



CADMIUM AS A CHEMICAL OF CONCERN

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EXECUTIVE SUMMARY

The Technical Committee for the Sudbury Soils Study established three criteria for the selection of Chemicals of Concern (COCs). These criteria must be satisfied in order to identify a substance as a COC:

1. Parameter must be above or equal to the Table A or Table B criteria published in the Ontario Ministry of the Environment (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;
2. Parameter must be present across the study area; and,
3. Parameter must scientifically show origin from smelter operations.

In 2003, the MOE reported to the Technical Committee that Table A and B soil quality criteria (e.g. Criterion 1 for evaluating a COC) only apply to soils with a pH range of 5.0 to 9.0. For soils with a pH outside this range, Table F criteria, or background levels, should be used as an alternative screening tool.

Preliminary soil data screening revealed that soil pH was below 5.0 in many of the regional or rural soil samples collected by Laurentian University. In addition, cadmium exceeded Table F (1.0 µg/g) in some urban Sudbury soils. Therefore, the SARA Group was requested to undertake a more detailed review of cadmium in Sudbury soils and other environmental media.

For the original 2001 soil survey, pH values were only available for 1 in 10 (10%) of the soil samples. However, pH was subsequently measured for all soil samples collected in the Regional Soil sampling program conducted by Laurentian University. This complete soil pH dataset was used as part of this evaluation.

In addition to soil cadmium concentrations, this review also evaluated the potential bioaccumulation of cadmium from soil to wildlife dietary items. This information was obtained from samples collected in the Sudbury region and from published literature.

Although the issue of cadmium in soil is primarily considered an Ecological Risk Assessment (ERA) matter, cadmium levels in other Sudbury-specific media related to the human health risk assessment (HHRA) were also reviewed as part of the evaluation. These databases include: bovine livestock tissue (liver, kidney and muscle), residential drinking water, and air filter samples.

The results of this evaluation of cadmium revealed:

1. Concentrations of cadmium in surface soil samples from across the Sudbury area did not exceed the MOE Table A (residential/parkland) criterion for cadmium.
2. Of 365 Regional Soil surface (0 - 5 cm) samples, 55 (15.1%) had pH less than 5 and cadmium concentrations that exceeded background (Table F). Most of the samples (85%) with cadmium levels above background concentrations (1.0 mg/kg) exceeded this value only marginally. Table F is not risk based. Therefore, it is appropriate to apply an alternative screening criterion.
3. Ecological Soil Screening Levels (Eco-SSL) (from US EPA) values are risk based and were used to screen the cadmium soil values. The Eco-SSL values for cadmium range from 0.38 µg/g for mammalian wildlife to 140 µg/g for soil invertebrates. None of the soil samples collected in the Sudbury area had cadmium levels which exceed either the plant or soil invertebrate Eco-SSL values.
4. The wildlife values (avian and mammalian) are at or below the background concentration for cadmium (MOE Table F: 1 µg/g). Therefore, they are not applicable to this situation.
5. A slight decrease in the level of conservatism in the Eco-SSL model by applying LOAELs rather than NOAELs resulted in acceptable soil cadmium concentrations greater than 2 µg/g. Only three samples with pH less than 5 had cadmium values which were marginally above 2 µg/g. The assumptions used in the alternate screening levels calculated remain conservative and show that the level of cadmium in the soil samples present little risk to ecological receptors.
6. By plotting and visually assessing the occurrence of soil samples with pH < 5.0 and cadmium > 1.0 µg/g, the samples appeared widespread throughout the Greater Sudbury area, with no obvious relationship to the smelter locations;
7. Statistical analysis revealed cadmium levels in soil were positively correlated to concentrations of copper and nickel, compounds known to be related to the smelter and were not correlated to vanadium, a compound not related to smelter operations;
8. Cadmium concentrations in the soil, irrespective of soil pH, tend to be higher in close proximity to the smelters. However, being emitted from the smelters is not sufficient reason, on its own, to merit an element becoming a COC.

9. Cadmium concentrations in wildlife dietary items collected for the ERA were not elevated. Cadmium did not display bioaccumulation from soils into grass then into grasshoppers.
10. Cadmium was measured in over 1,300 air filter samples collected in the Greater Sudbury area. The concentration of cadmium in air was much lower than the applicable provincial air quality criterion.
11. Cadmium was measured in over 100 samples of drinking water collected from private residential wells. The concentration of cadmium was much lower than the corresponding provincial drinking water standard.

In summary:

- Cadmium did meet the three criteria for the selection of a COC (with the application of Table F for low pH soils);
- Soil pH was less than 5.0 for urban and residential properties, and soil cadmium was greater than Table A;
- Cadmium levels were not elevated in samples of air or drinking water;

Therefore, cadmium in soil is not considered a COC for the Human Health Risk Assessment (HRHA).

A conservative comparison of soil cadmium levels with ecological soil screening levels (Eco-SSLs) indicated that a very small (3) number of Sudbury soil samples exceeded the Eco-SSL values.

Conclusion

Following this evaluation of cadmium in soil collected in Sudbury, there appears no justification to identify cadmium as a Chemical of Concern for the ecological risk assessment or human health risk assessment. Therefore, the SARA Group recommends to the Technical Committee that cadmium not be included as a Chemical of Concern in the Sudbury Soils Study.

Postscript

This report and the above recommendation were originally submitted to the Technical Committee (TC) for the Sudbury Soils Study in May 2005. While the majority of the TC accepted the SARA Group recommendation, the Ontario Ministry of the Environment (MOE) requested that cadmium be considered a COC for the terrestrial Ecological Risk Assessment (ERA).

Although this version of the report has been slightly modified to reflect editorial comments by the TC reviewers, the original conclusion of the SARA Group has been left unaltered. Notwithstanding our conclusion and recommendation, cadmium will be considered a COC for the ERA, and will be presented as such in Volume III of this report series (ERA).

**SUDBURY AREA RISK ASSESSMENT
CADMIUM AS A CHEMICAL OF CONCERN**

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1.0 INTRODUCTION

In recent years, several studies have shown there are areas in Sudbury with elevated metal levels in the soil. These areas are generally close to the historic smelting sites of Coniston, Falconbridge and Copper Cliff. Although these metals do occur naturally in all soils, the studies indicate that the higher amounts in surface soil (top 5 cm) are the result of local mining, smelting and refining operations. In 2001, the Ontario Ministry of the Environment (MOE) reported that the concentrations of nickel, cobalt, copper and arsenic exceeded the generic MOE soil quality criteria. Under Ontario legislation, this triggers the need for more detailed study. Therefore, the MOE made two recommendations: 1) that a more detailed soil study be undertaken to fill data gaps; and, 2) that a human health (HHRA) and ecological risk assessment (ERA) be undertaken.

The mining companies (Inco Ltd. and Falconbridge Ltd.) voluntarily accepted the recommendations and partnered with four other major stakeholders in Sudbury to establish what is commonly referred to as “The Sudbury Soils Study”. A comprehensive soil sampling and analysis program was undertaken in 2001 by the MOE and the mining companies. Approximately 9,000 soil samples were collected from urban and remote areas and analyzed for 20 elements. These data form the basis for the study. Early in 2003, a consortium of consulting firms working together as the SARA (Sudbury Area Risk Assessment) Group was retained to undertake the risk assessment portion of the study.

As part of the problem formulation stage of the Sudbury Soils Study, the SARA Group reviewed available information to determine if additional substances should be considered as Chemicals of Concern (COCs). An initial set of COCs was established by the Technical Committee (TC) based on existing sampling data and the MOE 2001 report entitled *Metals in Soil and Vegetation in the Sudbury Area (Survey 2000 and Additional Historic Data)*. The COCs identified by the Technical Committee were nickel (Ni), copper (Cu), cobalt (Co), and arsenic (As). Later, lead (Pb) and selenium (Se) were identified by the SARA Group as COCs.

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

1. Parameter must be above or equal to the Table A or Table B criteria 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;
2. Parameter must be present across the study area; and,

3. Parameter must scientifically show origin from smelter operations.

In 2003, the MOE reported to the Technical Committee that Table A and B soil quality criteria (e.g. Criterion 1 for evaluating a COC) only applied to soils with a pH range of 5.0 to 9.0. For soils with a pH outside this range, Table F criteria, or background levels, should be used as an alternative screening tool.

Preliminary soil data screening exercises conducted by the SARA Group identified that cadmium exceeded Table F (1.0 µg/g) in Sudbury soils. Therefore, the SARA Group was requested to undertake a more detailed review of cadmium in Sudbury soils and other environmental media.

A review of soil pH revealed that the pH of the residential soils within the urban area of Sudbury was above pH 5.0. This likely can be attributed to homeowners amending residential soils with lime, organic matter and fertilizers. However, soils from the regional survey conducted by Laurentian University often had a pH < 5.0 in areas outside the urban areas. Therefore, it was agreed: a) to conduct the more detailed review of cadmium on regional soil survey data only; and, b) that the matter was related to the ERA and not the HHRA. Although the matter was related to ERA, data specific to the HHRA were also reviewed, and are discussed herein, to provide additional support to the analysis.

The objective of this document is to review cadmium concentrations in Sudbury soils, biological material, air and water. This review will determine whether the concentration of cadmium in soil collected in Sudbury conforms to the three criteria outlined. A review of the cadmium concentrations present in water, air, animal, insect, plant and produce tissue was also conducted and compared to existing literature. This review provides the basis for evaluating cadmium as a potential Chemical of Concern.

2.0 EVALUATION APPROACH

2.1 Criteria

In order to determine whether a chemical should be designated as a COC, it must meet the three criteria previously outlined. The approach used to assess whether cadmium meets these criteria is summarized below and illustrated in Figure 2-1:

Criterion 1: Cadmium concentrations must be equal to or above MOE Table A criterion

The Table A (residential/parkland) criterion for cadmium from the *Guideline for Use at Contaminated Sites in Ontario, (1997)* is 12 µg/g. The Table B criterion (also 12 µg/g) is applied in areas where the land use specifies non-potable groundwater which is not the case in Sudbury. The Table A and B criteria for cadmium are the same, therefore only Table A will be referred to for the remainder of the report. Table A can only be used for comparative purposes in soils that have a pH value that is above 5. The 2001 urban soil database contains pH values for only 1 in every 10 soil samples collected. For the remote samples, all samples have pH data, and many of these soil samples have a pH below 5. When the metal levels in the soil cannot be compared to Table A due to low pH, they should be compared to Table F (Ontario background, 1 µg/g) criteria. Table F is not a risk-based criterion, so the SARA Group has provided a rationale and approach to evaluating cadmium concentrations in soil samples using the latest United States Environmental Protection Agency (US EPA) ecologically-based soil screening levels (the Eco-SSL).

