaches of TNC resulted in temporary acutely toxic conditions immediately downstream of contaminated floodplain areas. To minimize the potential for occurrence of similar future toxicity events the Xstrata Copper–Kidd Metallurgical Site (Kidd Metsite) voluntarily undertook action to prepare a Remedial Action Plan (RAP) to address the occurrence of such upset conditions.

## BACKGROUND AND HISTORICAL SETTING

A general plan of TNC including sampling points for this study is shown in Figure 1. The creek is a riverine system made up of an open creek channel, associated floodplain soils, sediments and beaver dams. The main channel is intermittent in the upstream reaches but receives additional flow in the downstream area from two additional sources identified as the Buffalo Paddock Tributary and the Re-aligned Branch (Figure 1). The Buffalo Paddock Tributary joins the main creek from the north approximately 2.2 km upstream from the Porcupine River. This tributary historically drained a field located immediately south and adjacent to the Kidd Metsite known as the Buffalo Paddock Area. The drained area of the Buffalo Paddock is now reduced due to stormwater control measures. The re-aligned Branch of TNC contains redirected flow from Three Nations Lake and re-joins the original creek from the south approximately 1.3 km upstream from the Porcupine River. Xstrata has four primary environmental monitoring stations for TNC (Hwy 101, 3ND-1, 3ND-2 and 3ND-4). Three Nations Creek decreases in elevation from approximately 284 m (masl) at the headwaters on the west falling to 276 m where it meets the Porcupine River in the east. This represents a total elevation drop of approximately 8 m over the 6 km length of TNC (i.e., about 0.13% average grade).

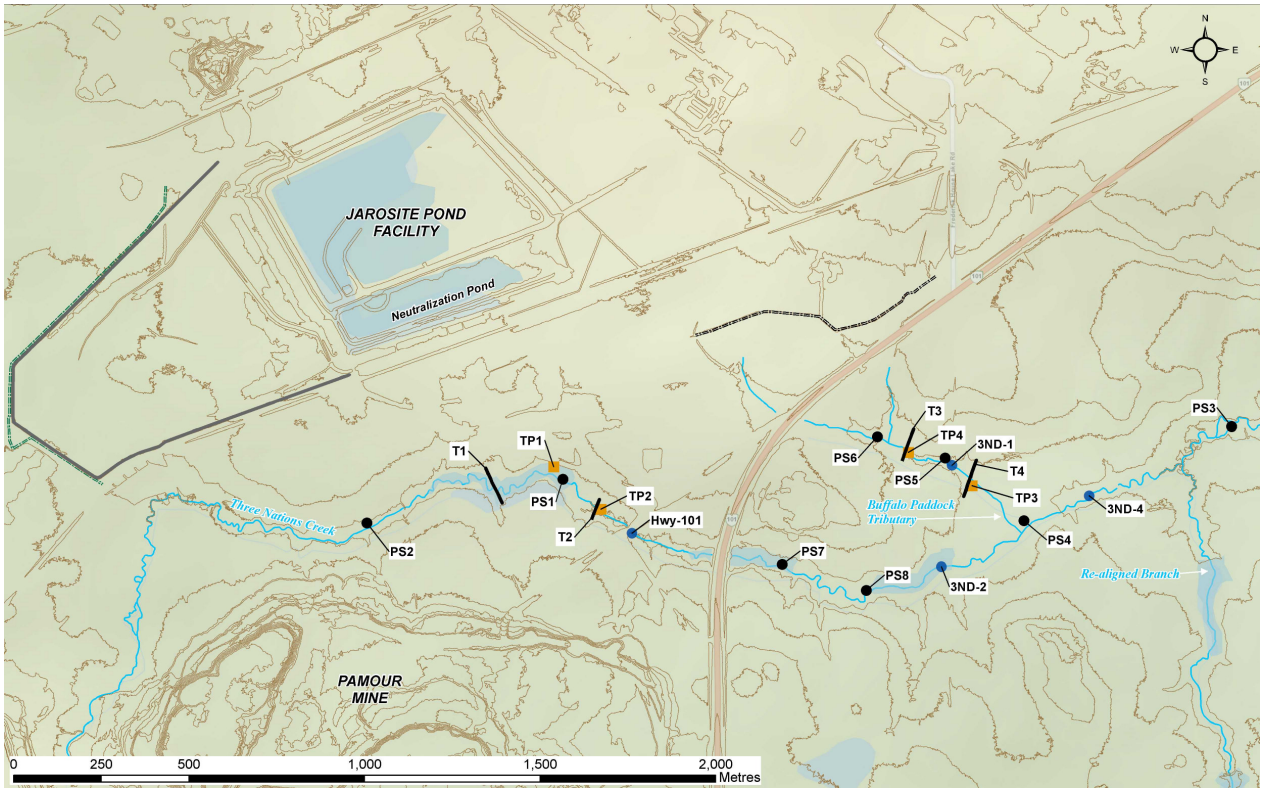


Figure 1. General Overview of Three Nations Creek

The original creek historically received surface runoff, and seepage from areas of the Pamour Mine, and the Kidd Metsite which resulted in elevated concentrations of metals, primarily Zn, with Cu, Cd, and Se, all of which accumulated in the sediments within TNC channel and the surrounding floodplain soils. Kidd Metsite implemented several source control programs to mitigate the sources of Zn contamination from the Jarosite Pond Facility including: establishment of seepage collection ditches around the Jarosite Pond Facility and containment ditching 1990-1998; construction of the West Containment Berm, and West Diversion Ditch east of the Jarosite Pond in 2002; improvements to seepage collection systems and

