SELENIUM AS A
CHEMICAL OF CONCERN

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SARA GROUP

HHRA/ERA Document
Selenium as a Chemical of Concern
Version 3.1
July 25, 2005

EXECUTIVE SUMMARY

At the beginning of the Sudbury Soils Study, four Chemicals of Concern (COCs) were put forth by the Technical Committee (TC) for detailed evaluation in the Human Health Risk Assessment (HHRA) and Ecological Risk Assessment (ERA). These included arsenic, cobalt, copper and nickel. This recommendation was based on a review of historical soil quality data in the Sudbury area.

An extensive survey of soil quality in the Sudbury area was undertaken in 2001. Approximately 8150 soil samples were collected from over 1000 locations. The survey was undertaken by three different groups (Ontario Ministry of the Environment, Laurentian University and Golder Associates Ltd.) utilizing similar methodology. All samples were analyzed for 20 inorganic parameters by the same analytical laboratory.

For a compound to be considered a COC in the risk assessment, it must fulfill 3 criteria established by the TC:

- Parameter must be above or equal to the Table A or Table B guidelines published in the MOE's Guideline for Use at Contaminated Sites in Ontario (1997), depending on whether the specified study area has surface or well water sources for potable water;
- Parameter must be present across the study area; and,
- Parameter must scientifically show origin from smelter operations.

The results of the 2001 survey were screened against these three criteria to identify whether any additional COCs should be considered for the risk assessments.

Following this screening exercise, it was determined that selenium (Se) met all three criteria. In 2004, the SARA Group recommended to the TC that Se be considered a COC for the Sudbury Soils Study.

This document reports on the screening approach and results which indicates that Se should be considered as a COC for the Sudbury Soils Study. The central reasons why Se is recommended as a COC are:

- A small proportion of soils samples (1.4%, or 113 of 8148) had concentrations of selenium that were greater than or equal to the generic soil quality guideline (10 mg/kg).
- Selenium is present across the study area. However, the majority of samples that meet or exceed the guideline are located in the vicinity of the smelter at Copper Cliff.
- The concentration of Se in soil generally decreases with increasing distance away from the smelters. There is a high positive correlation between Se and Ni, as well as Se and Cu levels in soil. These relationships indicate that elevated soil Se levels are linked to smelting operations.

In summary, the SARA Group recommends that Se should be considered a COC for the Sudbury Soils Study.

SARA GROUP

SUDBURY AREA RISK ASSESSMENT
SELENIUM AS A CHEMICAL OF CONCERN

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1.0 BACKGROUND

The Request for Proposal (RFP) for the Sudbury Soils Study identified four Chemicals of Concern (COCs): nickel (Ni), copper (Cu), cobalt (Co), and arsenic (As). The initial set of COCs was established by the Technical Committee for the Sudbury Soils Study based on existing sampling data and the Ontario Ministry of the Environment (MOE) 2001 report entitled *Metals in Soil and Vegetation in the Sudbury Area (Survey 2000 and Additional Historic Data)*.

As part of the problem formulation stage of the Sudbury Soils Study, the SARA Group has reviewed the combined database of 2001 soil sampling results to determine if additional substances should be considered as COCs. The database consists of soil sampling by the MOE, Laurentian University and Golder Associates Ltd. During this process, lead (Pb) was identified as a potential COC and further analysis by scanning electron microscopy (SEM) on anomalous samples has been completed.

Three criteria have been identified by the Technical Committee and all must be satisfied in order to identify additional substances as COCs. The three criteria are:

- Parameter must be above or equal to the Table A or Table B guidelines published in the MOE's *Guideline for Use at Contaminated Sites in Ontario* (1997), depending on whether the specified study area has surface or well water sources for potable water;
- Parameter must be present across the study area; and,
- Parameter must scientifically show origin from smelter operations.

The objective of this document is to demonstrate that selenium (Se) satisfies all three of the outlined criteria and should be included as a COC in the integrated Human Health Risk Assessment and Ecological Risk Assessment.

2.0 METHODOLOGY

To evaluate whether selenium meets the criteria as a COC, data from three sources were incorporated into a combined database and were reviewed by the SARA Group. One source of data was the results of a comprehensive soil monitoring program conducted in the Sudbury area in 2001 by the MOE. These results are presented in a report entitled *City of Greater Sudbury 2001 Urban Soil Survey* (MOE, 2004). The MOE sampling stations established in this study were in predominantly urban areas. The second data source was provided by Laurentian University and consisted of samples collected in rural and remote areas within the Greater Sudbury Area in 2001. The third data source was from a sampling program in the Falconbridge area by Golder Associates Ltd. All sampling programs followed the same sampling protocol, which included the collection of composite samples comprising a minimum of fifteen cores taken at three depths (0-5 cm, 5–10 cm and 10–20 cm), with most samples taken in duplicate.

The databases were combined, and the concentrations of selenium in all soil samples compared to the MOE's *Guideline for Use at Contaminated Sites in Ontario* (1997), specifically Table A soil criteria for residential/parkland land use for a potable groundwater condition. The Table A soil guidelines are effects-based and were derived to protect both human health and the natural environment, whichever is potentially affected at the lowest observed effect concentration (LOEC).

Selenium is an essential trace metal for some mammals but can be toxic at elevated levels. The range between deficiency and toxicity can be quite narrow (Ripley *et al.*, 1996). The MOE guidance level derived for selenium is 10 mg/kg in Table A for both industrial/commercial and residential/parkland sites. For agricultural sites, it is recommended that selenium concentrations be less than 2 mg/kg where there is a possibility that vegetation may be consumed by livestock. For the current evaluation, the Table A criteria for residential/parkland land uses were used as benchmark.

