

An Assessment of Long-term Risks of Metals in Sudbury: A Critical Loads Approach

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Abstract Over a century of metal processing activity has resulted in widespread metal contamination of soils in Sudbury, ON, Canada. To assess the potential for recovery from the large reductions in metal deposition, critical loads were estimated for metals at 415 sites in Sudbury using an ‘effects based’ approach that is based on exceedance of provincial soil guidelines using multiple independent estimates of metal partitioning (K_d) for each metal. Sudbury soils are heavily contaminated with copper (Cu) and nickel (Ni), with 74 % of samples currently exceeding the provincial soil guideline for Cu and 87 % of samples exceeding the guideline for Ni. Both metals are strongly correlated with other metals (zinc (Zn), cadmium (Cd), lead (Pb)), although they rarely exceed provincial guidelines. Copper and Ni are also strongly correlated with organic matter but not soil pH. Based on the most recent Cu and Ni deposition estimates (mid-1990s), it is estimated that between 20 % and 51 % of the sites receive deposition in excess of the ‘effects based’ critical load for Cu and between 5 % and 97 % of

sites receive atmospheric deposition in excess of the ‘effects based’ critical load for Ni. These results suggest that Cu and Ni concentrations in soil will generally decrease resulting in slightly fewer sites that exceed the provincial soil guideline, but that the timeframe of this response will be very slow, with relatively little change occurring over the next 100 years. Even assuming a best case deposition scenario whereby Cu and Ni deposition were to immediately fall to background levels, the percentage of sites with Cu and Ni levels in excess of the OMOE guideline would still be between 69 % and 72 %, and 56 % and 86 %, respectively, demonstrating that while recovery of the Sudbury soils is possible, greater reductions in metal deposition are needed and even so, it will be a process that takes several centuries.

Keywords Metals · Critical loads · Copper · Nickel · Soils · Dynamic models · Sudbury

1 Introduction

The increased emission of metals, such as cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) into the atmosphere from nearly all industrial endeavors results in the disruption of the metal balance in biogeochemical cycles and ecosystem function (Freedman and Hutchinson 1980; Nriagu 1996; Pacyna and Pacyna 2001).

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Metal contamination is a global concern, but local impacts from major emissions sources clearly demonstrate the negative effects that metals can have on the environment (Thornton 1996). One example is Sudbury, Ontario, which has been home to various mining and smelting activities for over a century since the discovery of major ore deposits of Ni and Cu and metallic sulphides in the 1880s (Gundermann and Hutchinson 1995; Hutchinson and Whitby 1977). As a result of metal processing activities in the Sudbury region, metals have greatly contaminated the surrounding soil with Cu, Ni, Cd and Zn (Dudka et al. 1995). Due to improved technologies and installation of the ‘super-stack’ metal emissions from the Sudbury stacks has been reduced dramatically (Keller et al. 1999; Larssen et al. 2003) and a number of studies have been conducted in an attempt to characterize and possibly identify ‘expected’ decreases in the concentration of metals in Sudbury’s soils, sediments and surface waters (Gundermann and Hutchinson 1995; Shuaihmi-Othman et al. 2006). The findings have been inconclusive even though ‘recovery’ is expected (Doyle et al. 2003).

Ultimately, metals emitted into the atmosphere are deposited to either the terrestrial or aquatic ecosystems. The fate of metals in the terrestrial environment is contingent on a number of transport and transformation processes, which determine the exposure of metals to receptors of potential concern (Lofts et al. 2007). These processes include the complexation of metals with natural ligands, sorption mechanisms governing the movement from soil water to soil solid phase, the competitive electrostatic interaction between ions in soil solution and the soil colloid through ion exchange (Bradl 2004; Lofts et al. 2007). The knowledge of these processes is central for assessing both the current and future impact of metal contaminated soils to various environmental compartments and processes.

The critical load (CL) concept has emerged recently as a tool for assessing the potential long-term impacts of metals on both terrestrial and aquatic ecosystems (de Vries and Groenenberg 2009). Fundamentally, the CL concept is a risk assessment approach that has been successfully used for negotiating the link between emission controls and environmental benefits (Bull 1993), or more

specifically, for assessing the risks associated with metal input into the environment by quantitatively estimating the highest input flux of metal into a region that does not exceed a defined chemical threshold (Bull 1993; de Vries et al. 1998; Lofts et al. 2007). The CL of a metal can be calculated based on several criteria: (1) an effects-based CL, defined by Lofts et al. (2007) as “the input flux of metal to a defined area and depth of soil that does not cause a defined critical limit to be exceeded when the system is in steady state” or (2) a stand still CL, defined as the input flux of metal where no further metal accumulation in the soil will occur (Reinds et al. 2001). A critical limit for a receptor of potential concern is a concentration in the soil below which the receptors (i.e., soil microbes) are affected. These limits are determined based on total metal content in soil or a free metal-ion concentration (Cd^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+}) found in soil pore water using a mechanistic model that accounts for the competitive binding between soil solids and solution ligands. In Ontario, soil guidelines are based on the ‘total’ metal concentration in surface soil and it is the exceedance of these guidelines that triggers an ecological risk assessment such as the one recently undertaken in Sudbury. Therefore, consideration of the change in sites exceeding these guidelines is a practical application of the critical load concept for the Sudbury region.

Doyle et al. (2003) conducted a risk assessment for trace metals from Cu and Zn production facilities for several sites in Canada, including Sudbury. In this study, CLs were based on effects-based concentrations in soil. In the terrestrial environment, assessment endpoints were related to (1) the growth of native tree species and the efficacy of their root symbionts and (2) the population of litter invertebrates and decomposers capable of maintaining steady-state levels of litter. Critical loads were established using input parameters selected to reflect boreal forest and Canadian Shield conditions rather than site-specific soils data (Doyle et al. 2003). Doyle et al. (2003) expressed exceedance of the critical load as a risk quotient (deposition divided by the critical load) and found that the risk was close to or exceeded 1 (based on the 25th percentile critical load) for Cu, Ni, and Cd.