removal of contaminated soil from the general Jarosite Pond Area in 2002-2003; and construction of a runoff diversion and collection system in the Buffalo Paddock Area in 2004-2010. The source control activities related to the Jarosite Pond Area have successfully abated the principal source of Zn loading. Buffalo Paddock source abatement works have also significantly reduced metal releases to TNC. The monitoring program indicated that the elevated Zn levels within the TNC sediments and floodplain soils extend approximately 3.5 km downstream of the historical seepage point from the Jarosite Pond Facility. Zinc contamination was confirmed to persist in the creek and floodplain soils from the surface to 8 to 10 cm in depth. Despite the elevated concentrations of Zn in the floodplain soils and creek sediments, relatively diverse benthic invertebrate and fish communities were observed, consistent with what might be expected in such a habitat in Northern Ontario. It was also concluded that the concentrations and loadings leaving the Buffalo Paddock Area did not have a significant impact on water quality conditions in TNC. In 2005 a severe summer drought in the Timmins area resulted in intermitted flow in TNC and caused the TNC floodplain to dry out. With the onset of fall rains and resumption of saturated and flowing conditions, an apparent flushing of Zn from the previously dried areas occurred within a limited time window, producing elevated concentrations of Zn in parts of TNC resulting in a series of acute toxicity events at permanent surface water monitoring stations Hwy 101 and 3ND-1 in the upstream area, but not the downstream 3ND-4 station.

Preparation of a remedial action plan (RAP) with reference to occasional acute toxicity events in TNC required collection of extensive support data, including benthic and aquatic studies, an environmental risk assessment, and soil, sediment, and water analyses. The primary objective of the soil, sediment and water study presented herein was to verify the sources and the functional mechanism (at a practical level) triggering the release of Zn and other metals of concern from the soils and sediments of the creek. This information was used to develop a remedial option for TNC to address the issue of temporary acute toxic conditions.

## SAMPLE TESTING AND RESULTS

A series of floodplain soil and sediment samples e were collected to conduct several interrelated laboratory tests and measurements. Water quality samples for surface water and piezometers were also collected and, in combination with historical water quality data for the site, were used to interpret the results within the context of determining the release mechanism for zinc and other metals to the creek water. The following sections describe sampling and testing methods along with the results for each.

### Soil Sampling

Soil samples (see Figure 1) were collected from four test pits (TP 1 – TP 4) and from a series of soil cores collected along four transects (T1 – T4). Two test pits (TP1 and TP2) and two transects (T1 and T2) were located in the upstream region of the TNC and two of each (TP3, TP4, T3 and T4) were located on the Buffalo Paddock Tributary. Transects were made up of eight sample holes positioned roughly perpendicular to the creek channel with four sample holes located to the south of the creek channel and four located to the north. Transects ranged in total length from about 70 to 110 m centered on the creek channel. All samples were submitted for analyses for total carbon, total organic carbon and total metals.

The content of organic matter in the samples ranged from 11.2% to 34.4%, assuming 58% organic carbon in soil organic matter. All samples contained elevated concentrations of Cd, Cu, Se, Ag and Zn at least an order of magnitude greater than their respective average crustal abundance. The total concentration of Zn in the samples ranged from 2,400 mg/kg (TP3) to 7,200 mg/kg (TP1) compared to background concentrations in mineral soil of 50 mg/kg. The samples containing the highest (TP1) and lowest (TP3) concentrations of Zn were selected for use in the sequential extraction analyses and leaching column analyses discussed below.

Distances between sample locations along transects varied; but were identified relative to increasing distance from the creek channel as follows:

- Creek Edge (immediately adjacent to the open water of the creek channel);
- Mid Point (midway between Creek Edge and Tree Line);
- Tree Line (at the edge of the floodplain where trees and scrubs were established); and,
- Woods (within the trees growing on the creek banks furthest from the creek channel).

Analyses were conducted on core samples from transects representing depth increments of 0 to 5 cm and 5 to 10 cm, from each sample hole. Where possible, a third 5 cm thick layer sample was also collected for analyses. This third sample, if present, was located immediately above the contact of glaciolacustrine clay which underlays the entire area. When available, samples were collected from the 10 cm up to 28 cm depth interval. A total of 77 samples were analyzed for content of total organic carbon and total metals. Soil samples collected from the four transects contained elevated concentrations of As, Cd, Cu, Se, and Zn relative to average crustal abundances. It was generally found that the concentrations within the first two sample depths (0 to 5 cm and 5 to 10 cm) were at least one order of magnitude greater than the average crustal abundance for soil for Cd, Cu, Se and Zn.

Samples from the 0 to 5 cm and 5 to 10 cm depths contained the highest concentrations of As, Cd, Cu, Se and Zn. The concentrations of As, Cd, Cu, Se and Zn decreased with depth to values near background for samples collected at 10 cm depth or more. The concentrations of Zn and Cu in each profile versus the relative distance from the creek channel for each of the four transect are shown in Figures 2. The majority of contamination occurred near the uppermost layers of the organic soil horizon decreasing with depth.