Criterion 2: Cadmium must be present across the study area.

All soil samples have Global Positioning System (GPS) coordinates associated with the sampling area where they were collected. The locations of surface soil samples were plotted using ArcGIS 9. This mapping was used to determine whether samples with pH below 5 and cadmium above Table F were distributed across the study area.

Criterion 3: Parameter must scientifically show origin from smelter operations.

To evaluate Criterion 3, various statistical analyses were performed to determine:

1. If there is a relationship between cadmium levels and distance from smelter operations; and,
2. If there is a correlation between cadmium concentrations and concentration of other COCs already determined to be linked to smelter operations.

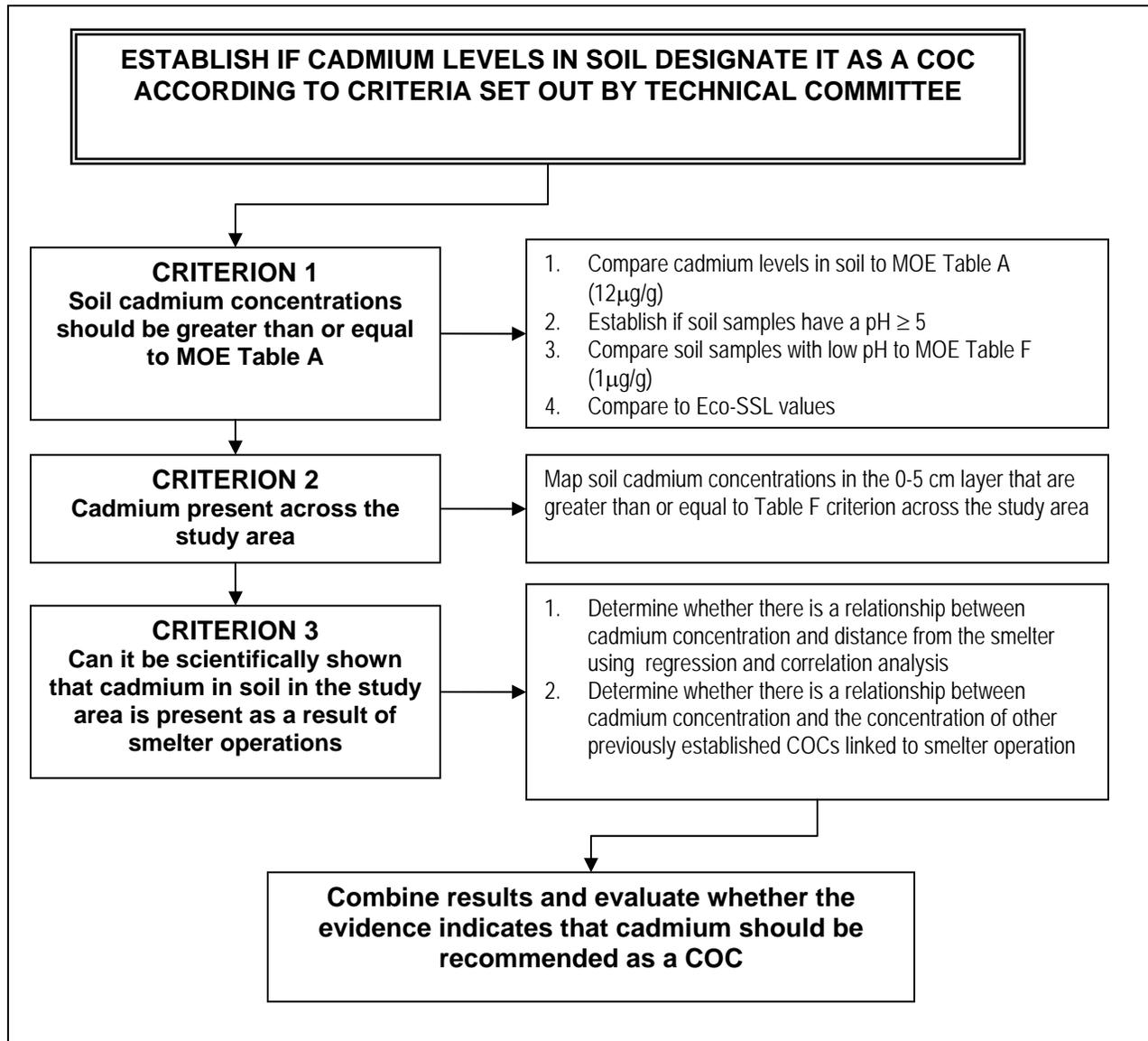


Figure 2-1 Evaluation Approach

2.2 Soil Samples Used in Evaluation

Three separate soil surveys were conducted in 2001 using similar methodologies. The data analyses are provided in three reports, covering urban soils (collected by the MOE), regional soils (collected by researchers from MIRARCO, Laurentian University), and Town of Falconbridge soils (collected by Golder Associates Ltd.). These data have been combined in an integrated database, referred to as the 'Combined Soils Database'.

During the problem formulation stage of the HHRA and ERA, various field studies were undertaken to fill recognized data gaps. Soil results from these additional studies were also considered in this review. All programs followed the same sampling protocol, including 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 sampling methods used in each study are provided in separate SARA Group data reports. In the Combined Soils Database, pH values are available for only 1 in 10 samples. The other surveys provide a pH value for each sample collected. Recently, complete soil pH data for the regional soil samples was obtained (February, 2005) by the SARA Group from researchers at Laurentian University.

In summary, surface soil samples from the following studies were evaluated in this review:

- 2001 Combined Soils Database;
- 2003 Wildlife Dietary Item Survey Database; and,
- 2004 ERA Field Collection Program Database.

2.3 Additional Information Used in the Evaluation

Additional evaluation was conducted to assess potential bioaccumulation from soil into other media as part of the ERA. This included a review of cadmium levels in wildlife dietary items (grass roots and shoots, and grasshoppers). Although the issue of cadmium in soil is primarily considered an ERA matter, cadmium levels in other Sudbury-specific media, collected as part of the HHRA, were reviewed as part of this evaluation. These databases include bovine livestock tissue (liver, kidney and muscle), residential drinking water, and particulate air samples.

3.0 EVALUATION OF COC CRITERIA

3.1 Criterion 1 - Comparison of Cadmium levels with various Regulatory Criteria

In the following sections, the cadmium levels in the various soil samples are compared to MOE Criteria Table A and Table F and to the US EPA Eco-SSL (ecologically-based soil screening level) values.

Comparison to Table A

The Table A soil criterion is effects-based and was derived to protect both human health and the natural environment, whichever is potentially affected at the lowest observed effect concentration (LOEC). The Table A criterion for cadmium is listed as an ecotoxicology based criterion; it was not developed by the MOE phytotoxicology group, but instead was derived from the Netherlands C criterion.

The concentrations of cadmium in surface soil samples (n = 1,993) were compared to the Table A (residential/parkland) criterion, 12 µg/g (Table 3.1). No samples exceeded the Table A (residential/parkland) criterion for cadmium. The highest measured cadmium concentration was 6.15 µg/g.

Table 3.1 Cadmium levels in soil compared to MOE Table A (12µg/g)

Database		Sample size (n) ^{bc}	Range of Cd Concentration (µg/g)	# above Table A ^a	% above Table A
Combined Soils Database (2001)	Urban Soil	1534	< DL - 6.15	0	0.00%
	Regional Soil	365	< DL - 3.2	0	0.00%
	Falconbridge Soil	33	< DL - 2.75	0	0.00%
ERA Field Collection (2004)	Homogenized Soil	22	< DL - 1.1	0	0.00%
	Core Samples	22	< DL - 1.3	0	0.00%
Wildlife Dietary Item Soil (2003)		17	0.17 - 0.68	0	0.00%
Total for all Soil Databases		1993	< DL - 6.15	0	0.00%

^aTable A Residential/Parkland, (MOE, 1997)

^bIf duplicate samples were taken, the mean of the two samples was used

^cfrom surface soil only for all databases

DL = 0.8 µg/g

The MOE soil quality guidelines (Table A) contains a disclaimer stating “inorganics in this table apply only where surface soil pH is 5.0 to 9.0”. Many of the soil samples collected, particularly in rural areas, have pH below 5. MOE (1997) states that when a sample cannot be compared to Table A values (for instance, because pH is too low), it should instead be compared to Table F, Ontario background values.

Comparison to Table F

Soil pH values were available for 688 of the 1993 samples considered in this review (Table 3.2). Of those samples, 418 or 60.7% had pH < 5.0. It should be noted, however, that the majority of soils with low pH were found in rural (regional) or natural sites. Only 5 (2%) of 229 samples from the urban residential sites had pH < 5.0. Therefore, low soil pH was considered an issue related to the ecological risk assessment and not the human health risk assessment.