For selenium to be classified as a COC, three criteria need to be met:

- Criterion 1: Are selenium concentrations above or equal to MOE's Table A?
- Criterion 2: Is selenium present across the study area?
- Criterion 3: Can it be shown that elevated levels of selenium are the result of smelter operations in the study area?

To evaluate Criterion 1, the combined database was compared to Table A guidelines as published in the MOE's *Guideline for Use at Contaminated Sites in Ontario* (1997).

To evaluate Criterion 2, all selenium values above or equal to 10 mg/kg (Table A guidelines) were plotted across the study area.

To evaluate Criterion 3, statistical analysis was performed to determine if the origin of elevated levels of selenium was related to smelter operations in the study area.

3.0 DETERMINATION OF CRITERIA

3.1 Criterion 1

Parameter must be equal to or above the Table A or Table B guidelines published in the MOE's *Guideline for Use at Contaminated Sites* in Ontario (1997), depending on whether the specified study area has surface or well water sources for potable water.

Selenium was present in the study area at levels equal to or above the MOE Table A guidelines (10 mg/kg); levels were equal to or above Table A in 106 samples collected by the MOE and in 7 samples collected by Laurentian University. Further analysis of the combined database was undertaken to determine the spatial and depth variation between the samples which contained elevated selenium levels. This analysis considered:

- 6532 samples taken from 1531 sites (located on 633 properties) (collected by the MOE);
- 1422 samples taken from 369 sites (collected by Laurentian University); and,
- 194 samples taken from 33 sites (collected by Golder and Associates).

The sampling locations that contained selenium in excess of or equal to the Table A guideline are summarized in Table 3.1. A complete list of these properties and the selenium levels for each sample at these locations is provided in Appendix A.

These results show that selenium fulfills Criterion 1 for 113 (1.4%) out of 8148 soil samples. The majority (91.1%) of the properties with selenium in excess of or equal to the Table A guidelines are located in Copper Cliff.

Table 3.1 Summary of Properties with Samples Containing Selenium Above or Equal to MOE Table A Value (10 mg/kg)

Area	Property No.	Depth (cm)	Total # of Samples	# Samples above or equal to Table A	Range (mg/kg)
Copper Cliff	Property 1	0-5	4	2	11-12
Copper Cliff	Property 2	0-5	4	1	11
Copper Cliff	Property 3	0-5	2	1	13
Copper Cliff	Property 4	5-10	4	1	10
Copper Cliff		0-5	4	4	10-15
Copper Cliff	Property 5	0-5	4	4	14-20
Copper Cliff	Property 6	0-5	4	2	10
Copper Cliff	Property 7	0-5	4	2	16-19

Table 3.1 Summary of Properties with Samples Containing Selenium Above or Equal to MOE Table A Value (10 mg/kg)

Copper Cliff		5-10	4	2	11-12
Copper Cliff	Property 8	0-15	2	2	11-12
Copper Cliff		0-5	2	2	16-18
Copper Cliff	Property 9	10-20	4	1	11
Copper Cliff	Property 10	0-5	4	2	13-14
Copper Cliff	Property 11	0-5	2	1	10
Copper Cliff	Property 12	0-5	4	2	10-12
Copper Cliff	Property 13	0-5	4	3	19-20
Copper Cliff	Property 14	10-20	4	1	10
Copper Cliff		0-5	4	4	14-18
Copper Cliff	Property 15	0-5	4	2	27-35
Copper Cliff	Property 16	0-5	4	4	12-15
Copper Cliff	Property 17	5-10	4	1	10
Copper Cliff	Property 18	0-5	24	1	13
Copper Cliff	Property 19	0-5	4	4	11-15
Copper Cliff	Property 20	0-5	4	1	10
Copper Cliff	Property 21	0-5	4	2	10
Copper Cliff	Property 22	0-5	4	4	11-16
Copper Cliff	Property 23	5-10	4	3	15-21
Copper Cliff		0-5	4	2	12-14
Copper Cliff	Property 24	0-5	4	4	12-13
Copper Cliff	Property 25	0-5	2	2	12
Copper Cliff	Property 26	5-10	4	1	10
Copper Cliff		0-5	4	2	13-14
Copper Cliff	Property 27	0-5	4	1	11
Copper Cliff	Property 28	0-5	2	2	11-12
Copper Cliff	Property 29	0-5	4	1	10
Copper Cliff	Property 30	0-5	4	1	11
Copper Cliff	Property 31	0-5	2	2	36-49
Copper Cliff	Property 32	0-5	16	1	12
Copper Cliff	Property 33	0-5	4	3	12-14
Copper Cliff	Property 34	0-5	4	2	12
Copper Cliff	Property 35	0-5	4	4	11-13
Copper Cliff	Property 36	0-5	4	2	11-12
Copper Cliff	Property 37	0-5	4	2	10-11
Copper Cliff	Property 38	5-10	2	1	10
Copper Cliff		0-5	2	2	33-36
Copper Cliff	Property 39	0-5	4	1	10
Copper Cliff	Property 40	0-5	4	1	10

Table 3.1 Summary of Properties with Samples Containing Selenium Above or Equal to MOE Table A Value (10 mg/kg)

Copper Cliff	Property 41	0-5	4	1	12
Copper Cliff	Property 42	0-5	4	1	10
Copper Cliff	Property 43	5-10	4	1	13
Copper Cliff		0-5	4	2	21-22
Copper Cliff	Property 44	0-5	2	2	20-22
Copper Cliff	Property 45	0-5		1	12.5
Copper Cliff	Property 46	0-5		1	17
Copper Cliff	Property 47	0-5	2	2	15-19
Sudbury (Core)	Property 48	0-5	25	1	11
Sudbury (South)	Property 49	0-5	2	2	12-13
Sudbury (East)	Property 50	0-5	2	1	11
Falconbridge	Property 51	0-5	5	3	10-12
Falconbridge		5-10	4	1	11
Falconbridge	Property 52	0-5	2	1	10
Not Listed*	Property 53	0-5	2	1	10

* at the time of publication, no area information available for this property.