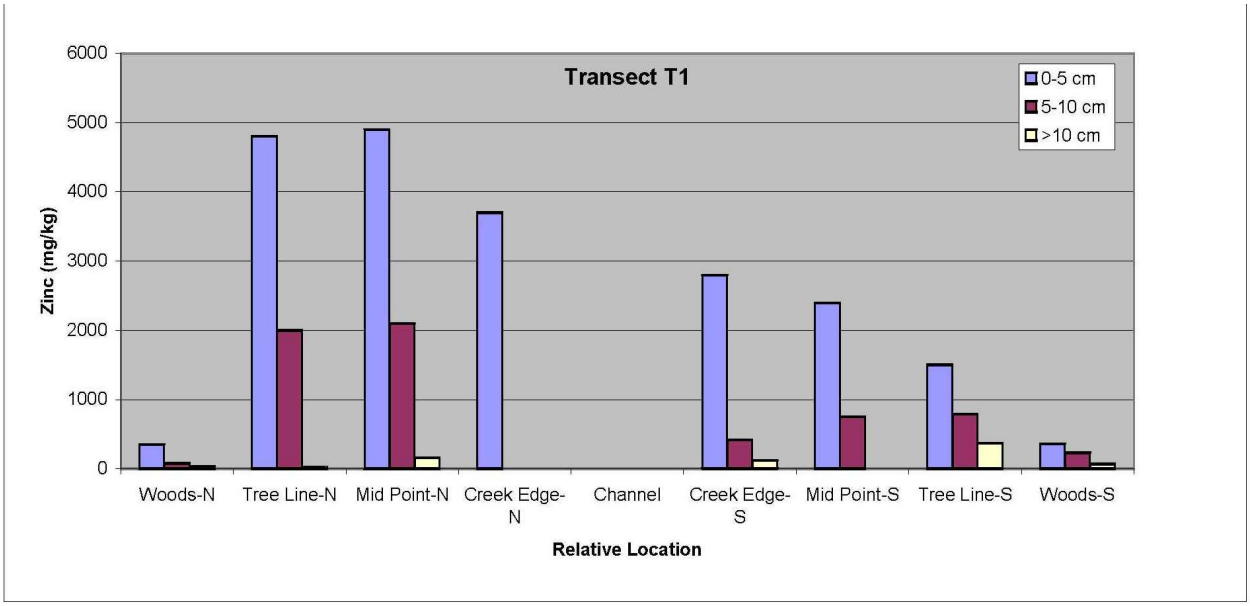


Figure 2. Concentration of zinc with depth in soil at Transect T1

**Piezometer Transects**

To assess possible mechanisms contributing to metal loadings to TNC from shallow groundwater sources a total of 13 stainless steel drive-point piezometers (approximately 1 m long) were installed along transects T1 and T4. The piezometers were installed within the organic layer with the filter screens immediately above the glaciolacustrine clay contact and sealed at the soil surface using bentonite plugs.

The piezometers were sampled eight times (about once a week) during the fall of 2007. Samples were analyzed for total concentrations of metals, pH, and dissolved organic carbon.

Analytical results for total Zn from the piezometer samples are summarized in Figure 3. Measured pH values in all piezometer samples ranged from 6.6 to 8.3 with no apparent trends in the data. In the case of transect T1 the concentrations of Zn were highest in the piezometers next to the creek channel (creek edge) decreasing with distance away from the creek channel. Concentrations of Zn were significantly higher on the north side adjacent to the creek channel at transect T1 compared to the south side. The concentrations of Zn were highest during the first (September 28, 2007) sampling at most piezometer locations. The profile for Cu was similar to Zn, although the absolute concentrations of Cu were lower than Zn and the concentration of Cu in the transect T1 piezometers were higher on the south side of the creek compared to the north side of the creek.

