THE EFFECTS OF ACID RAINFALL AND HEAVY METAL PARTICULATES ON A BOREAL FOREST ECOSYSTEM NEAR THE SUDBURY SMELTING REGION OF CANADA

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Abstract. Sulphur dioxide and particulate pollution have been occurring over a wide area in the Sudbury region, Ontario, as a result of massive smelting operations. In excess of 3½ million short tons of SO_2 were released into the atmosphere in the area in 1972, and this pollutant is now discharged through a 1250-foot smokestack. The particulate contribution is an additional complicating and phytotoxic factor. For example, in 1971, 192 tons of nickel, 145 tons of copper, 1130 tons of iron and 4.5 tons of cobalt per 28 days from two of the smelters were released as airborne pollutants (Hutchinson and Whitby, 1974). The natural vegetation of the area is a mixed deciduous boreal forest, with white pine (*Pinus strobus*), jack pine (*Pinus banksiana*), red maple (*Acer rubrum*), red oak (*Quercus rubra*), etc. as dominant trees. This forest, which previously surrounded the mining town of Sudbury, has been devastated over the past 50 yr, especially by the SO_2 emissions and the increased acidity of rainfall and soils. An area in excess of 100 mi^2 is now almost devoid of vegetation and damage to the forest vegetation is visible over an area of approximately 1800 mi^2. The increased stack heights to dilute local pollution problems have spread the problem more widely. The pH of rainfall sampled up to 12 mi east of the smallest smelter in 1970 was less than 4.3 and that within 2 mi of the stacks was frequently of less than pH 3.0. Soil erosion has occurred on a large scale as a consequence of loss of vegetation. Metal accumulation in the soils has also been a complicating and probably highly persistent phenomenon. Concentrations of nickel in excess of 3000 ppm and copper of 2000 ppm in surface soils occur widely. The increased acidity of these soils has increased metal mobility and solubility, presenting phytotoxic problems. The effects on the soil chemistry, especially of organic composition have been profound. They involve an increased metal binding capacity of these soils, and very high levels of sulphur in the purified 'fulvic acid' fraction itself. Indeed, the evidence is suggestive of the incorporation of sulphonic groups into the changed extracts. Such profound and damaging changes may be merely a consequence of the extreme conditions experienced at Sudbury or they may be a harbinger of things to come in many potentially podsolic soils in areas of increasing acidity of rainfall.

1. Introduction

The Sudbury area of Ontario contains one of the world's major ore deposits of Ni and Cu, as well as sizeable quantities of many other metallic sulphides. Initial discoveries were made in the 1880's and smelting dates back some 80 yr. Three smelters have operated, with the largest one being at Copper Cliff, 8 km west of Sudbury, a smaller one, also owned by the International Nickel Company of Canada, at Coniston, 14.4 km east of Sudbury, and a third, owned by Falconbridge Nickel Company, 16 km north-east of Sudbury at Falconbridge. Because of the massive quantities of ore smelted each year and because of its high S content, the emissions of SO_2 have been on a scale unmatched elsewhere in the world. Production figures have mounted steadily since 1939. In 1972, in excess of 3×10^6 short t of SO_2 gas was emitted into the atmosphere.

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This potentially phytotoxic gas has caused extensive damage over a very large area, with widespread destruction of the mixed boreal forest of the region, and damage to forests over an even greater area. Despite the improvements brought about in pollution control, the introduction of H_2SO_4 and S-producing plants and the construction of increasingly tall smokestacks, damage to vegetation continued to spread, at least until the introduction of the world's tallest smokestack of 1250 ft (403 m) at Copper Cliff in 1972 and the closing down of the Coniston smelter also in 1972.

Dreisinger (1970) reported that in the region during the period 1964–68, the area having at least an atmospheric average SO_2 concentration of 0.005 ppm covered 2181 mi^2 (5600 km^2), while 246 mi^2 (630 km^2) had average levels of 0.020 ppm or more. In terms of potentially injurious fumigations during the May–September growing season, an area of 2136 mi^2 (5470 km^2) was found to be subjected to one or more fumigations and 569 mi^2 (1400 km^2) were subjected to 10 or more such episodes.

The SO_2 emissions in the area amount to a significant fraction of the total for North America. Estimates range as high as 25% of the smelter total and 10% of the SO_2 total. Damage to the forests has been partially selective, in that outside the central core of almost total destruction, a range of species susceptibilities has been shown. The coniferous species and especially white pine (*Pinus strobus*) are the most susceptible. White pine is almost absent within 12 mi (19.3 km) of the smelters and growth is poor and damage frequent for a further 7 mi (11 km) (Linzon, 1958). There appeared to be reduced radial and volume increments and increased tree mortality of this tree, in direct proportion to the closeness of the source of SO_2. Some tree species, such as red maple (*Acer rubrum*) and red oak (*Quercus rubra*) are more resistant, perhaps as a result of their deciduous nature, and survive to within 5 km of the smelters. They are partially defoliated in most years and the crowns die back, with new shoots developing from basal branches. LeBlanc and Rao (1966) suggested that the SO_2 fumigations are responsible for the paucity of lichens near Sudbury.

The soils of the area are incipient podzols and range in pH, in non-fumigated areas, from 3.8 to 5.2. They are shallow and with a low organic content. The area was glaciated within the last 12 000 yr and glacial till fills some of the valleys to a depth of 30 ft. The whole region is dotted with innumerable lakes, which previously had a high reputation for sports fishing. Apart from Sudbury itself, with approximately 90 000 inhabitants, the population of the area is sparse. Soil erosion has taken place over a very large central area, so that much of the higher ground over at least 160 mi^2 (416 km^2) is devoid of soil and vegetation and consists of blackened rocks.