3.2 Criterion 2

Parameter must be present across the study area.

To determine the distribution of the samples that had selenium levels greater than or equal to the MOE Table A guideline (10 mg/kg), the easting and northing location of each sample was plotted (Figure 3-1). This mapping confirms that the samples with elevated selenium levels occur mainly in the vicinity of Copper Cliff. However, selenium levels above or equal to the MOE Table A guideline were present at 58 properties in Copper Cliff, three properties in Falconbridge, one in Sudbury Core, one in Sudbury South, one in Sudbury East and one property currently without an area listing.

The concentration of selenium in samples above or equal to the Table A guideline in Copper Cliff ranged from 10 mg/kg to 49 mg/kg. The concentration in the Falconbridge and Sudbury Core samples exceeding or equal to Table A ranged from 10 mg/kg to 11 mg/kg. The majority of the samples with selenium levels above or equal to the MOE Table A occurred in surface soils (0-5 cm, 101 out of 113 samples), while 10 samples occurred at 5-10 cm, and two samples at 10-20 cm. The elevated selenium levels were therefore confined primarily, though not exclusively, to the uppermost soil layer (0-5 cm) suggesting atmospheric deposition as the likely source.

The results of the analysis show that selenium fulfills Criterion 2; it exists within the study area although elevated levels are predominantly in the Copper Cliff area.

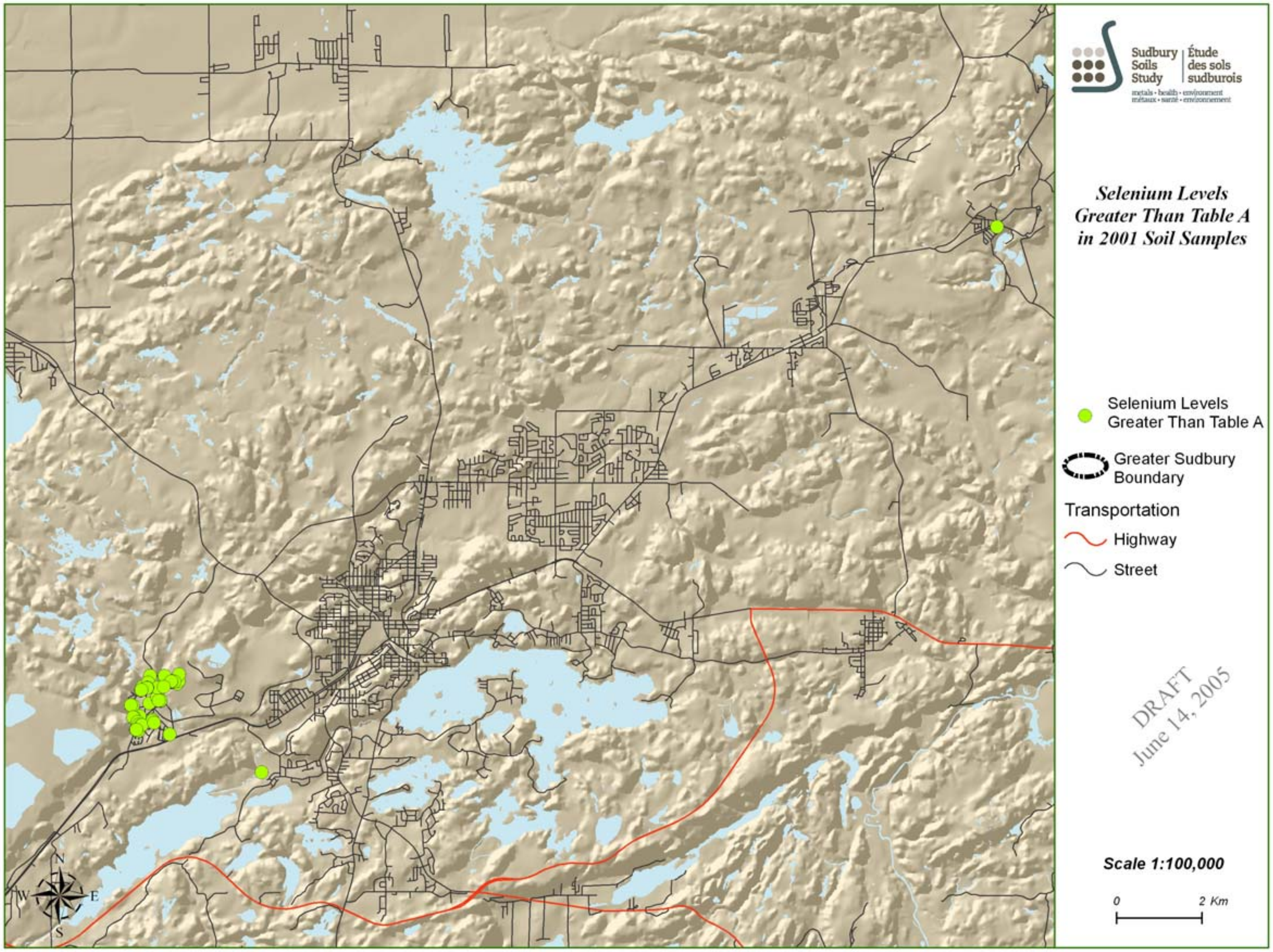

Figure 3-1 Distribution of Soil Samples with Selenium Concentrations >10 mg/kg

3.3 Criterion 3

Parameter must scientifically show origin from smelter operations.

