Soil acidity (pH) as influenced by point-source pollution from a base-metal smelter, Flin Flon , Manitoba

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Abstract: This study examines possible spatial variations in soil pH around Flin Flon, Manitoba, that might result from SO_2 deposition coming from the non-ferrous metal smelter located in the town. Ten study sites were selected to reflect decreasing ridge-crest ecosystem pollution damage along a 37.5 km east-southeast transect downwind from Flin Flon to Cranberry Portage. Two control sites were also selected at 33.2 and 47.3 km northeast of Flin Flon to reflect locations where no detectable modifications to ridge-top ecosystems were observed. At each study site eight soil samples were collected at ridge crest, eight at mid-slope, and sixteen at lower slope subsites. In addition, small ridge-top runoff conduits and depressions filled with organic residues were sampled. Linear regression did not confirm any correlation between pH and distance from the pollution source. While SO_2 and base metal fallout are implicated in the death of higher plants and cryptogams (lichen and mosses) on ridge-crest sites near the smelter, it is concluded that base metal/fly ash fallout is sufficient to counteract any SO_2 induced hydrogen buildup that would lower soil pH. Results support the normal base nutrient/base metal shedding properties of ridges as pH values increase significantly downslope.

Introduction

Many studies have documented acid fallout impacts on both vegetation and soil across eastern North America and Europe. While results are ambiguous, it is generally concluded that as SO_2 fallout increases, soils that are not well buffered against pH change experience SO_4^{2-} adsorption and increased acidity (lowered pH) over extended periods of time, and impacts to vegetation result (DeHayes *et al.* 1999; Eriksson *et al.* 1992). While such impacts tend to be regional, locally the soils most affected are those which are non-calcareous, coarse textured, have low cation exchange capacities, and low base saturations (Reuss *et al.* 1986).

More dramatic local pollution impacts are associated with increasing SO_2 and base metal particulate fallout as point-source non-ferrous smelters are approached (e.g. Sudbury, Flin Flon and Thompson -- Dudka *et al.* 1995, 1996; McMartin *et al.* 1996; Orlandini 1998; Henderson *et al.* 1995; Hocking *et al.* 1977). Despite the dramatic impacts on vegetation close to smelters, influences on pH are still ambiguous even though many studies conclude, or imply, that soil pH increases away from these same point sources (Amiro *et al.* 1981). In fact, it seems that increased acidification close to smelters is a basic assumption in many studies. Hogan *et al.* (1984), using data from eight lowland forest soils downwind of the Flin Flon smelter, were unable to confirm such a pH trend however, expressing surprise at a result so contradictory to that found for most other non-ferrous smelters. Zoltai (1988) also concluded that SO_2 emissions were not reflected in the surface peats throughout the Flin Flon region, even though within 5 km of the smelter soil sulfur levels were 3 to 12 times higher than background levels. This present study was therefore initiated to determine if any spatial trend in soil pH really exists near Flin Flon. Unlike these last two studies, which only sampled forested soils in run-off receiving lowland mineral and wetland soils, this study selected upland ridges many of which had lost their tree cover due to pollution. Ridges were selected because it was considered runoff shedding sites might better reflect direct fallout, and therefore provide a clearer view of any spatial pH variations resulting from pollution. Field studies were carried out during the summer of 1989, 1995, and 1996, with one winter visit in 1996.