The lakes of the area have received increasing attention, with the realization that many of them to the south-west of Sudbury have become acidic within the past 15 yr, and their fish populations eliminated! (Beamish, 1976.) This effect has damaged lakes in Killarney Provincial Park as far as 50 mi (80 km) away. The prevailing winter wind directions are to the south-west and snow analyses have indicated highly acidic snows melting, with resultant acidic run-off into lakes in spring time. Gorham and Gordon (1960) found acidic lakes with high sulphate values to the north-west of Falconbridge. Stokes, Hutchinson and Krauter (1973) and Stokes and Hutchinson

1976) have found lakes with pH values as low as 4.0 within a few kilometres of the smelters, and have described depletion of phytoplankton populations in these lakes. They also showed the heavy metals, Ni and Cu, to be present in toxic concentrations in many of these lakes. Isolates of some surviving algal strains (of a small number of species) were found to be much more tolerant of heavy metals, especially the locally contaminating ones, Ni and Cu, as well as being more tolerant of low pH than similar non-Sudbury strains.

Both Gorham (1976) and Norton (1976) have already referred (this Symposium) to the theoretical possibility of solubilization of aluminum compounds, and of Mn components of clay minerals at excessivley low soil pH's. Norton stressed the necessity of soil pH's below 3.0 and the presence of free H_2SO_4 to achieve this, and concluded that such extremes were unlikely to be achieved by acid rains, in view of the normal buffering capacity of soils (lakes in the Sudbury region are mainly, but not exclusively, poorly buffered and naturally oligotrophic). A similar mobilization of other potentially toxic heavy metals could be anticipated at such low soil pH's, whether these metals were naturally present in the soils or were anthropogenic additions.

The large SO_2 emissions in the Sudbury area and their effects on vegetation and soil chemistry have been studied in some detail (Hutchinson and Whitby, 1974; Whitby and Hutchinson, 1974; Whitby, 1974). They concluded that widespread acid rains were occurring in the Sudbury area, with pH levels down to less than 3.0 in the years 1970 and 1971. Soil pH values and pH values through the soil profile from the surface downward, and with distance from the Coniston smelter (the one studied) showed an increase with depth and distance. Heavy metals were a serious and complicating factor. For example, in 1971, 192 t of Ni, 145 t of Cu, 1130 t of Fe, and 4.5 t of Co per 28 days were released as airborne contaminants from two of the three smelters at Sudbury. Soils are toxic to seedling establishment over a wide area. Metals have accumulated in the foliage of naturally-occurring living vegetation. The effects on soil chemistry, especially on organic composition, have been profound.

The possibility of metal contamination around smelters has been recognized for a long time, e.g. Harkins and Swain (1908). More recently, the long distance dispersal of metal particulates from smelters has also been recognized. Kerin (1971) and Djuric *et al.* (1973) reported on Pb, Zn, and Nm contamination in the vicinity of Pb, Zn, and steel works in Yugoslavia. Lead was found to be very finely dispersed and spread over an even greater area than SO_2 near Mĕzica, Yugoslavia. Buchauer (1971) reported on Zn and Cd contamination near the Zn smelter at Palmerton, Pennsylvania, U.S.A., and concluded that metal contamination caused greater vegetational damage than did SO_2. Acid rain-metal interactions have been rather neglected to date. This paper attempts to consider the consequences for the Sudbury region, an area of normally acidic incipient podzolic soils, of massive inputs of both potentially toxic metals and acidic rainfall.

It should be noted that much of the damage has been caused as a result of past fumigations and that the new 1972 403 m stack at Copper Cliff has markedly improved air quality in the town of Sudbury itself.

2. Methods

2.1 SITES

The main study was carried out along transects from the Coniston smelter, which was chosen because it is situated off the main ores bodies of the Sudbury basin and provides largely uninhabited areas to the east, south and north. The sample sites for both soil, vegetation and rainfall were chosen at the tops of the numerous small hills in the area. Unlike the valley, glacially derived soils, those on the hill tops are less glacially contaminated and are largely derived from the parent bed rocks. The soils originally were grey-wooded podzols. Most soil horizons were severely eroded around Coniston. In all, 25 sites were sampled and profiles taken. Samples were taken at least 100 m from roads to minimize traffic inputs.

2.2 VEGETATION AND SOIL ANALYSES

Vegetation samples were collected in 1969–1971, in June and August each year. Species selection was complicated by the lack of many species common to the mixed coniferous forests at sites close to the smelters. This zone of species impoverishment extends 16 to 24 km from the Coniston smelter, due to SO_2 damage. Nine sites were sampled for vegetation, leaves from separate trees or herbs of the same species were mixed and the composite sample washed with a dilute detergent, rinsed in five changes of distilled water and dried at 60°C. Homogenized samples were used for metal analysis.

Rainfall samples were collected during the summers of 1970 and 1971 in 2-l polyethylene containers set above the ground. Samples were collected monthly and stored at 4°C prior to analyses. Those for metal analyses were acidified with a small quantity of HNO_3, to prevent deposition of metals on the surface of the container.

The pH and conductivity of the soils were measured on field-wet samples, with addition of enough water to produce a water: soil ratio of 1:1 for pH and 2:1 for conductivity. Soils for metal and sulphate analysis were dried at 105° for 24 h, sieved through a 0.2 mm mesh and homogenized. 2 g samples were placed in Teflon dishes, digested with Analar 40% HF: 40% H_2SO_4, and dissolved in 18% HNO_3. A dilution to 50 ml was made and analyzed for 18 metals by atomic absorption spectrophotometry. Duplicates were run of all samples and reagent blanks and background corrections lines used where necessary. 0.2 g plant samples were used, pre-digested for 16 h in 1:1 73% HNO_3:73% $HClO_4$, heated to 75°C for completion of the digestion and then diluted to 10 ml. Metals were analyzed as above.

