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The effects of acidification on metal budgets of lakes and catchments

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Abstract. Metal (Cu, Ni, Zn, Fe, Mn and Al) budgets were measured for 5 lakes and their catchments near Sudbury, Ontario, an area severely affected by the emission and deposition of strong acids (H_2SO_4/SO_2) and metals. Three of the lakes were circum-neutral (pH 6.3–7.1) during the study period, while one lake had a pH of ~ 4.8 and a fifth had very low pH (~ 4.4).

The lakes' catchments were all sources of Al, Mn and Ni, but were sinks for Cu and Zn. The Fe results were inconsistent; two lakes' catchments were sources while three were sinks.

The acidic lakes were conservative (i.e. net retention of zero) with respect to Cu and Ni, while the circum-neutral lakes were effective sinks for these 2 metals. All of the lakes were sinks for Zn and Al, but the acidic lakes were less effective. All lakes were also Fe sinks. While there was no pattern relative to the lakes' pH's, there was a trend towards increasing Fe retention with increasing water replenishment time. The most acidic lake was actually a source of Mn, while the others were sinks.

Introduction

The interaction between the biogeochemical effects of both the wet and dry deposition of acids to the earth's surface (i.e. "acid precipitation") and the increase in trace metals of anthropogenic origin has been a topic of numerous investigations (Anon. 1985). For example, the loss of fish from acidified, metal-contaminated lakes in Ontario, Canada (Beamish & Harvey 1972), the effects of trace metals on the survival of freshwater zooplankton (Biesinger & Christensen 1972; Baudouin & Scoppa 1974), the result of increased acidity on the mobility of trace metals in lake sediments and watersheds (Cronan & Schofield 1979; Schindler et al. 1980; Johnson et al. 1981) and the effects of high acidity and metal levels on terrestrial flora (Hutchinson & Whitby 1977; Linzon 1978; Freedman & Hutchinson 1980) have been studied extensively.

To date, however, few attempts to quantify the fluxes of metals to and from any lake, acidic or not, have been made. The few exceptions include Lee (1962) who measured the Fe and Mn budgets of Lake Mendota, Nriagu et al. (1979, 1983) who measured metal budgets for Lake Erie and a portion of Lake Ontario, Cross & Rigler (1983), who reported on the Fe budget of Bob Lake, Ontario, and White & Driscoll (1985, 1987a, b), who measured the budgets for several metals in Dart's Lake, New York. With the exception of Dart's Lake, these lakes were not affected by acidic deposition.

In addition, a few metal budgets for catchments have been measured (Andren et al. 1975; Swanson & Johnson 1980; Calles 1983; Schut et al. 1985) while input-output budgets for strong acids and related substances (eg. SO_4) have been quantified more frequently for both lakes and catchments (eg. Schindler et al. 1976; Wright & Johannessen 1980; Galloway et al. 1983; Wright 1983). The scarcity of metal mass balance information is unfortunate because these data could be used to assess the relative importance of the different sources and loss mechanisms to and from a lake (LaZerte 1986) or to predict metal concentrations in lakes as a function of source strength. They may also be useful for studying the effects of acidic deposition on the behaviour of trace metals in both terrestrial and aquatic systems.

The purpose of this study was to construct the input-output budgets for Cu, Ni, Zn, Fe, Mn, and Al for five lakes (two acidic lakes with average annual $\mathrm{pH} < 4.8$ and three circum-neutral lakes with average annual $\mathrm{pH} > 6.3$), and their catchments, and to use these mass balances to evaluate the effects of lake acidification on the behaviour of these metals.

Study area

Major Cu and Ni deposits were discovered near Sudbury, Ontario, Canada over 100 years ago. The resulting mining and smelting activities have resulted in the emission of extremely large quantities of SO_2, the precursor of H_2SO_4 (0.5–2.5×10^6 tonnes yr^{-1} during the 1970's), and of Cu and Ni (500–1100 tonnes yr^{-1}; Jeffries 1984; Ontario Ministry of the Environment 1982). As a consequence, there are elevated metal and acidity levels in the surrounding aquatic and terrestrial ecosystems (eg. Allan 1974; Beamish 1974; Hutchinson & Whitby 1977; Scheider et al. 1979; Amiro & Courtin 1981). Levels of many metals in the lake waters are extremely high; for example Yan & Miller (1984) measured Cu, Ni, Zn, Fe, Al and Mn levels in Clearwater Lake in 1977 of 81, 280, 39, 88, 380 and 290 $\mu\mathrm{g\ L}^{-1}$ respectively. This lake, and many others in the region, have been acidified such that their pH in 1973–74 was between 4.1 and 4.4.

Hydrologic and chemical budgets were measured for five lakes within a 30 km radius of Sudbury (Fig. 1) during the period June 1977-December 1979. Only data from the 12-month period June 1977-May 1978 are reported here because the shutdown of the Inco Ltd. smelter from September 1978 to June 1979 resulted in drastically reduced atmospheric deposition of some metals (Scheider et al. 1981). As a result, the lakes were not in steady-state with respect to the metal fluxes after September 1978 (Dillon 1984).

The study lakes and catchments, which are described in detail in Dillon et al. (1979, 1982), Jeffries (1984) and Jeffries et al. (1984), lie entirely on the Precambrian Canadian Shield. Hannah, Middle, Lohi and Clearwater Lakes are situated south of Sudbury and are underlain by quartzite, gabbro and metagabbro with gneiss, migmatite and/or granitic intrusions in large parts of the Clearwater Lake basin. Nelson Lake lies to the north of Sudbury; a large portion of the drainage basin is underlain by granophyre while volcanic tuff and breccia occur along the south shore.