Materials and Methods

a) Study Area: Flin Flon is located on the Saskatchewan/ Manitoba boundary at 54° 45' N (Figure 1). This part of the Precambrian shield is dominated by granitic and metavolcanic

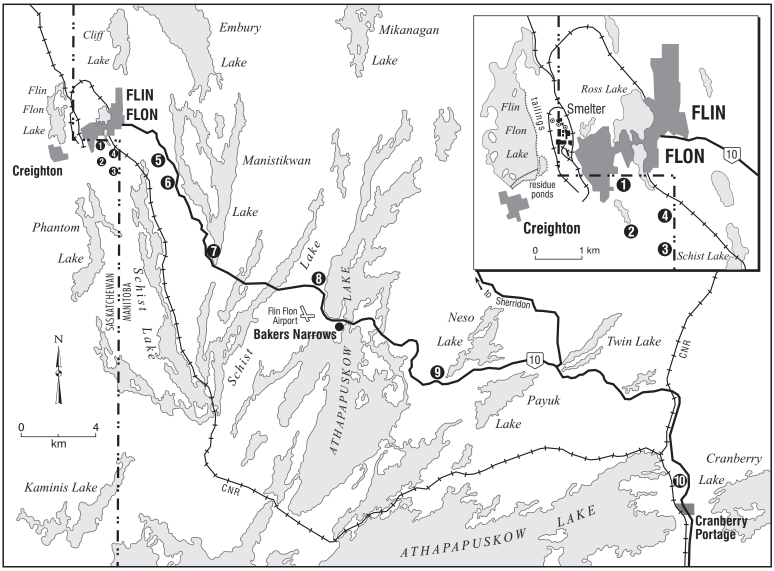

Figure 1: *Location of study sites 1-10 between Flin Flon and Cranberry Portage. The Sherridon road control study sites #11 and 14 are located off the top right corner of the mapped area.*

(greenstone) rocks containing sulphide orebodies rich in non-ferrous metals such as zinc, copper and cadmium. In1927 Hudson Bay Mining and Smelting Company (HBMS), began construction of a zinc-copper smelter which became operational in 1930, with atmospheric emissions being released from 30 m tall stacks. These were replaced in 1974 by a single 251 m stack. In addition to $SO_{2,}$ Zn, Cu and Cd, emissions include arsenic, nickel, iron, lead and mercury, with dry and wet base metals deposition taking the form of metal particulate, metal oxide and metal sulfates (Franzine *et al.* 1979). Emissions levels for SO_2 have always been high, but the addition of electrostatic precipitators in 1982 has reduced particulate emissions by approximately seven fold (Schultz *et al.* 1983). In 1996, 202,032 tonnes of SO_2 were released into the atmosphere (Krawchuk 1998), reflecting a gradual increase during the last decade in both yearly mean totals, and in the 1-Hr and 24-Hr maximum SO_2 levels.

Shield-bedrock outcrops as low rolling hills with glacially scoured crests that have been scratched relatively clean of any regolith. Intervening depressions are filled with discontinuous Quaternary and Holocene tills, glaciolacustrine sediments, peats, and numerous lakes. South of Cranberry Portage bedrock consists of Ordovician carbonates completely buried by till and outwash, and without outcrops. The dominant winds are towards the southeast and southwest, with strong components towards the north-northwest and south (Henderson *et al.*1995). This results in an oval pattern of decreasing base metal contaminated soil centered on Flin Flon, with a northwest to southeast axis (Zoltai 1988). Undisturbed ridge crests include soil-free areas (with crustose lichen cover) and thin Folisol-like organic profiles developed from accumulations of dead cryptogams together with some conifer residues. These Folisols are protected from erosion by the living cryptogam cover and provide a substrate sufficient to support scattered jack pine, and occasionally spruce. Better drained regolith on forested mid- and lower slopes have Degraded Dystric Brunisols often showing signs of gleying, while in lowlands Peaty Gleysols, Fibrisols and Mesisols dominate (Figure 2A).

