Saturation of ecosystems with toxic metals in Sudbury basin, Ontario, Canada

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Abstract

Mining and resource recovery activities have not been kind to ecosystems in the Sudbury basin, Ontario. The combination of logging, smelting, fires and erosion resulted in an unusual anthropogenic ecosystem of denuded barren land with lifeless lakes, or a micro-desert. Since the 1970s, however, the concerted efforts made to reduce the emissions and rehabilitate parts of the degraded ecosystem have resulted in improvements in water quality, and recoveries in phytoplankton, zooplankton, zoobenthos and fish communities but have had little impact on toxic metal concentrations in many lakes. We show that most of the catchments in the Sudbury basin have become saturated with Cu and Ni, and some with Zn and Pb. It is estimated that mobilization of metals stored in soils and glacial overburden by surface runoff, groundwater drainage and wind re-working of tailings can sustain the high concentrations of Cu and Ni in many lakes for well over 1000 years. Strategies to immobilize the pollutant metals in the watershed rather than further emission controls may be required for dealing with high levels of toxic metals in surface waters of the saturated ecosystems.   © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Mining and resource recovery activities have not been particularly kind to ecosystems in the Sudbury basin, Ontario. Extensive logging and forest fires and the use of open-bed roasting for ores depleted the vegetation and increased soil erosion (Nriagu et al., 1982; Courtin, 1994). Subsequent installation of smelters with low stacks resulted in extensive acidification and toxification of local soils and surface waters. Careless disposal of fine-grained tailings gave rise to metalliferous wind-blown dusts that were sprayed throughout the area. The combination of logging, smelting, fires and erosion resulted in an unusual anthropogenic ecosystem of denuded barrenland with lifeless lakes, or a micro-desert. From a scientific

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perspective, the Sudbury basin had become an opportunistic macrocosm (a unique laboratory) for mechanistic research on effects of severe acidification and metal pollution on ecosystems. Data obtained for the deteriorated ecosystems of Sudbury provided the scientific underpinning to much of the early Canadian thinking, debate and activism on long-range transport of pollutants and effects of acid rain.

The defiled ecosystems of Sudbury are now changing in response to public pressure, legislative measures and innovative technology. Since the 1970s, concerted effort has been made to reduce the emissions and rehabilitate parts of the degraded ecosystem. Emission of SO_2 increased from approx. 14 t day^{-1} in 1950s, peaked around 6000 t day^{-1} in 1971 and has since declined to approx. 2000 t day^{-1} in 1980 and further down to < 1000 t day^{-1} in 1995 (Courtin, 1994; Mallory et al., 1998). Between 1973 and 1981, annual emissions from the smelters averaged approx. 670 t year^{-1} for Cu, 500 t year^{-1} for Ni, 204 t year^{-1} for Pb, 125 t year^{-1} for As and 15 250 t year^{-1} for total particulates (Chan and Lusis, 1986); current emissions amount to a small fraction of the rates during the 1973–1981 period. Mine tailings have been stabilized, lakes have been limed and land patches revegetated. These control and remedial measures have resulted in improvements in water quality, and recoveries in phytoplankton, zooplankton, zoobenthos and fish communities in many lakes (Griffiths and Keller, 1992; Matuszek et al., 1992; Nicholls et al., 1992; Locke et al., 1994). The Sudbury basin is now becoming less of

an environment for the study of adverse effects of acid rain and metal deposition and more of a field laboratory for examining the beneficial effects of emission control and environmental rehabilitation (Gunn et al., 1995; Havas et al., 1995; Keller and Gunn, 1995; McNicol et al., 1995).

The chemistry and dynamics of pollutant metals in surface waters of the Sudbury basin are still not well understood. In 1978 and 1979, we did a detailed study of the distribution and chemical behavior of trace metals in water, seston (suspended particulates) and sediments of selected lakes in the Sudbury basin. These measurements were repeated during 1993/1994. The results of the two sets of measurements are compared in this report to ascertain the effects of various emission control measures on trace metals in lakes during the 15-year interval. The yield of metals from heavily contaminated ecosystems over a relatively long period of time was of major interest in this study.

2. Methodology

The lakes studied are located within a radius of 30 km of the city of Sudbury and encompass a wide range of physical and chemical properties (Table 1). Samples were collected in July 1993 and February 1994 at approximately the same locations used in the 1978/1979 study. The collection, handling and analysis of water samples followed the ultraclean laboratory procedure and involved stringent protocols to minimize the risks of sample contamination. Details of the method

Table 1
Physical characteristics of lakes in the Sudbury basin used in this study

Lake	Distance (km)	Area (ha)	Shoreline (km)	Max depth (m)	Mean depth (m)	Volume (km³)	pH
Clearwater	12	76	5.0	22	8.4	642	4.7
Kelley	4.3	339	15				7.4
Lohi	20	41	4.5	20	6.2	250	4.6
McFarlane	10	141	11	20	7.2	1020	7.5
Nelson		309	33	51			6.6
Ramsay	8.0	795		21	8.4	6683	7.4
Richard	12	79	5.4	9.5	3.9	298	7.1
Silver	6.5	23	8.6				4.2
Windy	30						6.3

used are described in Nriagu et al. (1993). All field procedures used in sample acquisition and handling were performed inside a mobile clean laboratory which was trailed to the shore of each lake. The mobile laboratory had a plastic interior, several HEPA filters and operated at better than Class 1000 level. Subsequent sample analyses were made in a Class 100 laboratory dedicated to research on trace metals in the environment.

In August, surface water samples were obtained from a rubber raft rowed to the sampling station. Gloved hands were used to open, fill and cap the sample bottle under water. Subsurface samples were obtained using carefully decontaminated 5-l, Go-Flo bottles (General Oceanics Inc., Miami, FL) attached to Kevlar rope and tripped using a Teflon messenger. In February, a power auger was used to drill a hole through the snow cover. The snow and slush were allowed to drift away before any samples were collected. To avoid any residual effects of the drilled hole, water samples were taken at depths of at least 4 m below the ice cover. All the winter samples were obtained by means of Go-Flo bottles. Upon retrieval, each water sample was quickly taken to the mobile clean laboratory and filtered through 0.45-μm polycarbonate membrane housed in an in-line teflon support (Nriagu et al., 1993). The filtered sample was acidified with Seastar nitric acid (Seastar Inc., Sydney, British Columbia) and triple-bagged and stored in a plastic cooler box in a cold room until analyzed.

Depending on the Secchi disk reading, between 1000 and 2000 l of lake water were pumped directly into a 4-bowl Westfalia continuous flow through centrifuge to remove the suspended particulates. The extraction efficiency for particles with diameter > 0.4 μm is believed to be over 90% at the flow rate of $6 \, l \, min^{-1}$ used during the study (Nriagu et al., 1982). The seston collected were frozen and subsequently freeze dried.

A light-weight corer was used to obtain undisturbed samples of the lake sediment (Nriagu et al., 1982). Immediately after retrieval, each core was subsectioned at 1.0-cm intervals. The subsections were frozen in plastic vials and freezed-dried later.

Aliquots of the freeze-dried sediments and seston were digested with concentrated HNO_3 in sealed Teflon vessels of a microwave digestion system. Metal concentrations in the leachates from sediments were determined using an ICP spectrometer and those from the seston by a graphite furnace atomic absorption spectrometer (GFAAS). Each batch of 12 samples analyzed included Buffalo River sediments (NIST 2704) as reference standard. The concentration obtained for each element during each run was within ± 10% of the certified value for the reference material. If not, digestion of the samples was repeated.

Metal concentrations in water samples were determined using a GFAAS equipped with a Zeeman background correction system. Standard addition methods were used for samples with low metal contents. Field blanks were used to estimate the amount of each metal that was introduced into samples from the reagents, bottles, filtration unit and during instrumental analysis. The blanks for this study consisted of aliquots of Milli-Q water which were filtered, stored, processed and analyzed exactly as the actual samples. Nine field blanks were processed during each of the July 1993 and February 1994 sampling campaigns. Average concentrations in field blanks were found to be $< 5 \, ng \, l^{-1}$ for Ni, Cu, Cd and Pb during both campaigns. For Zn, average blank values were $31 \, ng \, l^{-1}$ in July 1993 and $9.6 \, ng \, l^{-1}$ in February, 1994; for Fe $60 \, ng \, l^{-1}$ in July and $15 \, ng \, l^{-1}$ in February; and for Mn $19 \, ng \, l^{-1}$ in July and $14 \, ng \, l^{-1}$ in February. The mean blank values for Zn, Fe and Mn were subtracted from the sample results presented in this report.