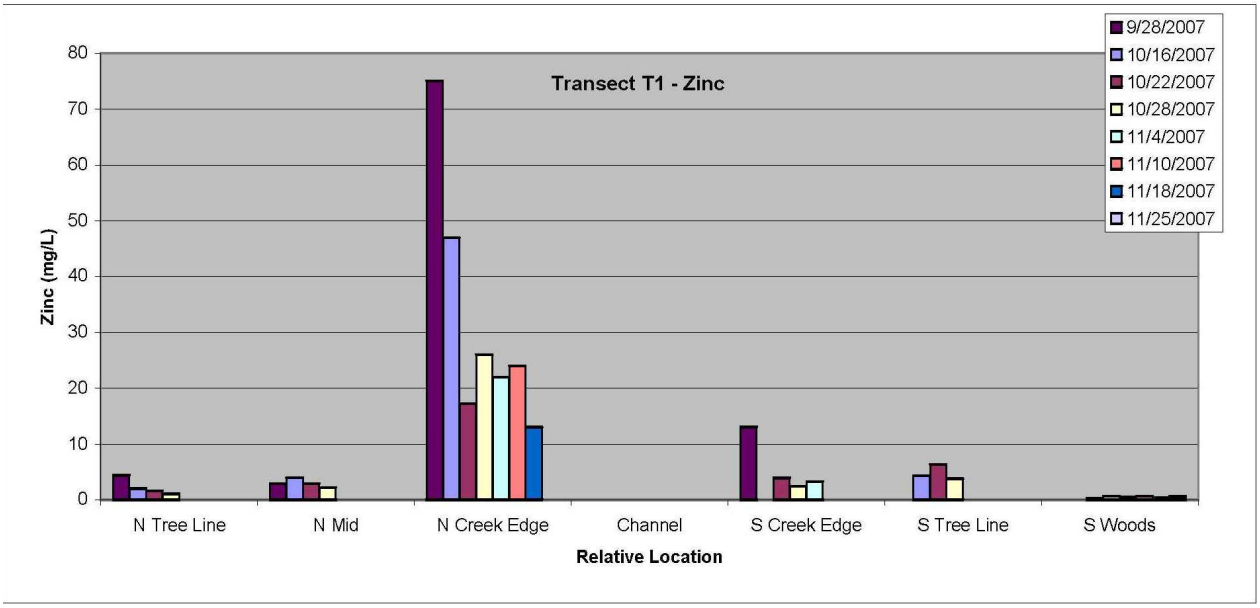


Figure 3. Concentration of zinc in Transect T1 piezometers.

**Beaver Pond Sediments**

Core samples of sediments were collected from the creek bed representing sediments deposited on the upstream side of eight existing beaver dams on TNC. Samples were collected approximately 10 to 30 m upstream of the beaver dams in an effort to avoid areas were sediments had been removed by beavers during dam building. Analyses were conducted on the surface organic layer (typically 0 to 5 cm depth) of the sediments.

The highest concentrations of Zn and Cd appear to occur in sediments upstream of the 3ND-2 and Hwy 101 monitoring points. Although concentrations of Cu are elevated the highest concentrations appears to be localized in a ditch receiving drainage from the culvert immediately south of the Kidd Metsite. Total concentrations of As, Cd, Cu, and Zn exceeded Severe Effects Level (SEL) guidelines (MOE, 1993b). The highest concentrations of Zn, Cd and As in the sediments samples were found in locations upstream (westerly) of the Hwy 101 monitoring point. The concentrations of Cu and Se in the pond sediments (comparable to those of the transect soils) were highest in the sediments associated with the Buffalo Paddock Tributary and downstream (easterly) positions of TNC. Based on these results the highest

concentrations of As, Cd and Zn appear to be in upstream areas of the creek, while Cu and Se appear to be more associated with the Buffalo Paddock Tributary.

**Leaching Columns**

Soil samples from two test pits (TP1 and TP3) were selected for leaching column analyses. Duplicate columns were analyzed for each of the test pit soils. The columns were treated with TNC water (collected at Hwy 101 monitoring point, August 30, 2007) on a weekly basis with the exception of the drying (Dry) treatment (see below). Sample selection was based on the total metals content of the soils where the TP1 sample contained highest concentrations of metals and the TP3 sample represented lower concentrations. All the soil samples had elevated concentrations of metals compared to the average background abundance in soils. Sample TP1 contained the highest total concentrations of Zn, Cu, Cd and As at 7,200, 750, 19, and 31 mg/kg, respectively. Sample TP3 contained the lowest total contents of Zn, Cu, Cd and As at 2,400, 350, 17 and 8 mg/kg, respectively.

Soil sub-samples of approximately 25 to 30 g (dry mass equivalent) each were placed in 7.62 cm (3 inch) diameter by 20 cm high opaque leaching columns (about 900 ml capacity). The initial moisture content of the organic soil samples was approximately 300 to 450% (dry mass basis) at the time of placement in the columns. Soils were leached on a scheduled basis with increments of about 250 ml water from TNC. Soil samples (TP1 and TP3) were subjected to three treatments in duplicate as follows:

- Maintained Water Cover (WC) Treatment. Soils were submerged with sufficient water to cover the soil and drained weekly without exposing the soil to the atmosphere. Water was collected from the bottom of the columns sampled weekly for nine weeks.
- Weekly Flushing (Flush) Treatment. Soils were flushed with water on a weekly basis allowing the soil to drain freely to approximately field capacity between flushes. Columns were sampled weekly for a total of nine weeks.
- Soil Drying (Dry) Treatment. After an initial flushing with TNC water, the soil was allowed to dry through evaporation at ambient temperature and humidity for approximately four weeks. The columns were then flushed with a single 250 ml increment of TNC water followed by another drying period of about five weeks when the columns were flushed again with a second 250 ml increment of TNC water. Water passing through the columns was sampled on three occasions: initial, after four weeks and after nine weeks.

All leachate samples (about 250 ml each) collected from the columns were analyzed for pH, total organic carbon, dissolved organic carbon, total metals, and dissolved metals.

The concentrations of Zn in leachate for soils TP1 is shown in Figure 4. The concentrations of Zn released from the TP1 soil decreased with progressive leaching. The lowest concentrations of Zn in the TP1 soil (high total Zn) were observed in columns with water cover (WC series). It should be noted that the soils with water cover were anaerobic as evident by the presence (smell) of hydrogen sulphide ($H_2S$ gas) when the columns were disassembled. Concentrations of Zn were lowest in the water cover (WC) treatment. The concentrations of Cu changed little over the entire leaching period, remaining less than 0.03 mg/L in all leachates. The highest concentrations of Cu were released from the columns subjected to drying (Dry) while concentrations released from the water column (WC) and periodic flushing (Flush) treatments were lower but similar.