Selenium is principally obtained as a by-product of copper refining (Doull *et al.*, 1975). It is known to occur in association with copper, from which it is separated during the electrolytic refining process (Ripley *et al.*, 1996).

Therefore, statistical analysis was conducted on the distribution of samples containing selenium with respect to distance from the Copper Cliff smelter. A two variable regression and correlation analysis was performed to evaluate the possible relationship between concentration of selenium and distance from the smelter.

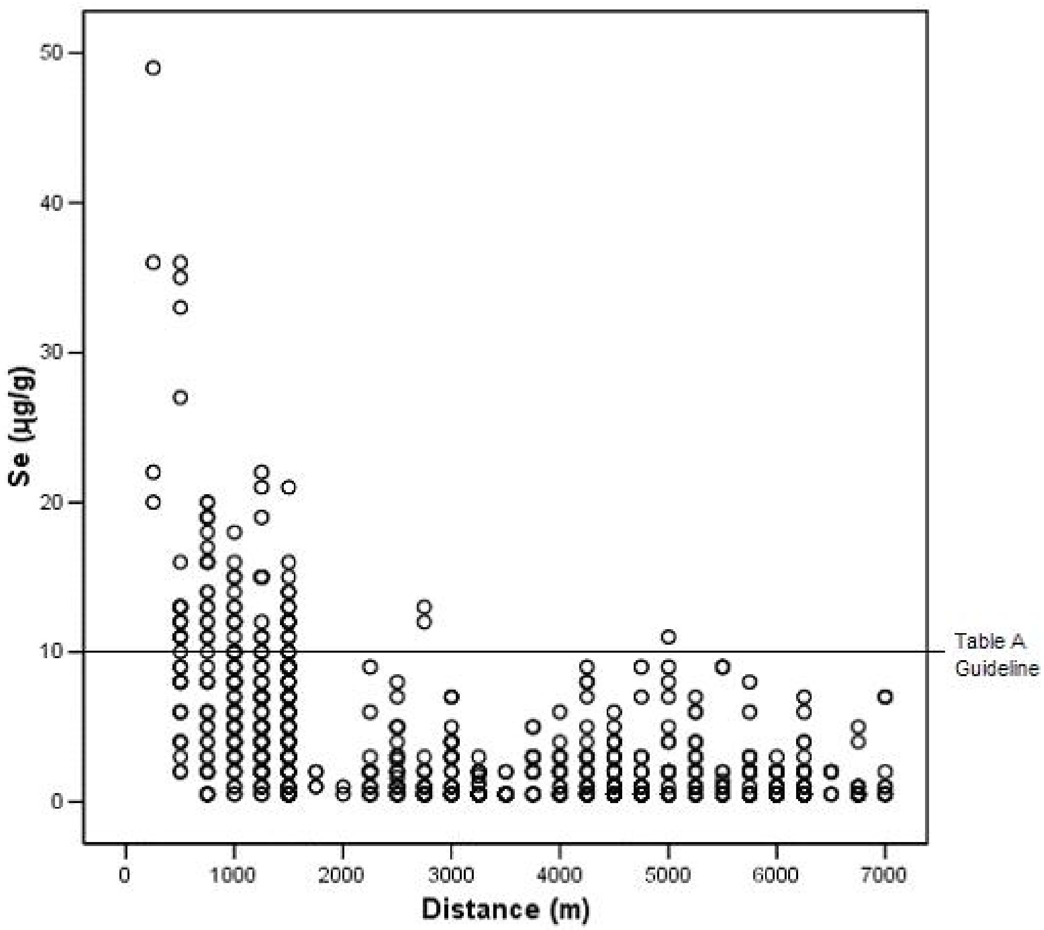

Figure 3-2 Selenium Concentration vs. Distance within a 7 km Radius from the Copper Cliff Smelter

Figure 3-2 indicates that most of the samples containing selenium exceeding the MOE Table A value occurred at a distance of less than 5000 m from the smelter. Beyond 5000 m, most samples contained selenium levels below Table A.

A 3D representation of selenium levels versus distance from the smelter is provided in Figure 3-3. The UTM coordinates of all points within a 10 km radius of the smelter were plotted.