3. Results and discussion

A number of recent studies have documented some improvements in water quality in lakes around Sudbury which are attributable to reduced smelter emissions. Keller et al. (1992) reported that during the period 1981–1989, there were measurable increases in pH and acid-neutralizing capacity (ANC) in over 90% of the lakes they surveyed. Decreases in concentrations of dissolved SO_4, Ca, Mg, Al and Mn were also found in over 80% of the lakes. Locke et al. (1994)

showed that the geometric mean pH has increased from 4.65 during 1971–1976 to 5.06 in 1988–1990 in the 80 lakes they studied. Improvements in water quality have been linked to biological recovery and changes in species richness and community structure in many of the lakes (Neary et al., 1990; Conlon et al., 1992; Griffiths and Keller, 1992; Nicholls et al., 1992; Gunn et al., 1995; McNicol et al., 1995).

A large number of lakes in the Sudbury basin, however, still display classic symptoms of acidification stress: low pH (≤ 5.0), low buffering capacity (negative alkalinity), elevated levels of toxic metals, high Secchi disk readings (> 6.0 m), absence of fish and limited growth of benthic algae (Neary et al., 1990; McNicol and Mallory, 1994; Havas et al., 1995; Gunn et al., 1995). Some of the lakes included in this study fall into this category. For instance, the pH of Silver, Lohi and Clearwater Lakes are still < 5.0 (see Table 1) and the Ni concentrations in these lakes vary from 133 to 631 μg l^{-1}, Cu from 82 to 282 μg l^{-1}, Zn from 20 to 83 μg l^{-1} and Pb from < 0.1 to 18 μg l^{-1} (Table 2). This study also includes lakes that are better buffered with pH values > 7.0 and alkalinities > 20 mg l^{-1} (Table 1). One common feature in all the lakes, irrespective of their buffering capacity, are the high levels of dissolved Ni and Cu, and to a lesser extent, Zn and Pb (Table 2). The levels in Sudbury lakes are many times higher than the concentrations in the Great Lakes which are typically < 15 ng l^{-1} for Cd, < 25 ng l^{-1} for Pb, < 300 ng l^{-1} for Zn and < 1000 ng l^{-1} for both Cu and Ni (Nriagu et al., 1996). The concentrations of Ni and Cu in most of the lakes sampled in this study exceed the Ontario Provincial Water Quality guidelines of 15 μg l^{-1} for Ni and 5 μg l^{-1} for Cu required to protect fish and aquatic life (Dudka et al., 1995). Decrease of metal levels with distance from Sudbury, documented in the previous studies (Nriagu et al., 1982; Keller et al., 1992) can still be seen in spite of the small sample size (Table 1).

Table 3 compares the average dissolved trace metal concentrations in 1978/1979 and 1993/1994 samples. One remarkable feature is the little change shown by Cu and Ni concentrations in the lakes during the 15-year period in spite of the

massive emission control and ecosystem rehabilitation efforts. The Zn concentrations have declined significantly in some of the lakes (Ramsey, Richard and McFarlane) but stayed constant in others (Clearwater, Silver and Lohi). Except for Silver Lake, the Pb concentrations have generally been low (< 0.7 μg l^{-1}), making it difficult to establish a definite temporal trend. Bearing in mind the major reductions in smelter emissions, one can invoke the following processes to account for high and unchanging levels of metals in lakes: (a) regeneration from heavily contaminated sediments and (b) transfer from metal-saturated soils and rocks in lakes' catchment. The potential importance of each process is discussed in detail below.

In a previous study of benthic fluxes of trace metals in these lakes, Carignan and Nriagu (1985) found that downward flux accounted for 24–52% of the accumulated Cu in sediments of acidic Clearwater Lake but had a negligible influence on Cu deposition in sediments of McFarlane Lake where the pH of water was neutral. Approximately 76–161% of the estimated Ni accumulation in Clearwater Lake, and 59% in McFarlane Lake were attributed to diffusional flux into the sediments. Carignan and Nriagu (1985) concluded that regeneration of pollutant metals from sediments was insignificant compared to downward flux from the water column, and that diffusion of dissolved metals into the sediments was an important mechanism for metal deposition especially in acidic lakes in the Sudbury basin. The study suggests that release from sediments by diffusion cannot be a viable explanation for the continuing high levels of Cu, Ni and sometimes Zn in the lakes.

Figs. 1–4 show the profiles of Cu, Ni, Pb and Zn concentrations in sediments of Ramsey, Nelson and McFarlane Lakes. Historical relationships between changes in metal concentrations and the outputs of Cu and Ni from the smelters in Sudbury have been discussed in detail elsewhere (Nriagu et al., 1982). The feature most pertinent to the present discussion is the continuing high accumulation rates (Table 4) and enrichments of metals in the surficial sediments. The profiles of Cu and Ni in Ramsey and Nelson

Table 2
Dissolved trace metal concentrations in water samples collected during 1993–1994 from lakes in the Sudbury basin

Lake	Depth (m)	Ni ($\mu g\,l^{-1}$)	Cu ($\mu g\,l^{-1}$)	Zn ($\mu g\,l^{-1}$)	Mn ($\mu g\,l^{-1}$)	Cd ($\mu g\,l^{-1}$)
13–15 July 1993						
Ramsey, east Basin	0.9	114	14	1.5	0.94	0.058
	9	116	16	2.3	1.2	0.099
Ramsey, west Basin	0.5	127	14	1.8	0.99	0.068
	10	127	17	2.8	0.64	0.087
	17	118	18	3.5	3.9	0.078
Kelley	0.5	379	7.8	1.3	82	0.074
	15	354	30	21	223	0.091
Silver	0.5	631	282	82	175	0.96
	6	631	282	83	175	1.1
McFarlane, east Basin	0.5	76	7.0	0.19	0.96	0.003
	8	83	7.7	2.7		0.003
McFarlane, west Basin	0.7	73	6.6	0.23	0.51	0.005
	7	82	7.8	1.4	2.5	0.019
	15	87	8.0	3.6	2.2	0.051
Clearwater	0.5	188	86	23	240	0.40
	12	144	81	23	210	0.45
Lohi	0.5	142	87	20	146	0.38
	6	133	82	22	147	0.34
Richard	0.5	72	6.1	0.83	0.92	0.024
	6	86	6.6	1.3	2.1	0.036
Windy	0.5	12	1.7	3.7	0.51	0.019
	10	13	2.4	4.6	5.3	0.022
	25	12	2.3	4.6	4.8	0.036
Nelson	0.5	5.1	2.3	2.5	4.3	0.016
	15	5.8	2.5	3.2	11	0.029
	25	5.7	2.7	3.3	14	0.029
22–24 February 1994						
Ramsey, east Basin	4	107	13	2.3	2.7	0.063
	9	110	14	2.8	8.1	0.086
Kelley	10	427	23	20	119	0.16
Silver	4	608	290	82	171	1.18
McFarlane, west Basin	4	48	6.1	2.1	1.8	0.010
	12	55	5.5	1.6	6.0	0.012
Clearwater	4	152	23	17	210	0.36
	12	139	22	14	213	0.38
Richard	4	162	7.8	5.9	8.9	0.074

Lakes show maximal concentrations at depths that vary from 1 to 3 cm below the sediment–water interface. Peaking of concentrations was not discernible in the 1978/1979 profiles (see Nriagu et al., 1982). The reduction in pollutant metal concentrations in the most recent (0–3 cm) sediment layers can be attributed to reduced inputs rather than to the release of their metal contents to the overlying water. The reason why the profiles of metal concentrations in sediments of the eastern basin (all four metals) and western basin (Zn and Ni) of McFarlane Lake (Figs. 3 and 4) have not peaked is unknown, but may be related to large mounds of mine tailings nearby. The absence of drastic changes in Pb concentrations in the most recent sediments is significant in suggesting that the regional effects of removing lead from gasoline sold in Canada are not being reflected in the

Table 3
Comparison of average dissolved trace metals in lakes in the Sudbury basin during 1979/1980 and 1993/1994