The surficial deposits are composed generally of thin, unconsolidated Pleistocene tills plus more recent stream and lacustrine deposits. Early smelting practices (i.e. open, surface roasting) led to destruction of most of the vegetation in the immediate vicinity of Sudbury, resulting in erosional

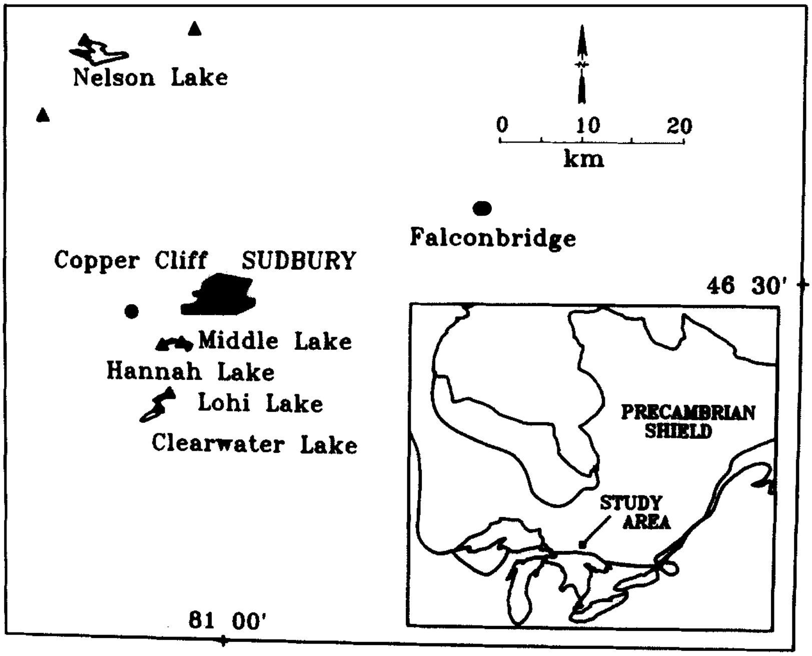

Fig. 1. Location of study lakes, precipitation collectors △, and the 2 major smelters in the Sudbury area, Copper Cliff and Falconbridge (●).

redistribution of surficial material in the Middle and Hannah basins and, to a lesser degree, in the Lohi and Clearwater basins (Dillon & Smith 1984). Glacial material has been washed into low-lying areas resulting in a large proportion of exposed bedrock (65–82%) in these basins. The Nelson Lake basin was much less affected by smelting events and is fully forested with only minor bedrock exposure (about 1%).

The locations and morphometries of the lakes are given in Table 1. All are small (27 to 309 ha) with mean depths between 4 and 12 m and maximum depths between 9 and 55 m. Clearwater, Hannah and Nelson are headwatrer lakes while Middle Lake is downstream of Hannah Lake and Lohi Lake is downstream of Clearwater Lake. All the lakes except Clearwater were treated with neutralizing agents and/or nutrients in the period 1973–1977. Details of the lake manipulations and their effects on the chemistry of the study lakes have been discussed previously (Dillon et al. 1979; Yan & Dillon 1984; Yan & Lafrance 1984). In summary, during the study period Clearwater Lake was the most acidic of the five lakes (pH ~4.4), Lohi Lake had reacidified to pH ~4.75 while Middle, Hannah and Nelson Lakes had remained circum-neutral, with pH's of 6.3–7.1.

Methods

Hydrologic budgets

The lakes' water budgets have been described elsewhere (Scheider 1984); a brief summary follows.

Precipitation. Precipitation depth was measured at eight sites using standard rain gauges from May to November 1977 and Nipher snow gauges in the winter. A gauge was located on or near each of the five study lakes and at three additional sites. Data from the eight gauges were pooled into three

Table 1. Distance from Copper Cliff smelters (d), morphometry, water replenishment time (τ_w), and catchment area (A_d) of the study lakes.

Lake	d (km)	Lake area (ha)	Lake volume ($10^5 m^3$)	Mean depth (m)	Maximum depth (m)	τ_w (yr)	A_d (ha)
Hannah	4.3	27.3	10.8	4.0	8.5	3.0	104
Middle	5.0	28.2	17.5	6.2	15.0	1.8	275
Lohi	11	40.5	25.0	6.2	19.5	1.3	558
Clearwater	13	76.5	64.2	8.3	21.5	4.4	419
Nelson	28	309	359	11.6	51.0	9.3	1110

stations: Sudbury North (30–50 km north of Sudbury), Sudbury South (10–12 km south) and Sudbury Centre (4–5 km south). Precipitation depth at the Sudbury Centre station was used for Hannah and Middle Lakes, data from the Sudbury South station were used for Clearwater and Lohi Lakes and data from the Sudbury North station were used for Nelson Lake. Where depth data were missing from the station records, data from the closest Environment Canada meteorological station were used.

Streamflow. Watershed boundaries for all the lakes and sub-watersheds were delineated by stereoscopic inspection of airphotos and by field observation. Weirs or flumes were installed at two inlet streams to Clearwater Lake and three inlet streams to Nelson Lake as well as at the outlet stream of each lake. Continuous stage was measured at these 10 sites using either a Brott bubble-type recorder or a Leopold and Stevens Type A Model 71 float-operated recorder (Scheider 1984). Discharge was measured using either a current meter (Ott C2) or, during low flow, by catching the entire volume of the stream in a bucket as the water passed over the weir notch. Measurements were taken at weekly to bi-monthly intervals except during periods of peak flow in the spring and fall when measurements were taken several times per week. Stage-discharge curves were established for each weir and flume. The continuous stage records were converted to continuous discharge using the STREAM programme (Water Survey of Canada 1977).

Some (18%–74%) of the terrestrial drainage area of each lake was not gauged. The ungauged areas either drain directly into the lake via overland flow or drain via wide, swampy streams where water velocity could not be measured. To estimate the annual discharge for these areas, the mean value of the annual areal runoff (per unit area) for the five gauged headwater streams was used. Monthly discharge was then calculated by pro-rating the annual discharge according to the monthly pattern observed in the gauged streams.

Storage. Changes in lake storage were determined from lake level measurements made at regular intervals using staff gauges, permanently installed in each lake.

Evaporation. Net evaporation rates (evaporation loss − condensation gain) for each lake were calculated as the residual term in the energy balance equation assuming that the heat exchange due to precipitation and to runoff (both into and out of the lake) and the heat loss to the sediments were negligible. Net radiation was measured continuously.

The evaporation calculations were carried out over time periods corresponding to measurements of the lakes' heat budgets (approx. weekly). Daily evaporation for each period was determined as the total evaporation for the time period divided by the number of days in the period. Monthly evaporation was obtained by summing the daily values.

Chemical budgets

Atmospheric loading. Atmospheric depositions of Al, Mn, Fe, Cu, Ni and Zn were measured at eight sites using bulk deposition collectors (Galloway & Likens 1976). The samples, after collection in an open funnel, drained into glass bottles which were housed in boxes to exclude light and discourage the growth of algae. The funnels (0.034 m^2 in 1977; 0.054 m^2 in 1978) were mounted 1 m above ground level and fitted with 500 μm Nitex mesh to prevent contamination by insects. Bulk snow samples were obtained using a 'bucket-type' collector with a collection area of 0.15 m^2.