The study by Doyle et al. (2003) suggests that metal deposition still poses an environmental risk to soils in the Sudbury region but lacked site-specific soils data. The objective of this work was to calculate standstill and ‘effects-based’ CLs for Cd, Cu, Ni, Pb, and Zn using soil data collected from 415 sites in the Sudbury region. The standstill approach effectively estimates the amount of deposition that will not cause any further increase in soil metal concentration (de Vries and Groenenberg et al. 2009). The effects-based CLs were calculated using Ontario Ministry of the Environment (OMOE) critical limits for total soil concentration concentrations. Exceedance values were expressed as the total number of sites where these criteria were exceeded based on the most recent available metal deposition estimates in Sudbury to determine CL exceedance. Finally, a simple dynamic modelling approach was used to assess the potential change in soil metal concentration over the next 100 years assuming no change in metal deposition or a complete cessation of activities and a reduction in Cu and Ni deposition to background levels (Landre et al. 2010).

2 Materials and Methods

Soil samples were collected from the surrounding Greater Sudbury region (Fig. 1) during the months of September and October 2001 by the OMOE (2004a, b). Samples were obtained from the surface soil (0–10-cm depth) of front, side, and back yards of residential properties. The retrieval of soil samples was focused around three point sources of metal pollution in Sudbury, specifically the Inco Superstack, Coniston Smelter stacks, and the Falconbridge stack (Fig. 1) rather than a representative sampling design. Consequently, the data preclude an estimation of regional critical loads and exceedances. Additional soil samples were obtained from 59 Sudbury parks, school, and day care areas in the Greater Sudbury region during the months from July 5th, 2001 to October 26th, 2001 (OMOE 2004a, b). A total sample set of 415 soil samples was obtained.

The air-dried soil was then sieved to a 2-mm size fraction and ground using a mortar and pestle then passed through a 355- μm sieve. The quantity of organic matter in the soil was determined by loss on ignition, where approximately 5 g of processed soil

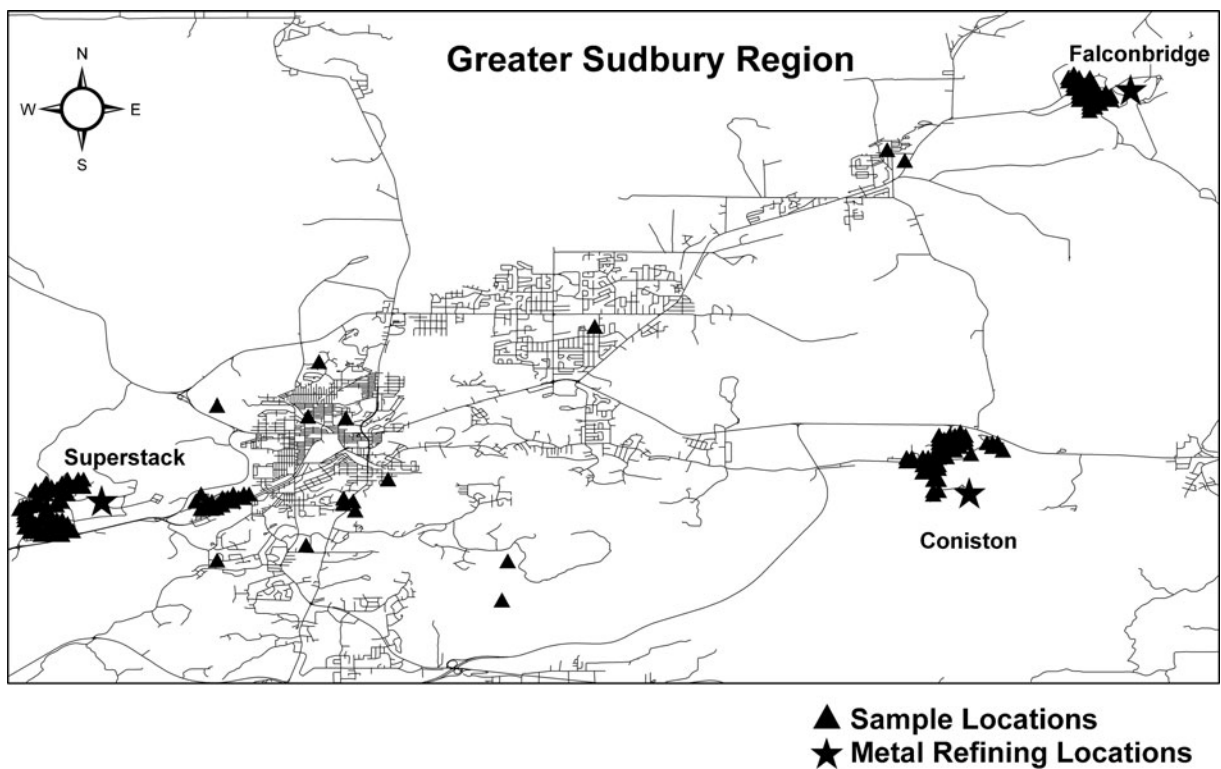


Fig. 1 Location of the 415 soil sampling sites in Sudbury, Ontario

(2- and 355- μm fraction) was weighed into ceramic crucibles and placed in a muffle furnace (Fisher Scientific Isotemp Muffle furnace 550 series) for 8 h at 450°C and left overnight and weighed the following day. Soil pH was measured using a water digestion method with a soil/solution ratio of 1:4. The digestion method was performed by adding 20 mL of deionized water to 5 g of soil in a paper cup, then stirred every 2 min for 20 min and left undisturbed for 40 min. The soil solution was measured potentiometrically using an Oakton pH meter. The total soil metal content of the soil samples was determined using a 1:3 ratio of nitric acid (HNO_3)/hydrochloric acid (HCl) microwave assisted aqua regia digestion procedure, similar to EPA Method 3501. Samples were analyzed for Pb, Ni, Cu, Cd and Zn using ICP-MS. Precision and accuracy for soil metal extracts were confirmed by systematic analysis of TILL-2 reference (Scission's Brook, New Brunswick), method blanks, sample replicates and split samples. Recoveries for all metals were typically ~80 %. Blanks and sample replicates were kept within a 20 % tolerance. Relationships between metal concentrations, pH, and organic matter were explored using simple correlation analysis on log-transformed data (except pH).