Lake	Year	Cu (μg l^{-1})	Ni (μg l^{-1})	Zn (μg l^{-1})
Ramsey, west Basin	1978/1979	16	220	8.0
	1993/1994	14	127	1.8
McFarlane	1978/1979	11	90	9.0
	1993/1994	7.0	76	0.19
Clearwater	1977[a]	81	278	39
	1978/1979			
	1993/1994	86	188	23
Lohi	1973[a]	84	254	42
	1978/1979	61	223	25
	1993/1994	87	142	20
Kelley	1978/1979	17	92	4.0
	1993/1994	7.8	79?	1.3
Silver	1978/1979	102	512	100
	1993/1994	282	631	82
Richard	1978/1979	7.0	146	10
	1993/1994	6.1	72	0.83
Nelson	1978/1979	2.1	6.8	4.0
	1993/1994	2.3	5.1	2.5
Windy	1978/1979	3.0	15	7.0
	1993/1994	1.7	12	3.7

[a] From Yan and Miller (1984).

sedimentary records in the Sudbury basin. In the three lakes (Ramsey, eastern basin of McFarlane and Nelson) where measurements were made in 1978 and 1993, the deposition rates increased in four instances, decreased in four cases and were unchanged in four others (Table 4), implying no systematic change in metal accumulation in the sediments. Data from solid sediments do not argue against the conclusion that release of pollutant metals from sediments cannot explain the unchanging high levels of the metals observed in the water column.

Figs. 5–8 show the profiles of Fe, Mn, Cd and Al in the three lakes. The concentrations of Al and Fe reflect the amounts extracted by the digestion method used rather than total concentrations in the sediments. Cadmium profiles are similar to those of the other pollutant metals in the basin (see Figs. 1–4). The enrichment factors [ratio of concentration in most recent (0–3 cm layer) sediments to concentration in pretechnological layers] of Cd fall in the range of 4–10, comparable to those of the other pollutant metals in the lake sediments. Increased accumulation of Fe in the most recent sediments reflects the fact that large quantities of this element are emitted by the Fe smelters in the Sudbury basin. The enrichment factors of 2–5 are unusual for a major component of sediments. Recent reduction in Fe emission in the basin is reflected by changes (downward) in Fe levels in the most recent (0–1 cm, layers) sediments of the lakes (Figs. 5–7).

Table 4
Accumulation rates (mg m^{-2} year^{-1}) of trace metals in sediments of lakes around the smelters in Sudbury, Ontario

Lake	Sediment flux (g m^{-2} year^{-1})	Ni	Cu	Pb	Zn
1978					
Ramsay, WB[a]	185	386	301	27	48
McFarlane, EB[a]	157	115	75	10	32
Nelson	37	13	1.9	23	27
Kelley	72	595	258	9.8	38
Vermillion	425	298	60	20	62
Windy	43	26	2.6	40	7.4
1993					
Ramsay	185	379	390	26	53
McFarlane, EB[a]	157	293	171	14	67
Nelson	35	24	34	8.1	9.5

[a] EB, eastern basin; WB, western basin.

Aluminum concentrations in sediments of all three lakes have declined by approx. 40% in recent years (Figs. 5–8). The decline can be linked to reduced weathering of bedrock associated with reduced deposition of hydrogen ions in the basin (Potvin and Negusanti, 1995; Boucard, 1997). The importance of Al in the chemistry of small lakes in particular in the Sudbury area is discussed by Mallory et al. (1998).

The concentrations of trace metals in seston collected in 1978/1979 and 1993/1994 are compared in Table 5. The most remarkable change is shown by lead, which declined sharply in all the lakes, from 165–562 μg g^{-1} in 1978/1979 to < 2.5 μg g^{-1} in 1993/1994. The sharp decline is comparable to the changes in concentrations of lead in ambient air and rainfall in central Ontario which have been attributed to the removal of lead from gasoline. Large changes in lead contents of seston suggest that a significant fraction of the lead in these lakes is derived from sources outside the Sudbury basin; such outside delivery of lead has declined substantially between 1978 and 1994. In contrast to Pb levels, there are no significant changes in Ni and Cu concentrations between the two sampling periods (Table 5). The trend for particulate Zn lies between those for Pb and Ni/Cu — the concentrations in some lakes (Ramsey and McFarlane) have increased while

those in others (including Nelson) have stayed constant. The trends for particulate metals thus tend to mirror the patterns for the dissolved phase. The contrasting behavior of Pb, Cu/Ni and Zn can be attributed to processes in the catchment rather than to changes in atmospheric inputs as the determining factor in the unchanging high levels of pollutant metals in the water column. It should be noted that the average concentrations of seston in 1978/1979 (0.16–0.66 mg g^{-1}) are similar to those of winter 1994 (Table 5). The higher concentrations of seston in summer of 1993 compared to winter of 1994 can be attributed to increased organic matter content and the dilution effect.

The discussions above rule out sediments as the major source of trace metals in the lakes studied. The alternative explanation for unchanging metal levels is that all the catchments in Sudbury basin have become saturated with Cu and Ni. Watershed where the Zn concentrations in lakes have remained constant (Clearwater, Lohi and Silver) are believed to have also become saturated with Zn, whereas only the Silver Lake watershed appears to have become saturated with Pb. Mobilization of metals stored in soils and glacial overburden by processes such as surface runoff, groundwater drainage and wind re-working of tailings is believed to be responsible for continuing the supply of large quantities of Cu, Ni and Zn to the lakes. With saturation, the catchments now act as sources and apparently yield enough metals to sustain the high levels of Ni and Cu observed in lakes. One would expect that once the buffering effects of the saturated catchments are exhausted, changes in levels of pollutant metals in the lakes will become manifested.

Several lines of evidence support the proposition that the reservoir of pollutant metals stored in the catchment are sustaining the high levels of toxic metals in these lakes. A study of many small (< 10 ha) and shallow (< 15 m) lakes downwind (northeast) of Sudbury has found no consistent, long-term change in pH, acid-neutralizing capacity (ANC) and trace metal concentrations (McNicol and Mallory, 1994; Mallory et al., 1998). In
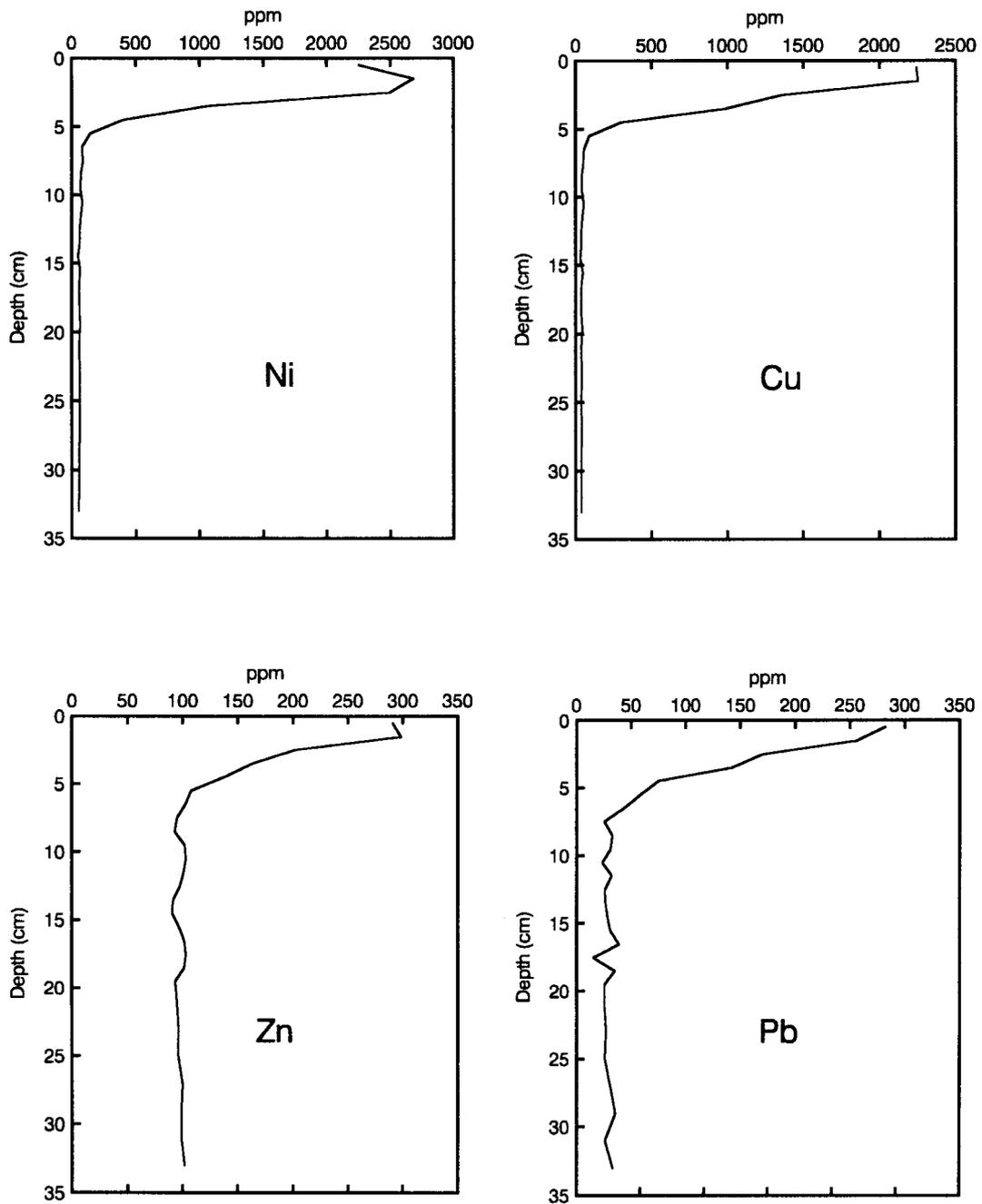
Fig. 1. Concentrations of Cu, Ni, Pb and Zn in sediments of Ramsey Lake, Sudbury basin, Ontario.