2.3 RAINFALL

Total volume, pH and conductivity of rainfall were measured shortly after collection. The samples were filtered to remove insoluble components and 5 ml of 73% HNO_3 was added to keep in solution those metals which tend to be precipitated or adsorbed. When precipitation was low, samples were made up to 50 ml and analyzed as for soil samples.

2.4 SOIL-WATER EXTRACTS

Soil water extracts were prepared for analysis by using a 1:3 ratio of air dried soil to distilled water and shaking for 2 h at room temperature. Samples were then filtered through Whatman No. 42 paper prior to use as a bioassay medium or for analysis.

2.5 WATER SOLUBLE SULPHATE

Soil water extracts were obtained as above but using a ratio of 1:5 dried soil to distilled water. A 1 ml extract was added to 9 ml reagent, consisting of 43 g ammonium acetate in 0.275 N acetic acid. 1 ml of 6 N.HCl 'seed' was added to each solution and stirred for 1 min. 0.5 g barium chloride was added and allowed to react for 2 min. The resulting suspension was stirred and absorbance measured in a Beckman spectrophotometer at a wavelength of 420 μm. Sample readings were compared with standard sulphate absorption curves and the results expressed as ppm dry soil weight.

2.6 BIOASSAYS

The simple techniques used for both field and laboratory bioassay experiments are described in Whitby and Hutchinson (1974).

2.7 EXTRACTION AND ANALYSES OF SOIL ORGANIC MATTER AND FULVIC ACID FRACTIONS

A somewhat complicated procedure was followed for the extraction and purification of the modified Sudbury soil organic matter. This was developed with the assistance of Dr M. Schnitzer and is a modification of his previously described methods. Details will be published elsewhere.

3. Results and Discussion

3.1 ACIDITY OF RAINFALL AND DRY PRECIPITATION

During the summers of 1970 and 1971 dustfall and rainfall collectors were located at a number of sites at increasing distance from the Coniston smelter. Two transects were used, one to the south, which would also be influenced by Copper Cliff, and one to the east, which is subject to Falconbridge influence as well as Coniston. Data are presented for two contrasting periods, i.e. (1) in 1970, June 23 to July 21, when rainfall was heavy and scrubbing of the atmosphere occurred, and (2) July 21 to August 4, 1970 when no wet precipitation occurred and the dry fallout was diluted to 50 ml with distilled water for analysis. Data for pH, conductivity and sulphate are given in Tables I and II. A comparative wet period is given for 1971, Table III.

It is clear that both conductivity and sulphate content of rainfall or dry fallout increase with proximity to the smelter sources, and that pH decreases to highly acidic levels. Rainfall is both strongly acidic and of a very high sulphate content in the Sudbury region. More complete analyses are given in Whitby (1974) but the data presented in Tables I–III are representative. Sulphate contents are highest when wet precipitation occurs, suggesting effective scrubbing of the SO_2 laden air during rainfall.

TABLE I

pH, conductivity and sulphate content of rainfall-dustfall in samples on a transect from the Coniston smelter during period June 23 to July 21, 1970

Distance			Amt. rainfall collected (ml)	Conductivity		Sulphate mg m^2/28 day
miles		km		pH	μ mhos	
1.0	S	1.6	628	2.85	450	2108
1.0	N	1.6	1290	3.67	186	1761
1.1	S	1.7	740	2.96	448	5456
1.2	S	1.9	1350	3.40	190	1536
4.6	S	7.4	1470	3.25	168	1761
8.4	S	13.4	834	3.72	64	329
12.0	E	19.2	580	4.34	45	347

TABLE II

pH, conductivity (μmhos) and sulphate content (mg m^{-2}/14 days) in dry precipitation following in transects from the Coniston smelter during the period July 21 to August 4, 1970. No rainfall fell in this period. Volumes were made to 45 ml with deionized water for pH and conductivity. 5 ml of dil. HNO_3 was added for sulphate and metal analyses

Distance					
miles		km	pH	Conductivity	Sulphate
0.95	S	1.6	1.60	11 100	94
1.0	S	1.6	2.79	930	62
1.0	N	1.6	2.36	2725	198
1.1	S	1.7	2.09	3650	136
1.2	S	1.9	2.74	950	75
4.6	S	7.4	3.80	129	87
8.4	S	13.4	4.64	42	74
12.0	E	19.2	6.16	65	93

TABLE III

pH, conductivity (μmhos) and sulphate content (mg m^{-2}/28 days) of dustfall-rainfall collected in the Coniston-Sudbury area in 1971, May 13 to June 10

Distance from Coniston			Volume rainfall collected			
miles		km	(ml)	pH	Conductivity	Sulphate
0.5	S	0.8	1250	2.93	1850	5456
1.0	N	1.6	1200	2.76	2170	1401
6.5	E	10.4	1080	3.53	320	620
8.4	S	13.4	960	3.70	335	620
35.0	S	56.0	1225	4.25	170	533
65.0	S	104.0	1100	4.10	94	131

The much lower dry precipitation values indicate a much wider dispersal of SO_2 during dry periods. The volumes of rainfall affect conductivity quite markedly, influencing both H ion concentration, dissolved salts and metallic ions. Rainfalls of less than pH 4.0 appeared the normal within at least 10 mi of Sudbury. Wind direction is of considerable importance with respect to point sources but was not measured in this study. Rather, bulk samples over 28 day periods were used.