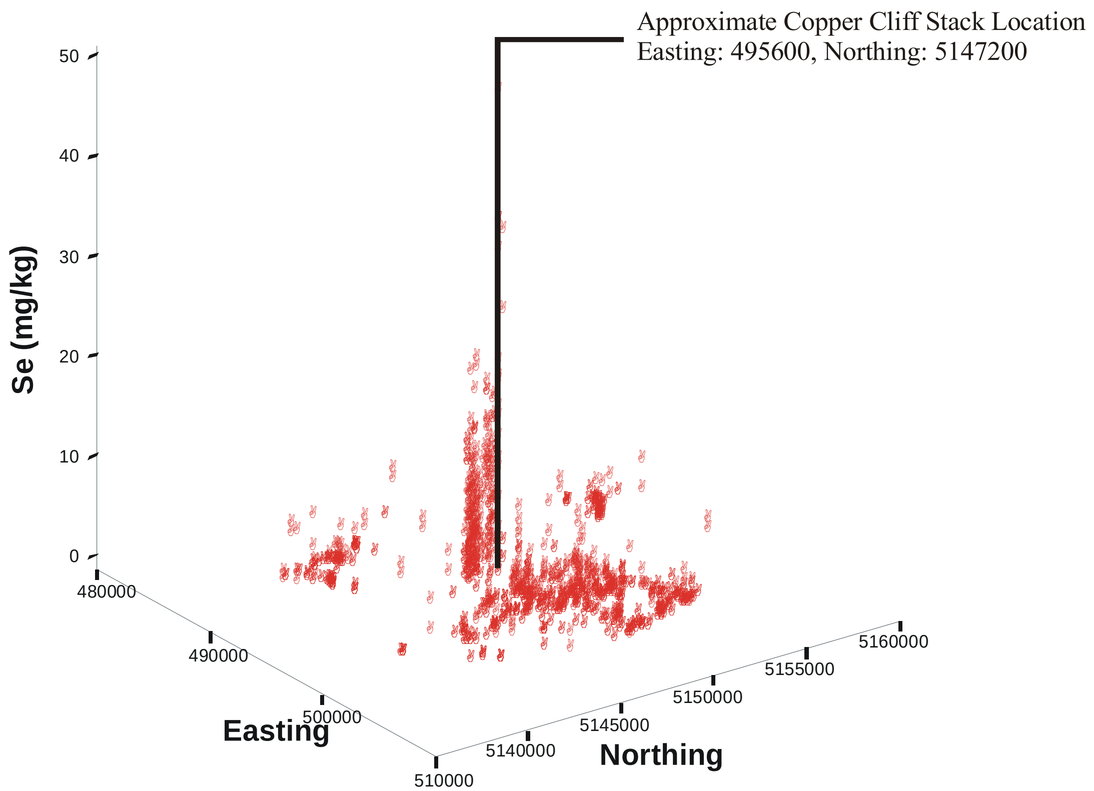

Figure 3-3 Se Concentration vs. Location within a 10 km Radius from the Copper Cliff Smelter

Statistical Analysis

Two regression and correlation analyses were performed. The first analysis included selenium concentration greater than or equal to 10, in relation to distance from the smelter. The second analysis evaluated selenium concentration in relation to other metals. Samples used were contained within a 10km radius from the smelter. The correlation analysis was performed using SPSS v.12.

Determining the spatial link between elevated levels of selenium and the smelter source:

Spearman's rank correlation was used to correlate the levels of selenium and distance from the smelter. For details on the selection of correlation tests, see Appendix B. The test value for a Spearman's rank correlation can range anywhere from -1 to +1. A value of -1 indicates a perfect negative correlation (as one variable increases, the other decreases); a value of +1 indicates a perfect positive correlation (as one variable increases, the other increases); a value of 0 indicates that no correlation exists between the two variables in question. The closer the test value is to -1 or +1 is also an indication of the strength of the correlation between the two variables being tested. A general scale for determining the strength of the correlation is as follows:

Table 3.2 A General Scale* for Classifying the Strength of a Spearman's Rank Correlation

Test statistic (r value)	Strength of correlation
0.9 – 1.0	very high correlation, very dependable relationship
0.7 – 0.9	high correlation, marked relationship
0.4 – 0.7	moderate correlation, substantial relationship
0.2 – 0.4	low correlation, relationship definite but small
< 0.2	slight, almost negligible correlation

* From Senter (1969).

The level of confidence is the probability by which the results are not due to random chance alone. For this analysis, a confidence level of 99% was used. This statistical significance is also reflected in the α value (α = 0.01), which is the probability of the results occurring due to random chance alone.

A one-tailed test was used in this analysis (*i.e.* it was assumed that concentrations of selenium would not decrease closer to the smelters or as levels of the other COCs increased). Therefore the parameters for this test were n = 1536, α = 0.01 (99% level of confidence), using a one-tailed test.

The results of the analysis are summarized in Table 3.3. The full details of the statistical analysis are provided at the end of this report.

Table 3.3 Correlation of Selenium Levels in the 0-5 cm Depth Layer to Distance from the Smelter

α	0.01
Test type	One-tailed
Correlation Coefficient Test Value (r)	-0.601
n	1536

The correlation coefficient for selenium versus distance from the smelter was r = -0.601 with $p<0.01$ which implies a significant, negative correlation between selenium and distance from the smelter. The negative sign in the test value signifies that the correlation is negative in nature (*i.e.* as the distance to the smelter decreases, selenium levels increase).

<u>Determining the correlation between levels of selenium and levels of other established COCs associated with the smelter:</u>

An additional comparison between selenium and other COCs associated with smelter operation was performed based on the premise that if selenium follows a similar distribution pattern as the established COCs already associated with smelter operation, then the results would suggest that the source of selenium was also due to smelter operations.

Spearman's coefficient was used to correlate the levels of selenium and levels of other established COCs associated with the smelter. The same parameters used in the first correlation also apply here (*i.e.* n = 1536, α = 0.01, and one-tailed test). Although a one-tailed test was also used in this correlation, it should be noted that a positive correlation was anticipated this time, as selenium levels were not expected to decrease as levels of the other COCs increase. The results of the analysis are summarized in Table 3.4. Full details of this statistical analysis are provided in Appendix B.