Undisturbed forests throughout this Subhumid Mid-Boreal Ecoclimatic Region are characteristic of the mixed-woods section of the boreal forest, and are dominated by jack pine, (*Pinus banksiana)*, black spruce *(Picea mariana)*, white spruce *Picea glauca)*, trembling aspen *(Populus tremuloides)*, balsam poplar *(Populus balsamifera)*, and white birch *(Betula papyrifera)* (Scott 1995). Ridge crests close to Flin Flon have been devegetated primarily because of pollution with their cryptogam cover killed, thin Folisols eroded, and conifers toppled. These remaining ridge-crest conifers survive only on remnant Folisol patches or on organic-filled depressions, and are aided by developing basal skirts which are protected during the fumigation winter months intranivally. Lower slopes with deep soils retain a forest cover even close to Flin Flon, although closed mixed forest gives way to a more open hardwood cover of birch and aspen within 3 km of the smelter.

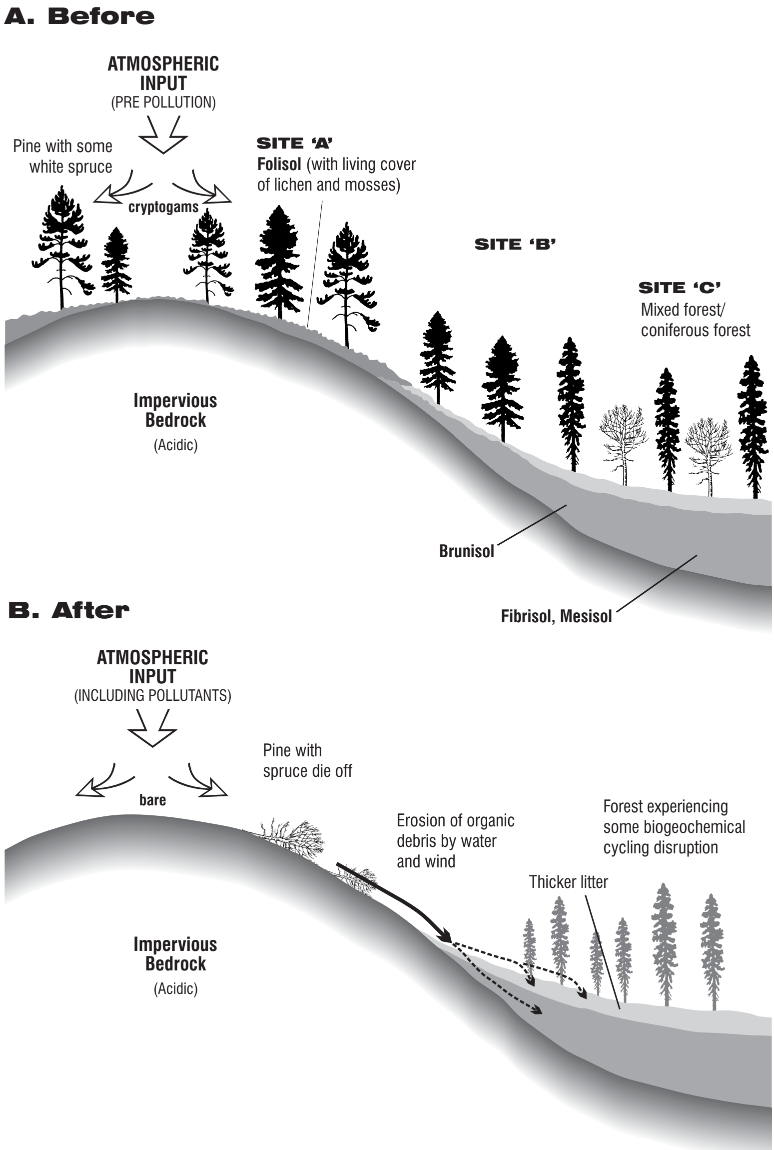

Figure 2: *A. Typical ridge ecosystem conditions in the Flin Flon region before (or without) pollution impacts. B. Typical ridge ecosystem conditions close to Flin Flon after seventy years of smelter pollution.*