Table 3.2 Cadmium levels in soil^a compared to MOE Table F^b value (1 µg/g)

Database		Total sample size	Above DL ^c	Maximum Concentration	# Samples with pH	# with pH < 5	# above Table F	# with pH < 5 and Cd above Table F
		n		µg/g	n	n		
Combined Soils Database (2001)	Urban Soil	1534	362	6.15	229	5	253	1
	Regional Soil	365	135	3.2	365	347	59	55
	Falconbridge Soil	33	17	2.8	33	7	12	1
ERA Field Collection (2004)	Homogenized Soil	22	20	1.1	22	21	1	1
	Core Samples	22	22	1.26	22	21	2	2
Wildlife Dietary Item Soil (2003)		17	17	0.68	17	17	0	0
Total for all Soil Databases		1993	573	6.15 ^d	688	418	327	60 (8.72% ^e)

^aSurface soil (0 - 5 cm)

^bTable F Background (MOE, 1997)

^cDL = detection limit = 0.8 µg/g

^dTotal value for Maximum Concentration represents the highest value for the dataset

^ePercentage of total number of samples with pH results that contain a pH < 5 and Cd above Table F

Of the 688 samples for which pH values were measured, only 60 samples (8.7%) had both a pH < 5 and a cadmium concentration greater than 1.0 µg/g (Table F). Of these 60 samples only three samples had cadmium concentration > 2 µg/g, five samples had cadmium concentrations between 1.55 and 2 µg/g, and the remaining 52 samples had cadmium concentrations between 1 and 1.54 µg/g. Therefore, most (87%) of samples with cadmium concentrations above background levels, actually exceeded background only marginally and had cadmium concentrations which were less than or equal to 1.54 µg/g.

This analysis showed that cadmium concentrations in soil samples were generally low but there were some samples with concentrations marginally above MOE Table F background concentrations. The Table

F values were developed from an Ontario-wide sampling program at rural and urban parks unaffected by local point sources of pollution (MOE, 1997). These values are not based on the risk that these concentrations might pose to human or ecological receptors. When conducting a risk assessment, the selection of Chemicals of Concern should be based upon their potential risk. Therefore, another level of screening was undertaken using the latest risk-based criteria applicable to soils with a pH < 5, as developed by the US EPA.

Cadmium Eco-SSLs

Many jurisdictions around the world are developing screening or guideline values for concentrations of chemicals in soil which are protective of terrestrial invertebrates, plants and wildlife. These Soil Protection Values (SPVs), variously known as "critical loads", "precautionary soil values", "soil criteria", "ecological soil screening levels", or "soil quality objectives", are generally based on total recoverable concentrations of chemicals measured from bulk soils. At or below the SPV, there is no reason to believe that adverse effects will occur to ecological receptors. At concentrations above the SPV, there may or may not be adverse effects, depending upon local conditions. One example of SPVs is the Ecological Soil Screening Levels (Eco-SSLs), recently developed by the US Environmental Protection Agency (US EPA).

Eco-SSLs are screening values that can routinely be used to identify COCs in soils requiring further evaluation in an ERA. Eco-SSLs apply to soils where the pH is greater than or equal to 4.0 and less than or equal to 8.5. The Eco-SSL represents the concentration of a chemical in soil which is protective of ecological receptors that come into contact with soil or ingest biota that live in or on soil (US EPA, 2003). Eco-SSLs for wildlife are derived to be conservative and are intended to be applied at the screening stage of an ecological risk assessment (US EPA, 2003). For cadmium, Eco-SSL values have been derived for all receptor groups, as summarized in Table 3.3. The values in Table 3.3 were obtained by the SARA Group from the USEPA webpage. The Eco-SSL values for cadmium range from 0.38 µg/g for the most sensitive mammalian wildlife to 140 µg/g for soil invertebrates.

Table 3.3 Eco-SSL values for Cadmium

Category		Eco-SSL ($\mu\text{g/g}$) d.w. in soil
Plants		32
Soil Invertebrates		140
Wildlife (Avian)	Herbivore	20
	Carnivore	180
	Insectivore	1.0
Wildlife (Mammalian)	Herbivore	12
	Carnivore	120
	Insectivore	0.38

Almost all soil samples collected from the regional areas had a $\text{pH} > 4$ and can be compared to these values. None of the soil samples collected in the Sudbury area contained cadmium at levels exceeding either the plant or soil invertebrate Eco-SSL values, or the mammalian or avian herbivore or carnivore Eco-SSL values.

The insectivorous wildlife values are both at or below the Ontario background concentration for cadmium ($1 \mu\text{g/g}$) provided in Table F (MOE, 1997). The wildlife cadmium Eco-SSL values were derived following a comprehensive literature search that identified 1,953 papers with possible toxicity data for either avian or mammalian species. Of these papers, 1,766 were rejected for use due to unacceptable quality or documentation. Of the remaining studies, 35 papers contained data for avian test species and 145 contained data for mammalian test species which could be used in the derivation of an Eco-SSL (US EPA, 2003).

The presumptions made in the derivation of the wildlife Eco-SSL values were examined by the SARA Group to determine their level of conservatism. A summary of this investigation is provided in the following sections.

Wildlife Eco-SSL: Avian

There were 35 selected studies with adequate data for the derivation of an Eco-SSL. The actual values used are provided in Appendix A (Table A1). The endpoints examined were reproduction, growth and survival. The studies reported no observed adverse effect levels (NOAELs) and lowest observed adverse effect levels (LOAELs). The allocations of these values within the selected studies were: reproduction endpoint, 6 NOAELs and 9 LOAELs; and growth endpoints, 14 NOAELs and 18 LOAELs.

To derive the Eco-SSL value the geometric mean of NOAELs from these studies was calculated as 1.47 mg Cd/kg/day. This value was lower than the lowest bounded LOAEL for reproduction, growth, or survival of 2.37 mg/kg/day. The term “bounded” refers to studies where both a NOAEL and a LOAEL were derived in the same study. The NOAEL (1.47 mg Cd/kg bw/day) was used to back-calculate a soil concentration for an avian herbivore (dove), avian ground insectivore (woodcock), and an avian carnivore (hawk). The resulting Eco-SSLs for these three groups were: herbivore, 20 mg Cd/kg dw soil; insectivore, 1.0 mg Cd/kg dw soil; and, carnivore, 180 mg Cd/kg dw soil.

The cadmium concentrations in the soil collected in Sudbury do not exceed the Eco-SSLs for avian herbivores or carnivores. The value for the avian insectivores is equivalent to background cadmium concentrations and warranted further investigation.

It is common in an ERA to use a LOAEL as the toxicity reference value (TRV) instead of a NOAEL (except when evaluating threatened or endangered species). The database used in the derivation of the Eco-SSL was reviewed to consider LOAELs in the calculations rather than the more conservative NOAELs. Six cases were calculated, three using earthworms as the food source and three using arthropods. Earthworms, while present in the Greater Sudbury area, are not abundant in Sudbury. Arthropods likely represent the predominant food source for avian insectivores in the Sudbury region. The cases presented are:

Case 1: The base case of the Eco-SSL, provided for comparative purposes. Uses earthworm as the food source and NOEL in the calculation;

Case 2: Derived using the lowest bounded LOAEL and earthworms as the food source but maintains all other assumptions used in the calculation of the Eco-SSL;

Case 3: Derived using the geometric mean of LOAELs after four highest values were removed and earthworms as the food source but maintains all other Eco-SSL assumptions;

Case 4: Modified base case using NOEL and arthropods as the food source;

Case 5: Derived using the lowest bounded LOAEL and arthropods as the food source; and,

Case 6: Derived using the geometric mean of LOAELs, after 4 high values were removed and arthropods as the food source.

The model used to estimate earthworm concentrations, based on soil concentrations, was taken from Sample et al. (1998). Sample used a similar method to derive uptake models for arthropods (Sample and Arenal, 2001). The cadmium concentration ($\mu\text{g/g}$) in soil for each case where the ecological risk is equal to or greater than 1, is presented in Table 3.4, along with the corresponding toxicity reference values (TRV).

Table 3.4 Estimation of risk-based soil screening levels: avian insectivores

	TRV (mg/kg/d)	Cadmium Soil Concentration ($\mu\text{g/g}$)
Case 1: Eco-SSL using NOAEL and earthworm model	1.47	1
Case 2: Lowest bounded LOAEL with earthworm model	2.37	2
Case 3: Geometric mean of LOAELs with earthworm model	3.05	2.7
Case 4: Eco-SSL using NOAEL and arthropod model	1.47	14
Case 5: Lowest bounded LOAEL and arthropod model	2.37	28
Case 6: Geometric mean of LOAELs and arthropod model	3.05	65

The soil concentrations in Table 3.4 show that a slight decrease in the level of conservatism in the Eco-SSL model using LOAELs in place of NOAELs results in acceptable soil cadmium concentrations which are greater than $2 \mu\text{g/g}$. Using arthropods as the food source in the model raises the acceptable cadmium concentrations in soil to a minimum of $14 \mu\text{g/g}$, a level which exceeds all the soil samples collected in Sudbury (maximum concentration found is $6.15 \mu\text{g/g}$). Of the soil samples collected during the regional sampling program in Sudbury, there are only three samples which have $\text{pH} < 5$ and cadmium $> 2 \mu\text{g/g}$. This means that 52 of 55 samples from the Regional Survey identified as having $\text{pH} < 5$ had cadmium levels between 1- $2 \mu\text{g/g}$. The remaining three cadmium values are only marginally above $2 \mu\text{g/g}$ (2.25 , 2.8 and $3.2 \mu\text{g/g}$). The assumptions used in calculating the alternate screening levels remain conservative. This is because the Eco-SSL model incorporates several conservative assumptions into its design, such as: 100% bioavailability of cadmium in the soil to the organism; and 100% of the organism's diet is comprised of earthworms. This differs from the diet of most avian insectivores which includes arthropods, insects and some plant matter.

Wildlife Eco-SSL: Mammalian

There were 145 selected studies which contained adequate data for the derivation of an Eco-SSL. The actual values used are provided in Appendix A (Table A2). The endpoints examined were reproduction, growth and survival. The studies reported NOAELs and/or LOAELs values, with 11 bounded LOAELs with reproduction as an endpoint, and 12 bounded LOAELs with growth as an endpoint. Three of the reproduction LOAELs and four of the growth LOAELs were much greater than the other data points (doses greater than 40 mg/kg/d), and were, therefore, removed from the analysis in order to remain conservative.