particular, it was observed that connected, rapid-flushing lakes, those on low or moderately sensitive bedrock, and peatlands showed the greatest

improvement in pH and ANC whereas glacial headwaters and lakes on highly sensitive bedrock showed the least improvement (Mallory et al.,
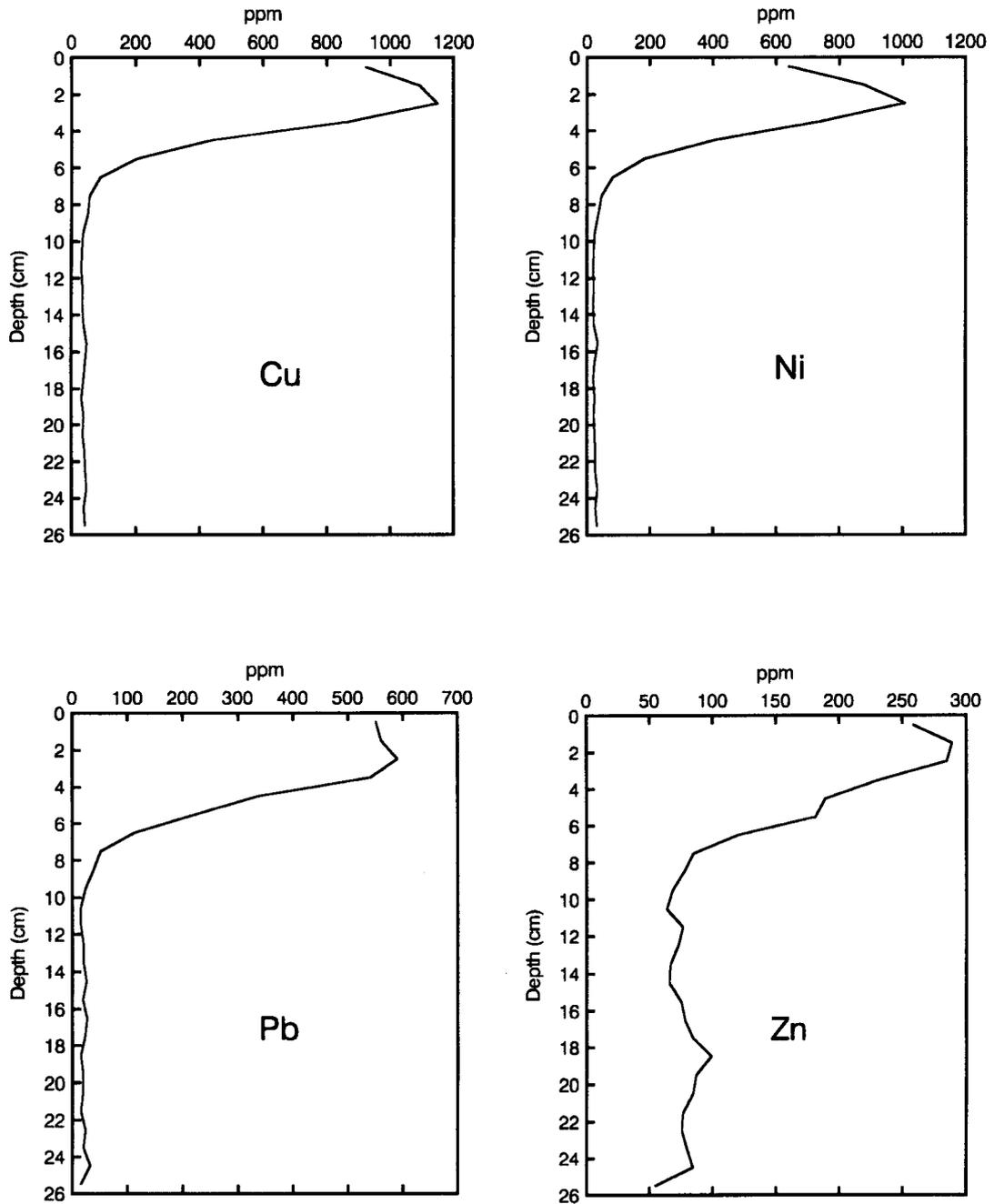
Fig. 2. Concentrations of Cu, Ni, Pb and Zn in sediments of Nelson Lake, Sudbury basin, Ontario.

1998). The lakes found to be most vulnerable are apparently those in which the chemistries are more likely to be susceptible to inputs from the catchment. Peats for instance serve to ameliorate contaminant input into lakes. The fact that pH and metal (especially Ni and Cu) concentrations
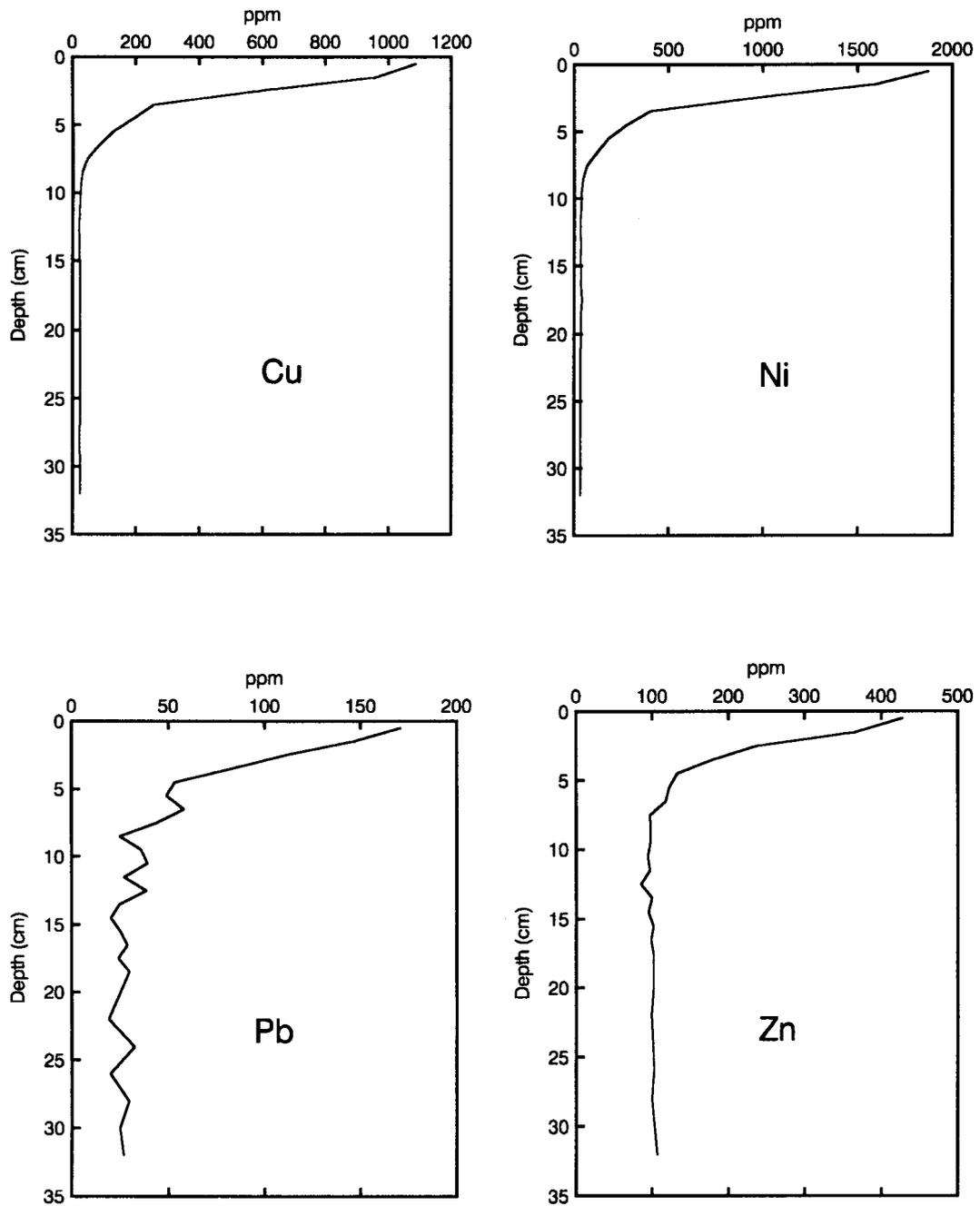
Fig. 3. Concentrations of Cu, Ni, Pb and Zn in sediments of the eastern basin of McFarlane Lake, Sudbury basin, Ontario.