Table 3.4 Correlation of Selenium in the 0-5 cm Depth Layer to Levels of the Established COCs and Non-COCs

α	0.01								
Test type	One-tailed								
n	1536								
	Se	**As**	**Co**	**Cu**	**Ni**	**Pb**	**Be***	**V***	**Al***
Correlation Coefficient Test Values (r)	1.000	0.763	0.762	0.827	0.813	0.769	-0.072	0.168	0.193

*not a COC

There was a significant, positive correlation between levels of selenium and the other COCs (r values >0.7, p<0.01).

For comparison purposes, metals not related to the smelting process were included in the analysis. Beryllium (Be), vanadium (V) and aluminium (Al) were chosen. The correlation between selenium and beryllium, selenium and vanadium, and selenium and aluminium according to Table 3.2 is classified as a slight, almost negligible correlation. These results indicate little or no association between the levels of selenium and metals not associated with smelter operations.

The results of the analysis show that selenium fulfills Criterion 3; the spatial distribution analysis, scatterplots, and correlation analysis all strongly indicate that selenium is related to smelting operations in Copper Cliff.

4.0 SUMMARY

The data suggest that elevated selenium levels present in Sudbury soil samples are a result of smelter activity in Copper Cliff. Selenium meets all three of the criteria necessary to designate it as a Chemical of Concern. It is apparent that:

1. A proportion of selenium samples exceeded MOE Table A criteria;
2. These samples are present in the study area; and,
3. Elevated selenium concentrations in soil samples appear to have originated from smelter operations.

5.0 RECOMMENDED ACTION

It is recommended that selenium be designated as a COC and that it be carried forth for detailed analysis in the Sudbury area risk assessment.

6.0 REFERENCES

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Ripley E.A., R.E. Redman, A.A. Crowder. 1996. Environmental Effects of Mining. St. Lucie Press, Florida.

Senter, R.J., 1969. Analysis of Data. Scott, Foresman and Company, Glenview, Illinois.

APPENDIX A:

PROPERTIES WITH SAMPLES CONTAINING SELENIUM ABOVE MOE TABLE A VALUE (10 MG/KG)

Table A.1 Properties With Samples Containing Selenium Above MOE Table A Value (10 mg/kg)

Area	Easting	Northing	Depth (cm)	Se Concentration (mg/kg)
Copper Cliff	494435	5146567	Soil 0-5	12
Copper Cliff	494421	5146567	Soil 0-5	11
Copper Cliff	494450	5146560	Soil 0-5	11
Copper Cliff	494768	5147381	Soil 0-5	13
Copper Cliff	494748	5147266	Soil 5-10	10
Copper Cliff	494745	5147259	Soil 0-5	12
Copper Cliff	494748	5147266	Soil 0-5	15
Copper Cliff	494748	5147266	Soil 0-5	14
Copper Cliff	494745	5147259	Soil 0-5	10
Copper Cliff	495157	5147539	Soil 0-5	16
Copper Cliff	495157	5147539	Soil 0-5	20
Copper Cliff	495142	5147534	Soil 0-5	17
Copper Cliff	495142	5147534	Soil 0-5	14
Copper Cliff	494450	5146527	Soil 0-5	10
Copper Cliff	494450	5146527	Soil 0-5	10
Copper Cliff	495018	5146962	Soil 0-5	19
Copper Cliff	495018	5146962	Soil 5-10	12
Copper Cliff	495018	5146962	Soil 5-10	11
Copper Cliff	495018	5146962	Soil 0-5	16
Copper Cliff	494812	5147539	Soil 0-5	18
Copper Cliff	494812	5147539	Soil 0-5	16
Copper Cliff	495010	5146444	Soil 10-20	11
Copper Cliff	494547	5146389	Soil 0-5	14
Copper Cliff	494547	5146389	Soil 0-5	13
Copper Cliff	495199	5147382	Soil 0-5	10
Copper Cliff	494992	5147266	Soil 0-5	10
Copper Cliff	494992	5147266	Soil 0-5	12
Copper Cliff	495060	5146953	Soil 0-5	19
Copper Cliff	495060	5146953	Soil 0-5	19
Copper Cliff	495059	5146964	Soil 0-5	20
Copper Cliff	495047	5147286	Soil 10-20	10
Copper Cliff	495076	5147268	Soil 0-5	14
Copper Cliff	495076	5147268	Soil 0-5	18
Copper Cliff	495047	5147286	Soil 0-5	16
Copper Cliff	495047	5147286	Soil 0-5	16
Copper Cliff	495494	5147575	Soil 0-5	27
Copper Cliff	495494	5147575	Soil 0-5	35
Copper Cliff	494868	5146509	Soil 0-5	12
Copper Cliff	494868	5146509	Soil 0-5	15

Table A.1 Properties With Samples Containing Selenium Above MOE Table A Value (10 mg/kg)