The process used in the derivation of a mammalian Eco-SSL was as follows. The geometric mean of NOAELs was calculated as 1.86 mg Cd/kg/day. This value was greater than the lowest bounded LOAEL, and therefore the TRV for Eco-SSL derivation was selected as the highest bounded NOAEL that was less than the lowest bounded LOAEL for reproduction, growth, or survival of 0.91mg/kg/day. Therefore, the NOAEL of 0.77 mg/kg bw/day was used as the TRV to back-calculate a soil concentration for a mammalian herbivore (vole), mammalian ground insectivore (shrew) and mammalian carnivore (weasel). The resulting Eco-SSLs for these three groups were: herbivore 12 mg Cd/kg dw soil, insectivore 0.38 mg Cd/kg dw soil, and carnivore 120 mg Cd/kg dw soil.

The cadmium concentrations in the soil collected in Sudbury do not exceed the Eco-SSLs for mammalian herbivores or carnivores. The value for the mammalian insectivores is less than the Ontario background cadmium concentration and warranted further investigation.

It is common in ERA to use a LOAEL as the TRV instead of a NOAEL (except when evaluating threatened or endangered species). Therefore, the database used in the derivation of the Eco-SSL was reviewed to consider LOAELs instead of NOAELs.

Eight cases were calculated, four using earthworms as the food source and four using arthropods. Earthworms are present in the Greater Sudbury area, but are not abundant. Arthropods represent the predominant feeding scenario for mammalian insectivores in the Sudbury region. The cases presented are:

Case 1: The base case of the Eco-SSL, provided for comparative purposes. Uses earthworm as the food source and NOEL in the calculation;

Case 2: Derived using the lowest bounded LOAEL for reproduction and earthworms as the food source, maintains all other assumptions used in the calculation of the Eco-SSL;

Case 3: Derived using the geometric mean of LOAELs (after 7 high values were removed; n = 28) and earthworms as the food source, maintains all other assumptions used in the calculation of the Eco-SSL;

Case 4: Derived using dose-response data (EC₂₀ value) and earthworms as the food source, maintains all other assumptions used in the calculation of the Eco-SSL;

Case 5: Modified base case using NOAEL and arthropods as the food source in the calculation;

Case 6: Derived using the lowest bounded LOAEL for reproduction and arthropods as the food source but maintains all other assumptions used in the calculation of the Eco-SSL;

Case 7: Derived using the geometric mean of LOAELs (after 7 high values were removed; n = 28) and arthropods as the food source, maintains all other Eco-SSL assumptions; and,

Case 8: Derived using dose-response data (EC₂₀ value) and arthropods as the food source, maintains all other assumptions used in the calculation of the Eco-SSL.

The dose-response data (EC₂₀) used in Case 4 and 8 was calculated in US EPA (2001) for use in an ERA in the Coeur d'Alene. The value pertaining to reproductive effects (number of live fetuses) in rats (Sutou et al., 1980) was used to derive the EC₂₀ of 2.9 mg/kg/d (US EPA, 2001). The cadmium concentration (µg/g) in soil for each of these cases where the ecological risk is equal to 1 is presented in Table 3.5 with the corresponding toxicity reference values (TRV).

Table 3.5 Estimation of risk-based soil screening levels: mammalian insectivores

	TRV (mg/kg/d)	Cadmium Soil Concentration (µg/g)
Case 1: Eco-SSL using NOAEL and earthworm model	0.77	0.38
Case 2: Lowest bounded LOAEL for reproduction, with earthworm model	2.28	1.5
Case 3: Geomean of LOAELs with earthworm model	5.4	2.1
Case 4: EC ₂₀ with earthworm model	2.9	4.6
Case 5: Eco-SSL using NOAEL and arthropods as food source	0.77	5
Case 6: Lowest bounded LOAEL for reproduction, with arthropod model	2.28	28
Case 7: Geomean of LOAELs with arthropod model	5.4	100
Case 8: EC ₂₀ with arthropod model	2.9	40

The soil concentrations presented in Table 3.5 show that even a slight decrease in the level of conservatism in the Eco-SSL model results in acceptable soil cadmium concentrations which are greater than 1.5 µg/g. Once arthropods are used as the food source in the model the acceptable cadmium concentrations in soil rise to a minimum of 5 µg/g. Of the soil samples collected during the regional survey in Sudbury, there are only three soil samples with pH < 5 and cadmium > 1.5 µg/g. The assumptions used in the alternate screening levels calculated remain conservative. This is because the Eco-SSL model incorporates several conservative assumptions into its design, such as: 100% bioavailability of cadmium in the soil to the organism and 100% of the organism's diet constituting of earthworms. This differs from the varied diet of most mammalian insectivores, which includes arthropods, insects and some plant matter.

Summary of Results for the Evaluation of Criterion 1

The results of this evaluation show:

MOE Table A: The concentrations of cadmium in 1993 surface soil samples from across the Sudbury area were compared to the Table A (residential/parkland) criterion of 12 µg/g. No samples exceeded this criterion for cadmium. In addition, no soil samples at depth (below surface) exceeded Table A.

MOE Table F: Sixty surface samples with pH values reviewed had a cadmium concentration which exceeded Table F (1 µg/g) and had pH < 5. Most of these samples came from the Regional Soil survey. Of the 365 Regional Soil samples, 55 (15.1%) had both pH < 5 and a cadmium concentration that exceeded background (Table F). Most of the samples (85%) with cadmium above background actually exceeded this value only marginally and contained cadmium concentrations which were < 1.54 µg/g.

Using the amended Criterion 1 to address soil pH, cadmium does not meet this criterion. Therefore, ecologically-based soil screening levels were used as a next evaluation step.

Eco-SSL: The Eco-SSL values for cadmium range from 0.38 µg/g for mammalian wildlife to 140 µg/g for soil invertebrates. None of the soil samples collected in the Sudbury area contains cadmium at levels which exceed either plant or soil invertebrate Eco-SSL values. The lowest wildlife values (avian and mammalian) are both at or below the Ontario background concentration for cadmium (1 µg/g). A slight decrease in the level of conservatism in the Eco-SSL model results in a cadmium screening criterion of 2 µg/g. Using this level as a reasonable risk-based criterion, only 3 soil samples have pH

< 5.0 and cadmium > 2.0 µg/g. Therefore, the level of cadmium in Sudbury soil samples poses very little risk to ecological receptors.

3.2 Criterion 2 - Distribution of Cadmium throughout the Study Area

Figure 3-1 shows the location of all soil samples collected during the Regional Soil Sampling Program (Laurentian University, 2001). Most of these samples (95%) had pH below 5. Sample sites with cadmium above Table F (1 µg/g) and pH < 5 are highlighted in red.

This mapping reveals that soil samples with cadmium above Table F are distributed across the study area. The samples are relatively widespread throughout the southern portion of the City of Greater Sudbury with some samples occurring north to Lake Wanapitei. The distribution appears random with no obvious relationship to smelter location.

Therefore, cadmium distribution meets Criterion 2 for COC selection as it is present across the study area.

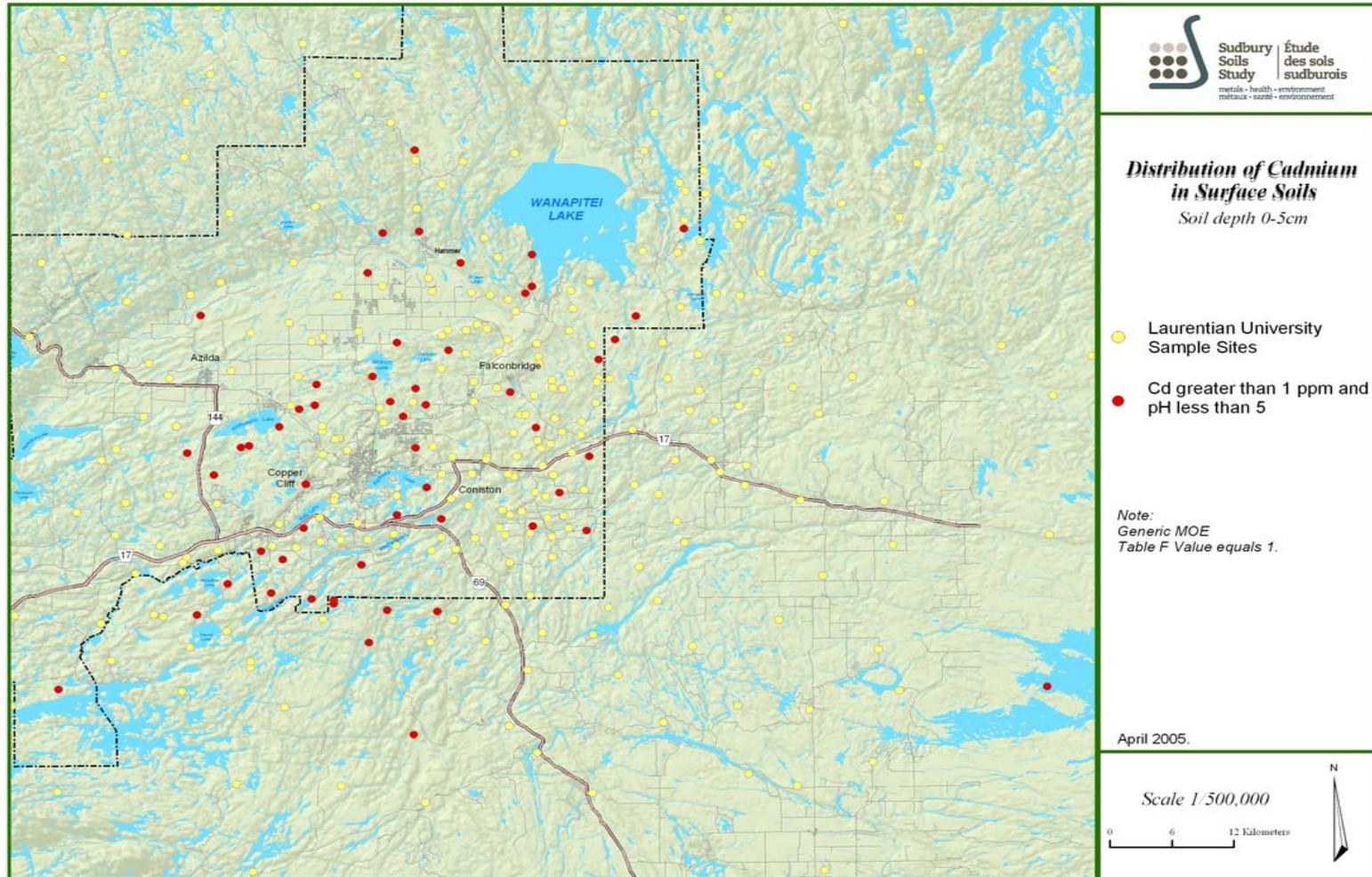


Figure 3-1 Distribution of Cadmium in Surface Soils (0-5 cm)

3.3 Criterion 3 - Parameter must scientifically show origin to smelter operations

Cadmium is known to enter the environment via copper and nickel smelting operations (Hoffman et al., 1995). A number of statistical analyses were conducted to determine if observed cadmium concentrations in Sudbury soil are related to the smelters. Statistical tests were performed using SPSS v.12 to:

- 1) Evaluate the possible relationship between distance from one of the three smelters (Copper Cliff, Coniston, and Falconbridge) and soil cadmium concentration (two variable regression and correlation analysis); and,
- 2) Evaluate the correlation between soil cadmium concentration and concentration of other metals known to be related to the smelter operations (i.e., copper and nickel).