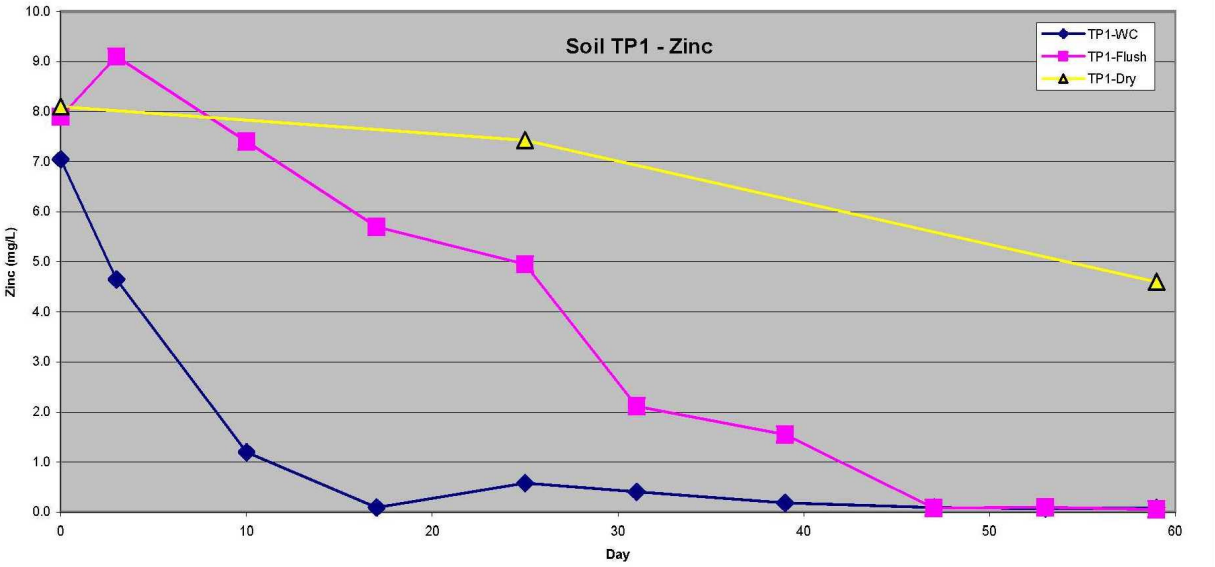


Figure 4. Concentration of zinc leaching column leachate with time.

**Sequential Extraction**

Sequential extraction is an analytical approach to estimate the partitioning metals among various soil fractions by treating soil samples with a series of extracts which attack and dissolve soil solids (and associated metals) with increasing vigour (Tessier, 1979). Each fraction is defined relative to the chosen extract used in the prescribed sequence, where each extract solution is designed to selectively dissolve one metal-containing soil fraction at a time. Several variations in extraction procedures have evolved (e.g., Evans and Wilson, 1985) and procedures are routinely varied depending on the application.

For the current application four samples from the TNC sampling program (two test pits soil samples and two of the beaver pond sediments) were subjected in duplicate to sequential extraction analyses to determine the distribution of metals of interest among five major fractions identified as follows:

1. The soluble and exchangeable fraction was determined by extraction with 0.01 mol/L sodium nitrate ($NaNO_3$).
2. Organically bound metals were extracted with 0.1 mol/L solution of sodium pyrophosphate with a pH value of 10.0.
3. Metals associated with carbonates were extracted with a 2.5% solution of acetic acid (initial pH = 2.6).
4. Metals associated with Fe and Mn oxyhydroxides were extracted using a mixture of 0.1 mol/L ammonium oxalate and 0.1 mol/L oxalic acid buffered at a pH of 3.0.
5. Total metal content was determined using a reverse aqua regia [3:1 nitric acid ($HNO_3$):hydrochloric acid (HCl)] digestion and the recalcitrant fraction determined by difference.

All extracts were analyzed for total concentrations of As, Cu, Cd, and Zn. The proportions of each element associated with each fraction identified above are summarized in Table 1. The greatest percentages (50 to 60%) of all metals in soil were associated with the organic fraction, while the greatest percentages of metals in sediments were associated with the recalcitrant fraction. With the exception of

Cu, the carbonate fraction (acetic acid extractable) contained between 20% and 30% of the other metals. Only a minor percentage of the Cu was associated with carbonate and almost 50% was associated with Fe and Mn oxyhydroxides. About 2% of the total Zn was associated with the exchangeable/soluble fraction while Cd, Cu and As were not detected in the exchangeable/soluble fraction.

Table 1. Percentage of total metals associated with five soil fractions

| Element | Material | Exch. | Organic Matter | Carbonate | Iron Oxide | Recalcitrant |
|---|---|---|---|---|---|---|
| Arsenic | Soil | <0.1 | 58.7 | 19.7 | 15.3 | 6.4 |
| | Sediment | <0.1 | 18.3 | 7.0 | 8.4 | 66.0 |
| Cadmium | Soil | <0.1 | 38.6 | 9.5 | <0.1 | 51.9 |
| | Sediment | <0.1 | 5.7 | 8.1 | 7.5 | 78.7 |
| Copper | Soil | <0.1 | 38.1 | 1.0 | 25.3 | 35.6 |
| | Sediment | <0.1 | 8.8 | <0.1 | 10.8 | 80.3 |
| Zinc | Soil | 1.8 | 48.3 | 7.3 | 13.2 | 29.4 |
| | Sediment | 0.05 | 34.0 | 15.5 | 14.4 | 36.1 |

**Distribution Coefficients (Kd values)**

Distribution coefficients (Kd values), also known as partition coefficients, provide a means and mathematical basis for estimating and assessing the ability of a soil to adsorb and release metals. Distribution coefficients (Kd) are defined as follows:

$$Kd = \text{mass adsorbed} / \text{mass in solution}$$

where the mass adsorbed is the mass of metal adsorbed per unit dry mass of solid phase and operationally defined in the laboratory as the mass of metal released from the solid phase on equilibration with solution at pH 2.0. The mass in solution is the concentration of dissolved metal in the solution contacting the adsorbed phase at a specified solution pH value. Values for Kd are commonly expressed in units of L/kg or ml/g.