2.1 Critical Load Calculations

2.1.1 Steady State Approach to Assess Standstill and Critical Loads

Standstill loads and CLs are calculated for the surface mineral soil horizon (0–10 cm) with a mass balance model on the basis of a present or critical metal leaching rate, respectively, which in turn is defined by a present or critical metal concentration in soil or soil solution (see de Vries and Groenenberg 2009). The steady state mass balance is described by:

$$M_{\text{td}} = -M_{\text{lf}} + M_{\text{fu}} + M_{\text{ru}} + M_{\text{le}}, \quad (1)$$

where M_{td} is the total load of metal M by atmospheric deposition and where M_{lf} , M_{fu} , M_{ru} , and M_{le} are the fluxes of metal by litterfall, foliar uptake, root uptake, and leaching, respectively (all in milligrams per square meter per year). Apart from the assumption of steady state, various other assumptions are implied by the model including (1) the soil system is homogeneously mixed, (2) the soil is in an oxidized state and metal partitioning can be described with equilibrium

sorption, (3) transport of water and metals only takes place in the vertical direction, (4) metal weathering and erosion is not considered, and (5) the deposited metal is chemically reactive and is 100 % available for exchange with the solution phase (deVries et al. 2007). In addition, potential changes in soil pH or organic matter content are not considered. For simplicity, internal metal cycling is usually ignored as these processes have little impact on critical load estimations (deVries and Groenenberg 2009). Consequently, the steady state mass balance can be expressed more simply as:

$$M_{\text{td}} = M_{\text{le}} \quad (2)$$

Metal leaching losses are defined by:

$$M_{\text{le}} = Q \cdot [M]_{\text{tot,ss}}, \quad (3)$$

where Q_{le} is the water flux leaching from the soil (meter per year) and $[M]_{\text{tot,ss}}$ is the total metal concentration in soil solution (milligrams per cubic meter). One approach used to determine the solution concentration of metals is the solid–solution partitioning coefficient (K_{d}), which is determined by the ratio between the total metal content in the soil solid (milligrams per kilogram) and the concentration of metal in the soil water (milligrams per liter), expressed in liters per kilogram. The assumptions of this approach are that the dissolved metals are mobile and are available for uptake by biota and plants; the dissolved metal has the potential to be leached from the soil and enter surface and/or ground waters. In addition, this approach assumes that the remaining portion of metal present in the soil solid is unavailable for biological uptake and movement into surface or groundwater.

The standstill or critical load based on total metal concentration in soil may then be expressed as:

$$\text{CL}(M) = \left[\frac{[M]_{\text{tot}}}{K_{\text{d}}} \right] \cdot Q, \quad (4)$$

where, $\text{CL}(M)$ standstill or critical load of metal M (milligrams per square meter per year), $[M]_{\text{tot}}$ =current metal or critical concentrations (milligrams per kilogram) according to OMOE (2004a, b) guidelines, Q =water runoff value (liters per square meter per year), K_{d} or $K_{\text{d(crit)}}$ =solid–solution concentration of soil metal (liters per kilogram). This approach quantifies all relevant metal fluxes out of the system due to leaching

from the product of the runoff (Q) and the solid–solution partition coefficient value (K_d) for each metal and sample site. The solid–solution partitioning approach (K_d) has been used extensively in the literature for determining the potential leaching and bioavailability of metals in soil (de Vries et al. 1998; Goody et al. 1995; Sauvé et al. 2000, 2003; Watmough et al. 2005). The advantage of using this approach instead of relying solely on total soil metal content is the dependency of the K_d coefficient on the key soil parameters that govern metal behavior in the soil, such as total soil metal content, organic matter content (OM), and pH (Goody et al. 1995; McBride et al. 1997; Sauvé et al. 2003, 2000; Watmough et al. 2005). Therefore, the values of K_d for each metal can vary by as much as six orders of magnitude due to the dependence of K_d values on soil parameters (Sauvé et al. 2000). For example, a review of the range of K_d values in the literature by Sauvé et al. (2000) illustrates this variation: Cd, 40–800; Ni, 300–1,100; Pb, 270–22,000; Zn, 200–2,400. Given the variability in reported K_d values, in this study K_d values were estimated using different solid–solution partition models from Watmough et al. (2005) and Sauvé et al. (2000).

The amount of water leaching through the soil column is assumed to be due to surface runoff (R) in meters per year, where runoff is equal to the difference between the input of water from annual precipitation (P) and the amount of water leaving the terrestrial environment from evaporation (E), evapotranspiration (E_t), and storage (S), expressed as $R=P-(E+E_t+S)$. Long-term mean runoff estimates were obtained for Ontario from a Global Environmental Multiscale grid at a resolution of 35×35 km, where runoff was estimated by subtracting the modeled actual evapotranspiration values from the precipitation values generated from the global land surface climatology at a scale of 0.5° latitude \times 0.5° longitude for the time period of 1961–1990 by New et al. (1999) (Posch, personal communication).

2.1.2 Critical Limits

The critical limits used to determine the toxicity endpoints for Cd, Cu, Ni, Pb, and Zn was based on either current (standstill approach) and the total metal content standards set by the Soil, Ground Water, and Sediment Standards for Use under Part XV.1 of the Environmental Protection Act, March 9, 2004 (OMOE

2004a, b). The critical limits for Cd, Cu, Ni, Pb, and Zn were 12, 225, 150, 200, and 600 mg kg^{-1} , respectively.

2.1.3 Metal Deposition

Deposition estimates of the total soluble metal particulate concentrations for Cu and Ni ($n=4$) in the Greater Sudbury Region were obtained from (Doyle et al. 2003), and a deposition surface was created for the area using an Inverse Distance Weighted (IDW) interpolation method in ArcMap 9.1. The IDW interpolation method is a deterministic local exact interpolator, which calculates predictions based on the assumption that locations close together are more alike than locations that are farther apart by weighting the value of existing points within a defined neighborhood. The Cu and Ni exceedance (milligrams per square meter per year) for all sample sites was calculated as the difference between the current annual metal deposition load and the calculated CL.

2.1.4 Dynamic Model

A simple dynamic modeling approach was used to evaluate temporal changes in soil metal concentration. The following dynamic model was used to estimate soil concentrations for Cu and Ni after 100 years based on a scenario where runoff and current metal deposition estimates in Ontario does not change. The following time series mass balance equation was used:

$$\rho z \frac{dM}{dt} M_{\text{tot}} = Q \cdot M_{\text{tot.ss}} + M_{\text{dep}}, \quad (5)$$

where $\rho z \frac{dM}{dx} M_{\text{tot}}$ is the change in the total concentration of metal in the soil at a depth z (10 cm) at a bulk density ρ (in kilograms per cubic meter) expressed in milligrams per kilogram. The bulk density for all soils was determined using a pedotransfer function $\rho = 1.775 - 0.173(\text{LOI})^{1/2}$ from de Vos et al. (2005). The flux of metal leaving the soil each year was determined by $Q \cdot M_{\text{tot.ss}}$, the product of natural water runoff (Q , liters per square meter per year) and the amount of metal partitioned from the soil solid ($M_{\text{tot.ss}}$, milligrams per liter). It was assumed that the only significant input of metal entering the soil system is from atmospheric deposition (M_{dep} , milligrams per square meter per year) and that metal deposition will

not change over a 100-year time period. It was assumed that the quantity of runoff will not vary over the next 100 years, and horizontal flow was neglected. In addition, it is assumed that the soil system is homogeneously mixed and the vertical variation of soil properties such as soil metal content, pH, and OM content does not take place, and the soil is in an oxidized state. The dynamic model was used to evaluate the change in soil metal content for all studied locations within a 100-year time period.