respond quickly to changes in the amount of rainfall has also been noted in several studies (Keller et al., 1992; McNicol and Mallory, 1994),

and can be related to the release of previously deposited pollutants from the catchment. During the very dry years of 1986 and 1987, for instance,
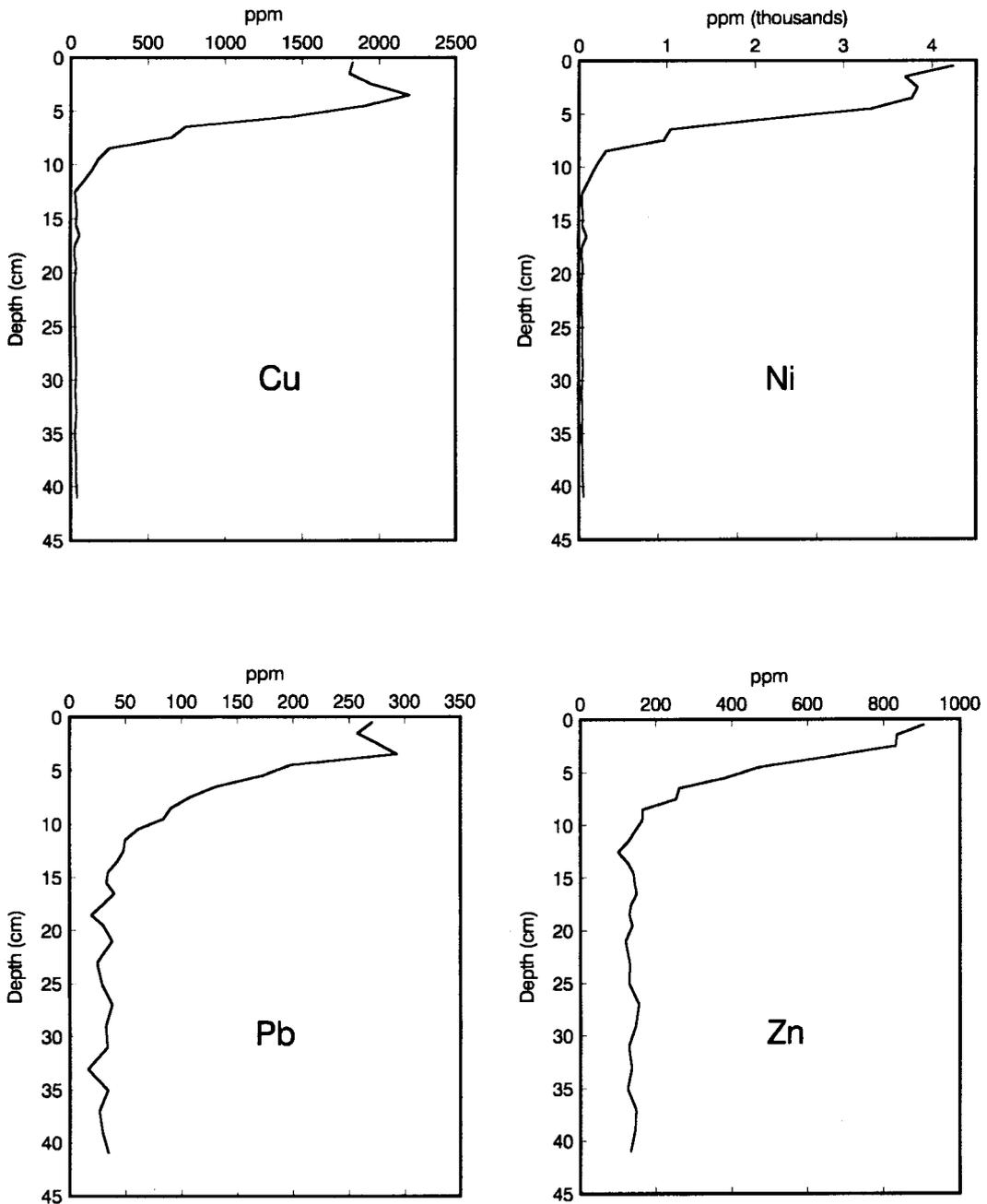
Fig. 4. Concentrations of Cu, Ni, Pb and Zn in sediments of the western basin of McFarlane Lake, Sudbury basin, Ontario.

low levels of hydrogen ions and trace metals were generally reported in the Sudbury basin. The return of abundant rainfall in 1988 and 1989 was followed by significant increases in the hydrogen ions and trace metal concentrations in many lakes (Keller et al., 1992; McNicol and Mallory, 1994).
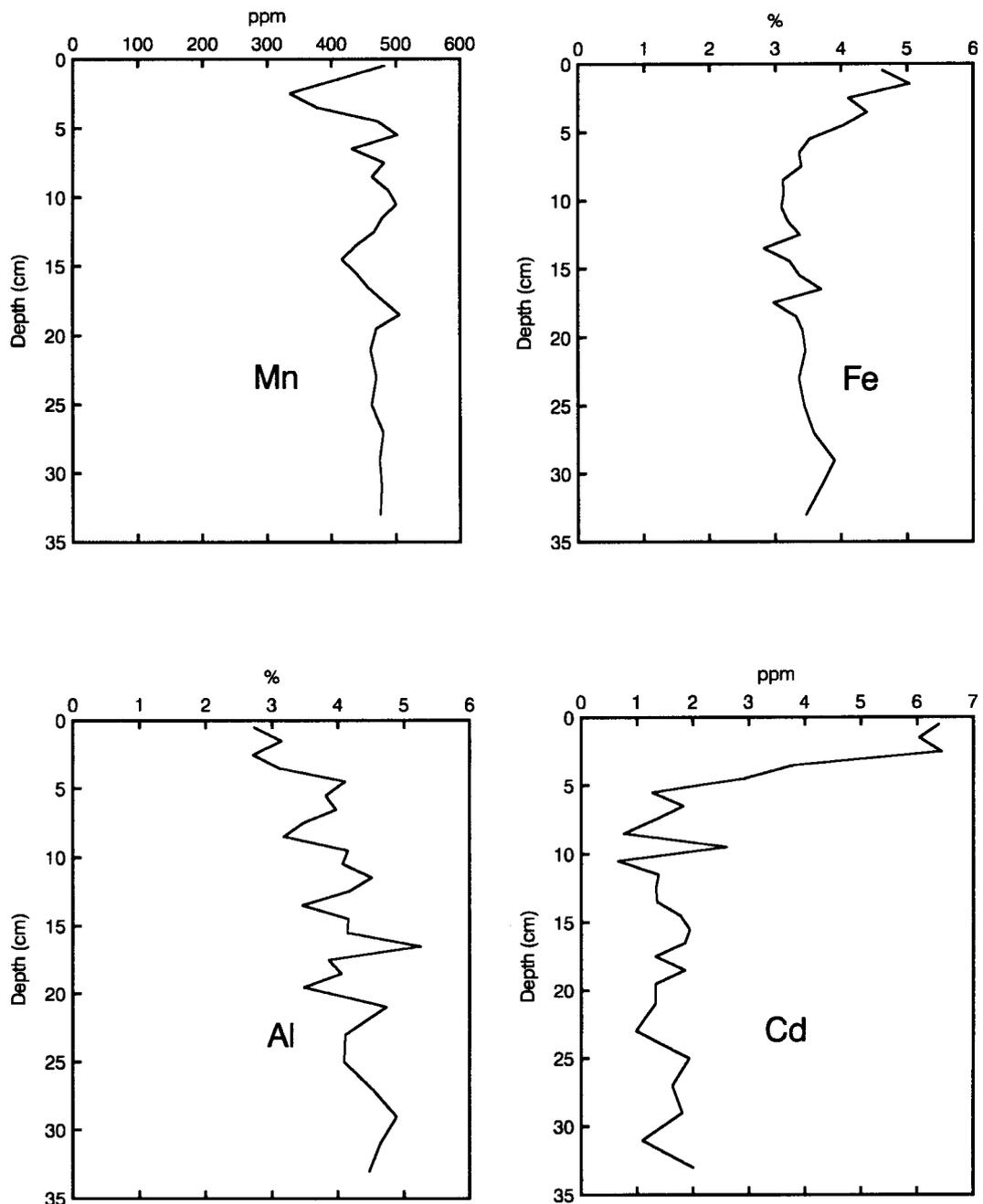
Fig. 5. Profiles of Mn, Fe, Al and Cd in sediments of Ramsey Lake.