b) Study Site Selection: Following a preliminary reconnaissance between Flin Flon and Cranberry Portage, ten ridge-crest study sites were selected where conditions were considered similar in all respects except for pollution impacts (Figure 1). Site selection was based to five criteria, 1) conformity to the downwind pollution fallout pattern, 2) similar acidic bedrock, 3) were/are dominated by lichen cover and open jack pine, 4) accessibility, 5) lack of disturbance by fire or other non-pollution anthropogenic impacts. Suitable sites could not be selected southeast of Cranberry Portage due to different bedrock/outcrop characteristics. As the control site (# 10) at Cranberry Portage was later considered to exhibit possible minor pollution impacts, two additional control sites, # 11 and 14, were selected 33.2 and 47.3 km respectively northeast of Flin Flon along the Sherridon road. Here no pollution impacts were noted, and soil base metal contents approach background levels (Zoltai 1988).

c) Soil Sampling and Analysis: To reflect the nutrient/runoff shedding characteristics of ridges at each study site, samples were collected at three subsites (A, B, and C in Figure 2). Figure 2 models the general pre- and post-pollution ecosystem conditions at the more seriously impacted sites within 6 km of Flin Flon. At each of subsites A, B and C, eight 0-5 cm deep soil samples were collected randomly within a 10x10 m area. At subsite C eight additional samples were collected at a depth of 5-10 cm (C_2). Additional samples were collected from small ride-top runoff swales and in depressions (1-5 m across) which had been partially filled with eroded organic debris. Ridge-crest samples were mostly organic except at study sites # 1-3 where much of the original Folisol had been removed by erosion. Here many samples consisted of mineral regolith found in crevices. Soil samples were immediately air dried, and on return to the laboratory the organic samples were ground and all samples sieved through a 2 mm mesh sieve. The 0.01M $CaCl_2$ method was used for pH determination, using a Radiometer Inc., Copenhagen, pH Meter (type PHM 29b).

d) Statistical Analysis: Linear regression was performed (using the statistical analysis software SPSS) on the data from study sites

Table 1: *Means and standard deviations for pH data at all study sites.*

Site #	distance from smelter (km)	mean pH for all 3 sub-sites	mean pH for sub-site A	S. D. for sub-site A	mean pH for sub-site B	S. D. for sub-site B	mean pH for sub-site C_1	S. D. for sub-site C_1	mean pH for sub-site C_2	S. D. for sub-site C_2
1	1.65	5.299	4.589	.305	5.449	.453	5.961	.159	5.198	.621
2	2.45	4.230	3.540	.142	3.508	.370	4.494	.608	5.38	.711
4	3.00	4.260	4.501	.282	4.574	.264	4.126	.344	3.840	.433
3	3.40	4.560	3.624	.190	3.824	.286	5.206	.573	5.610	.347
5	4.70	4.594	4.103	.278	4.326	.316	5.129	.670	4.851	.765
6	6.35	5.414	4.356	.469	5.300	.261	5.811	.522	6.189	.304
7	10.40	4.026	4.836	.351	4.645	.197	5.311	.354	4.511	.087
8	15.70	3.818	3.430	.253	4.139	.454	3.988	.137	3.718	.365
9	23.90	4.552	4.337	.323	4.995	.460	4.890	.438	3.984	.302
10	37.50	4.554	4.265	.287	3.770	.379	4.594	.707	5.591	.891
11	36.8	3.766	3.900	-	3.600	-	3.800	-	-	-
14	47.3	3.912	4.013	-	3.81	-	3.913	-	-	-

1 - 10 to determine if there is a statistically significant relationship between the soil pH of the ridge-crest samples (subsite A) and their distance from the smelter. The pH data from the mid- (subsite B) and lower slopes (subsite C) were tested in the same manner. Linear regression was also used to see if there is a relationship between soil pH and position on the hillside (i.e. between subsites A, B and C). As the control study sites 11 and 14 did not conform to the site-selection criteria established for these analyses, they were not used in the regression analyses.