3 Results

3.1 Current Soil Conditions

The Sudbury soils are generally moderately acidic (average pH, 5.6) and heavily contaminated with Cu and Ni (Table 1). Soil Cu concentrations exceed the OMOE guidelines at 74 % of the sites, whereas Ni exceeds the OMOE guidelines at 87 % of the sampled sites. A small number of sites (4 %) exceed the OMOE guidelines for Pb, but no sites exceed the OMOE guidelines for Cd or Zn (Table 1). Soil organic matter content averages 13 %, but like other soil properties it exhibits considerable variation ranging from a low of 1.8 % to a high of 43 % (Table 1). Even though Cu and Ni are the major soil contaminants at Sudbury all metals are strongly correlated with each other (correlation coefficients range from 0.68 to 0.96), with the strongest relationship observed between Cu and Ni (Table 2). Metal concentration data are described more fully in OMOE (2004a, b). Furthermore, concentrations of all metals are significantly positively correlated with organic matter (correlation coefficients range from 0.48 to 0.71), but exhibit no (Cd, Cu Ni, Pb) or a weak (Zn,

Table 2 Correlation coefficients for selected soil (0–10 cm) parameters from the Sudbury region

	Cd	Cu	Pb	Ni	Zn	pH	%OM
Cd	1						
Cu	0.76	1					
Pb	0.68	0.76	1				
Ni	0.81	0.96	0.80	1			
Zn	0.68	0.76	0.84	0.79	1		
pH	0.05	0.02	0.03	0.06	0.15	1	
%OM	0.71	0.54	0.48	0.64	0.53	-0.08	1

$r=0.15$) relationship with soil pH (Table 2). The need for a risk assessment of sites in Sudbury is based on exceedance of established guidelines for total metal concentration in surface soil, even though it is recognized that the free-metal ion concentration is more relevant for toxicity endpoints (Lofts et al. 2007). In order to provide an indication of potential ‘toxicity’ of the Sudbury soils we estimated the free metal ion concentration for all sites using empirical regression equations reported by Tipping et al. (2003) and compared these values to ‘critical’ free ion concentrations reported by de Vries and Groenenberg (2009) that are calculated based on soil pH and organic matter content. In this exercise, only five of the sites exceed the critical limit for Cu, three sites exceed the critical limit for Pb, and no sites exceed the critical limit for Cd or Zn. Empirical relationships and critical limits are not reported by de Vries and Groenenberg (2009) for Ni.

3.2 Critical Loads

Estimated critical loads vary considerably among sites and metals, which are strongly dependant upon the K_d

Table 1 Summary statistics for the 415 soil samples collected in the Sudbury region

	Average	Min	Max	Standard deviation	% of sites exceeding OMOE guidelines
pH	5.6	4.1	7.9	0.53	–
OM (%)	13	1.8	43	6.5	–
Soil, ground water, and sediment standards for use under Part XV.1 of the Environmental Protection Act, March 9, 2004, Cd ($12 \mu\text{g g}^{-1}$), Cu ($225 \mu\text{g g}^{-1}$), Pb ($200 \mu\text{g g}^{-1}$), Ni ($150 \mu\text{g g}^{-1}$), and Zn ($600 \mu\text{g g}^{-1}$)					
Cd ($\mu\text{g g}^{-1}$)	1.5	0.8	5.2	0.94	0
Cu ($\mu\text{g g}^{-1}$)	836	40	5,600	835	75
Pb ($\mu\text{g g}^{-1}$)	75	8	410	61	4
Ni ($\mu\text{g g}^{-1}$)	757	56	3,649	651	87
Zn ($\mu\text{g g}^{-1}$)	79	21	250	43	0

value used and whether the standstill or ‘effects based’ critical load is desired (Fig. 2). In order to prevent no further increase in metal concentration in surface soils at 50 % of the sites, atmospheric metal deposition must not exceed 0.1–2.3 mg m⁻² year⁻¹ for Cd, 78–169 mg m⁻² year⁻¹ for Cu, 1.0–1.4 mg m⁻² year⁻¹ for Pb, 34–730 mg m⁻² year⁻¹ for Ni and 6.2–59 mg m⁻² year⁻¹ for Zn (Fig. 2). Similarly, in order to prevent soils from exceeding the OMOE guidelines or allowing soil metal concentrations to decrease to these guidelines atmospheric metal deposition must not exceed 1.3–20 mg m⁻² year⁻¹ for Cd, 29–63 mg m⁻² year⁻¹ for Cu, 2.7–5.1 mg m⁻² year⁻¹ for Pb, 8.8–146 mg m⁻² year⁻¹ for Ni, and 54–385 mg m⁻² year⁻¹ for Zn (Fig. 2). As expected, standstill critical loads are generally lower for metals

that do not presently show exceedance of the OMOE guidelines (Cd, Pb, and Zn) while ‘effects based’ critical loads are lower for metals than generally currently exceed the OMOE guidelines.