Collection periods averaged less than 7 days but ranged from 1 to 83 days with extremely long sampling periods (> 30 days) occurring only rarely for winter snow collection when sample reactivity was minimal.

Daily deposition of each metal for each bulk collector was calculated by first multiplying the sample concentration by the cumulative precipitation depth for the sampling period and then by dividing by the number of days in the period. The daily deposition values for all the collectors within a station (i.e. Sudbury North, Sudbury Centre and Sudbury South) were averaged to yield an arithmetic mean daily value for that station. The mean daily values were then summed to give monthly deposition.

Watershed loading. The metal concentrations in the five gauged headwater streams (i.e. Clearwater inlets 1 and 2, Nelson inlets 1, 2 and 3) draining into the study lakes as well as the five outflows were monitored throughout the study period. All stream samples were retrieved at or below the notch of the weir or within the flume of the streams. Sampling frequency varied from bi-weekly or monthly during base flow conditions in the winter to 2–3 times per week during spring thaw, and weekly during the summer.

Because there were no significant relationships between stream discharge and stream metal concentration, loads (mg yr^{-1}) were calculated by multiplying the concentration of the metal in the stream measured during the midpoint of a time period by the total discharge over that time interval.

The chemistry of six ungauged headwater streams (Clearwater inlets 3 and 4, Middle inlet 1, Nelson inlets 4, 5 and 6) was also monitored. Sampling frequency varied from bi-weekly or monthly during base flow conditions in the winter to 2–3 times per week during spring snowmelt. Since discharge in these streams was estimated rather than measured, the load was calculated as the product of the mean monthly metal concentration and the total monthly discharge as estimated above.

The ungauged portion of the basin includes areas drained by intermittently flowing streams that were not sampled and areas that drain into the lake via direct overland flow. Inputs from these areas were estimated from the data available on the hydrologically gauged basins. For Clearwater and Lohi Lakes, inputs from the ungauged areas of the basin were estimated by prorating measured gross export (output per unit basin area) data for Clearwater Lake inlet 1, while for Hannah and Middle Lakes, inputs from the ungauged areas of the basin were estimated from gross export data from Middle Lake inlet 1. Inputs for the ungauged areas of Nelson Lake were estimated using the mean gross export of inlets 1, 2 and 3 prorated by the drainage basin areas.

Budgets for the terrestrial basins of Lohi and Hannah Lake were not constructed because neither had monitored headwater inlets.

Analytical methods

After collection, all samples (unfiltered) to be analyzed for Zn, Cu, Ni and Al were preserved with 1 mL HNO_3 L^{-1} and stored for 14–60 days in Nalgene bottles. Samples were digested overnight at 70 °C in a 2:1 mixture of $HCl:HNO_3$, and concentrated by 10X. After dilution with deionized, distilled water the digestate was analyzed using a Varian atomic absorption spectrometer (model 1250). These analytical techniques were described in detail in Ontario Ministry of the Environment (1981).

Samples to be analyzed for Fe and Mn were refrigerated in glass bottles after collection. For the measurement of Mn, the methods of Crowther (1978a) were followed. Fe was measured by colourimetry after autoclave digestion under acidic conditions (Crowther 1978b). The limit of detection for all of the metals was about 2 μg L^{-1}.

Results and discussion

Atmospheric deposition

During the study period, the strong acid deposition (much of it as SO_2) was $\sim$ 300 meq $m^{-2}yr^{-1}$ at Middle and Hannah Lakes, $\sim$ 200 meq $m^{-2}yr^{-1}$ at Clearwater and Lohi, and $\sim$ 150 meq $m^{-2}yr^{-1}$ at Nelson Lake (Table 2).

Table 2. Deposition of strong acid (meq $m^{-2}yr^{-1}$) and metals (mg $m^{-2}yr^{-1}$) in the study period (from Jeffries 1984 & Dillon 1984).

	Hannah/Middle	Lohi/Clearwater	Nelson
Strong acid	300	200	150
Cu	297	87.4	45.4
Ni	110	81.6	6.5
Zn	48.7	66.7	61.3
Fe	402	215	105
Mn	7.7	6.1	9.5
Al	53.2	40.6	62.8

These levels are extremely high relative to those measured in most other parts of the world affected by acidic deposition (eg. Andren & Lindberg 1977).

Jeffries & Snyder (1981) and Jeffries (1984) reported the measured bulk deposition rates of metals in the study area including the period June 1977 to May 1978. The deposition rates of Cu and Ni, the principal metals processed and emitted by the smelters, were extraordinarily high, ranging from 45 mg $m^{-2}yr^{-1}$ (at Sudbury North – Nelson Lake) to 297 mg $m^{-2}yr^{-1}$ (Sudbury Centre – Hannah, Middle Lakes) for Cu and from 6.5 (Sudbury North) to 110 (Sudbury Centre) mg $m^{-2}yr^{-1}$ for Ni (Table 2). These values are typically 20–250 times greater than those measured 200 km to the south-east of Sudbury and in other rural areas in North America (Jeffries 1984).

Significant amounts of Zn and Fe were also emitted from the smelters; however, deposition of Zn was only ~4 times greater than in the region remote from the smelters, and was roughly equal at all 3 Sudbury sites. Deposition of Fe was elevated above that measured 200 km to the south-east only at the 2 sites closest to the smelters, (4x at Sudbury Centre and 2x at Sudbury South), indicating a very rapid decline in deposition with distance from the source. The depositions of both Al and Mn were approximately equivalent at all 3 stations which were, in turn, very close to those measured at the Muskoka-Haliburton site 200 km from the Sudbury area (Jeffries 1984).

These results indicate that the smelters' metal emissions are a major factor in the observed Cu and Ni levels in the lakes, a lesser factor in the Zn and Fe levels and not responsible for the observed high Al and Mn levels. Interaction of the strong acid and acid precursors emitted by the smelters and deposited on the lakes' catchments with the overburden/bedrock, or perhaps the lakes' sediments is undoubtedly the driving force behind the observed lake Al and Mn levels, and at least partially responsible for the observed Fe and Zn concentrations.