Results

Table 1 summarizes pH data for all study sites sampled. For ridge-crest study sites 1-10 (subsite A, n = 80) the mean pH value is 4.16, while the comparable value for the two control sites # 11 and 14 (n = 16) is 3.96. Individual pH values for subsites A range from a low of 3.08 at site # 8, to a high of 5.29 at site # 1 (Figure 3). While the largest mean pH values were actually found at study sites # 1 and 7, the lowest ridge-crest mean values were at sites 2,

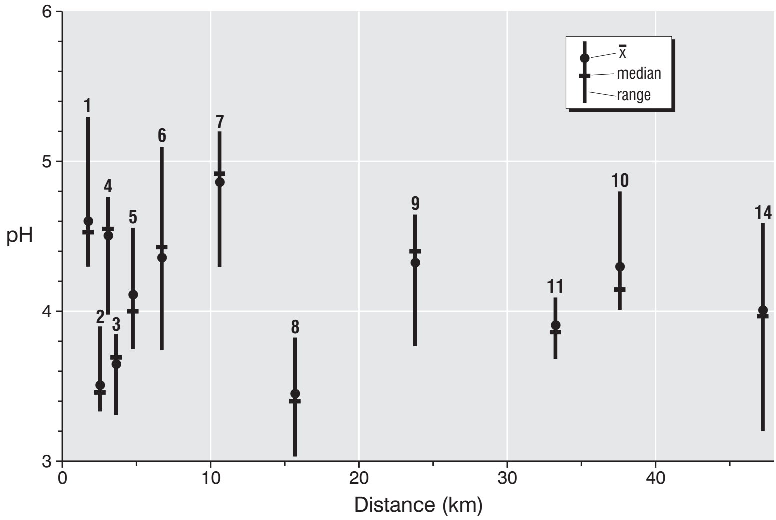

Figure 3: *Ridge-crest (subsite A only) pH values plotted against distance from the smelter.*

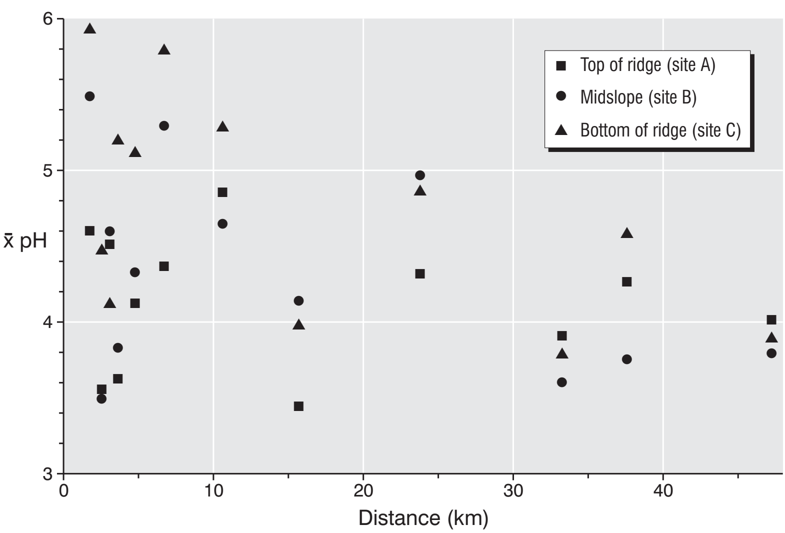

Figure 4: *Mean pH values at subsites A, B and C_1 plotted against distance from smelter. See Figure 3 for study-site numbers.*

Table 2: *Pearson Product Moment Coefficients (r) and Significance of r at the 0.01 level for linear regression analyses, study sites 1-10 only.*

Dependent variable v independent	r	Significant at the 0.01 level?
pH values for subsites A v distance from smelter	0.05614	no
pH values for subsites B v distance from smelter	0.16816	no
pH values for subsites C_1 v distance from smelter	0.23956	no
pH values for subsites A v pH values for subsites B	0.49809	yes
pH values for subsites B v pH values for subsites C_1	0.46164	yes
pH values for subsites A v pH values for subsites C_1	0.3097	yes