Exceedance of the critical load was calculated as the difference between the calculated critical load and metal deposition estimate. Current metal deposition estimates are not available, and we estimated exceedance based on interpolated values from the most recent available deposition data for Cu and Ni (Doyle et al. 2003). The deposition of Cu ranged from 9.55 to 60 mg m⁻² year⁻¹, and the deposition of Ni ranged from 13.9 to 58 mg m⁻² year⁻¹. For Cu, between 20 % and 51 % of the sites receive deposition in excess of the ‘effects based’ critical load (Table 3). For Ni, it is estimated that between 5 %

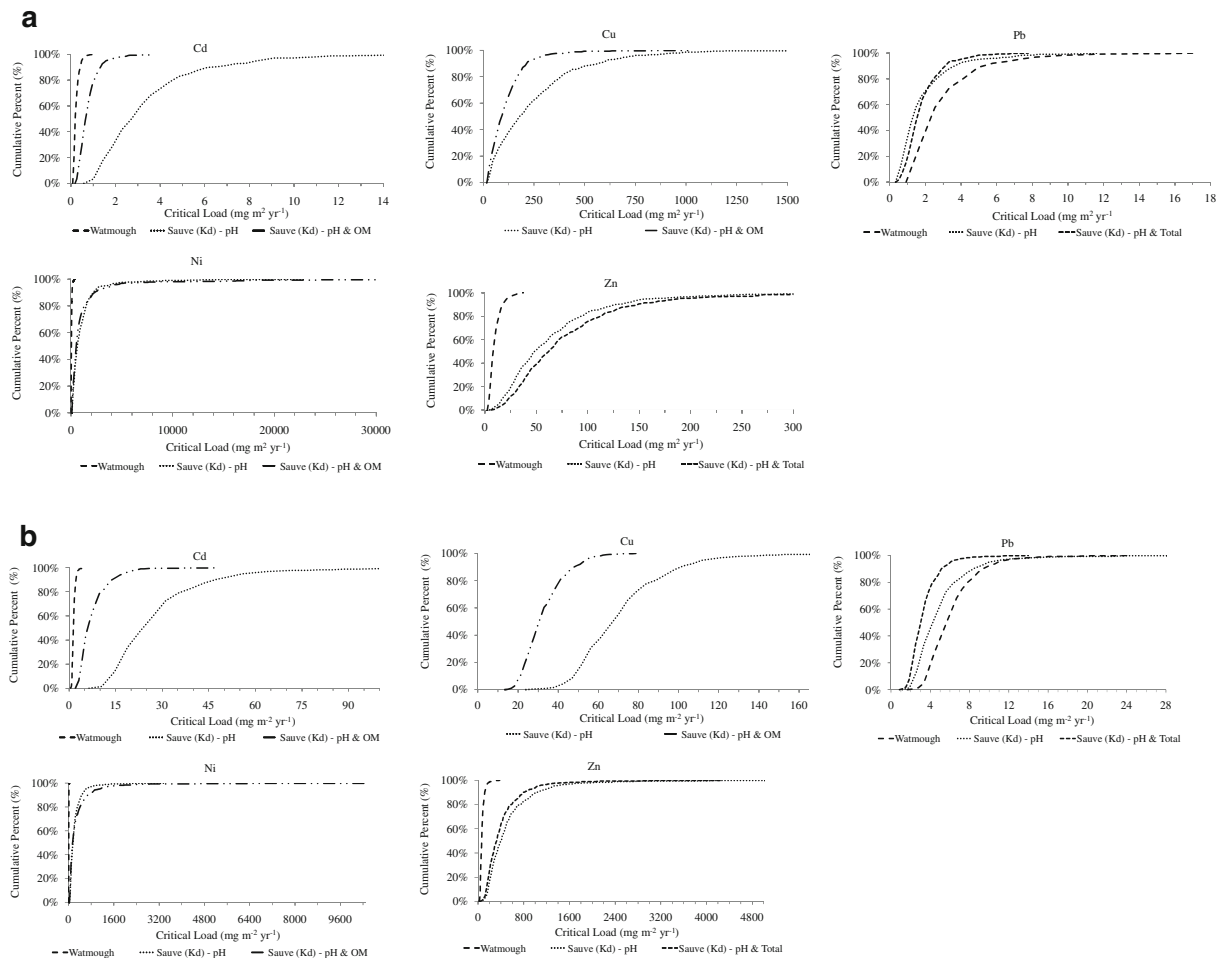


Fig. 2 Cumulative distribution of **a** standstill critical loads and **b** ‘effects-based’ critical loads for Cd, Cu, Pb, Ni, and Zn estimated using four different partitioning coefficients reported in the literature (Sauvé et al. 2003; Watmough et al. 2005)

Table 3 Percentage of sites in Sudbury ($n=415$) exceeding ‘effects-based critical loads’ based on OMOE soil Cu and Ni guidelines and on the most recent available metal interpolated metal deposition estimates using three different estimates for K_d

Model K_d	Cu	Ni
Watmough, pH	–	97 %
Sauvé, pH	20 %	5 %
Sauvé, pH and OM	51 %	17 %

and 97 % of sites receive atmospheric deposition in excess of the ‘effects based’ critical load. Assuming that deposition remains unchanged for the next 100 years, mean Cu concentrations are predicted to decrease slightly, from $835 \mu\text{g g}^{-1}$ to between 667 and $779 \mu\text{g g}^{-1}$ (depending upon K_d value used) and mean Ni concentrations are predicted to decrease from $758 \mu\text{g g}^{-1}$ to between 746 and $343 \mu\text{g g}^{-1}$ (Table 4). These results suggest that based on the most recent deposition data for Cu and Ni that metal concentrations in soil will generally decrease resulting in fewer sites that exceed the OMOE guideline, but that the timeframe of this response will be very slow, with relatively little change occurring over the next 100 years unless metal deposition decreases considerably. For example, between 72 % and 75 % of sites will still exceed the OMOE guidelines for Cu and between 61 % and 90 % of sites will exceed OMOE guidelines for Ni. If a best case scenario is assumed and Cu and Ni deposition were reduced to background levels as reported by Landre et al. (2010) ($\text{Cu}=0.88 \text{ mg m}^{-2} \text{ year}^{-1}$ and $\text{Ni}=0.59 \text{ mg m}^{-2} \text{ year}^{-1}$), the percentage sites exceeding the OMOE guidelines for Cu would still be between 69 % to 72 % and 56 % to 86 % for Ni.

4 Discussion

The sampled soils were heavily contaminated with both Cu and Ni with >70 % of samples exceeding the OMOE guidelines (OMOE 2004a, b). Concentrations of Cd and Zn were below the OMOE guidelines, while just 4 % of samples exceed the OMOE guidelines for Pb. Numerous studies have similarly shown that soils in the Sudbury area are primarily heavily contaminated with Ni and Cu due to more than 100 years of deposition from local mining and smelting operations (Adamo 2002; Dudka et al. 1995; Gundermann and Hutchinson 1995; Hutchinson and Whitby 1977; OMOE 2004a, b). Even though Cu and Ni are the primary contaminants at the sites, all metals are strongly correlated with each other and also with soil organic matter content. This indicates that a substantial proportion of the metals measured in the study are derived from a common source and that soils that are richer in organic matter have a greater capacity to retain the deposited metals (Watmough and Dickinson 1995). Soils in the region have also been reported to be generally acidic; based on 73 samples, Dudka et al. (1995) reported an average pH value of around 4.0 but with a range of 3.3 to 7.4. In the present study, we found a similar range in pH, but report a much higher average pH, which is more likely a result of different sampling locations although an increase in pH resulting from the dramatic reduction in SO_4 deposition (Larssen et al. 2003) cannot be ruled out completely. Furthermore, pH exhibited little to no relationship with metal concentrations suggesting local geological factors rather than acid emissions from the smelters are the primary cause of the observed differences in soil pH.