Terrestrial budgets

The output of all of the metals from the monitored catchments is given in Table 3. Measured output of Cu ranged from 115 mg m^{-2}yr^{-1} at Middle inflow 1, the site closest to the smelters, to 20.9–26.3 at the 4 Clearwater inflows to 1.8–4.2 at the 6 Nelson Lake inflows. Nickel export followed a similar pattern (404, 99–175, 5.2–16.7 at Middle, Clearwater and Nelson Lakes, respectively), decreasing with distance from the smelters. These Cu and Ni exports are extremely high relative to those measured anywhere in the world (Andren et al. 1975; Swanson & Johnson 1980).

The patterns of Zn, Mn and Al were similar to each other; the lowest output of each was measured at Nelson Lake (as for Cu and Ni), but the outputs at Middle and Clearwater were almost identical (Table 3). Iron was the only one of the 6 metals that did not have the highest outputs at Middle Lake; output at Middle Lake was similar to that at Nelson Lake, with the levels at Clearwater Lake being about twice as high. The high Fe export from the Clearwater Lake catchment results from very high Fe concentrations in streams draining 2 subcatchments (exports of 375 and 703 mg m^{-2}yr^{-1}). Both of these streams also had high dissolved organic matter (as DOC) and colour levels, indicating high levels of fulvic/humic material that originated in wetlands (beaver ponds) in the subcatchments. It is apparent that organic matter transport is the most important factor determining Fe output from terrestrial basins, since Fe is readily complexed by organic matter originating in soils (Schnitzer & Skinner 1966, 1967).

The retentions (the percent of the input to the catchment that does not leave via streamflow) of the metals by the terrestrial systems are shown in Table 4. In general, the Nelson Lake catchment had the highest metal retention, the exceptions being for Ni and Fe. The retention of metals in the Middle catchment was usually the same or less than that in the Clearwater catchment.

Table 3. Average and range of gross output of metals from the catchments at Middle Lake (inflow 1), Clearwater Lake (inflows 1 to 4) and Nelson Lake (inflows 1 to 6). All figures in mg m^{-2}yr^{-1}, and uncorrected for input by atmospheric deposition (from Jeffries et al. 1984). Figures for the Clearwater and Nelson catchments are a really weighted averages of the 4 and 6 sub-catchments respectively.

	Middle	Clearwater	Nelson
Cu	115	22.6 (20.9–26.3)	3.1 (1.8–4.20)
Ni	404	128 (99–175)	10.4 (5.2–16.7)
Zn	24.2	28.6 (11.7–48.2)	6.2 (3.0–13.4)
Fe	173	375 (124–703)	163 (46–284)
Mn	104	98.5 (87.0–126)	34.2 (16.3–72.6)
Al	275	260 (154–334)	110 (53–203)

Table 4. Retention (%) of each metal by the catchment of each study lake where terrestrial metal budgets were measured directly. A negative number means that the output in streamflow is greater than the input via atmospheric deposition.

	Middle	Clearwater	Nelson
Cu	61	75	93
Ni	−270	−48	−74
Zn	51	72	88
Fe	57	−72	−40
Mn	−1300	−1400	−345
Al	−420	−409	−95

There was net export of Al and Mn (i.e. the retention was negative) from all the catchments, reflecting the lithologic origin of these metals and their increased mobility under acidic conditions (Cronan & Schofield 1979; Driscoll & Schafran 1981). The large amount of Al supplied from these catchments was expected, since it has been well documented that under acidic conditions, Al is readily mobilized from soils (Schofield 1976; Hall and Likens 1981; Johnson et al. 1981). Jeffries et al. (1984) found a positive correlation between the H^+ concentration and the Al concentration in the 11 streams monitored in this study, reflecting the greater solubility and mobility of Al in acidic watersheds. Heinrichs & Mayer (1977) determined that Mn and Al were the only two metals of 20 elements measured that were not accumulating in both a central European beech forest and a spruce forest. Export from the Nelson Lake catchment was substantially less than that from the other catchments, probably because of the higher pH of the runoff water from the catchment. The mean pH of the 6 Nelson Lake inlets was 4.6–5.0 vs. 4.5–5.0 for the 5 Clearwater and Middle Lake inlets (Jeffries et al. 1984). In all the watersheds, Mn appears to have been retained the least effectively of all the metals. This is in agreement with the findings of Andren et al. (1975) which showed that Mn had the lowest terrestrial retention of seven metals measured. Mn also had the lowest stability constant for metal-fulvic acid complexes of five metals examined, both at a pH of 3.5 and 5.0 (Schnitzer & Skinner 1966, 1967), suggesting that, unlike Fe transport, Mn transport is not controlled by organic material.

On the other hand, Swanson & Johnson (1980), determined that the percent terrestrial retention of Mn in their acidic pine-oak, cedar-sphagnum forest in Pine Barrens, New Jersey, was about 60%. The higher retention observed by Swanson & Johnson may reflect differences in geology.

The retention of Cu, Ni and Zn generally followed the order of mobility of Cu $\leqq$ Zn $<$ Ni. Ni was exported from all the catchments while Cu and

Zn were accumulated. This order is in agreement with results of desorption and leaching experiments performed by Tyler & McBride (1982) on mineral and organic soil columns, and with the results of Andren et al. (1975) who observed that Cu was retained more efficiently by the Walker Branch Watershed than was Zn (82–84% and 73–75%, respectively). However, others (e.g. Tyler 1978) report alternate orders of mobility of these metals. The fact that all of the catchments were a source of Ni (i.e. retention was negative) is probably a reflection of the high deposition levels of Ni in the study area prior to 1972 when the emissions of metals and SO_2 were reduced significantly (Ontario Ministry of the Environment 1982). A second possibility is the existence of nickel ores in the catchments, although none are known to exist in at least the Nelson Lake area.

Zn retention by the Middle Lake watershed was lower than that of the other watersheds. In soil studies, Tyler & McBride (1982) found that metals such as Zn, which may have a larger portion present in the easily exchangeable form, may be more susceptible to minor pH changes so that accelerated deposition of acidity may be expected to decrease the retention of Zn in the the watersheds. Lindsay (1979) suggested that where there are sufficient quantities of SO_4 in the soil, as there are undoubtedly in the study area, $(ZnSO_4)_{aq}$ may be important, and may contribute significantly to the total Zn in solution. Sulphate is often added to Zn fertilizers because it increases the solubility and mobility of Zn in soils (Lindsay 1979). This would explain why the catchments with highest SO_4 input retain relatively less of the inputs than do the Clearwater and Nelson catchments.

The results for Fe retention in the catchments are different than for the other metals. The Clearwater and Nelson catchments exported Fe while the Middle watershed, the closest to the smelters, accumulated it (Table 4). The Fe retention pattern did not relate to distance from the smelters. As mentioned earlier, the flux of organic material likely controls the Fe budgets.