Copper Cliff	494870	5146489	Soil 0-5	15
Copper Cliff	494870	5146489	Soil 0-5	15
Copper Cliff	494730	5146237	Soil 5-10	10
Copper Cliff	495008	5147264	Soil 0-5	13
Copper Cliff	494609	5147212	Soil 0-5	15
Copper Cliff	494603	5147203	Soil 0-5	13
Copper Cliff	494609	5147212	Soil 0-5	12
Copper Cliff	494603	5147203	Soil 0-5	11
Copper Cliff	495110	5146442	Soil 0-5	10
Copper Cliff	494645	5147285	Soil 0-5	10
Copper Cliff	494645	5147285	Soil 0-5	10
Copper Cliff	495001	5147049	Soil 0-5	12
Copper Cliff	495001	5147049	Soil 0-5	11
Copper Cliff	494982	5147035	Soil 0-5	13
Copper Cliff	494982	5147035	Soil 0-5	16
Copper Cliff	494613	5146387	Soil 5-10	12
Copper Cliff	494613	5146387	Soil 0-5	16
Copper Cliff	494613	5146387	Soil 5-10	14
Copper Cliff	494613	5146387	Soil 0-5	21
Copper Cliff	494623	5146387	Soil 0-5	15
Copper Cliff	495166	5147410	Soil 0-5	12
Copper Cliff	495195	5147429	Soil 0-5	13
Copper Cliff	495166	5147410	Soil 0-5	13
Copper Cliff	495195	5147429	Soil 0-5	16
Copper Cliff	494518	5146455	Soil 0-5	12
Copper Cliff	494518	5146455	Soil 0-5	12
Copper Cliff	494538	5146250	Soil 5-10	10
Copper Cliff	494538	5146250	Soil 0-5	13
Copper Cliff	494538	5146250	Soil 0-5	14
Copper Cliff	494908	5146436	Soil 0-5	11
Copper Cliff	495322	5147421	Soil 0-5	12
Copper Cliff	495322	5147421	Soil 0-5	11
Copper Cliff	494607	5146346	Soil 0-5	10
Copper Cliff	495094	5147171	Soil 0-5	11
Copper Cliff	495480	5147419	Soil 0-5	36
Copper Cliff	495480	5147419	Soil 0-5	49
Copper Cliff	494367	5146850	Soil 0-5	12
Copper Cliff	494487	5146278	Soil 0-5	13
Copper Cliff	494487	5146278	Soil 0-5	14
Copper Cliff	494486	5146282	Soil 0-5	12
Copper Cliff	494496	5146272	Soil 0-5	12
Copper Cliff	494496	5146272	Soil 0-5	12

Table A.1 Properties With Samples Containing Selenium Above MOE Table A Value (10 mg/kg)

Copper Cliff	495307	5147415	Soil 0-5	13
Copper Cliff	495311	5147399	Soil 0-5	11
Copper Cliff	495311	5147399	Soil 0-5	13
Copper Cliff	495315	5147390	Soil 0-5	13
Copper Cliff	495138	5147281	Soil 0-5	11
Copper Cliff	495138	5147281	Soil 0-5	12
Copper Cliff	495271	5146166	Soil 0-5	11
Copper Cliff	495271	5146166	Soil 0-5	10
Copper Cliff	495383	5147398	Soil 5-10	10
Copper Cliff	495383	5147398	Soil 0-5	36
Copper Cliff	495383	5147398	Soil 0-5	33
Copper Cliff	495115	5146146	Soil 0-5	10
Copper Cliff	494758	5147252	Soil 0-5	10
Copper Cliff	494793	5146897	Soil 0-5	12
Copper Cliff	494787	5146653	Soil 0-5	10
Copper Cliff	494414	5146842	Soil 5-10	13
Copper Cliff	494414	5146842	Soil 0-5	21
Copper Cliff	494414	5146842	Soil 0-5	22
Copper Cliff	495445	5147351	Soil 0-5	20
Copper Cliff	495445	5147351	Soil 0-5	22
Copper Cliff	497423	5145275	Soil 0-5	12
Copper Cliff	497423	5145275	Soil 0-5	13
Copper Cliff	494571	5146598	Soil 0-5	15
Copper Cliff	494571	5146598	Soil 0-5	19
Not Listed*	496284	5132001	Soil 0-5	10
Sudbury (East)	506292	5146262	Soil 0-5	11
Sudbury (South)	497423	5145275	Soil 0-5	12
Sudbury (South)	497423	5145275	Soil 0-5	13
Sudbury (Core)	500367	5147088	Soil 0-5	11
Falconbridge	514420	5156546	Soil 0-5	10
Falconbridge	514632	5158085	Soil 0-5	12
Falconbridge	514641	5158069	Soil 5-10	11
Falconbridge	514641	5158069	Soil 0-5	10
Falconbridge	514641	5158069	Soil 0-5	10

* at the current time, no area information available for this property.

APPENDIX B:

STATISTICAL ANALYSIS

Correlation Analysis

A common statistical method for establishing relationships such as those in this study is through correlation analysis. Correlation analysis involves comparing a test value, determined from an equation based on the number of samples, and the two variables whose relationship is in question (in this case selenium concentration and distance) to critical values in published statistical tables. This comparison is often made by a statistical program. If the test value is greater than the critical value for a certain sample size, then it can be concluded that a correlation exists between the two variables in question. The test value is then compared to the scale provided below in Table B.1.

Table B.1 A General Scale* for Classifying the Strength of a Spearman's Rank Correlation

Test statistic (r value)	Strength of correlation
0.9 – 1.0	very high correlation, very dependable relationship
0.7 – 0.9	high correlation, marked relationship
0.4 – 0.7	moderate correlation, substantial relationship
0.2 – 0.4	low correlation, relationship definite but small
< 0.2	slight, almost negligible correlation

* From Senter (1969).

The significance of the correlation is determined by the p value or probability (as calculated by SPSS v.12), indicating the chance of the correlation results being due to random chance alone.

Correlation Method Selection

Two common methods of correlation analysis are Pearson's correlation and Spearman's rank correlation. Spearman's correlation analysis is a useful tool for finding relationships with non-parametric data. Spearman's rank correlation (as the name implies) must have the data presented by rank, where as Pearson's correlation analysis allows one to use the raw data. The ability of Spearman's rank correlation to determine the relationship between two variables without the assumption of linearity or normalized distributions made it more desirable for the analysis.

Correlations Performed
Spearman's rank correlation was calculated to determine:

1. If there is a spatial link between the concentration level of selenium and the distance from the smelter (*i.e.* the closer one gets to the smelter, the higher the concentration level of selenium).