In Ontario, soil guidelines are based on total soil metal concentration, although it is recognized that these are protective values and that the free metal ion

Table 4 Summary statistics for predicted Cu and Ni concentrations for the 415 soil samples (0–10 cm) in Sudbury in 100 years based on the most recent available interpolated metal deposition data and three different estimates for K_d

	Cu ($\mu\text{g g}^{-1}$)				Ni ($\mu\text{g g}^{-1}$)			
	Min	Max	SD	Mean	Min	Max	SD	Mean
Current concentration	40	5,600	835	835	56	3,649	651	758
Watmough, pH	–	–	–	–	72	3,519	619	746
Sauvé, pH	42	4,602	645	667	1.9	2,057	380	343
Sauvé, pH and OM	43	5,178	753	779	0.6	3,134	517	424

concentration in soil solution may be a more appropriate indicator of potential ecological damage if appropriate critical levels can be established (de Vries and Groenenberg 2009). Free metal ion concentrations can be calculated using models such as WHAM (Tipping et al. 2002) when data exist, or simple empirical relationships may be used based on simple soil properties, even though they have not been tested for Canadian soils. In the present study, we estimated the free metal ion concentration for Cu using empirical relationships reported by Tipping et al. (2002) whereby the free metal ion concentration increases with soil metal concentration, soil acidity, and reduced organic matter content. These values were compared with critical limits proposed by de Vries and Groenenberg (2009) that are also a function of pH such that higher critical limits are observed for acidic soils because of the potential of greater cation interaction in acidic soils (see Lofts et al. 2004). Using this approach, we estimate that even though 75 % of the sites exceed the OMOE guideline, only five sites (~1 %) exceed the critical free ion concentration. Data are not available to provide a similar estimate for Ni, but these findings suggest that a more detailed evaluation of soils in the Sudbury area along with estimates of free metal ion concentration is warranted.

Presently, however, critical free ion concentrations are not used for policy decisions in Ontario, so we used the critical loads approach to estimate the amount of deposition needed to (a) maintain current soil metal levels (standstill approach), (b) reach (increase or decrease) OMOE soil guidelines (effects based), and (c) how would the number of sites exceeding the OMOE guidelines for Cu and Ni change in 100 years assuming either current estimated deposition or a reduction in deposition to Ontario background levels (Landre et al. 2010). A key factor in these calculations is the metal partitioning between soil and soil solution (K_d) as this will determine the metal leaching rate. There are many published K_d values that are primarily a function of soil pH and in some cases organic matter; with K_d values increasing (less metal released into solution) as soil pH increases and soil organic matter increase (Goody et al. 1995; McBride et al. 1997; Sauvé et al. 2003, 2000; Watmough et al. 2005). In this study, we adopted to use a range of K_d values reported for Canadian soils.

The combination of different K_d values combined with different soil properties resulted in a wide range

of critical loads for the Sudbury soils. Critical load estimates for Pb were quite similar using the various K_d values, whereas critical load estimates for Cd and Zn tended to exhibit the greatest relative discrepancy. As we have no reason to assume that one particular estimate is more reliable than another, we used all three estimates in order to provide a reasonable range for critical metal deposition loads. For the two metals that were most enriched in the Sudbury soils (Cu and Ni), standstill critical loads were generally higher than the effects based critical loads as more metal leaching (and hence deposition) is allowed for soils that exceed the OMOE guideline. One consequence of this, however, is that potential leaching losses to surface waters may be much greater with possible adverse effects on aquatic biota.

Critical loads estimated in this study were compared with critical loads calculated for European soils, and some notable discrepancies were found. For example, de Vries and Groenenberg (2009) reported standstill critical loads for Cu for sandy soils to be $2 \text{ mg m}^{-2} \text{ year}^{-1}$ while the effects based critical load (based on free ion concentration) was $12 \text{ mg m}^{-2} \text{ year}^{-1}$. The higher standstill critical loads estimated in this study can be partly attributed to the higher Cu concentrations in soil. In general, it would be expected that effects-based critical loads calculated for European ecosystems will be greater than 'effects based' critical loads in this study as soil OMOE guidelines are meant to be protective (OMOE 2004a, b). For Cd and Zn, standstill critical loads reported by de Vries and Groenenberg (2009) of 0.44 and $34 \text{ mg m}^{-2} \text{ year}^{-1}$, respectively are much more similar to average standstill critical load estimates in the current study. There is, however, a notable difference in the standstill critical loads for Pb reported by de Vries and Groenenberg (2009) for sandy soils ($28 \text{ mg m}^{-2} \text{ year}^{-1}$) and the average standstill critical loads estimated in this study ($1\text{--}2 \text{ mg m}^{-2} \text{ year}^{-1}$). Our study suggests that Pb concentrations would continue to increase, even at deposition values around $1 \text{ mg m}^{-2} \text{ year}^{-1}$. A potential independent verification of our estimates comes from a mass balance study conducted approximately 200 km south of Sudbury that showed Pb is retained (and hence accumulating) in upper mineral soil at Pb deposition values around $1 \text{ mg m}^{-2} \text{ year}^{-1}$ (Landre et al. 2010; Watmough and Dillon 2007). As expected the standstill critical loads that we report for Sudbury ($0.1\text{--}2.3 \text{ mg m}^{-2} \text{ year}^{-1}$ for Cd, $78\text{--}169 \text{ mg m}^{-2} \text{ year}^{-1}$ for Cu, $1.0\text{--}1.4 \text{ mg m}^{-2} \text{ year}^{-1}$

for Ni, and 6.2–59 mg m⁻² year⁻¹ for Zn) are also generally higher than reported leaching losses from upper soil horizons (0.11 mg m⁻² year⁻¹ for Cd, 0.57 mg m⁻² year⁻¹ for Cu, 0.63 mg m⁻² year⁻¹ for Ni, and 16 mg m⁻² year⁻¹ for Zn) at this site (Landre et al. 2010). The higher modeled leaching losses for standstill conditions for Cu and Ni, in particular, arise from the higher metal concentrations in Sudbury soils compared with the reference site and lend support that modeled metal losses in this study are reasonable.