High rainfall apparently provided the vehicle for increased export of pollutant metals and hydrogen ions stored in the catchment.

Extensive contamination of soils around Sudbury with Cu and Ni has been documented in a number of studies (Freedman and Hutchinson,
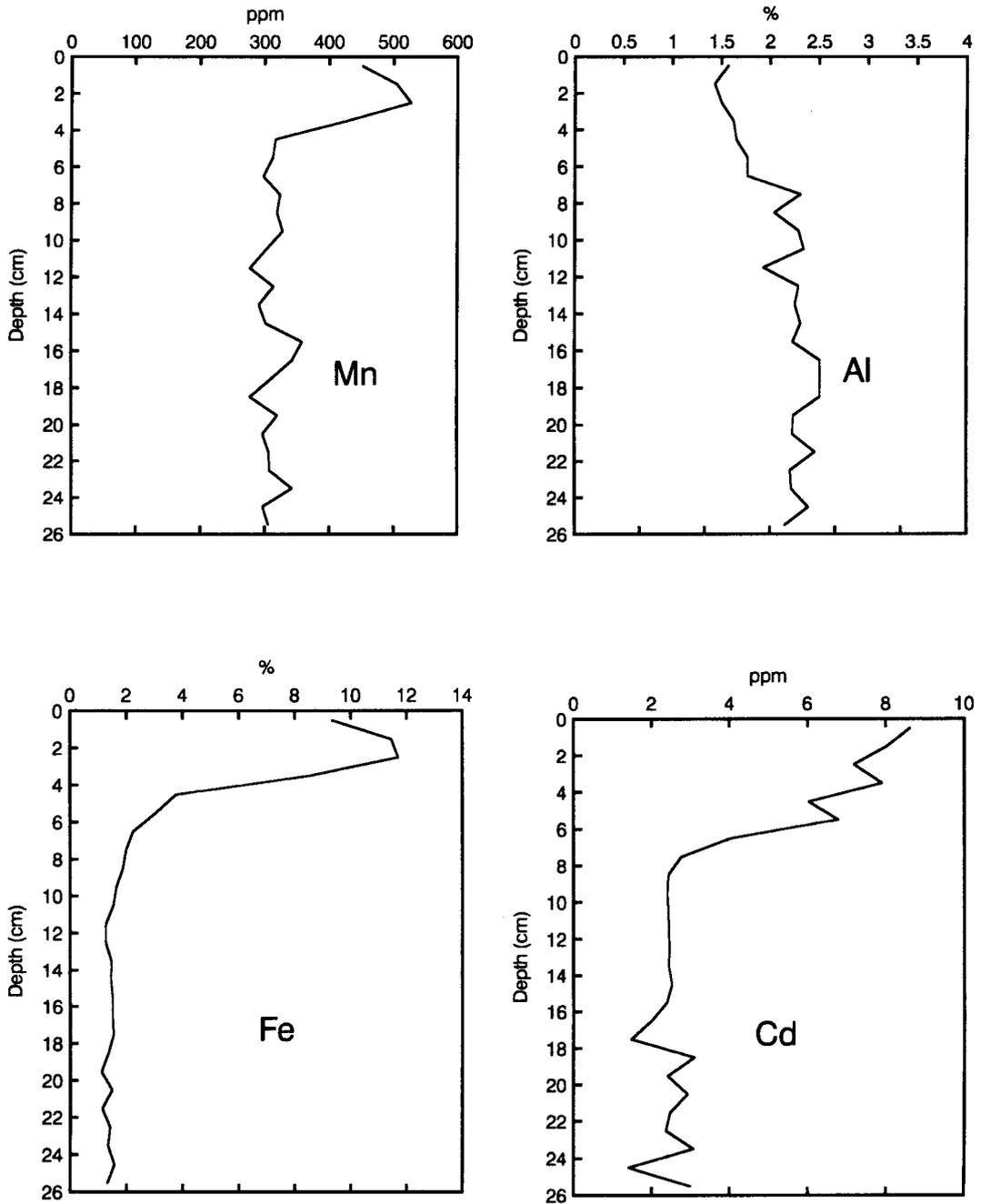
Fig. 6. Profiles of Mn, Fe, Al and Cd in sediments of Nelson Lake.

1980; McIlveen and Negusanti, 1994; Dudka et al., 1995). Table 6 shows the percentile distribution of trace metals in soils in the Sudbury basin.