3.2 HEAVY METALS IN RAINFALL

The airborne dispersal of heavy metal particulates in the Sudbury area was measured as influenced by distance from smelters, by wet or dry precipitation. Data are presented in Tables IV–VI for equivalent periods to those for pH etc. Ni, Cu, Co, and Fe are smelted in the area, while Zn and Pb are not, but are present in the ore in trace amounts. It is apparent from the data that the metals Ni, Cu, and Fe are deposited or

TABLE IV

Metal analyses of rainfall-dustfall collected at various distances from the Coniston smelter during the period June 23 to July 21, 1970 (expressed as mg m^{-2}/28 days)

Distance								
miles		km	Ni	Cu	Co	Fe	Zn	Pb
1.0	S	1.6	271	122	8.5	144	5.7	1.2
1.0	N	1.6	161	58	3.7	103	8.6	2.5
1.1	S	1.7	273	131	8.7	111	6.0	9.4
1.2	S	1.9	95	85	4.2	34	7.4	3.7
4.6	S	7.4	16	22	0.5	47	4.9	4.5
8.4	S	13.4	2	3	0.2	5	2.3	nd
12.0	E	19.2	8	2	0.1	7	5.4	nd

nd = below detection limit

TABLE V

Metal analyses of dry precipitation-dustfall collected at various distances from the Coniston smelter during the period July 21 to August 4, 1970. Data are given as mg m^{-2}/14 days

Distance								
miles		km	Ni	Cu	Co	Fe	Zn	Pb
0.95	S	1.6	2.6	2.5	0.2	10	0.7	nd
1.0	S	1.6	4.1	2.8	0.3	10	1.1	nd
1.0	N	1.6	23.3	10.2	0.6	28	1.0	nd
1.1	S	1.7	4.1	5.1	nd	9	0.7	nd
1.2	S	1.9	2.3	3.5	0.1	8	0.6	nd
4.6	S	7.4	1.7	3.9	0.4	7	0.4	nd
8.4	S	13.4	0.4	0.4	nd	0.4	nd	nd
12.0	E	19.2	0.9	0.7	0.1	3.0	0.5	nd

TABLE VI

Heavy metal concentration of rainfall-dustfall collections along transect from Coniston smelter, collected from May 13 to June 10, 1971. Concentrations are given in mg m^{-2}/28 days

Distance miles		km	Vol. rain ml.	Ni	Cu	Co	Fe	Zn	Pb
0.5	S	0.8	1250	288	205	5.5	53	6.9	8.9
1.0	N	1.6	1200	127	67	2.6	1513	3.6	5.7
6.5	E	10.4	1080	13	5	0.9	75	3.6	1.2
8.4	S	13.4	960	11	15	0.1	129	3.5	5.1
35.0	S	56.0	1225	3	3	0.3	69	2.5	3.5
65.0	S	104.0	1100	1	6	nd	74	5.1	2.9

TABLE VII

The pH, conductivity (µmhos) and percentage loss on ignition values for soils taken at three depths (0, 5, and 10 cm) along a transect running from the Coniston smelter

Distance from smelter miles	km	Depth (cm)	pH	Conductivity	L.O.I.
0.5	0.8	0	2.19	630	6.5
		5	2.43	220	5.8
		10	2.50	208	5.8
0.95	1.5	0	2.82	552	8.7
		5	2.87	386	9.1
		10	3.02	214	9.9
1.2	1.9	0	2.76	850	10.5
		5	3.04	356	11.5
		10	3.29	167	10.3
2.4	3.8	0	3.66	228	9.7
		5	3.59	216	9.2
		10	3.66	215	9.4
4.6	7.4	0	2.92	234	12.5
		5	2.96	146	26.3
		10	3.09	105	14.3
6.5	10.4	0	3.23	210	12.0
		5	3.35	59	8.4
		10	3.37	45	12.3
8.4	13.5	0	2.95	87	27.3
		5	3.18	39	16.3
		10	3.40	28	12.0
12.0	19.3	0	4.04	67	22.7
		5	3.95	51	10.6
		10	4.19	51	16.3
31.0	49.8	0	3.39	58	6.0
		5	3.27	33	6.4
		10	3.42	25	5.6

rescrubbed from the air in large quantities close to the smelter. Zinc and Pb did not show such a clear-cut trend. Location of site is an important variable. For example, Fe was deposited in large quantities at a site 1.6 km north of Coniston (Table VI) when, presumably, winds from the Falconbridge iron ore recovery plant were involved. Deposition during a dry period (Table V) was a good deal less at sites close to the smelter than during a wet period (Tables IV and VI. In dry periods the particulates were much more widely dispersed, presumably over a much greater area. It is apparent that metal inputs into the surrounding ecosystems are considerable and are combined with a highly acidic rainfall and very high sulphate inputs. These conditions could potentially lead to high solubility of the heavy metals in the soils and (a) their availability for plant uptake and (b) loss through run-off into water bodies.

3.3 EFFECTS ON SOIL pH AND HEAVY METAL CONTENT

Examples of the soil pH and its variation with profile depth and with distance from the smelter are given in Table VII. It can be seen that surface soils within approximately 7.4 km from the Coniston smelter now have a pH of less than 3.0. In some cases this very low pH is continued to a depth of 10 cm in the profile. In the data presented, 'normal' soil pH's for the region are only reached at distances in excess of 19 km. These very low pH's appear to be the result of both wet and dry precipitation of SO_2 contaminated air, and indicate the strong likelihood of free H_2SO_4 in many surface soils.

Conductivity values are very elevated close to the smelter, compared with those of soils distant from it. Despite the variability, conductivity was generally highest in surface soils, where mobilization of cations and anions and deposition of heavy metals are greatest.

The heavy metal content of the transect soils are given in Table VIII. A marked soil-profile effect was shown for Ni, Cu and Co, with highest concentrations usually occurring in surface soils. These three metals also showed a decline in concentration at soil depths as a function of distance from the smelter. Concentrations of Ni and Cu were very high, being in excess of 1000 ppm to a distance of 13.4 km. Nickel was generally at higher concentrations than Cu, and is smelted in larger quantities. The pattern of change with distance parallels that for rainfall-dustfall analyses for these metals. Elevated levels of soil Ni and Cu compared with expected background levels for uncontaminated igneous rocks are exceeded at all sites except that at 50 km. This suggests long distance dispersal of airborne particulates, especially as the pattern is that of surface loading.