In order to calculate exceedance of the critical load, metal deposition estimates are needed and for the Sudbury area only data for Cu and Ni from four locations collected in the mid-1990s are available (Doyle et al. 2003) leading to considerable uncertainty in current site-specific metal deposition estimates. Nevertheless, based on these estimates, the number of sites that receive deposition in excess of the effects based critical loads ranges from 20–51 % (Cu) and from 5–97 % (Ni), although two of the three calculations for Ni estimate the number of sites that exceed the critical load is less than 17 %. Overall, these results are suggestive that over time considerably fewer sites will have soil Cu and Ni concentrations in excess of the critical load. Doyle et al. (2003) previously conducted a risk assessment for the Sudbury region using general (rather than site specific) soil parameters for boreal forest soils and ‘effects-based’ critical limits. They estimated effects-based critical loads using a probabilistic approach for metal transport and fate and reported geometric mean critical loads for Cu and Ni to be 25 and 86 mg m⁻² year⁻¹, respectively. These values are within the range of average ‘effects-based’ critical loads estimated in this study (29–63 mg m⁻² year⁻¹ for Cu and 8.8–146 mg m⁻² year⁻¹ for Ni). Furthermore, Doyle et al. (2003) reported that there was an elevated risk of Cu toxicity from current metal deposition within a distance of up to 6 km from the smelters.

Our results and those reported by Doyle et al. (2003) indicate that at current deposition levels there will be a gradual reduction in soil Cu and Ni concentrations but that the risk of negative impacts close to the smelters may persist. A key question that arises from this work is the time for this ‘recovery’ to take place. Dynamic models have been developed for predicting changes in soil metal concentration and target loads (Posch and De Vries 2009; Tipping et al. 2010). In this study, we applied a very simple dynamic

approach to assess the potential change in soil metal concentration in 100 years assuming deposition remains constant or declines to background levels (Landre et al. 2010). These calculations indicate that while there will be a general improvement in soil chemistry over the next 100 years, average Cu concentrations will only decline by approximately 10–20 % at current deposition levels although average Ni concentrations may decrease up to 50 %. These rates of chemical recovery are much lower than have been observed for lakes in the region (Keller et al. 1999). Even assuming a best case deposition scenario whereby Cu and Ni deposition were to fall to background levels, the percentage of sites with Cu and Ni levels in excess of the OMOE guideline would still be between 69 % and 72 %, and 56 % and 86 %, respectively, demonstrating that while recovery of the Sudbury soils is possible, it will be a process that takes several centuries.

The critical loads approach used in this study is an effective method to assess the risk of heavy metal deposition to the environment—an environmental issue of local, regional, and global importance (Kaste et al. 2005; Hall et al. 2006; Johnson and Richter 2010). Critical loads may be used effectively to assess the potential risk of metal contamination at multiple scales (Hall et al. 2006) as long as soil and metal deposition data are available.

5 Conclusions

Sudbury soils are heavily contaminated with Cu and Ni, with 74 % of samples ($n=415$) exceeding the OMOE soil guideline for Cu and 87 % of samples exceeding the guideline for Ni. Both metals are strongly correlated with other metals (Zn, Cd, Pb), organic matter but not soil pH. Based on the most recent Cu and Ni deposition estimates, we estimate that between 20 % and 51 % of the sites receive deposition in excess of the ‘effects-based’ critical load for Cu and between 5 % and 97 % of sites receive atmospheric deposition in excess of the ‘effects-based’ critical load for Ni. These results suggest that based on the most recent deposition data for Cu and Ni that metal concentrations in soil will generally decrease resulting in fewer sites that exceed the OMOE guideline, but that the time frame of this response will be very slow, with relatively little change occurring over the next 100 years unless metal

deposition decreases considerably and even assuming a best case deposition scenario whereby Cu and Ni deposition were to fall to background levels, the percentage of sites with Cu and Ni levels in excess of the OMOE guideline would still be between 69 % and 72 %, and 56 % and 86 %, respectively, demonstrating that while recovery of the Sudbury soils is possible, it will be a process that takes several centuries. These ‘effects-based’ critical loads, however, are recognized as being overprotective as they are based on total metal content rather than free-metal ion concentration and there are indications that only about 1 % of sites currently exceed the critical free ion concentration for Cu. Furthermore, potential changes in climate, hydrology, soil pH, and organic matter are not considered. We suggest that future work should focus on a more regionally representative soil sampling program, more detailed chemical analyses to estimate free ion concentrations in soil solution and obtaining better and more recent metal deposition data to more fully assess the current risk and recovery of Sudbury soils.