In summary, the output of metals from the catchments was influenced not only by the amount of metal deposited at that site from the atmosphere, but also by the amount of strong acid and acid precursors (SO_2) deposited at each site. The Cu and Ni deposition and the strong acid deposition followed the same pattern, being highest at Middle and Hannah Lakes (Sudbury Centre), the lowest at Nelson Lake (Sudbury North: Scheider et al. 1981; Dillon 1984; Jeffries 1984). The output of Mn and Al from the catchments greatly exceeded their atmospheric deposition rates; the excess was undoubtedly generated by reactions of strong acid with lithologic material. The same appears to be true for Ni. On the other hand, a significant portion of the Cu and Zn was stored in the catchments, with the absolute amounts exported (Table 3) decreasing and the proportion stored (Table 4) increasing with decreasing metal and acid deposition rates. The Fe results were inconsistent with the patterns observed for the other metals; some catchments were Fe sinks (i.e. retention was positive) while others were Fe sources (negative retention), with no apparent relationship to either Fe or strong acid deposition.

Some metals are more soluble and more mobile under acidic conditions (Lindsay 1979; Swanson & Johnson 1980; Tyler 1981; Tyler & McBride 1982; Anon. 1985). The low pH of the runoff water coming from the Middle and Clearwater Lake catchments could be enhancing the mobility and thus the net export of some of these metals. For example, Jeffries et al. (1984) obtained a positive correlation between Ni and H^+ concentrations in the 11 streams sampled in our study. The results in Table 4 generally support this hypothesis.

Lake budgets

Importance of sources

The proportion of the total input of each of the 6 metals to each of the lakes that was contributed by that lake's catchment via runoff water is shown in Table 5. The source of aluminum to these lakes was almost exclusively the catchment which supplied between 82 and 100% of the total input of Al to the lakes. Similarly, virtually all of the Mn input and most of the Ni input to each lake was supplied from the catchment. On the other hand, direct atmospheric deposition to the lakes' surfaces was an important source of Cu and Zn to most of the lakes (17 to 85% of the Cu, 24 to 76% of the Zn). This was especially important for Nelson Lake with its very low catchment area: lake area ratio (Tables 1 and 2), but also for Clearwater and Hannah Lakes, the other 2 headwater lakes. Direct atmospheric deposition was an important source of Fe for Hannah Lake, a moderate source for Middle and Nelson Lakes, but less important for Clearwater and Lohi Lakes.

Table 5. Proportion (%) of the total input of metal to the lakes contributed by the catchments of each of the five lakes.

	Hannah	Middle	Lohi	Clearwater	Nelson
Cu	52	73	83	52	15
Ni	91	96	95	87	82
Zn	59	76	76	55	24
Fe	55	74	87	89	78
Mn	97	99	100	99	92
Al	93	97	98	96	82

Metal retention in the study lakes

The total inputs and losses of Cu, Ni, Zn, Fe, Mn and Al to and from the five study lakes are summarized in Table 6. In Table 7, the percent retention of each metal by the lake is shown.

In the acidic lakes (Clearwater and Lohi), Cu and Ni behaved like conservative substances; that is, the measured retention in the lakes, with the possible exception of Cu in Lohi Lake, was close to zero. In fact, 3 of these 4 measured retentions were actually slightly negative, indicating the possibility of a small net loss of these metals from the lakes. The net loss of Cu and Ni, in part, may be attributed to the slight decreases in lakewater concentrations from 1973–1978 as a result of decreases in atmospheric deposition rates over this time period (Ontario Ministry of the Environment 1982); i.e. a residual wash-out of metals accumulated in the lakewater reflecting older, higher deposition rates. Although it is not possible to do more than guess the potential error in these figures, these retentions are probably not significantly different than (number zero) 0.

These results are consistent with the observed sediment chemistries (Dillon & Smith 1984). In Clearwater and Lohi Lakes, there was a decrease in

Table 6. Total input from watersheds and precipitation and loss via outflow (mg m^{-2}yr^{-1}) during the period June 1977–May 1978.

		Hannah	Middle	Lohi	Clearwater	Nelson
Cu	input	619	1,053	514	184	53
	loss	179	298	430	199	12
Ni	input	1,242	2,755	1,538	616	36
	loss	619	1,436	1,605	626	11
Zn	input	117	206	277	149	80
	loss	37	113	217	95	7.1
Fe	input	894	1,525	1,620	1,856	485
	loss	242	567	770	363	74
Mn	input	300	691	1,943	418	119
	loss	161	656	1,523	644	32
Al	input	821	1,656	2,069	962	379
	loss	220	372	1,126	876	52

Table 7. Retention (%) of each metal in the five study lakes.

	Hannah	Middle	Lohi	Clearwater	Nelson
Cu	71	72	16	−8	78
Ni	50	48	−4	−2	68
Zn	69	45	21	36	91
Fe	73	63	52	80	85
Mn	46	5	22	−54	73
Al	73	78	46	9	86

the Cu and Ni contents of the sediments deposited within the most recent 1–3 decades, reflecting the lower retention of these metals by the lakes when they are acidic. The fact that Cu and Ni levels in relatively recent sediments were greater than background levels (i.e. pre-smelter emissions) is attributable almost certainly to mixing of the sediments; that is, recent sediments (post-acidification in the 1940's) are mixed with older sediments (1880's–1940's) deposited when Cu and Ni were accumulating. Jackson et al. (1980) have postulated that competition between H^+ ions and metal cations for binding sites may explain why acidification interfered with the uptake of certain metal radionuclides by suspended particles in experiments conducted by Schindler et al. (1980). This sort of mechanism would inhibit the transfer of metals from the water column to the sediments and subsequently decrease their retention in the lake. The fact that, in Clearwater Lake, about 70% of the total Cu was labile, as determined by anodic stripping voltametry (Yan & Miller 1984), supports this hypothesis.

On the other hand, in the non-acidic lakes, a significant portion of the Cu (71–78%) and Ni (48–68%) was retained even though, in the case of Ni, the catchments were a net source. Since the Cu and Ni levels in the water column either didn't change or decreased, but never increased, during the study (Yan and Dillon 1984), the Cu and Ni retained must have been stored in the lakes' sediments. This is again consistent with observed increases in the metal levels of the surficial sediments of these lakes (Dillon & Smith 1984).