Comparisons of the significance values for regression lines of concentration on distance for 18 metals, showed significant decline curves for soil Ni, Cu, Co, Ag, Fe, Pb, Cd, Mn and K, but no significant distance effect for Zn, Al, and V, none of which are smelted at Sudbury. A particularly interesting aspect was that where a variety of data transformations were used to compare goodness of fit, a $\log_e$ transformation of concentration gave the best fit for Ni and Ag, and a $\log_e$ transformation of distance gave the best fits for Cu, Fe, and Pb. Reciprocal and square root transformations also

TABLE VIII

Metal contents of Sudbury area soils collected at 3 depths along transects from the Coniston smelter. Analyses are of total digests, expressed in ppm

Distance		Depth							
miles	km	cm	Ni	Cu	Co	Fe	Zn	Pb	Mn
0.4	0.6	0	1789	1365	84	22 238	63	40	176
		5	1038	1318	52	25 025	58	28	149
		10	955	1452	53	25 713	62	33	146
0.5	0.8	0	2835	1528	127	43 000	67	68	232
		5	2809	1238	124	49 088	66	64	242
		10	1522	935	82	28 150	57	42	202
0.7	1.0	0	1166	1140	59	19 463	55	45	211
		5	929	1193	50	24 643	57	38	207
		10	662	950	41	26 750	55	38	185
0.95	1.5	0	1847	2007	72	38 350	73	56	207
		5	1611	1864	69	38 080	72	47	204
		10	1163	1740	6	36 460	69	35	204
1.0	1.6	0	2679	1291	122	43 438	75	56	290
		5	1710	1478	88	43 438	78	68	276
		10	1097	1630	67	28 150	92	47	316
1.2	1.9	0	2161	2071	85	18 655	73	58	251
		5	730	1772	34	18 350	53	41	249
		10	649	1578	31	18 600	51	31	251
2.4	3.8	0	831	1140	42	26 750	53	47	161
		5	842	1104	58	26 750	57	42	167
		10	732	1166	43	20 850	55	38	162
4.6	7.4	0	3309	1425	154	76 788	84	52	360
		5	2330	1621	98	68 625	80	78	343
		10	613	944	36	50 463	64	31	354
6.5	10.4	0	356	392	33	28 763	68	28	336
		5	69	21	24	25 725	60	14	317
		10	79	3	24	29 188	63	9	295
8.4	13.5	0	103	1177	6	40 825	78	75	316
		5	409	568	6	38 415	72	35	349
		10	212	191	6	41 395	72	35	353
12.0	19.3	0	652	730	38	22 250	62	66	146
		5	553	597	20	18 075	57	75	146
		10	198	285	20	11 125	46	38	134
31.0	49.8	0	83	31	19	8 170	46	17	125
		5	71	27	17	8 185	51	17	122
		10	63	23	19	8 120	50	15	124

gave significant regression lines. The distance decline curves are typical of fallout patterns of particles with a logarithmic normal size distribution, and differences between Ni and Cu suggest differences in their particulate sizes.

The site at 7.4 km is anomalous in its high values, but is influenced by both Coniston and Falconbridge.

3.4 METAL CONTENT OF NATURAL VEGETATION

Fumigations have resulted in a major loss of vegetation in the Sudbury area. However, collections were made in 1970 and 1971 of surviving naturally-occurring species of the forests, including those able to survive close to the smelter zones. Washed material was analyzed for its metal content, to determine whether the elevated Ni and Cu levels etc. in soil and air were also reflected in the foliage. A total of 14 species were found at sufficient sites to make distance comparisons of metal content feasible. Data for four of these are given in Table IX. The data for Al are given because of the possibility of mobilization of Al ions at the excessively acidic pH's of some of the soils, and because Al is known to be a major controlling toxic metal for plant growth on acidic soils, e.g. Rorison (1960) and Clarkson (1968).

TABLE IX

Content of Ni, Cu, Co, Zn, and Al in foliage of four species along a transect from the Coniston smelter, collected in June 1970. Values in ppm on homogenized samples

	Distance						
Species	miles	km	Ni	Cu	Co	Zn	Al
Comptonia peregrina	1.0	1.6	113	57	7	30	250
	1.4	2.2	243	175	12	28	560
	4.6	7.4	—	—	—	—	—
	6.5	10.4	13	11	4	77	55
	8.4	13.5	74	70	5	36	90
	12.0	19.3	59	36	7	50	40
	18.0	28.8	28	29	5	54	90
	31.0	49.8	17	14	4	56	145
Deschampsia flexuosa	1.0		902	726	33	50	2500
	1.4		—	—	—	—	—
	4.6		160	103	12	28	280
	6.5		14	11	6	36	60
	8.4		138	66	8	31	90
	12.0		43	18	6	30	60
	31.0		37	13	6	31	60
Acer rubrum	1.0	North	109	61	7	28	220
	1.0	South	91	38	9	21	125
	1.4		88	42	11	26	220
	4.6		35	17	6	19	40
	6.5		35	26	6	30	35
	8.4		—	—	—	—	—
	12.0		33	28	3	22	80
	18.0		14	16	12	42	40
	31.0		14	20	6	46	20
Betula papyrifera	1.0		148	95	12	98	215
	4.6		111	37	8	90	160
	6.5		101	39	8	100	130
(collected Aug. 1970)	8.4		72	25	8	150	200
	12.0		64	32	8	188	100
	18.0		35	14	7	248	30
	31.0		16	14	5	340	60