Statistical Tests Used for Analysis

A detailed description on the selection and interpretation of the statistical approach is provided in Appendix B. To correlate cadmium concentration and distance from the smelter, a Spearman's rank correlation was applied. 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 shown in Table 3.6.

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

¹ Taken 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 p value ($p = 0.01$) which is the probability of the results occurring due to random chance alone.

Soil Samples Used for Analysis

Surface soil samples (0 - 5 cm) from the 2001 combined soils database, 2003 Wildlife Dietary Items Survey, and the 2004 ERA Sampling Program were used in this analysis (original and duplicate samples were included). Sample points without detectable levels of cadmium were allocated a number which was half of the minimum detection limit (MDL).

Distance from the Smelter and Soil Cadmium Concentration

There are two operational smelters (Copper Cliff and Falconbridge) and one inactive smelter (Coniston) in the Greater Sudbury area. Regression and correlation analyses were performed on the cadmium concentration in the soil in relation to the distance from each of these smelters.

Distance from the smelter was determined using the GPS coordinates of each sample in ArcGIS 9. Due to the large number of samples, the distance from the smelter was allocated into 250 m distance increments, up to 10,000 m from each smelter. Once grouped into the appropriate distance allocation, the cadmium concentrations were compared.

Cadmium Concentration Related to Distance from the Copper Cliff Smelter

The results of the correlation analysis for the cadmium samples within 10,000 m of the Copper cliff smelter are shown in Figures 3-2 and 3-3. In Figure 3-3, a three-dimensional representation of the cadmium levels in the soil samples versus distance from the Copper Cliff smelter is shown. The stack location is shown on the plot for reference purposes.

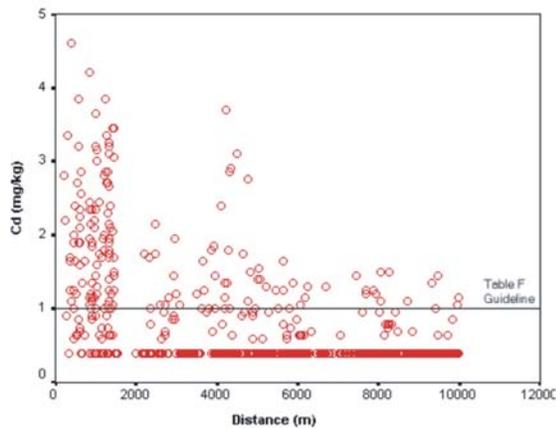


Figure 2

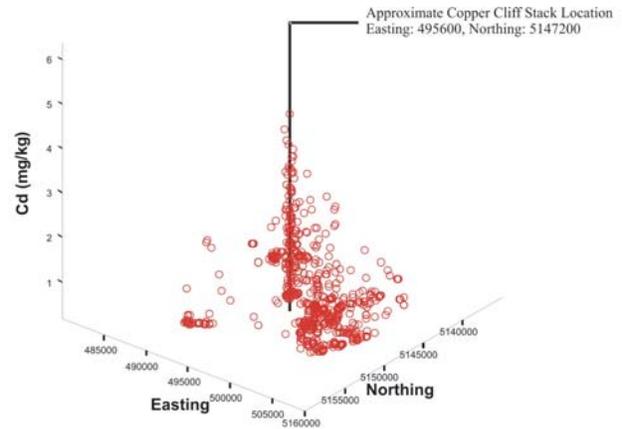


Figure 3

Figure 3-2 Cd vs. distance within a 10,000m radius from the Copper Cliff smelter

Figure 3-3 Cd vs. location within a 10,000m radius from the Copper Cliff smelter

The results illustrate that cadmium levels tend to be higher in the area 0 - 5,000 m from the Copper Cliff smelter. Greater than 5,000 m away, there are fewer samples with cadmium concentrations above 1 $\mu\text{g/g}$.

Cadmium Concentration Related to Distance from the Coniston Smelter

The results of the correlation analysis for the cadmium samples within 10,000 m of the Coniston smelter are shown in Figures 3-4 and 3-5. Figure 3-4 suggests that soil cadmium concentrations in some samples within 2 km of the Coniston smelter are higher than $> 2,000$ m distance from the smelter. In Figure 3-5, a three dimensional representation of the cadmium levels in the soil samples versus distance from the Coniston smelter is shown. The stack location is shown on the plot for reference purposes.

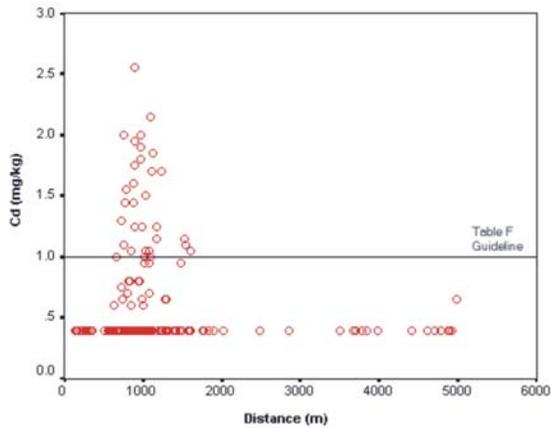


Figure 4

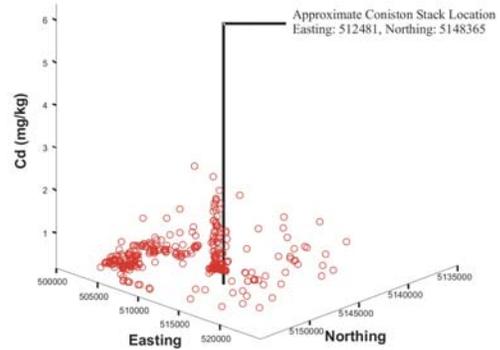


Figure 5

Figure 3-4 Cd vs. distance within a 10,000 m radius from the Coniston smelter

Figure 3-5 Cd vs. location within a 10,000 m radius from the Coniston smelter

These results indicate that cadmium levels tended to be higher in the area 0 – 2,000 m from the Coniston smelter. There are no samples with cadmium concentrations above 1 $\mu\text{g/g}$ between 2,000 – 6,000 m from the smelter.

Cadmium Concentration Related to Distance from the Falconbridge Smelter

The results of the correlation analysis for cadmium samples within 10,000 m of the Falconbridge smelter are shown in Figures 3-6 and 3-7. Figure 3-6 suggests that any soil containing cadmium concentrations above 1.0 µg/g occurs within 2,000 m of the Falconbridge smelter. In Figure 3-7, a three dimensional representation of the cadmium levels in the soil samples versus distance from the Falconbridge smelter is shown. The stack location is shown on the plot for reference purposes.

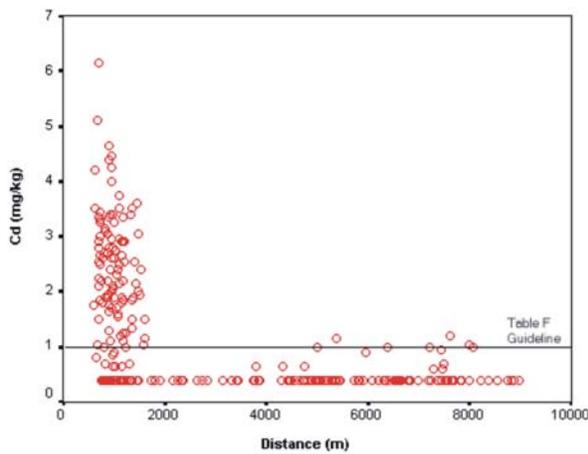


Figure 6

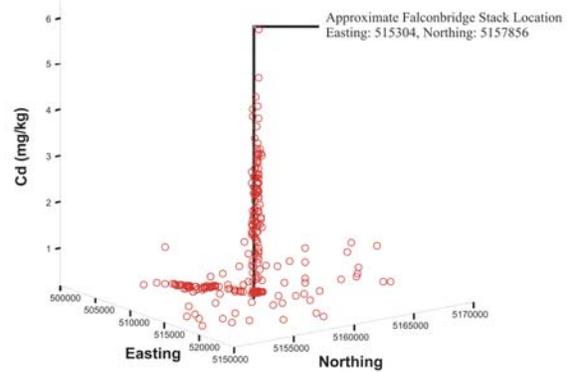


Figure 7

Figure 3-6 Cd vs. distance within a 10,000 m radius from the Falconbridge smelter

Figure 3-7 Cd vs. location within a 10,000 m radius from the Falconbridge smelter

These results indicate that cadmium levels tended to be higher in the area 0 – 2,000 m from the Falconbridge smelter. Greater than 2,000 m away, there are fewer samples with cadmium concentrations above 1 µg/g.

The correlation between the cadmium concentration in soil and distance from each of the smelters is summarized in Table 3.7. Given the large sample size (n), each of the correlations are significant and highly negative, demonstrating that Cd levels tend to be higher closer to each of the smelter sources.