Unlike Cu and Ni, Zn was retained by the acidic lakes. This is in contrast to the results from Dart's Lake, New York (pH 5.0–5.5) where there was no retention of Zn (White and Driscoll 1987a). It is possible that there may be Zn accumulation in our acidic lakes by diffusion from the water column to the sediment's interstitial water followed by precipitation as a sulphide (Carignan & Tessier 1985), although the same mechanism would be expected to occur in the cases of Cu and Ni. Nevertheless, Zn retention in Clearwater and Lohi Lakes (36% and 21%, respectively) was lower than in the neutral lakes (45%, 69% and 91%). Schindler et al. (1980) found that when the pH of lakewater in experimental enclosures was decreased from 5.72 to 5.12, there was a 30% increase in the half removal time of Zn-65 and a 78% decrease in the proportion of Zn-65 retained by a 0.45-μm membrane filter. These data are consistent with our findings that retention of Zn decreases under acidic conditions and with Dillon and Smith's (1984) observations. However, the Zn retention in these two acidic lakes is comparable to that measured in one very large non-acidic lake; Nriagu et al. (1979) determined the retention of Zn in Lake Erie, Canada, to be about 43% (the value of 35% given in the abstract of their paper appears to be an error).

The retention of Al in the acidic lakes was much lower than in the other three lakes, with virtually none being retained in the most acidic lake (Clearwater Lake 9%) and 46% being retained in Lohi Lake. The relatively low Al retention in the two acidic lakes is supported by data from Borg (1983) who found a significant negative correlation between pH and dissolved (dialysable) Al fractions for lakes in Sweden. Higher dissolved Al concentrations at lower pHs would be expected to result in an overall lowering of the lake retention. Again, the results are consistent with Dillon & Smith (1984), who found depletion of Al in the surface sediments of the acidic lakes. Similarly, Schindler et al. (1980) observed a release of Al from sediments when the lakewater pH was lowered to 5.1.

Lake pH does not appear to be affecting Fe retention; between 52% and 85% of the Fe inputs were retained in all the lakes. Nelson Lake had the highest retention of Fe (85%) while Middle and Hannah Lakes retained 63% and 73%, respectively, of the total Fe input. Interestingly, there is a trend towards increasing Fe retention with increasing water replenishment time (Tables 1, 7).

A very high retention of Fe (80%) was observed in the most acidic lake (Clearwater), the lake whose catchment yielded more than twice the amount of Fe per square metre than that of any of the other four lakes ($375\,\mathrm{mg\,m^{-2}}$ vs 110–$180\,\mathrm{mg\,m^{-2}}$). One inflow to Clearwater Lake, which drains approximately 20% of the watershed, had Fe concentrations which were much higher than those measured in all the other streams as well as much higher levels of DOC. It may be that Fe is efficiently lost to the lakes' sediments in conjunction with the organic matter, even in acidic lakes. Santschi et al. (1986) observed that the ratio of particulate to soluble concentrations for ^{59}Fe were similar at pH's of 6.5 and 4.3 in limnocorral experiments. Thus, reducing the pH apparently did not increase the proportion of Fe in readily settlable form. It appears that Fe may be retained efficiently in all lakes. In other studies, the Fe retention was measured as 75% for Bob Lake, a soft, headwater, oligotrophic lake in Ontario (Cross and Rigler 1983), 82% in Lake Mendota, a hardwater, eutrophic lake in Wisconsin (Lee 1962) and, on average, 86% for Lake Rawson, a softwater, oligotrophic lake in Ontario (Schindler et al. 1976).

The retention of Mn in Lohi Lake (22%) was lower than in neutral Hannah (46%) and Nelson (73%) Lakes. However, the low (5%) retention in circum-neutral Middle Lake does not fit the pattern established by the other study lakes. The reason for the latter finding is unclear although one possible explanation may be that anoxic conditions in the hypolimnion of Middle Lake during the summer months may have favoured the formation and subsequent loss via outflow of the more soluble manganous ion species (LaZerte 1987). These observations generally support the findings of

Schindler et al. (1980) who noted that at a pH of about 5.1, a greater proportion of the Mn was found in dissolved form and that its residence time in the water column was longer than under non-acidic (pH = 6.7) conditions.

In Clearwater Lake, the most acidic lake, there was a net loss of Mn from the lake. In other words, considerably more Mn left the lake via outflow than entered through precipitation and streamflow (retention = −54%). There are two mechanisms which can give rise to this situation.

Firstly, the system was not in steady state such that lakewater concentrations of Mn are constantly decreasing. While the average concentration of Mn in Clearwater decreased by about $30\,\mu g\,l^{-1}$ since 1973 (Yan & Miller 1984), this decrease in the water column concentration is not nearly large enough to account for the net loss of Mn from the lake in 1977–78.

Secondly, the sediments of the lake may be releasing Mn to the overlying water. Carignan & Nriagu (1985) demonstrated Mn efflux from the sediments of Clearwater Lake and attributed it to the effects of the overlying acidic water. In fact, of 6 metals studied, they proposed that the lake was a net source of only Mn, a result consistent with our mass balances.

During enclosure experiments, Schindler et al. (1980) observed mobilization of Mn from the sediments at a pH of 5.0. They also suggest that release of Mn from the sediments is occurring at pH = 6.0, although the increase in Mn levels in their enclosures can be accounted for by the relative increase in the dissolved Mn fraction rather than a net release from the sediments.

In addition, Dillon & Smith (1984) reported that the surficial sediments of Clearwater Lake had Mn levels that were much lower than those deeper in the sediment profile. On the other hand, White & Driscoll (1987b) reported that the input and output of Mn to and from acidic Dart's Lake, New York, were almost identical (i.e. retention ~0%) although the very short hydraulic retention time (22–90 days) may account for the retention being lower than that we measured for Lohi Lake.

Based on these data, two generalizations can be made. First, retention of almost all the metals in the acidic lakes (Clearwater and Lohi) was less than in the three neutral lakes (Middle, Hannah and Nelson). There were only two exceptions to this generalization; Fe retention in Clearwater Lake, which is high (80%), and Mn retention in Middle Lake, which was comparatively low at only 5%.

The second generalization which can be made about these results is that the retentions of all the metals in Middle and Hannah Lakes were always similar to, but slightly lower than, those in Nelson Lake.