The data show a highly significant decrease in Ni, Cu, and Al concentration with distance from the smelter ($p > 0.01$). Cobalt shows a significant but weaker correlation. Zinc shows a trend the other way for *Betula papyrifera,* probably caused by its normal availability through organic complexes in soil humus, much of which is lacking at sites close to the smelter. Aluminum is especially interesting in that it appears that considerable mobility of this element has occurred in soils within 2 km of the smelter, with resultant uptake by plants from soluble Al compounds released from clay minerals by the very low pH's of these soils. This will increase soil toxicity markedly and also be a potential problem to water bodies. Bowen (1966) quotes normal metal levels for land plants as follows: Ni 3 ppm, Cu 14 ppm, Co 0.5 ppm, and Zn 100 ppm. Aluminum in foliage may occur at levels up to 200 ppm in plants on acidic soils. These levels were regularly exceeded in Sudbury plants for Cu, Ni and Co, and for Al at sites close to the smelter. Zinc, our control metal, did not exceed the norms of Bowen.

It needs to be emphasized that the species tested for metal content are those species capable of surviving in areas of extensive and, previously, repetitive fumigations by SO_2, and at the same time, capable of tolerating highly acidic and heavy metal polluted soils.

3.5 pH, SULPHATE AND METAL CONTENT OF SOIL-WATER EXTRACTS

The previous data suggest highly acidic and metal contaminated rainfall and dry fall-out, soil contamination over a very large area and highly elevated levels of Ni and Cu in the vegetation growing on these soils. Generally, total metal concentrations of soils are a poor reflection of the availability of these metals in the soil for plant uptake. Many methods of extraction are available, with appropriate claims for their close reflection to true availability for plant uptake. As a simple but probably low estimate of the availability of potentially toxic metals in the Sudbury soils, a simple water extraction technique was used. These extracts were both analyzed and used as a growth medium for seedling growth in laboratory experiments.

Data on analyses are given in Table X. For all of the soils, except that at 50 km the surface soil yielded the extract with the lowest pH and with the highest Ni, Cu, Co, and Al concentrations. Nickel occurred in the highest concentrations followed by Al and Cu. pH increased with depth and distance, as did (generally) sulphate and metal concentrations. Even Zn showed this pattern, suggesting its mobilization at the acidic pH's. Nickel and Al were extractable from surface soils at levels greater than 5 ppm out to 10.4 km. Since the extraction technique involves a three-fold dilution of the soil extract, one can well consider the levels available in the soils to be even higher than those reported here. Sulphate levels were excessive within 2 km of the smelters and elevated to 10 km.

3.6 PLANT GROWTH ON SOILS AND EXTRACTS

The soil extraction data indicate that potentially toxic heavy metals are available in the Sudbury soils as a result of their aerial deposition and especially as a result of acidic rainfall. The potential effects on the boreal forest ecosystem of the presence of

TABLE X

Analyses of water extracts of soils collected along a transect from the Coniston smelter. Total analyses of metal and pH values are given in Tables VII and VIII. Metals are given in ppm of extract. A 3 : 1 water : soil extraction was used for metal analyses

Distance from Coniston smelter		Depth cm	pH	Sulphate	Ni	Cu	Co	Al	Zn
miles	km								
0.5	0.8	0	3.08	780	127	42	4.6	51	1.0
		5	3.36	100	14	8	0.2	7	0.1
		10	4.48	75	11	6	nd	6	nd
0.95	1.5	0	3.40	325	107	60	3.4	77	0.9
		5	3.59	220	56	20	1.5	52	0.5
		10	3.69	115	19	10	0.4	23	0.1
1.2	1.9	0	3.25	3200	142	60	4.4	99	1.4
		5	3.48	190	36	10	1.0	31	0.3
		10	3.86	430	17	6	0.2	14	0.1
2.4	3.8	0	3.59	80	14	8	0.2	10	0.2
		5	3.57	75	12	6	0.1	10	0.2
		10	3.67	60	14	7	0.1	10	0.2
4.6	7.4	0	3.41	60	9	3	nd	7	0.1
		5	3.54	70	4	2	nd	7	0.1
		10	3.65	60	2	1	nd	4	0.1
6.5	10.4	0	3.86	65	7	1	nd	15	0.4
		5	4.11	50	1	nd	nd	6	nd
		10	4.22	20	1	nd	nd	6	nd
8.4	13.5	0	3.93	20	1	nd	nd	2	nd
		5	4.32	20	nd	nd	nd	nd	nd
		10	4.69	30	nd	nd	nd	nd	nd
12.0	19.3	0	4.39	25	nd	nd	nd	nd	nd
		5	4.46	40	nd	nd	nd	nd	nd
		10	4.70	40	nd	nd	nd	nd	nd
31.0	49.8	0	4.79	30	nd	nd	nd	0.5	nd
		5	4.69	35	nd	nd	nd	0.5	nd
		10	4.44	20	nd	nd	nd	0.5	nd

widespread acidic and metal contaminated soil need to be considered. Seedlings are very rare in the Coniston region. Both Ni and Cu are toxic at low concentrations to many aquatic plants, e.g. Hutchinson, 1973; Stokes *et al.*, 1973. Indeed, Cu is both an algicide and a fungicide. Levels as low as 0.1 ppm are inhibitory to many algae. Nickel is somewhat less toxic to algae, but levels of 1 ppm are inhibitory. Aluminum is a further toxic heavy metal, present in quantity in the soil water extracts.

A series of experiments were carried out involving (a) studies of germination, growth and metal uptake of naturally-occurring and cultivated plants at field sites along the Coniston transect, (b) studies of germination, growth and plant metal uptake into seedlings grown on these soils brought to the laboratory, where SO_2 fumigations could be excluded as complicating factors, (c) studies of germination, growth and metal uptake of four cultivated plants, radish, tomato, cabbage and lettuce, on the water extracts of Sudbury soils, and (d) growth of these same four species on single salt: Ni, Cu, Co, Al, and sulphate solutions, at a range of concentrations and in the presence of a nutrient solution. The concentrations of the metals ranged from 0 to 75 ppm. Details of these experiments are given in Whitby and Hutchinson (1974) and Whitby (1974).