3 and 8. Linear regression between ridge-crest pH data (which were considered to be the most likely to demonstrate any pH changes attributable to SO_2 adsorption) and distance from the smelter, reveal no linear relationship at the 0.01 level (Table 2). Figure 4 illustrates mean pH values for each of the subsites A, B and C_1 plotted against distance from the pollution source. While these data (n = 239) might suggest greater scatter in mean values between subsites close to the smelter, again linear regression shows no correlation at the 0.01 level between pH for either subsite B or C with distance from the smelter.

When individual subsites from ridge-crest to slope-bottoms at study sites 1-10 are compared with each other (without regard to distance from the smelter), the base nutrient shedding (and most likely the bases metal/fly ash shedding) characteristics of these ridges is evident (Figure 5). Mean pH values for subsites A, B and C_1 are 4.158, 4.453 and 4.956 respectively. Regression analysis reveals that this downslope increase in pH is significant at the 0.01 level (Table 2). The pH data from control sites # 11 and 14, however, show no particular trend (Figure 5). Results obtained from small depressions at A subsites show great variation in pH values depending on the extent each acts as small collecting basins, or runoff swales. While most of the depressions have strongly acid soils (pH 3.5 - 4.2), runoff swales for both sites # 1 and 6 exhibited high values. Just below the ridge-crest at site # 1 one swale contained eroded organic debris through which metal particulate

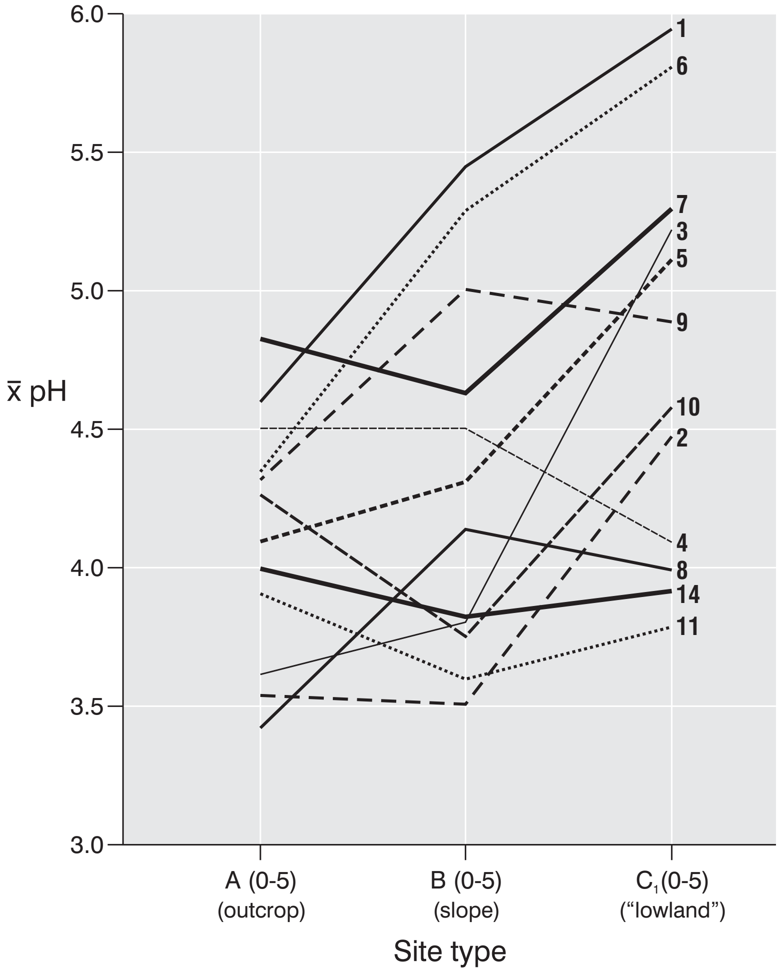

Figure 5: *Mean pH values for subsites A, B and C_1 for each of the twelve study sites plotted against topographic position.*

and fly ash were washed following rain. Three samples taken at its centre of this swale had pH values of 5.5, 6.0 and 6.1. A similar swale at study site # 6 had a pH of 5.8.