Distribution coefficients are site specific coefficients that are dependent on the nature of the soil, ionic strength and solution pH. Values for Kd may be used to estimate the mass of a metal adsorbed onto soil solids for a given concentration of metal in solution and vice versa. In the present case the Kd values were used to determine if the floodplain soils are acting as a source or sink for metal loading to the creek. The values may also be used to estimate the concentrations in the solution phase based on soil metal content.

Four samples (two floodplain soils, two beaver pond sediments) were submitted to the University of Guelph for determination of Kd values for the three elements of interest (Zn, Cu and Cd) based on the total metals content. Values for Kd were determined in a background ionic strength of 0.008 mol/L (as $LiNO_3$) at pH values ranging from 5.5 to 8.0 in steps of 0.5 pH units.

Results for Zn are provided in Figure 5 and calculated values for Kd along with the distribution of Zn at pH 6.6 are summarized in Table 2. Adsorption of Zn decreased with decreasing pH values for the floodplain soil samples and the beaver pond sediments. Equations for Zn in the sediment sample and all samples except the sediment in the case of Cu did not follow the typical trend with respect to pH. The high variability in the data for Cu and the atypical relationship between Kd and pH for Cu in most samples indicated that the predictions for Cu would be unreliable. Although total concentrations of Zn in the pond sediments were typically higher compared to the floodplain soils, the proportion of adsorbed metal was

lower in the beaver pond sediments indicating that much less of the total metals is found in the adsorbed form compared to the proportion found in the floodplain soils.

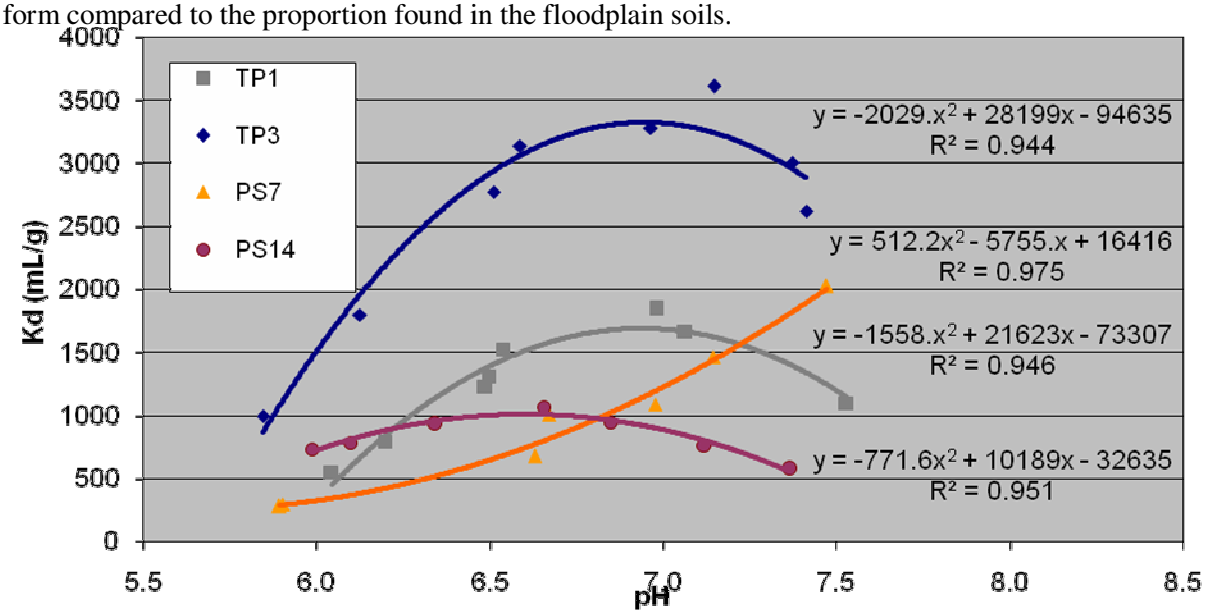


Figure 5. Overview of Three Nations Creek showing locations of grade control structures.