The findings were complementary in that it was found impossible to keep either naturally-occurring or cultivated plants alive for even a few weeks on soils collected within 8 km of the Coniston smelter. Germination did not seem to be affected but symptoms typical of heavy metal damage (Rorison, 1960) appeared immediately upon radicle emergence. These included recurvature, growth of roots out of the solution, a blackening of root tips and necrosis of cotyledons. In field experiments, lime additions had a marked effect in improving growth and in decreasing metal uptake (and metal content of water extracts). Oats (*Avena sativa*) survived even at 1.5 km from Coniston and are here used as an example of lime effects. The shoots (tops) of plants grown for 8 weeks in the field on unamended soil contained 385 ppm of Ni and roots contained 1381 ppm Ni. Plants grown on limed soil at the same site contained 43 ppm Ni in the shoot and 424 ppm in the roots. In contrast, at 7.4 km unlimed plants had shoot levels of 88 ppm and 451 ppm Ni in their roots, compared with 19 ppm in shoots and 248 ppm in roots of limed plants. Copper and Co levels were also found to be excessive. When grown in the laboratory on these soils, most seedlings died on soils collected from within 7.4 km of Coniston. Lettuce and tomato were especially sensitive and accumulated more than 500 ppm of Ni, Cu, and Al in their tops on the soil from 7.4 km. Liming, which increases pH and reduces heavy metal solubility, had a notable effect in reducing soil toxicity and metal uptake.

The effect of soil water extracts was similar to direct soil testing, in bioassays using tomato and radish. At all sites located closer than 3.8 km from the smelter and irrespective of the depth from which the soil was obtained, there was an almost total inhibition of radicle elongation. Morphological and anatomical symptoms typical of heavy metal toxicity were noted. At distances greater than 3.8 km, the relative inhibition of root elongation compared with the controls, was found to relate to distance from the smelter and to soil depth from which extracts were made. Surface soils were inhibitory to growth (caused 50% reduction in root elongation compared with 50 km controls) to a distance of 10.4 km. This would coincide with water extract levels greater than 5 ppm for both Ni and Al in surface soils.

Single salt solutions were used in similar bioassays to test the toxicity of Ni, Cu, Co, Al and sulphate to the test species (Whitby and Hutchinson, 1974). Aluminum and Ni were found to be the metals most toxic to tomato, followed by Co and Cu. Levels of only 2 ppm Ni reduced root elongation by nearly 70% and complete inhibition occurred at 10 ppm. Aluminum reduced growth by approximately 80% at only 2 ppm and by 90% at 4 ppm. Cobalt reduced growth 60% at 2 ppm and caused total inhibition at 15 ppm. (Cobalt was present at 4.4 ppm in soil extracts from 1.9 km, Table X.) Copper reduced root growth by 30% at 2 ppm and almost completely inhibited elongation at 15 ppm.

Variation within treatments was fairly high, often ±50%, but reflected differing germination times within a species. Sulphate levels of 250 ppm were not found to be inhibitory.

The high toxicity of soil extracts and the proven toxicity of their heavy metal constituents at levels which were often markedly exceeded in many of the soil extracts, leads to the conclusion that the Sudbury soils are probably directly toxic to establishment of seedlings of most species over a very wide area. The seedling establishment experiments in the field and the laboratory, and the improved performance with lime amendments would support this conclusion. One could account for the data by either Ni (a major aerial contaminant) or Al alone. Copper and Co are also present in sufficient quantities to create serious problems over a more limited area. The Al problem is of especial interest in that it seems to be an indirect result of smelter activities. Aluminum toxicity is apparently caused by highly acidic rainfall mobilizing Al from clay minerals in the Sudbury soils. This effect was unforeseen and may well be a salutary warning for those concerned with acidic rainfall problems on ecosystems both aquatic and terrestrial, in Scandinavia and in the eastern United States.

The problem is severe enough, without the added complication of synergistic interactions between certain of the polluting metals at Sudbury. The synergistic interactions of Ni and Cu have already been described (Hutchinson, 1973).

Heavy metal toxicity problems in soils tend to be long term and almost semi-permanent. The ongoing major SO_2 emissions from the new superstack at Copper Cliff have undoubtedly improved local air quality. The new resultant prospect of increasingly widespread acidic rainfall over hundreds of square kilometres, with attendant mobilization of metals such as Al in soil, is not one to be taken lightly.

3.7 EFFECTS ON SOIL ORGANIC MATTER

The chemical and physical properties of organic matter extracted from soils collected at 1.6, 7.4 and 52 km from Coniston have been studied in detail. The work was done in collaboration with Dr M. Schnitzer of Agriculture Canada, Soil Research Institute. Attention has focused especially on the properties of fulvic acid extracts obtained from the Sudbury soils. Schnitzer and Khan (1972) point out that the bulk of organic matter in most soils and water consists of humic substances. Important characteristics exhibited by all humic fractions are their resistance to microbial degradation, ability to form stable water-soluble and water-insoluble salts and complexes with metal ions and hydrous oxides, and to interact with clay minerals and organic chemicals which may be toxic pollutants. Humic substances are critical to soil fertility, both physically and chemically. They facilitate the transport and availability of nutrients, especially trace metals, and improve aeration and drainage. Factors which may affect the functioning of humic substances in a deleterious way deserve special attention.

Details of the analyses of the extracted organic matter will be given elsewhere, and a general résumé will merely be presented here. The properties of the soils and the water extracts used for organic matter extractions are given in Table XI. The soil from 1.6 km was of particularly low pH, i.e. 2.4.