Table 3.7 Cadmium levels ($\mu\text{g/g}$) in surface soil (0 - 5cm) correlated to distance from the smelters

Smelter source	Correlation Coefficient (r) ^a	p Value
Copper Cliff (n = 796)	-0.508	0.000
Coniston (n = 618)	-0.233	0.000
Falconbridge (n = 360)	-0.488	0.000

^aTest type= one-tailed, $\alpha = 0.01$

Relationship between Cd, Cu, Ni and V in Soil

The relationship between the concentration of cadmium in the soil samples and other metals known to originate from the smelters (e.g. copper and nickel), and one element (vanadium) not related to smelter emissions was investigated. The premise for this analysis is that if cadmium follows a similar distribution pattern as the established COCs already associated with smelter operations, then the results would suggest that the source of cadmium may also be due to smelter operations.

Table 3.8 Correlation between Cd, Cu, Ni and V in soil (0 - 5 cm)

Smelter source	Correlation coefficient test values (r) [*]		
	Cu	Ni	V ^{**}
Copper Cliff (n=796)	0.752	0.755	0.206
Coniston (n=618)	0.688	0.707	-0.102
Falconbridge (n=360)	0.814	0.831	0.211

^{*}Test type= one-tailed, $\alpha = 0.01$
^{**}not a COC (chemical of concern).

Spearman's coefficient was used to correlate the levels of cadmium and levels of other established COCs associated with the smelter, out to a radius of 10,000 m. Full details of this statistical analysis are provided in Appendix B. The results of the analysis show that Cd levels in soil are highly positively and significantly correlated with both Cu and Ni (Table 3.8). In contrast, there was no consistent or statistically significant relationship between Cd and V levels in soils. Vanadium has not been linked to smelter emissions.

Summary of Criterion 3 Analysis

The analysis completed to evaluate whether cadmium in soil fulfills Criterion 3 shows that:

- Higher soil cadmium concentrations were observed in closer proximity (< 2,000 m) to each of the smelters;
- There was a significant, highly positive correlation between levels of cadmium with levels of both nickel and copper (r values > 0.6) for each smelter; and,
- There was low to negligible correlation (r value < 0.22, p<0.01) between the levels of cadmium and vanadium in the soil.

The results of the analysis show that cadmium meets Criterion 3 in that the origin of cadmium in Sudbury soils could be linked to companies operations.

4.0 REVIEW OF CADMIUM IN WILDLIFE DIETARY ITEMS COLLECTED FOR THE ERA

Cadmium is a relatively rare element (0.2 µg/g in the earth crust) and is not found in its pure state in nature. It occurs mainly in association with the sulfide ores of zinc, lead and copper. It is a divalent metal that is insoluble in water, although the chloride and sulphate salts of cadmium are freely soluble. The availability of cadmium to organisms in the environment is dependant on a number of factors including pH, Eh, and chemical speciation (Eisler, 1985). Cadmium can be taken up into plants from soils and translocated with subsequent transfer through the terrestrial food chain (Shore and Douben, 1994).

Some metals pose little hazard to food-chain contamination because of their strong phytotoxic effects, that is, increasing metal concentrations cause plant mortality before transfer to the next trophic level has an opportunity to occur (McLaughlin, 2002). This has been termed the soil-plant barrier and allows metals to be classified into four groups based on retention in soil and metal translocation into the plant. Cadmium, however, poses a health risk at concentrations which are not generally phytotoxic (McLaughlin, 2002). This means that cadmium has the potential to bioaccumulate through the soil-plant-animal food chain.

Many small mammals, particularly insectivores, are vulnerable to cadmium accumulation in areas with high soil cadmium concentrations (Shore and Rattner, 2001). As part of the ERA, the SARA Group collected items that could constitute a portion of the diet of a small mammal living in the Sudbury area. The objective was to collect targeted wildlife dietary items (WDI) with co-located soil samples. Sites were established at seventeen regions around the three smelters, with each site encompassing various soil metal concentrations, site conditions and soil types. Composite samples of grasshoppers (*Melanoplus sp.*) and the roots and shoots of a widespread grass species (*Deschampsia sp.*) were collected in the same area as the soil samples.

Table 4.1 presents a summary of the range of cadmium concentrations in surface soil (0 - 5cm), grass (roots and shoots) and grasshoppers. The cadmium concentration in the soil is below both MOE Table A and Table F values.

Table 4.1 Cadmium in soil and wildlife dietary items

Wildlife Dietary Items (n = 17)	Range	Mean
	µg/g	
Soil (0 - 5 cm)	0.17 - 0.68	0.41
Grass Roots	0.27 - 5.87	1.97
Grass Shoots	0.071 - 0.55	0.24
Grasshoppers	0.14 - 1.4	0.45

The data show that cadmium concentrations in grass roots and grasshoppers are higher than the soil concentration at each site, with the exception of two sites (5 and 10). Grass roots accumulated higher concentrations of cadmium than did shoots or grasshoppers. The mean accumulation of cadmium in roots was 4.7 times higher than that found in soil at the corresponding site, although at times the cadmium concentration in the roots was up to 14 times higher. In shoots, cadmium concentrations were comparable to that in the soil. Although the mean accumulation of cadmium from the soil to the shoots was 0.6 times, indicating that at some sites shoot concentration was lower than soil concentration, the highest accumulation was 2.5 times higher than the soil concentration. The concentration of cadmium found in grasshoppers at the sites was also comparable to that in the soil, with the mean accumulation only 1.2 times higher.

These results indicate that, although cadmium can bioaccumulate in the soil-plant-animal food chain, the levels found during the site-specific collection in Sudbury showed little accumulation in grass shoots and grasshoppers in comparison to soil cadmium concentrations. Although variable, cadmium levels in grass roots were generally higher than soil cadmium levels.

Correlation analysis (Spearman correlation, SPSS v.12) was used to determine whether a relationship existed between total cadmium in the soil and cadmium in grass or grasshoppers. A summary of the results of the correlation analysis is shown in Table 4.2.

**Table 4.2 Correlation between Cadmium in soil, grass and grasshoppers
Wildlife Dietary Item Survey, Summer 2003**

	Soil	Grass Shoots	Grass Roots	Grasshopper
Cd Concentration (µg/g)				
Soil (n = 17)	1	0.225	0.288	0.078
Grass Shoot (n=15)	0.225	1	0.56	0.197
Grass Roots (n=17)	0.288	0.56	1	0.197
Grasshopper (n =17)	0.078	0.197	0.197	1

This analysis shows that total cadmium in soil is not strongly related to cadmium concentration in grass roots or shoots ($r = 0.288$ and 0.225 respectively) and is not related to cadmium concentration in grasshoppers ($r = 0.078$). Cadmium in grass roots and shoots, unsurprisingly, is related to each other ($r = 0.560$).

The absence of a relationship between total metal concentration in soil and concentrations measured in plants is well documented. Experimental data have demonstrated that the bioavailability of a metal is highly dependent on soil physicochemical conditions. The cadmium concentration in the plants is likely governed by factors such as soil pH, cation exchange capacity and organic carbon content (McLaughlin, 2003). The range of cadmium in soils at the WDI sites was also very low ($0.1 - 0.7 \mu\text{g/g}$) and is below the background concentrations set out by the MOE ($1 \mu\text{g/g}$). Therefore, it is not surprising there is no clear indication of bioaccumulation of cadmium from Sudbury soils into plants or herbivorous insects.

5.0 REVIEW OF CADMIUM IN SAMPLES COLLECTED FOR HHRA

Soil pH levels in residential yards in the urban areas were above 5.0, indicating that Table A cadmium levels could be used to screen the soil data. All soil Cd values were below Table A.

Therefore cadmium is not considered a COC for the HHRA in Sudbury. However, the concentration of cadmium in various media such as air, water, and animal tissue was assessed to further evaluate the potential significance of cadmium in the study area. The samples were collected by the SARA Group in response to data gaps for the HHRA in Sudbury.

5.1 Cadmium in Drinking Water

Drinking water usually contains very low concentrations of cadmium. The concentration of cadmium in drinking water in Ontario is regulated under the Safe Drinking Water Act (2002), via the Ontario Drinking Water Standards (ODWS). The primary objective of the ODWS is to protect public health through the provision of safe drinking water. The ODWS has identified a Maximum Acceptable Concentration (MAC) for cadmium of 5 µg/L.

As part of the HHRA, the SARA Group conducted a survey of the metal concentrations in drinking water in Sudbury. Drinking water in the City of Greater Sudbury comes from either surface water or groundwater. The majority of homes are on a municipal supply, with water tested by the City of Greater Sudbury and the MOE. A portion of homes obtain their drinking water from private wells or lakes, which are not tested by the City or the MOE. The aim of the drinking water survey was to collect samples from residences with private water supplies. Tap water was sampled to be representative of water being consumed by the residents. Water was collected from 106 residences during the autumn and winter of 2004-2005. Table 5.1 provides a summary of the results.

Table 5.1 Concentration of Cadmium (µg/L) in drinking water from Sudbury area homes

Sample size (n)	106
Range	< 0.1 - 0.7
Mean	0.1
MAC	2

The results of the SARA Group drinking water survey show that concentrations of cadmium in drinking water samples were low. Both the mean cadmium concentration (0.1 µg/L), and the maximum value measured (0.7 µg/L) were well below the MAC of 2 µg/L. The World Health Organization (WHO) reports that the typical concentration of cadmium in drinking water is in the range 0.0 1- 1 µg/L (WHO, 1992). Therefore, cadmium in drinking water from private wells in the Sudbury area is not considered a concern for human health

5.2 Cadmium in Air

Cadmium is emitted to the atmosphere predominantly as elemental cadmium and cadmium oxide and from some sources as cadmium sulfide or cadmium chloride. In air, cadmium is rapidly oxidized into cadmium oxide. Most of the cadmium that occurs in air is associated with particulate matter in the respirable range (diameter 0.1 - 1 µm). The residence time of cadmium in air is relatively short (days to weeks) but sufficient to allow long-range transport in the atmosphere (WHO, 2000).