Table 2. Distribution coefficients (Kd values) and distribution of Zn at pH 6.6 in soils and sediments.

| Sample | Total Zinc (mg/kg) | Adsorbed Zinc (mg/kg) | Adsorbed:Total Ratio (%) | Kd (L/kg) |
|---|---|---|---|---|
| Soil | 7,200 | 4,000 | 56% | 1,517 |
| Sediment | 21,000 | 429 | 2% | 741 |

Predicted concentrations of Zn in solution based on the Kd values for the floodplain soils were highest at 2.9 mg/L for the soil sample. Consequently, based on this analyses, that there is sufficient Zn adsorbed on the organic matter of the TNC floodplain soils upstream of the Hwy 101 monitoring station to support solution concentrations of Zn in TNC in excess of 2 mg/L. Values for Kd in the field were back-calculated from field data for comparison. Adsorbed concentrations for Zn were calculated based on the total concentrations of 3,200 mg/kg, assuming that the proportion of adsorbed Zn (56%) is consistent for all soil in the system. The measured concentration of Zn found in the pore water of the piezometers (Figure 3) were higher compared to values predicted from the Kd values determined in the laboratory and the concentration in the water of the open channel of TNC was lower compared to values predicted from the Kd values determined in the laboratory.

The following average annual data was assumed for floodplain soils upstream of the Highway 101 crossing:

| | |
|---|---|
| Estimated flow at Highway 101 (average annual) | 2.2M $m^3$/year |
| Difference in the concentration of Zn between upstream and downstream positions (average annual) | 0.1 mg/L |
| Estimated area of floodplain soil | 63,403 $m^2$ |
| Volume of organic layer in floodplain soils upstream of Highway 101 | 14,582 $m^3$ |
| Mass of available Zn in floodplain soils upstream of Highway 101 | 7,323 kg |

| | |
|---|---|
| Dry Bulk density of organic soil in TNC Floodplain | 600 kg/$m^3$ |
| Floodplain soil porosity (organic layer) | 0.8 |

Based on the above assumptions it was calculated that more than 30 years would be required to flush all available (adsorbed) Zn from the floodplain soils upstream of Highway 101.

**Loading Calculations**

Metal loadings calculations for Zn and Cu were constructed for TNC using meteorological data obtained from Environment Canada for the Timmins Airport. Annual precipitation is estimated at 840 mm and the mean annual lake evaporation is estimated at 537.5 mm. These data were based on means calculated from the Timmins Airport daily precipitation data from 1955 to 2000. The loadings of Zn and Cu to the creek from individual catchment areas were calculated using water quality data from previous reports (Golder, 2004; 2005). Data for key stations on the creek (Hwy 101, 3ND-1, 3ND-4 and Porcupine River) were used to calculate loadings in TNC for the combined catchment areas. Upstream loading inputs were calculated and compared to four key stations:

- Hwy 101: 2.2 million $m^3$/year.
- 3ND-1: 356,000 $m^3$/year.
- 3ND-4: 3.6 million $m^3$/year.
- Porcupine River: 10 million $m^3$/year.

Total annual flow from TNC to the Porcupine River is estimated at 10 million $m^3$ with more than 50% occurring during spring runoff in the months of April and May. Another 10% of the total annual flow occurs during October.

Zinc

The loading calculations indicated that the concentration of Zn measured in TNC at the Hwy 101 crossing (Figure 1) exceeded the loadings received from the sum of the component upstream catchment areas. This observation is also apparent from high concentration spikes observed in March-May of 2006 after the extremely dry summer of 2005. The difference suggests that the source of Zn during these specific events was derived from the contaminated floodplain areas of TNC itself upstream of Hwy 101 estimated at about 63,400 $m^2$. The highest proportion of Zn loading to TNC upstream of Hwy 101 occurs in the spring primarily due to the high volume of runoff.

Further downstream at 3ND-4 (Figure 1) the sum of inputs from component upstream catchments appear to exceed the measured concentration at the 3ND-4 monitoring station indicating that Zn derived from upstream catchment areas contributing to the Zn load is attenuated upstream of the 3ND-4 monitoring station. This indicates that the floodplain soils and sediments of TNC between monitoring stations Hwy 101 and 3ND-4 appear to act as a major sink for Zn in the system, at least under some runoff conditions. Limited data is available for catchments downstream of 3ND-4 to the Porcupine River, however, average Zn loading from upstream catchments appears similar to those measured at the Porcupine River convergence with the exception of the averaged values for March.

Copper

The loading calculations indicated that the concentration of Cu measured from the upstream inputs exceed the Cu loadings at all four monitoring points indicating that Cu is attenuated by floodplain soils and sediments of TNC under most conditions. Although loadings from upstream area appear to exceed the proposed benchmark for Cu during some periods of the year, the averages for the monitoring stations do not; with the exception of 3ND-1 in the spring of 2005. The majority of Cu loading to TNC appears to occur in the spring during snow melt. The largest proportion of Cu at 3ND-1 is apparently derived from the area upstream with the largest proportion of the total contributed during the spring.

The toxicity of Cu is dependent on water hardness. For example, guidelines for Cu are 0.002 mg/L at hardness values less than 120 mg/L, 0.004 mg/L between hardness values between 120 and 180 mg/L and 0.004 mg/L at hardness values >180 mg/L as $CaCO_3$ (CCME, 2003). Water hardness in snowmelt reporting to TNC is likely to be low during spring runoff while hardness will likely be higher during the remainder of the year. Consequently, toxicity events may occur at low concentrations of Cu during spring runoff while they may not be observed at higher concentrations during other periods of the year. Increasing water hardness, particularly during snow melt may provide a means to avert toxicity events associated with Cu during spring runoff.

## CONCLUSIONS

The following conclusions were based on the data discussed herein.