Discussion

This study confirms the more general findings of Hogan *et al.* (1984) and Zoltai (1988) that despite the trend apparently found close to point-source polluting smelters elsewhere, here around Flin Flon there is no statistically significant spatial variation in pH downwind of the pollution source (Figure 3). The study also confirms the expected situation that ridges shed bases and pollutants downslope, a factor which helps account for both higher and more variable pH values in lowland soils (Figure 5, Table 2).

A number of factors may account for this lack of any downwind pH variation. The first possibility is that the 251 m stack, which was constructed precisely to distribute pollutants more widely, has been effective in creating a more even SO_2 fallout pattern, thereby impacting soils equally. This explanation, however, is considered unlikely for two reasons. First, it would require a regional depression of pH values, not supported when pollution transect values are compared to the Sherridon road control sites, and second it is not supported by the earlier results of Hogan *et al.* (1984) and Zoltai (1988).

A more plausible explanation is that buffering by both fly ash and base metal particulate and cations, which have been documented to decrease exponentially away from the smelter (Zoltai 1988; McMartin *et al.* 1996; Orlandini 1998), are in sufficient quantities to neutralize induced hydrogen ion buildup in the soil solution (Buchauer 1973). It should be noted that the highest single pH value recorded for any ridge crest was at study site # 1 only 1.65 km from the HBMS stack. It is at this same site that the highest pH values for runoff swales were also recorded. This implication of fly ash is supported by Zoltai's findings that the higher levels of sulfur found in peats within 5 km of the HBMS smelter were associated with ash contents also much above background levels. In addition, Hogan *et al.* (1984) suggest that for Flin Flon, zinc may be responsible for the ameliorating effects of sulfur deposition. In the USA, Legge *et al.* (1986) also noted that at least half of the sulfur acids deposited by precipitation are neutralized by base metal pollutants precipitated at the same time, while Jordan *et al.* (1975)

found that the amphoteric properties of zinc oxide may cause pH to actually rise near a base metal smelter!

While this study demonstrates no linear relationship between soil acidity and distance from the smelter, the cocktail of sulfur and base metal particulate has clearly been demonstrated to seriously impact the soil-vegetation complex to the point that close to the smelter almost all ridge-crest vegetation has been killed. Particularly significant is the impact of these pollutants on the thin cryptogam-formed and protected Folisols, on which these ridge-crest ecosystems depend (Scott, 1995). Cryptogam death leads to the 'death' of these Folisols and they are then eroded. This soil loss, combined with impacts of atmospheric sulfur to tree leaves, and the effects of elevated base metal levels on roots, free-living soil microflora (Wright *et* al. 1996; Hocking *et al.* 1977), and root mycorrhizal associations (Klein 1983) , may account for such ecosystem destruction.

It may well be that the contradictory statements about pH trends close to base metal smelters found in the literature may be partly the result of the amount and type of data used in each study. Often these pH data were obtained both from few samples, and samples collected as secondary to studies performed to show plant cover damage differences regardless of topographic position. This current study demonstrates that combining data from a variety of topographic sites is inappropriate as they would include the pre- and post-pollution nutrient cation and base metal pollutant shedding properties of ridges.

Acknowledgments

The author wishes to thank Lynn Christenson, Rosa Orlandini, Gregory Scott and David Wright, who greatly assisted with field sampling and lab analyses. Special thanks to Brian McGregor who performed the statistical analysis, and Weldon Hiebert for his excellent cartography.

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