In general, average Cu and Ni concentrations vary from > 100 μg g^{-1} at a distance of < 7 km to over 1000 μg g^{-1} close to the Coniston smelter.
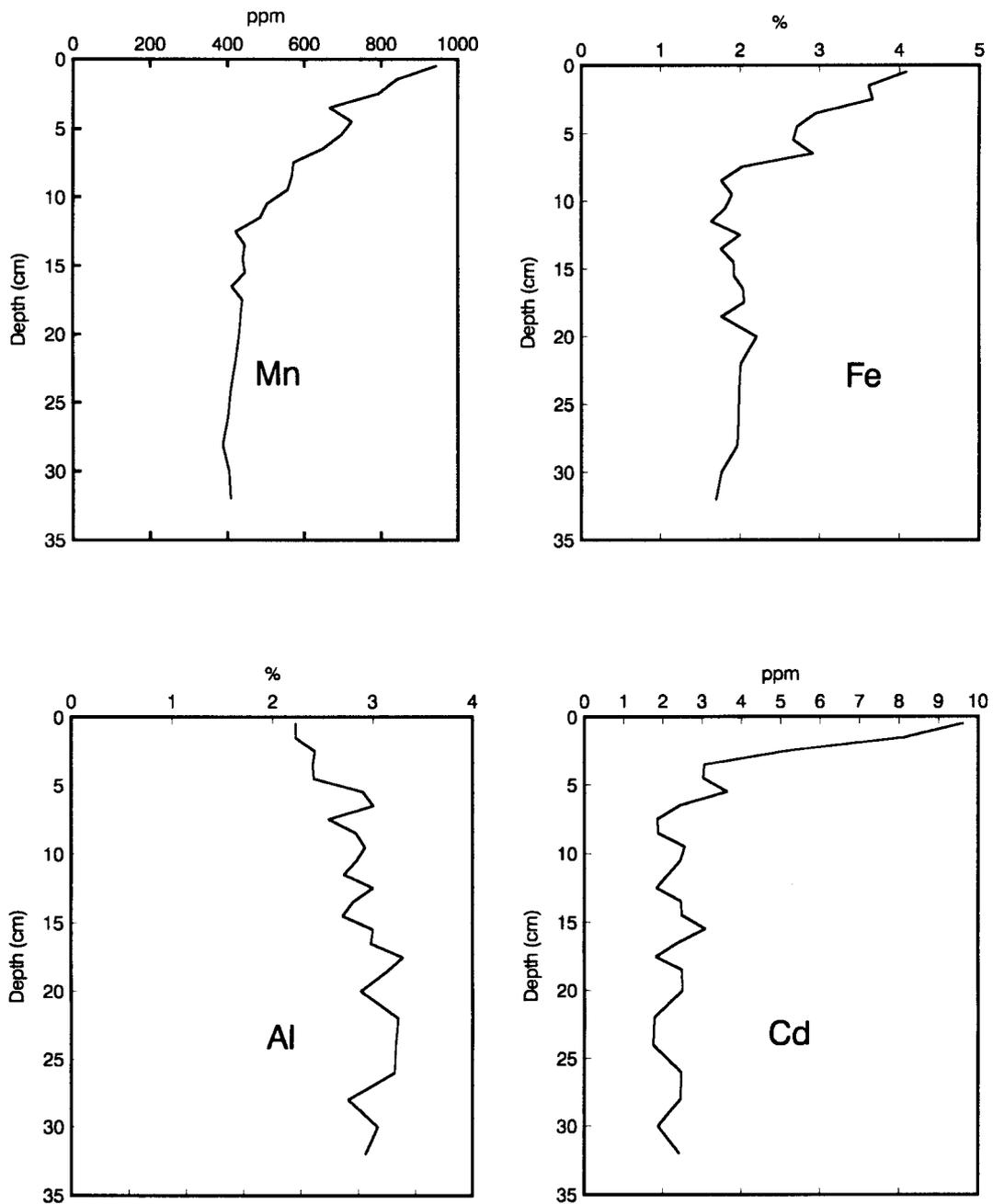
Fig. 7. Profiles of Mn, Fe, Al and Cd in sediments of the eastern basin of McFarlane Lake.

Soil levels for the Sudbury basin are much higher than the guideline values of 60 $\mu g\ g^{-1}$ for both Cu and Ni that have been set for non-agricultural soils by Ontario Ministry of Environment (MOE, 1992). Most of the Cu and Ni pollution in soils of the Sudbury basin is geochemically mobile. Ap-
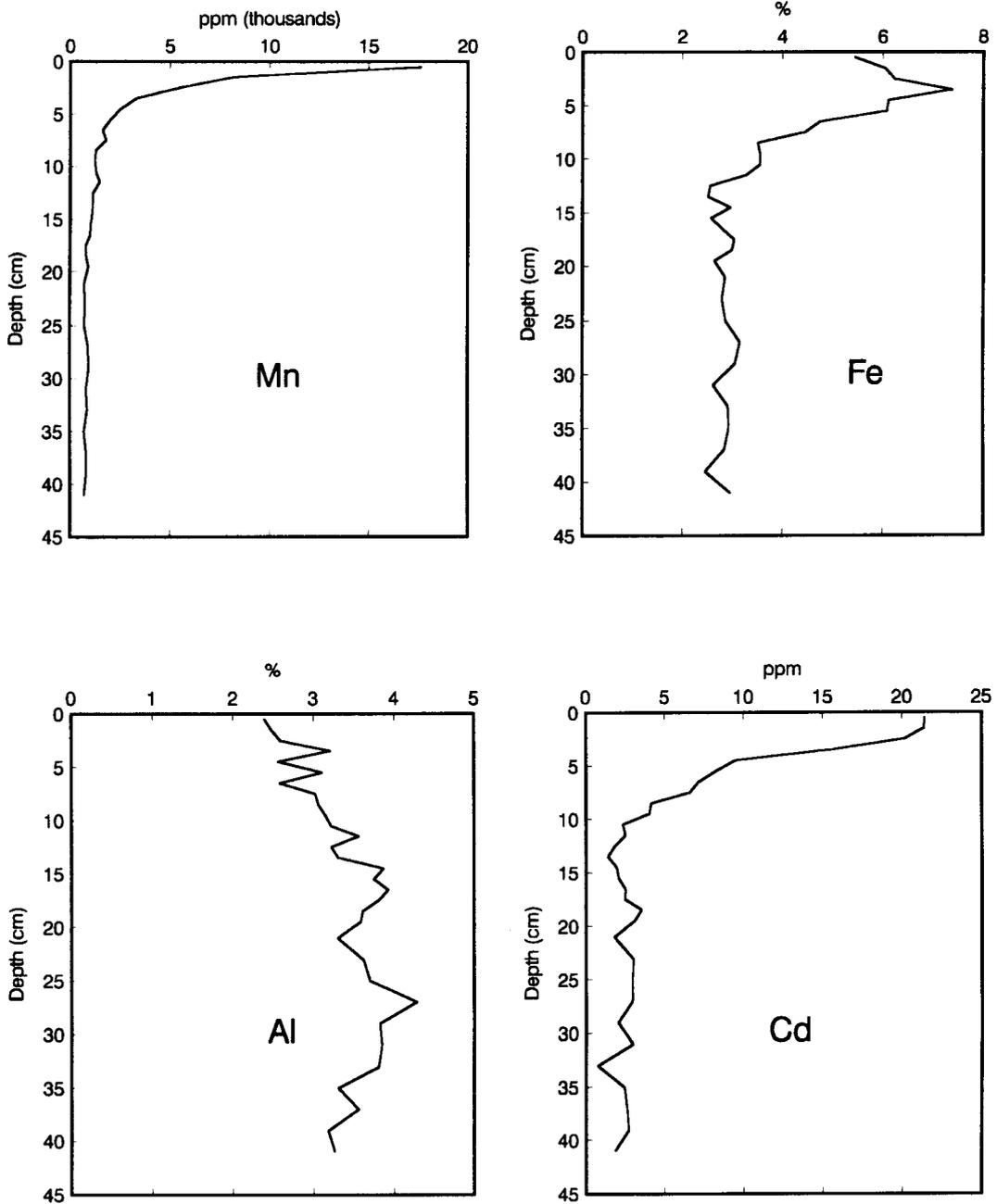
Fig. 8. Profiles of Mn, Fe, Al and Cd in sediments of the western basin of McFarlane Lake.

proximately 75% of the Cu and 40% of the Ni in the soils have been shown to be associated with non-residual extractable forms (Adamo et al., 1996). Mobility of bioavailable forms of Cu and Ni is greatly enhanced by high acidity (average pH is 4.0) of the soils (Dudka et al., 1995).

Table 5
Average trace metal concentrations in suspended particulates from lakes around the smelters in Sudbury, Ontario

Lake	Seston load (mg l^{-1})	Ni ($\mu g\ g^{-1}$)	Cu ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)	Pb ($\mu g\ g^{-1}$)	Fe (%)
Summer 1993						
Ramsay	1.03	1173	451	65	0.57	2.1
Nelson	0.18	602	656	314	2.1	1.4
McFarlane	1.28		442	101	0.55	2.2
Winter 1994						
Ramsay	0.21	1757	688	138	2.1	1.9
McFarlane	0.51	919	565	28	0.47	2.0
Richard	0.32	1439	535	165	2.3	2.3
Silver	0.44	585	380	253	0.74	2.5
Clearwater	0.34	259	753	129	1.8	1.4
Summer 1978						
Ramsay	0.42	1520	570	693	235	3.1
McFarlane	0.66	2170	237	587	357	2.6
Nelson	0.16	368	53	347	562	2.5
Windy	0.20	578	55	556	490	2.4
Wavy	0.23	624	630	234	358	3.4
Vermillion	0.57	2580	256	548	165	3.1

Table 6
Percentiles of elemental concentrations in soils in the Sudbury basin Ontario ($n = 73$; concentrations in $\mu g\ g^{-1}$)[a]

Element	Geometric mean	Percentiles					
		5th	25th	50th	75th	90th	95th
Cd	0.29	0.04	0.04	0.49	0.93	1.6	2.5
Co	11	1.7	6.5	11	18	33	45
Cr	49	21	41	52	66	85	98
Cu	116	16	61	109	215	460	646
Ni	105	22	45	97	218	504	622
V	52	30	43	51	64	79	86
Zn	35	6.6	22	39	61	90	147

[a] From Dudka et al. (1995).