As part of the HHRA, the SARA Group measured the concentration of metals in ambient air samples from October 2003 to October 2004. A network of 9 monitoring sites and 1 reference site was established throughout the Greater Sudbury area. At each monitoring station hi-volume and lo-volume air samplers collected total suspended particulate matter (TSP - less than 44 microns in diameter), respirable particulate matter (PM_{2.5} - less than 2.5 microns in diameter), and particulate matter (PM₁₀ - less than 10 microns in diameter). These monitoring sites were situated close to residences, schools, agricultural areas, and smelting operations across the region. Over 1,350 air samples were collected during the year-long sampling program, with samples being collected over a 24-hour period every six days. A full description of the sampling methods and results is presented elsewhere in this series of reports for the Sudbury Soils Study.

The MOE has established Ambient Air Quality Criteria (AAQC) to assess general air quality in Ontario. These criteria are based on the best available scientific information and are set at a level that safeguards the natural environment and protects sensitive populations, such as children and the elderly. The 24-hour AAQC for cadmium is 2.0 µg/m³. The maximum 24-hour cadmium concentrations (µg/m³) in the air samples collected from each station during the air monitoring program are presented in Table 5.2.

Table 5.2 Maximum 24-hour Cadmium concentration ($\mu\text{g}/\text{m}^3$) in Sudbury ambient air samples

Air Monitoring Station	Cadmium Concentration ($\mu\text{g}/\text{m}^3$)		
	PM ₁₀	PM _{2.5}	TSP
Algonquin	----	----	0.0042
Coniston	----	----	0.0031
Copper Cliff	0.0103	0.0078	0.0098
Falconbridge/Edison	0.055	0.0361	0.0602
Garson	0.0028	0.003	0.0031
Hanmer	----	----	0.0019
Skead	----	----	0.0037
Travers/West End	0.0144	0.0171	0.0139
Walden	----	----	0.0032
Windy Lake (Reference Site)	0.0046	0.0033	----

The results show that there were no exceedences of the AAQC for cadmium at any of the sampling locations during the one year program. The highest 24-hour cadmium concentration was $0.06 \mu\text{g}/\text{m}^3$ (approximately 3% of the current AAQC) from a sample collected at the Falconbridge/Edison station. Therefore, cadmium levels in air in the Sudbury area is not considered a concern for human health.

5.3 Cadmium in Tissue

The WHO (2000) reviewed data on concentrations of cadmium in various media and reported that for nonsmokers, food constitutes the principal environmental source of cadmium. The concentration of cadmium is in the range of 1 - 50 $\mu\text{g}/\text{kg}$ in meat, fish and fruit and 10-300 $\mu\text{g}/\text{kg}$ in staple foods such as wheat, rice and potatoes (WHO, 2000). The highest cadmium levels (100-1000 $\mu\text{g}/\text{kg}$) are found in the internal organs (kidney and liver) of mammals and in certain species of mussels, scallops and oysters. The average daily intake of cadmium *via* food for people in North America is 15-25 μg . The gastrointestinal absorption of cadmium in humans amounts to about 5%, but may be increased by nutritional factors (up to 15% in iron deficient people). The average amount of cadmium absorbed *via* food can thus be estimated at about 1 $\mu\text{g}/\text{day}$ (WHO, 1992; WHO, 2000; Bernard and Lauwerys, 1992).

As part of the HHRA, Sudbury-specific studies were conducted to determine the concentration of metals in cattle tissue (liver, kidney and muscle) produced locally. Existing literature outlining cadmium concentrations was reviewed to assess cadmium levels in wild game.

Livestock Tissues

Knowledge of cadmium levels in livestock tissues is important for quantifying intake for humans. Metal levels in cattle and other livestock have been measured in a number of studies including industrial areas (Farmer and Farmer, 2000; Kottferova and Korenekova, 1995; Lopez Alonso et al., 2000). The kidney and, to a lesser extent, the liver are the critical organs for cadmium concentration, as cadmium predominantly accumulates because rate of elimination from these organs is low (Friberg et al., 1979). Differences in the rate of cadmium accumulation is often related to sex (females accumulate higher levels than males) and age of the animal (the older the animal the higher the kidney and liver cadmium levels (Wren, 1983)). Cadmium levels are generally low in blood and muscle.

As part of the Sudbury HHRA, a Livestock Tissue Survey was conducted to obtain site-specific data on the range of metal concentrations found in tissue of beef cattle raised in the Sudbury Area. The samples were collected from animals raised and destined to be consumed within the local area. The samples were collected in a manner consistent with how they are normally collected by residents, and then analyzed for metal content. Tissue samples were collected from 10 animals, including kidney (composite the medulla and the cortex), liver (left lobe), and muscle (left cheek). The results are summarized in Table 5.3 and described in more detail elsewhere in this study.

Table 5.3 Cadmium (µg/g w.w.) in livestock tissue

Tissue	Sample Size (n)	Mean	Range
Liver	8	0.086	0.05 - 0.15
Kidney	6	0.57	0.25-1.29
Muscle	10	0.002	< DL - 0.0030

The highest cadmium concentrations were found in kidney (maximum 1.29 µg/g w.w.). It is not common for people to eat the kidney or liver of cattle, but in order to determine whether these levels were elevated, they were compared to levels found in peer-reviewed literature. Alonso *et al.* (2000) measured background concentrations of cadmium in livestock tissue from Galicia Spain, an area with little or no industrial inputs. The mean cadmium concentrations in muscle (0.07 µg/g w.w.), liver (0.1 µg/g w.w.), and kidney (0.212 µg/g w.w.) were greater than the mean concentrations in Sudbury, with the exception of the kidneys. In a similar study, Kreuzer (1976) measured the natural background cadmium levels in meat, liver and kidney from 287 cattle in non-impacted areas of the sub-alpine regions of Bavaria. Background cadmium concentrations in meat (< 0.005 µg/g f.w.), liver (< 0.005 - 1.65 µg/g f.w.), and

kidney (0.008 – 1.95 µg/g f.w.) were in the same range as the levels measured by the SARA Group. However, higher maximum concentrations in liver and kidney tissues were reported in the Kreuzer (1976) study.

Studies and surveys have been conducted worldwide to determine the concentrations of cadmium in livestock and other items. Cadmium concentrations measured in livestock tissues in other studies are shown in Table 5.4. The cadmium values observed in Sudbury cattle are consistent with levels measured in other studies around the world.

In another study by Frank *et al.* (1989), cadmium levels in bovine kidney and liver tissues from cattle raised in regions across the Canadian Shield (northeastern Ontario) were compared to tissue concentrations in cattle raised on farms further south of the shield, with soil derived from glacial deposits (southwestern Ontario). Mean cadmium concentrations in liver and kidney tissues (n = 244) measured from regions across the Canadian Shield ranged between 0.11 - 0.48 µg/g and 0.51 - 4.47 µg/g, respectively. Mean cadmium concentrations measured in regions south of the Canadian Shield in liver and kidney tissues (n = 253) ranged between 0.07 - 0.24 µg/g and 0.24 - 2.58 µg/g, respectively. Cadmium concentrations in liver and kidney tissues from regions across the Canadian Shield were consistently greater than levels in tissues from south of the shield, however, the differences were not significant. The soils of the Canadian Shield are poorly buffered against acidification and, therefore, have higher levels of bioavailable cadmium and have shown increased cadmium in surficial soils and plants due to natural enrichment (Shilts, 1981; Kovalesky, 1984). The livestock tissues measured in Sudbury are well below the ranges reported in cattle by Frank *et al.* (1989) for other parts of Ontario.

Table 5.4 Cadmium (µg/g) in livestock tissues from other studies.

Animal	Tissue (no. of samples)	Cadmium Concentration (µg/g wet weight)		Location	Reference
		Mean	Range		
LIVER					
Calves	Liver (312)	0.0307	0.00339 - 0.221	Asturias* (North Spain)	Miranda <i>et al.</i> (2001)
Dairy cattle	Liver (39)	0.0516	0.0236 - 0.265	North Spain	Lopez Alonso <i>et al.</i> (2000)
Beef cattle	Liver (16)	0.0357	0.017 - 0.187	North Spain	Lopez Alonso <i>et al.</i> (2000)
Cattle	Liver (196)	0.066	NR	Finland	Tahvonon and Kumpulainen (1994)
Cow (heifer)	Liver (151)	0.036	NR	Finland	Tahvonon and Kumpulainen (1994)
Cattle	Liver (101)	1.22 (d.w.)	NR	Netherlands*	Spierenburg <i>et al.</i> (1988)
Cattle	Liver (24)	0.56 (d.w.)	NR	Netherlands (control group)	Spierenburg <i>et al.</i> (1988)
Beef cattle	Liver (30)	0.119	0.038 - 0.320	Campania, Italy	Amodio-Cocchieri and Fiore (1987)
KIDNEY					
Calves	Kidney (312)	0.161	0.0042 - 0.717	Asturias* (North Spain)	Miranda <i>et al.</i> (2001)
Dairy cattle	Kidney (36)	0.194	0.0298 - 0.866	North Spain	Lopez Alonso <i>et al.</i> (2000)
Beef cattle	Kidney (16)	0.186	0.0423 - 1.388	North Spain	Lopez Alonso <i>et al.</i> (2000)
Cattle	Kidney (89)	9.58 (d.w.)	NR	Netherlands*	Spierenburg <i>et al.</i> (1988)
Cattle	Kidney (24)	3.90 (d.w.)	NR	Netherlands (control group)	Spierenburg <i>et al.</i> (1988)
Beef cattle	Kidney (30)	0.342	0.060 - 0.900	Campania, Italy	Amodio-Cocchieri and Fiore (1987)
MUSCLE (MEAT)					
Calves	Meat (119)	0.00203	< 0.00096 - 0.0207	Asturias* (North Spain)	Miranda <i>et al.</i> (2001)
Dairy cattle	Muscle (41)	0.00812	< 0.0129 - 0.0296	North Spain	Lopez Alonso <i>et al.</i> (2000)
Beef cattle	Muscle (16)	0.0071	< 0.0129 - 0.0363	North Spain	Lopez Alonso <i>et al.</i> (2000)
Beef cattle	Muscle (30)	0.038	0.020 - 0.120	Campania, Italy	Amodio-Cocchieri and Fiore (1987)
()	indicates number of tissues sampled				
*	indicates regions near industrial emissions or mining activities				
NR	not reported				
d.w.	only dry weight concentrations were reported				

The SARA Group was unable to find published Canadian standards or maximum permissible concentrations for cadmium in bovine organs, specifically liver and kidney tissues, for human consumption. Despite repeated efforts to contact individuals at the Chemical Health Hazard Assessment Division of Health Canada and the Regulations & Procedures Department of the Canadian Food Inspection Agency (CFIA), no response was received.