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References

- Adamo, P. (2002). Distribution of trace elements in soils from the Sudbury smelting area (Ontario, Canada). *Water, Air, and Soil Pollution*, *137*, 95–116.
- Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, *277*, 1–18.
- Bull, K. R. (1993). *Development of the critical loads concept and the UN-ECE mapping programme. Critical Loads: Concept and Applications* (pp. 8–10). London: HMSO.
- de Vos, B., Van Meivenne, M., Quataert, P., Deckers, J., & Muys, B. (2005). Predictive quality of pedotransfer functions for estimating bulk density of soils. *Soil Science Society of America Journal*, *69*, 500–510.
- de Vries, W., Bakker, D. J., Groenenberg, J. E., Reinds, G. J., Bril, J., & van Jaarsveld, J. A. (1998). Calculation and mapping of critical loads for heavy metals and persistent organic pollutants for Dutch forest soils. *Journal of Hazardous Materials*, *61*, 99–106.
- de Vries, W., Lofts, S., Tipping, E., Meili, M., Groenenberg, J. E., & Schutze, G. (2007). Impact of soil properties on critical concentrations of cadmium, lead, copper, zinc, and mercury in soil and soil solution in view of ecotoxicological effects. *Reviews of Environmental Contamination and Toxicology*, *191*, 47–89.
- de Vries, W., & Groenenberg, J. E. (2009). Evaluation of approaches to calculate critical metal loads for forest ecosystems. *Environmental Pollution*, *157*, 3422–3432.
- Doyle, P. J., Gutzman, D. W., Sheppard, M. I., Sheppard, S. C., Bird, G. A., & Hrebenyk, D. (2003). An ecological risk assessment of air emissions of trace metals from copper and zinc production facilities. *Human and Ecological Risk Assessment*, *9*, 607–636.
- Dudka, S., Ponce-Hernandez, R., & Hutchinson, T. C. (1995). Current level of total element concentrations in the surface layer of Sudbury’s soils. *The Science of the Total Environment*, *162*, 161–171.
- Freedman, B., & Hutchinson, T. C. (1980). Pollutant inputs from the atmosphere and accumulations in soils and vegetation near a nickel–copper smelter at Sudbury, Ontario, Canada. *Canadian Journal of Botany*, *58*, 108–132.
- Goody, D. C., Shand, P., Kinniburgh, D. G., & Riemsdijk, W. H. (1995). Field-based partition coefficients for trace elements in soil solutions. *European Journal of Soil Science*, *46*, 265–285.
- Gundermann, D. G., & Hutchinson, T. C. (1995). Changes in soil chemistry 20 years after the closure of a nickel–copper smelter near Sudbury, Ontario, Canada. *Journal of Geochemical Exploration*, *52*, 231–236.
- Hall, J. R., Ashmore, M., Fawehinmi, J., Jordan, C., Lofts, S., Shotbolt, L., Spurgeon, D. J., Svendsen, C., & Tipping, E. (2006). Developing a critical load approach for national risk assessments of atmospheric deposition. *Environmental Toxicology and Chemistry*, *25*, 883–890.
- Hutchinson, T., & Whitby, L. (1977). The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. *Water, Air, and Soil Pollution*, *77*(7), 421–438.
- Johnson, A. H., & Richter, S. L. (2010). Organic-horizon lead, copper, and zinc contents of mid-atlantic forest soils, 1978–2004. *Soil Science Society of America Journal*, *74*, 1001–1009.
- Kaste, J. M., Friedland, A. J., & Miller, E. K. (2005). Potentially mobile lead fractions in montane organic rich soil horizons. *Water, Air, and Soil Pollution*, *167*, 139–154.
- Keller, W., Heneberry, J. H., & Gunn, J. M. (1999). Effects of emission reductions from the Sudbury smelters on the recovery of acid- and metal-damaged lakes. *Journal of Aquatic Ecosystem Stress and Recovery*, *6*, 189–198.
- Landre, A. L., Watmough, S. A., & Dillon, P. J. (2010). Metal pools, fluxes, and budgets in an acidified forested catchment on the Precambrian Shield, Central Ontario, Canada. *Water, Air, and Soil Pollution*, *209*, 209–228.
- Larssen, T., Brereton, C., & Gunn, J. M. (2003). Dynamic modelling of recovery from acidification of lakes in Killarney Park, Ontario, Canada. *Ambio*, *32*, 244–248.
- Lofts, S., Chapman, P. M., Dwyer, R., & McLaughlin, M. J. (2007). Critical loads of metals and other trace elements to terrestrial environments. *Environmental Science and Technology*, *41*, 6326–6331.
- Lofts, S., Spurgeon, D. J., Svendsen, C., & Tipping, E. (2004). Deriving soil critical limits for Cu, Zn, Cd, and Pb: a method based on free ion concentrations. *Environmental Science and Technology*, *38*, 3623–3631.

- McBride, M., Sauvé, S., & Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, *48*, 337–346.
- New, M., Hulme, M., & Jones, P. (1999). Representing twentieth-century space-time climate variability. Part I: development of a 1961–1990 mean monthly terrestrial climatology. *American Meteorological Society*, *12*, 829–856.
- Ontario Ministry of the Environment (OMOE). (2004a). *City of Greater Sudbury 2001 Urban Soil Survey Report*. Toronto, Ontario: Ecological Standards and Toxicity Branch, Standards Development Branch, Ontario Ministry of the Environment. Report Number SDB-008-3511-2003.
- Ontario Ministry of the Environment (OMOE) (2004). Soil, Ground Water and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act. Queens Printer for Ontario.
- Nriagu, J. O. (1996). A history of global metal pollution. *Science*, *272*, 223–224.
- Pacyna, J. M., & Pacyna, E. G. (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environmental Reviews*, *9*, 269–298.
- Posch, M., & de Vries, W. (2009). Dynamic modelling of metals—time scales and target loads. *Environmental Modelling and Software*, *24*, 86–95.
- Reinds, G.J., de Vries, W., Groenenberg, B.J. (2001). Critical loads of lead and cadmium for European forest soils. RIVM Rep. 259101010, p 81–92.
- Sauvé, S., Manna, S., Turmel, M., Roy, A. G., & Courchesne, F. (2003). Solid–solution partitioning of Cd, Cu, Ni, Pb, and Zn in the organic horizons of a forest soil. *Environmental Science and Technology*, *37*, 5191–5196.
- Sauvé, S., Hendershot, W., & Allen, H. E. (2000). Solid–solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environmental Science and Technology*, *34*, 1125–1131.
- Shuaihmi-Othman, M., Pascoe, D., Borgman, U., & Norwood, W. P. (2006). Reduced metals concentrations of water, sediment and *Hyaella azteca* from lakes in the vicinity of the Sudbury metal smelters, Ontario, Canada. *Environmental Monitoring and Assessment*, *117*, 27–44.
- Thornton, I. (1996). Impacts of mining on the environment: some local, regional and global issues. *Applied Geochemistry*, *11*, 355–361.
- Tipping, E., Rey-Castro, C., Bryan, S. E., & Hamilton-Taylor, J. (2002). Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochimica et Cosmochimica Acta*, *66*, 3211–3224.
- Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M. R., Lofts, S., & Hill, M. T. R. (2003). The solid–solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environmental Pollution*, *125*, 213–225.
- Tipping, E., Rothwell, J. J., Shotbolt, L., & Lawlor, A. J. (2010). Dynamic modelling of atmospherically-deposited Ni, Cu, Zn, Cd and Pb in Pennine catchments (northern England). *Environmental Pollution*, *158*, 1521–1529.
- Watmough, S. A., & Dickinson, N. M. (1995). Dispersal and mobility of heavy metals in relation to tree survival in an aerielly contaminated woodland soil. *Environmental Pollution*, *90*, 135–142.
- Watmough, S. A., Dillon, P. J., & Epova, E. N. (2005). Metal partitioning and uptake in central Ontario forests. *Environmental Pollution*, *134*, 493–502.
- Watmough, S. A., & Dillon, P. J. (2007). Lead biogeochemistry in a central Ontario forested watershed. *Biogeochemistry*, *84*, 143–159.