TABLE XI

Properties of soils and water extracts used for organic matter extractions

	1.6 km	7.4 km	52 km
Soil pH	2.4	2.8	3.2
% L.O.I.	20.5	15.1	7.6
% Ash	79.5	84.9	92.4
% C	5.30	8.40	2.33
% N	0.32	0.81	0.15
% S	0.92	0.34	0.09
% Organic Matter	10.60	16.80	4.66
Total Ni (ppm)	1847	1809	83
Total Cu (ppm)	2007	1425	31
Water Extract pH	2.7	3.2	3.5
Water Soluble Ni (ppm)	321	25	nd
Water Soluble Cu (ppm)	180	9	nd
Water Soluble Sulphate (ppm)	1300	500	60

nd = not detectable

The normal range of N values for podsolic soils is 0.10 to 0.20%, and an approximate S value for podsolic soils is 0.1%. The S content of soil from 52 km was 0.09%, that from 7.4 km 0.34% and that from 1.6 km 0.90%.

The results of percentage loss on ignition, ash and ash reaction with concentrated HCl at room temperature for unpurified organic matter are given in Table XII. Notable findings were the high ash content of the 1.6 km soil, the color of the ash, its solubility in cold conc. HCl and the excessively high Cu and Ni contents in the ash compared with the 52 km control. The soil from 7.4 km was intermediate but closer to the control in its properties.

The titratable acidity of purified podsolic fulvic acid to pH 7.0 is normally 7.15 meq g^{-1}. When titrated with 0.05 N NaOH in the presence of 0.1 N KCl, unpurified samples from 1.6 km gave 6.5 meq g^{-1} and from 52 km gave 1.4 meq g^{-1}.

TABLE XII

Properties of unpurified organic matter

Soils	1.6 km	7.4 km	52 km
% Loss of ignition	35.4	50.2	46.3
% Ash	64.6	49.8	53.7
Colour of Ash	grey-green	bright red	brick red
Reaction with cold conc. HCl	soluble	partially soluble	insoluble
Ni (ppm) in unpurified extract	76 300	1380	160
Cu (ppm) in unpurified extract	15 460	340	170
Ni (ppm) in ash	118 100	2770	295
Cu (ppm) in ash	23 930	680	315

TABLE XIII

Chemical composition of purified organic matter

	1.6 km	7.4 km	52 km
% Ash	32.3	5.6	3.8
% C*	15.9	36.6	43.8
% N*	0.2	1.7	1.5
% H*	5.8	5.2	5.3
% O*	47.5	54.8	48.2
% S*	30.6	1.7	1.3

* corrected for ash content

This suggests significant differences in the acidic functional groups – COOH and phenolic-OH.

Purified extracts of organic matter were prepared by treatment with diluted HCl-HF and dissolution by 0.5 N NaOH. Because of the high ash content, 6N HCl was also used on the samples from 1.6 km to separate the organic matter from the ash. The chemical composition of purified organic matter is given in Table XIII, together with the titratable acidity. The C content of the 1.6 km soil was very low as was its N content. In contrast, the S concentration was abnormally high. Titratable acidity also differed markedly between the soils. It remained high for the sample from 1.6 km, indicating a large number of functional groups, but was normal (for fulvic acid) in the purified extracts of soils from 7.4 and 52 km. This indicates the effect of unlocking the functional groups by removal of metallic ions (ash).

The IR spectra of the purified fulvic acid fractions were examined following methylation. Major differences were found between the methylated samples from 1.6 km and that of normal fulvic acid. Methylated samples were also prepared for gas chromatograph. Again, the sample from 1.6 km was atypical for fulvic acid. Not only were many of the components of podsolic fulvic acid absent but there are a large number of $S=O$ groups (not present in fulvic acid) and many compounds that were detected at low temperatures, some of which probably contain S groups. It seems that S has replaced C atoms and it is likely that the control benzene rings are now surrounded by sulphonic groups (SOH_3) rather than carboxylic groups. Peaks for tri, penta and hexa-benzene carboxylic methyl esters were missing. The resultant drastically modified organic matter tends to act as a sulphonic ion resin, with very strong metal binding capacity. Exchange properties will be very different from those of fulvic acid and the role as nutrient reservoir and sink for plant growth will have been drastically altered. Further studies are needed into many of these aspects of organic matter changes in the Sudbury soils.

If the long distance dispersal of SO_2 leading to acid rainfalls and acidic soils, and of heavy metals was merely a land and air problem, it would be sufficiently serious as regards the destruction of the forest ecosystem and contamination, in view of the vast acreages involved. However, the problem does not stop there. Lakes as far as 80 km from the town have become acidic in recent years. Metals accumulate in the snow and run-off in acidic melts in the spring. Sheet erosion of thousands of acres has already occurred. Sediment loads in the Wanapitei River which drains the eastern end of the area are very high. Nickel concentrations in the river water 80 km away averaged 42 ppb in 1974. Sediment cores taken in the same river have a surface 10 cm with Ni content ratios of up to 400 ppm and Cu to 150 ppm. Large quantities of Ni and Cu are released in solution as fine particulates into Georgian Bay of Lake Huron. This erosion and leaching of metals from the acidic soils is likely to continue for the foreseeable future. The severity of the Sudbury effects, especially as regards (a) mobilization of Al in the soil, (b) the profound changes in organic matter structure found, and (c) the widespread phytotoxicity of the soils as a result of Ni and Cu accumulations may be merely a consequence of the severity of the Sudbury conditions experienced at least up to 1972. The disturbing implications would be if these changes and effects were to be repeated on even wider scales in areas with appropriate soils and levels of precipitation, and with SO_2 or N oxide inputs. Both Scandinavia and Eastern North America are such areas and one hopes that useful lessons for the future may be gleaned from the Sudbury studies.

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