- Floodplain soils from 0 to 5 cm and 5 to 10 cm depths contain the highest concentrations of As, Cd, Cu, Se, and Zn decreasing with depth to values near background levels for samples collected at depths greater than 10 cm.
- The greatest percentages of all metals in TNC floodplain soils were associated with the organic fraction as determined by the sequential extraction procedure. The greatest percentages of metals in TNC sediments were associated with the recalcitrant fraction as determined by the sequential extraction procedure.
- Although total concentrations of Zn, Cu, and Cd in the beaver pond sediments were typically higher compared to the floodplain soils, the amount of exchangeable metal available to go into solution was lower compared to the floodplain soils indicating that a higher percentage of total metals in the floodplain soils are available to solution.
- Maintaining a water cover over the floodplain soils would be expected to attenuate the release of Zn, particularly from soils with highest contents of Zn. The experiments confirmed that allowing the soils to dry for prolonged periods of time would lead to highest releases of Zn in soils with highest concentrations of total Zn (i.e., upstream areas).
- All sampled beaver pond sediments contained elevated concentrations of As, Cd, Cu, and Zn that exceeded Severe Effects Level (SEL) guidelines for sediments (MOE, 1993b). The relative distribution of metals among the beaver pond sediment samples indicate highest concentrations of Zn, Cd and As occur in the area of the creek upstream of the Hwy 101 monitoring station while highest concentrations of Cu and Se were observed in sediments associated with drainage from the Buffalo Paddock Tributary.
- The main sources of available Zn, Cd and As appear to be the floodplain soils associated with the creek channel upstream of Hwy 101 monitoring station.
- Based on calculations using distribution coefficients (Kd values), the floodplain soils upstream of Hwy 101 could contribute and maintain Zn in solution at concentrations to a maximum of about 2.9 mg/L. Aqueous concentrations of Zn in TNC at Hwy 101 are typically much lower than 2.9 mg/L but higher compared to concentrations in water from upstream. The increased concentrations at Hwy 101 indicate that metals are released from the floodplain soils based on the concentrations observed in the creek with the exception of the seasonal flushing.
- Using average conditions for flow and measured soil properties it was calculated that more than 30 years would be required to flush all available Zn from the floodplain soils upstream of Hwy 101 assuming average flow conditions and water quality with current levels of contamination of the floodplain soil.
- Based on the loading calculations, Zn released from floodplain soils upstream of Hwy 101 appear to be derived from areas associated with the immediate vicinity of creek channel and is released from the soils with flushing particularly after prolonged dry periods.
- The loading calculations developed for TNC suggest that Zn contributed from upstream catchment areas is currently attenuated (accumulated) in the floodplain soils and sediments of TNC mostly

between Hwy 101 and 3ND-4 monitoring points indicating that this region of TNC is currently acting as a major sink for Zn in this riverine system.

**Remedial Works**

Based on the information provided in this study and others, a remedial option that included flooding soils in TNC with the highest zinc concentrations was approved by regulatory agencies. Flooding was accomplished by construction of two grade control structures to control the flow of water from the upper regions of the creek (Figure 6). Construction was completed in 2011 at a cost of $1.3M. Performance monitoring is ongoing to provide assurance that the objective has been met.

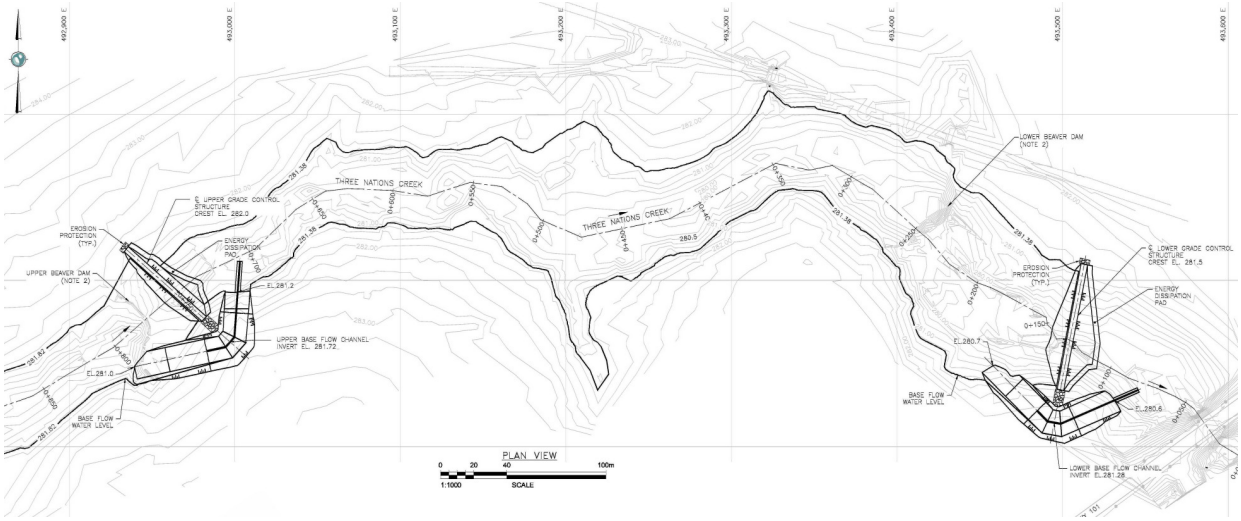


Figure 6. Overview of Three Nations Creek showing locations of grade control structures.

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