The loss of trace metals from soils can be approximated using the equation:

$$\text{Annual Loss }(R) = C_s F_s + C_d F_d + C_g F_g + C_v F_v \tag{1}$$

where C is concentration, F is annual material flux, s is suspended solids, d is dissolved (in runoff), g is groundwater and v is vegetation. The decontamination time (T) is given by

$$T = Q/R \tag{2}$$

where Q is the trace metal burden in the given soil. Little of the contaminated soils in the Sudbury basin are used for agriculture so that decontamination by crop harvesting ($C_v F_v$) can be neglected. The water budgets for many watersheds in the Sudbury basin have been well characterized. Long-term annual precipitation in the basin is approx. 0.84 m, or 840 l m^{-2} (Scheider, 1984). Terrestrial runoff supplies most of the water to lakes, average contributions ranging from 60 to 90%. Approximately 70% of total annual flow into lakes occurs in spring months of March, April and May. Direct precipitation on lake surface ranges from 10 to 40% of total water supply. Outflow accounts for 65–90% of water loss from lakes while evaporation losses range from 9 to 35% (Scheider, 1984). Groundwater accounts for < 10% of the water loss in watershed so that decontamination by this route (i.e. $C_g F_g$) can also be neglected.

Little is currently known about soil decontamination due to suspended particles in air or runoff. As a first approximation, lake sediments can be

considered as the principal sink for soil particles mobilized in each catchment. Sedimentation rates in lakes studied vary from 30 to over 425 g m^{-2} year^{-1} and average 120 g m^{-2} year^{-1} (Nriagu et al., 1982). The surficial sediments contain approx. 25% organic matter (believed to be derived mainly autochthonously) so that average allochthonous flux is estimated to be 92.2 g m^{-2} year^{-1}. Average lake surface area to watershed area in the basin is estimated to be 0.2 so that the average yield of suspended solids from the catchment is estimated to be 18 g m^{-2} year^{-1}. Geometric mean concentrations in soils are 116 μg g^{-1} for Cu, 105 μg g^{-1} for Ni and 35 μg g^{-1} for Zn (Dudka et al., 1995), from which the average removal associated with suspended particles are estimated to be 2.1 mg m^{-2} year^{-1} for Ni and 0.52 mg m^{-2} year^{-1} for Ni and 0.52 mg m^{-2} year^{-1} for Zn.

Average annual unit runoff from the watershed is estimated to be 0.4 m year^{-1}, or 400 l m^{-2} year^{-1} (Scheider, 1984). Assuming that the average metal concentrations in runoff water is similar to that of the lakes, the average yield of dissolved metals in the catchment is estimated to be 14 mg m^{-2} year^{-1} for Cu, 67 mg m^{-2} year^{-1} for Ni and 6.8 mg m^{-2} year^{-1} for Zn. Average decontamination rates due to the removal of both dissolved and suspended phases ($C_s F_s + C_d F_d$) of the metals are then estimated to be 16 mg^{-2} year^{-1} for Cu, 69 mg m^{-2} year^{-1} for Ni and 7.3 mg m^{-2} year^{-1} for Zn and <8 mg m^{-2} year^{-1} for Pb. It is rather interesting that the critical loading rates for European soils of 1.3–35 mg m^{-2} year^{-1} for Cu, 14–200 mg m^{-2} year^{-1} for Cd, and 19–410 mg m^{-2} year^{-1} for Pb (Reinds et al., 1993) are similar to the natural decontamination rates in the Sudbury basin. In view of the difference in soil characteristics and climatic conditions, the yield and loading rates are not directly comparable, however. The large disparities in the figures nevertheless do emphasize the need for considering the saturation index in any attempt to estimate the resilience of soils to heavy metal pollution. The concept of critical loading of heavy metals into soils assumes that soils have an unlimited ability to absorb heavy metals at certain loading rates. Such a concept may need to be re-evaluated in some instances in light of the 'new' phenomenon of catchment saturation.

From the percentile distributions of metals in soils in the Sudbury basin (Table 6), and assuming mean soil density of 2.5 g ml^{-1}, the average burdens corresponding to the 50th, 75th and 90th percentiles have been calculated (Table 7). From these data, the excess metal pools (Q) between the 50th and the 90th and 75th percentiles have also been derived (Table 7). It needs to be noted that the average baseline concentrations of these three metals in Sudbury soils (Dudka et al., 1995) are well below the 50th percentile values used in our calculation. By substituting the decontamination rates and excess metal pools into Eq. (2), the times required to reduce the metal concentrations from the 75th percentile to the 50th percentiles values are estimated to be 810 years for Cu, 220 years for Ni and 380 years for Zn. To lower the metal concentrations from the 90th percentile levels to the 50th percentile values will take much longer: 4190, 960 and 1920 years, respectively for Cu, Ni and Zn (Table 7). These estimates, though crude, point to the fact that the lifetimes of Cu, Ni and Zn in soils of the Sudbury basin are fairly long (hundreds of years). In other words, the contaminated soils are likely to sustain the high concentrations of trace metals in lakes for a very long time. Emission controls alone may no longer be enough to reduce the risks of heavy metal pollution of surface waters and a strategy for immobilizing the reservoir of pollutant metals in the watershed is needed to reduce the metal levels.

Historically, studies of trace metals (so-called microelements) in soils have generally focused on their deficiency status (see Nriagu, 1979, 1980). In such soils, an efficient internal cycle is developed leading to minimal export or loss of the particular microelement. This has led to the common belief that watersheds are efficient sinks for trace metals. The present study shows that soils, especially if acidic, become readily saturated with pollutant metals, resulting in increased leakage of metals to soil solution and surface waters. Elevation of heavy metal levels in soil solutions, especially in

Table 7
Average yields and lifetimes of pollutant metals in catchments of the Sudbury basin

Process or reservoir	Cu	Ni	Zn
Dissolved metal concentration ($\mu g\, l^{-1}$)	35	168	17
Metal concentration in suspended particulates ($\mu g\, g^{-1}$)[a]	116	105	35
Annual metal yield, dissolved (mg m^{-2})[b]	14	67	6.8
Annual metal yield, suspended solids (mg m^{-2})[c]	2.1	1.9	0.52
Total metal yield (mg m^{-2})	16	69	7.3
Metal concentration ($\mu g\, g^{-1}$)[d]			22
5th Percentile	16	22	6.6
25th Percentile	61	45	22
50th Percentile	109	97	39
75th Percentile	215	218	61
90th Percentile	4690	504	90
95th Percentile	646	622	147
Reservoir of excess metal in top (5 cm) soil (g m^{-2})			
75th to 50th percentile	13	15	2.8
90th to 50th percentile	67	66	14
Lifetime of metal (years):			
Decline from 75th to 50th percentile level	810	220	380
Decline from 90th to 50th percentile level	4190	960	1920

[a] Geometric mean concentrations for soils in the Sudbury basin (Ref. 15).
[b] Annual unit runoff in the basin is 400 l m^{-2} year^{-1}.
[c] Derivation of these values are given in the text.
[d] From Mallory et al. (1998).

the rooting zone, creates toxic conditions for plants, engenders accumulation of toxic metals to high levels in tissues of plants and their consumers, and leads to a disturbance in normal functioning of an ecosystem. It is not surprising that only few plants can thrive in the contaminated soils around Sudbury (McIlveen and Negusanti, 1994). Saturation of ecosystems with pollutant metals has thus far been ignored in the scientific literature. The phenomenon is believed to be common especially around mining/smelting centers and major industrial installations in many countries.

Our ability to manage and rehabilitate ecosystems around major mining/smelting areas has been hampered by a lack of adequate understanding of the chemistry and dynamics of the metal pollution. Gains on environmental quality of ecosystems around Sudbury have certainly been made by controls on smelter emissions. Our data suggest that the yields of pollutant metals from the catchment now exceeds the atmospheric inputs, and that the phenomenon of metal exhalation from catchment is dominating the metal levels in many surface waters of the Sudbury basin. The benefits of further emission controls must remain questionable until something is done about metal release from the saturated ecosystems.

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