2. If there is a similar distribution pattern in elevated levels of selenium as that of other established COCs associated with smelter operation, indicating that elevated selenium levels originate from smelter operations.

To perform Spearman's rank correlation test, the data for selenium, distance from the smelter, and data for the COCs corresponding to the same sites as the selenium data was ranked using SPSS and then the correlation coefficient determined. The tests were one-tailed and used a significance value of $\alpha = 0.01$. Beryllium, vanadium and aluminium were used in the second analysis as controls, as these metals are not associated with smelter operations and should therefore have no significant relationship with selenium.

The total number of samples (n) was 1536, consisting of all samples at the 0-5 cm depth out to a radius of 10 000 m from the Copper Cliff smelter. Samples with Se < 10 mg/kg were included to produce a better correlation coefficient.

Complete results of the statistical analysis are found in Table B.2.

Correlation analysis 1: Selenium levels and distance from the smelter.

Hypotheses

Null Hypothesis H_{o1}: There is no correlation between selenium and distance from the Copper Cliff smelter.

Alternate Hypothesis H_{a1}: There is a correlation between selenium levels and distance from the Copper Cliff smelter.

Results

The correlation coefficient associated with distance and selenium was -0.601, with $p<0.01$ (indicated by the "Sig. (1-tailed)" value) which implies a significant, negative correlation.

Complete results of the statistical analysis are found in Table B.2.

Correlation analysis 2: Selenium levels and other established COC levels.

Hypotheses

Null Hypothesis H_{o2}: There is no correlation between the concentration level of selenium in the soil and the concentration level of other established COCs associated with smelter operation.

Alternate Hypothesis H_{a2}: There is a correlation between the concentration level of selenium in the soil and the level of other established COCs associated with smelter operation.

Results

The correlation coefficients associated with Se and As, Co, Cu, Ni, Pb were all >0.7, with $p<0.01$ which implies a significant, positive correlation between Selenium and the other COCs associated with smelter operation.

The correlation coefficient for V was 0.168, with $p<0.01$ indicating that there was a negligible correlation between Se and V. The value of the correlation coefficient for Be was -0.072, with $p<0.01$, indicating that there was negligible correlation between Se and Be. The correlation coefficient for Al was 0.193, with $p<0.01$ indicating that there was negligible correlation between Se and Al.

Complete results of the statistical analysis are found in Table B.2.

Summary

The test for correlation using Spearman's correlation analysis suggests two things:

1. That there is a relationship between selenium and distance from the Copper Cliff smelter- the closer one gets to the smelter, the higher the levels of Se found in the soil.

2. That selenium follows the same trend as the other already established COCs, which increase in concentration level as the distance to the smelter decreases, therefore indicating a link between the presence of elevated levels of selenium and smelter operation.

Table B.2 Spearman's Correlation Coefficients for Se, Distance, and other COCs

		Se	As	Co	Cu	Ni	Pb	Be	V	Al	Distance
Se	**Correlation Coefficient**	**1.000**	**.763**	**.762**	**.827**	**.813**	**.769**	**-.072**	**.168**	**.193**	**-.601**
	Sig. (1-tailed)	**.**	**.000**	**.000**	**.000**	**.000**	**.000**	**.002**	**.000**	**.000**	**.000**
	n	**1536**	**1536**	**1536**	**1536**	**1536**	**1536**	**1536**	**1536**	**1536**	**1536**
As	Correlation Coefficient	**.763**	1.000	.773	.818	.822	.803	.003	.241	.157	-.424
	Sig. (1-tailed)	**.000**	.	.000	.000	.000	.000	.453	.000	.000	.000
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536
Co	Correlation Coefficient	**.762**	.773	1.000	.873	.872	.789	-.002	.350	.159	-.534
	Sig. (1-tailed)	**.000**	.000	.	.000	.000	.000	.466	.000	.000	.000
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536
Cu	Correlation Coefficient	**.827**	.818	.873	1.000	.982	.923	-.018	.202	.185	-.624
	Sig. (1-tailed)	**.000**	.000	.000	.	.000	.000	.237	.000	.000	.000
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536
Ni	Correlation Coefficient	**.813**	.822	.872	.982	1.000	.929	-.013	.194	.179	-.576
	Sig. (1-tailed)	**.000**	.000	.000	.000	.	.000	.299	.000	.000	.000
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536
Pb	Correlation Coefficient	**.769**	.803	.789	.923	.929	1.000	.013	.179	.161	-.475
	Sig. (1-tailed)	**.000**	.000	.000	.000	.000	.	.308	.000	.000	.000
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536
Be	Correlation Coefficient	**-.072**	.003	-.002	-.018	-.013	.013	1.000	.110	.008	.081
	Sig. (1-tailed)	**.002**	.453	.466	.237	.299	.308	.	.000	.000	.001
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536
V	Correlation Coefficient	**.168**	.241	.350	.202	.194	.179	.110	1.000	.026	-.058
	Sig. (1-tailed)	**.000**	.000	.000	.000	.000	.000	.000	.	.000	.011
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536
Distance	Correlation Coefficient	**-.601**	-.424	-.534	-.624	-.576	-.475	.081	-.058	1.000	1.000
	Sig. (1-tailed)	**.000**	.000	.000	.000	.000	.000	.001	.011	.	.
	n	**1536**	1536	1536	1536	1536	1536	1536	1536	1536	1536

* A significant value of 0.000 is directly from SPSS output and indicates that the p value was much lower than the alpha of 0.05.