As the pH's of the last 3 lakes are similar, we can possibly explain this observation simply on the basis of the hydraulic retention time (τ_w; Table 1) of the lakes. In other cases, e.g. phosphorus, it has been observed that retention in lakes is directly proportional to τ_w, i.e. a lake which flushes rapidly will have a lower retention than one with a slow flushing rate. The τ_w of Nelson Lake is ~ 9.3 years, over 3 times longer than Hannah Lake and over 5 times longer than Middle Lake (Table 1). On the basis of water movement alone, we would therefore predict that Nelson Lake should have the highest metal retention of all the lakes.

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References

Allan, R.J (1974) Metal contents of lake sediment cores from established mining areas: an interface of exploration and environmental geochemistry. Geol. Surv. Can. Paper 74–1, Part B: 43–49

Amiro, B.D. & G.M. Courtin (1981) Patterns of vegetation in the vicinity of an industrially disturbed ecosystem, Sudbury, Ontario. Can. J. Botany 59: 1623–1639

Andren, A.W., S.E. Lindberg & L.C. Bate (1975) Atmospheric input and geochemical cycling of selected trace elements in Walker Branch Watershed. Publ. No. 728, Oak Ridge National Laboratory, Oak Ridge Tennessee

Andren, A.W. & S.E. Lindberg (1977) Atmospheric input and origin of selected elements in Walker Branch Watershed, Oak Ridge, Tennessee. Water, Air Soil Pollut. 8: 199–215

Anon. (1985) Acid deposition. Effects on geochemical cycling and biological availability of trace elements. Subgroup on Metals of the Tri-Academy Committee on Acid Deposition. National Academy Press

Baudouin, M.P. & P. Scoppa (1974) Acute toxicity of various metals to freshwater zooplankton. Bull. Environ. Contamin. Toxicol. 12: 745–751

Beamish, R.J (1974) Loss of fish populations from unexploited remote lakes in Ontario, Canada as a consequence of atmospheric fallout of acid. Water Res. 8: 85–95

Beamish, R.J. & H.H. Harvey (1972) Acidification of the La Cloche Mountain Lakes, Ontario, and resulting fish mortalities. J. Fish. Res. Bd. Can. 29: 1131–1143

Biesinger, K.E. & G.M. Christensen (1972) Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. J. Fish. Res. Bd. Can. 29: 1691–1700

Borg, H (1983) Trace metals in Swedish natural fresh waters. Hydrobiologia 101: 27–34

Calles, U.M (1983) Dissolved inorganic substances: A study of mass balance in three small drainage basins. Hydrobiologia 101: 13–18

Carignan, R. & J.O. Nriagu (1985) Trace metal deposition and mobility in the sediments of two lakes near Sudbury, Ontario. Geochem. Cosmochim. Acta. 49: 1753–1764

Carignan, R. & A. Tessier (1985) Zinc deposition in acid lakes: the role of diffusion. Science 228: 1524–1526

Cronan, C.S. & C.L. Schofield (1979) Aluminum leaching response to acid precipitation: effects on high elevation watersheds in the Northeast. Science 204: 304–306

Cross, P.M. & F.H. Rigler (1983) Phosphorus and iron retention in sediments measured by mass budget calculations and directly. Can. J. Fish. Aquat. Sci. 40: 1589–1597

Crowther, J (1978a) Semiautomated procedure for the determination of low levels of total manganese. Anal. Chem. 50: 1041–1043

Crowther, J (1978b) Autoclave digestion procedure for the determination of total iron content of waters. Anal. Chem. 50: 658–659

Dillon, P.J (1984) The use of mass balances and mass balance models for quantification of the effects of anthropogenic activities on lakes near Sudbury, Ontario. In: J. Nriagu (Ed) Environmental Impacts of Smelters (pp. 283–347). Advances in Environmental Science Series, John Wiley and Sons, Inc.

Dillon, P.J., D.S. Jeffries & W.A. Scheider (1982) The use of calibrated lakes and watersheds for estimating atmospheric deposition near a large point source. Wat. Air Soil Pollut. 18: 241–258

Dillon, P.J. & P.J. Smith (1984) Trace metal and nutrient accumulation in the sediments of lakes near Sudbury, Ontario. In: J. Nriagu (Ed) Environmental Impacts of Smelters (pp. 375–426). Advances in Environmental Science Series, John Wiley and Sons, Inc.

Dillon, P.J., N.D. Yan, W.A. Scheider & N. Conroy (1979) Acidic lakes in Ontario, Canada: characterization, extent and responses to base and nutrient additions. Arch. Hydrob. Beih., Ergebn. Limnol. 13: 317–336

Driscoll, C.T. & G.C. Schafran (1981) The chemistry, transport and fate of aluminum in dilute acidified lake systems. Final report for USEPA/NCSU Acidic Deposition Program APP-0094-1981

Freedman, B. & T.C. Hutchinson (1980) Effects of smelter pollutants on forest leaf litter decomposition near a nickel-copper smelter at Sudbury, Ontario. Can. J. Botany 58: 1722–1736

Galloway, N.N. & G.E. Likens (1976) Calibration of collection procedures for the determination of precipitation chemistry. Wat. Air Soil Pollut. 6: 241–258

Galloway, J.N., C.L. Schofield, N.E. Peters, G.R. Hendrey & E.R. Altwicker (1983) Effect of atmospheric sulfur on the composition of three Adirondack lakes. Can. J. Fish. Aquat. Sci. 40: 799–806

Hall, R.J & G.E. Likens (1981) Chemical flux in an acid-stressed stream. Nature 292: 329–331

Heinrichs, H & R. Mayer (1977) Distribution and cycling of major and trace elements in two central European forest ecosystems. J. Environ. Qual. 6: 402–407

Hutchinson, T.C. & L.M. Whitby (1977) The effects of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. Wat. Air Soil Pollut. 7: 421–438

Jackson, T.A., G. Kipphut, R.H. Hesslein & D.W. Schindler (1980) Experimental study of trace metal chemistry in soft-water lakes at different pH levels. Can. J. Fish. Aquat. Sci. 37: 387–402

Jeffries, D.S (1984) Atmospheric deposition of pollutants in the Sudbury area. In: J. Nriagu (Ed) Environmental Impacts of Smelters (pp. 117–154). Advances in Environmental Science Series, John Wiley and Sons, Inc.

Jeffries, D.S., W.A. Scheider & W.R. Snyder (1984) Geochemical interactions of watersheds with precipitation in areas affected by smelter emissions near Sudbury, Ontario. In: J. Nriagu (Ed) Environmental Impacts of Smelters (pp. 195–241). Advances in Environmental Science Series, John Wiley and Sons, Inc.

Jeffries, D.S. & W.R. Snyder (1981) Atmospheric deposition of heavy metals in central Ontario. Wat. Air Soil Pollut. 15: 127–152

Johnson, N.M., C.T. Driscoll, J.S. Eaton, G.E. Likens & W.H. McDowell (1981) "Acid rain", dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire. Geochim. Cosmochim. Acta 45: 1421–1437

LaZerte, B.D (1986) Metals and acidification: an overview. Wat. Air. Soil Pollut. 31: 369–576

LaZerte, B.D (1987) Manganese in the freshwater environment. In: P. Stokes (Ed) Manganese in the Environment. National Research Council of Canada (in press)

Lee, G.F (1962) Studies on the iron, manganese, sulphate and silica balances and distributions for Lake Mendota, Madison, Wisconsin. Wis. Academy Sci. Arts Letts. 51: 141–155

Lindsay, W.L (1979) Chemical Equilibria in Soils. John Wiley and Sons

Linzon, S.N (1978) Effects of airborne sulfur pollutants on plants. In: J.O. Nriagu (Ed) Sulphur in the Environment. Part II. Ecological Impacts (pp. 109–162). John Wiley and Sons, New York

Nriagu, J.O., A.L.W. Kemp, H.K.T. Wong & N. Harper (1979) Sedimentary record of heavy pollution in Lake Erie. Geochim. Cosmochim. Acta 43: 247–258

Nriagu, J.O., H.K.T. Wong & W.D. Snodgrass (1983) Historical records of metal pollution in sediments of Toronto and Hamilton Harbours. J. Great Lakes Res. 9: 365–373

Ontario Ministry of the Environment (1981) Outlines of analytical methods. Laboratory Services Branch, Min. Environ.

Ontario Ministry of the Environment (1982) Sudbury Environmental Study. Synopsis (1973–80) Acidic Precipitation in Ontario Study Coordination Office.

Santschi, P.H., U.P. Nyffeler, R.F. Anderson, S.L. Schiff, P. O'Hara & R.H. Hesslein (1986) Response of radioactive trace metals to acid-base titrations in controlled experimental ecosystems: evaluation of transport parameters for application to whole-lake radiotracer experiments. Can. J. Fish. Aquat. Sci. 43: 60–77

Scheider, W.A (1984) Lake water budgets in areas affected by smelting practices near Sudbury, Ontario. In: J. Nriagu (Ed) Environmental Impacts of smelters (pp. 155–194). Advances in Environmental Science Series, John Wiley and Sons, Inc.

Scheider, W.A., D.S. Jeffries and P.J. Dillon (1979) Effects of acidic precipitation on precambrian freshwaters in southern Ontario. J. Great Lakes Res. 5: 45–51

Scheider, W.A., D.S. Jeffries & P.J. Dillon (1981) Bulk deposition in the Sudbury and Muskoka-Haliburton areas of Ontario during the shutdown of Inco Ltd. In: Sudbury. Atm. Environ. 15: 945–956

Schindler, D.W., R.W. Newbury, K.G. Beaty & P. Campbell (1976) Natural water and chemical budgets for a small Precambrian lake basin in central Canada. J. Fish. Res. Bd. Can. 33: 2526–2543

Schindler, D.W. R.H. Hesslein, R. Wagemann & W.S. Broecker (1980) Effects of acidification on mobilization of heavy metals and radionuclides from the sediments of a freshwater lake. Can. J. Fish. Aquat. Sci. 37: 373–377

Schnitzer, M. & S.I.M. Skinner (1966) A polarographic method for the determination of the carbonyl groups in soil humic components. Soil Sci. 101: 120–124

Schnitzer, M. & S.I.M. Skinner (1967) Organo-metallic interactions in soil: period stability constants of Pb^{2+}–, Ni^{2+}–, Mn^{2+}–, Co^{2+}–, Ca^{2+}–, Mg^{2+}– fulvic acid complexes. Soil Sci. 103: 247-252

Schofield, C.L (1976) Acid precipitation: effects on fish. Ambio 5: 228–230

Schut, P.H., R.D. Evans, & W.A. Scheider (1985) Variations in trace metal exports from small Canadian Shield watersheds. Wat. Air Soil Pollut. 28: 225–237

Swanson, K.A. & A.H. Johnson (1980) Trace metal budgets for a forested watershed in the New Jersey Pine Barrens. Wat. Resources Res. 16: 373–376

Tyler, G (1981) Leaching of metals from the A-horizon of a spruce forest soil. Wat. Air Soil Pollut. 15: 353–369

Tyler, L.D. & M.B. McBride (1982) Mobility and extractability of cadmium, copper, nickel and zinc in organic and mineral soil columns. Soil Sci. 24: 198–205

White, J.R. & C.T. Driscoll (1985) Lead cycling in an acidic Adirondack lake. Environ. Sci. Technol. 19: 1182–1187

White, J.R. & C.T. Driscoll (1987a) Zinc cycling in an acidic Adirondack lake. Environ. Sci. Technol. 21: 211–216.

White, J.R. & C.T. Driscoll (1987b) Manganese cycling in an acidic Adirondack Lake. Biogeochemistry 3: 87–103

Wright, R.F (1983) Input-output budgets at Langtjern, a small acidified lake in southern Norway. Hydrobiologia 101: 1–12

Wright, R.F. & M. Johannessen (1980) Input-output budgets of major ions at gauged catchments in Norway. In: D. Drablos & A. Tollan (Eds) Ecological Impact of Acid Precipitation (pp. 250–251)

Yan, N.D. & P.J. Dillon (1984) Experimental neutralization of lakes near Sudbury, Ontario. In: J. Nriagu (Ed) Environmental Impacts of Smelters (pp. 417–456). Advances in Environmental Science Series, John Wiley and Sons, Inc.

Yan, N.D. & C. Lafrance (1984) Responses of acidic neutralized lakes near Sudbury, Ontario to nutrient enrichment. In: J. Nriagu (Ed) Environmental Impacts of Smelters (pp. 457–521). Advances in Environmental Science Series, John Wiley and Sons, Inc.

Yan, N.D. & G.E. Miller (1984) Effects of deposition of acids and metals on chemistry and biology of lakes near Sudbury, Ontario. In: J. Nriagu (Ed) Environmental Impacts of Smelters (pp. 243–282). Advances in Environmental Science Series, John Wiley and Sons, Inc.