When compared with maximum permitted concentrations for human consumption of cattle liver and kidney from Australia (1.25 µg/g w.w. and 2.5 µg/g w.w., respectively) and the Netherlands (1.0 µg/g w.w. and 3.0 µg/g w.w., respectively) it can be concluded that levels of cadmium found in Sudbury livestock are well below these limits and are unlikely to be of concern for human health (Koh *et al.*, 1998; Baars *et al.*, 1988). Additionally, consumption of cow kidney and liver tissues is not expected to be a major human exposure pathway.

Wild Game

Various studies have documented cadmium levels in moose, deer and elk living in the Sudbury area (Glooschenko *et al.*, 1988; Parker and Hamr, 2001). Glooschenko *et al.* (1988) measured cadmium in deer and moose liver, kidney and muscle during 1984 and 1985 from various areas of Ontario. Mean cadmium concentrations in adult (4.5 years and older) moose liver, kidney and muscle in the Sudbury area (non-buffered soils) were 2.8, 16.0, and ND (not detected) µg Cd/g wet weight, respectively. Deer sampled in Loring, Ontario (non-buffered soil site south of Sudbury) had significantly higher cadmium concentrations in kidney and liver samples than other sample sites in Ontario, with maximum levels of 15.1 µg Cd/g w.w. and 1.1 µg Cd/g w.w., respectively.

Based on these results, the Ontario Ministry of Natural Resources (MNR) issued an advisory recommending that members of the Ontario public should not consume livers or kidneys of moose or deer due to cadmium concentrations. It is clear that the recommendations pertained to all of Ontario, and were not linked to point sources. Further, the advisory was not supported by any health studies or risk assessment.

Parker and Hamr (2001) reported on metal levels in elk located at Burwash-French River. The levels in the elk were low in comparison to the range of values for cervids residing in areas with little or no known source of pollutants (Wren, 1983; Wolkers *et al.*, 1994).

Cadmium concentrations measured in wild game tissues from various studies are summarized below.

Table 5.5 Cadmium concentrations in wild game tissues.

Animal	Tissue (no. of samples)	Cadmium Concentration (µg/g wet weight)		Location	Reference
		Mean	Range		
Moose	Liver (17)	2.31	NR	Northern British Columbia	Jin and Joseph- Quinn (2003)
Moose	Liver (105)	0.743	0.13 - 4.37	Finland	Vahteristo <i>et al.</i> (2003)
Moose	Liver (21)	0.960	NR	Sweden	Falandysz (1994)
Moose	Liver (69 - 79)	0.450	NR	Sweden	Falandysz (1994)
Moose	Liver	5.64 (d.w.)	NR	Maine	Scanlon <i>et al.</i> (1986)
Moose	Liver (13 - 21)	1.28-2.07 (d.w.)	NR	Norway	Scanlon <i>et al.</i> (1986)
Moose	Liver (306)	2.9-15.9 (d.w.)	NR	South of Quebec	Crete <i>et al.</i> (1987)
Moose	Liver (8)	2.8 (adult)	NR	Sudbury, Ontario (non- buffered soils)	Glooschenko <i>et al.</i> (1988)
Moose	Liver (7)	5.7 (adult)	NR	Algonquin, Ontario (non-buffered soils)	Glooschenko <i>et al.</i> (1988)
Moose	Liver (3)	5.0 (adult)	NR	Cornwall, Ontario (buffered soils)	Glooschenko <i>et al.</i> (1988)
Moose	Liver (228)	1.19 (d.w.)	0.01 - 4.70 (d.w.)	Manitoba	Crichton and Paquet (2000)
Deer	Liver	1.7 (d.w.)	NR	Connecticut	Musante <i>et al.</i> (1993)
Deer	Liver	4.0 (d.w.)	NR	New Jersey	Musante <i>et al.</i> (1993)
Deer	Liver	0.4 (d.w.)	NR	Illinois	Musante <i>et al.</i> (1993)
Deer	Liver	1.3 (d.w.)	NR	Maine	Musante <i>et al.</i> (1993)
Deer	Liver (86)	NR	0.07 - 23.2 (d.w.)	New Jersey	Stansley <i>et al.</i> (1991)
Caribou	Liver	1.1	NR	Northern Quebec	Archibald and Kosatsky (1991)
Moose	Kidney (6)	7.59	NR	Northern British Columbia	Jin and Joseph- Quinn (2003)
Moose	Kidney (105)	4.56	1.62 - 21.50	Finland	Vahteristo <i>et al.</i> (2003)
Moose	Kidney (21)	4.40	NR	Sweden	Falandysz (1994)
Moose	Kidney (69 - 79)	2.30	NR	Sweden	Falandysz (1994)
Moose	Kidney	26.76 (d.w.)	NR	Maine	Scanlon <i>et al.</i> (1986)
Moose	Kidney (13 - 20)	8.36 - 20.52 (d.w.)	NR	Norway	Scanlon <i>et al.</i> (1986)
Moose	Kidney (125)	31.8 - 100.5	NR	South of Quebec	Crete <i>et al.</i> (1987)

Table 5.5 Cadmium concentrations in wild game tissues.

Animal	Tissue (no. of samples)	Cadmium Concentration (µg/g wet weight)		Location	Reference
		Mean	Range		
		(d.w.)			
Moose	Kidney (6)	16.0	NR	Sudbury, Ontario (non-buffered soils)	Glooschenko et al. (1988)
Moose	Kidney (14)	51.4	NR	Algonquin, Ontario (non-buffered soils)	Glooschenko et al. (1988)
Moose	Kidney (3)	18.7	NR	Cornwall, Ontario (buffered soils)	Glooschenko et al. (1988)
Moose	Kidney (228)	6.84 (d.w.)	0.18 - 38.00 (d.w.)	Manitoba	Crichton and Paquet (2000)
Caribou	Kidney	11.0	NR	Northern Quebec	Archibald and Kosatsky (1991)
Moose	Muscle (6)	0.023	NR	Northern British Columbia	Jin and Joseph-Quinn (2003)
Moose	Meat (103)	0.004	0.001 - 0.035	Finland	Vahteristo et al. (2003)
Moose	Muscle (11 - 17)	0.03 - 0.13 (d.w.)	NR	Norway	Scanlon et al. (1986)
Moose	Muscle (6)	ND	NR	Sudbury, Ontario (non-buffered soils)	Glooschenko et al. (1988)
Moose	Muscle (4)	0.2	NR	Algonquin, Ontario (non-buffered soils)	Glooschenko et al. (1988)
Moose	Muscle (3)	Trace (< 0.1)	NR	Cornwall, Ontario (buffered soils)	Glooschenko et al. (1988)

() indicates number of tissues sampled
 NR not reported
 d.w. only dry weight concentrations were reported

The cadmium values in wild game reported from the Sudbury region suggest that the levels are not elevated in comparison to other regions of Ontario, Quebec or the northeastern United States. Therefore, there is no concern for cadmium in tissues of deer or moose specific to Sudbury or this study.

6.0 SUMMARY

Cadmium concentrations in the soil collected during the Sudbury Soils Study were below MOE Table A, but above background concentrations as determined by MOE Table F. A comparison to Table F was made because a large number of the soil samples collected in rural regions had a pH < 5.

Table F is not a risk-based screening level so the cadmium levels were compared to US EPA Eco-SSL values which are applicable to soils with a pH < 5 and are based on risk calculations. The concentrations of cadmium in Sudbury were below all screening values except those calculated to be protective of insectivores (avian and mammalian). Further analysis revealed that the Eco-SSL values were below Ontario background cadmium concentrations. A slight adjustment in the calculation of the Eco-SSL value using LOAELs rather than NOAELs produced a soil screening concentration for cadmium (2 µg/g) which is conservative yet above background. The newly calculated value maintains the conservative assumptions of the Eco-SSL and is protective of insectivores inhabiting the Sudbury region.

Of 1993 soil samples only three had a pH < 5 and a cadmium concentration > 2.0 mg/kg. Therefore, an insignificant number of soil samples exceeded the risk-based screening criterion developed for cadmium in Sudbury soils.

Examination of the spatial distribution of cadmium in Sudbury soils indicates that cadmium levels are elevated closer to the smelters, and is, therefore, likely emitted from the smelters. However, soil concentrations are still not considered high in the Sudbury area.

Cadmium levels in air and water in Sudbury are very low and below applicable provincial criteria.

Cadmium levels in tissues of cattle, deer and moose in the Sudbury area are comparable with levels reported elsewhere in Ontario and other parts of the world.

This review indicates that the levels of cadmium in the soil samples collected during the Sudbury Soils Study are unlikely to cause ecological risk. In addition, there is no apparent reason to consider ambient cadmium levels in Sudbury a human health concern. Therefore, the SARA Group recommends to the Technical Committee that cadmium is not considered a Chemical of Concern in the Sudbury Soils Study.

7.0 REFERENCES

- Amodio-Cocchieri, R. and Fiore, P. 1987. Lead and cadmium concentrations in livestock bred in Campania, Italy. *Bull Environ Contam Toxicol*, 39:460-464.
- Agency for Toxic Substances and Disease Registry (ATSDR). 1999. Toxicological profile for cadmium. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
- Archibald, C.P. and Kosatsky, T. 1991. Public health response to an identified environmental toxin: managing risks to the James Bay Cree related to cadmium in caribou and moose. *C J Public Health*, 82:22-26.
- Baars, A.J., Spierenburg, T.J., and de Graaf, G.J. 1988. Some heavy metals in liver and kidneys from cattle in a cadmium-polluted area in the Netherlands. *Proceedings of the University of Missouri 22nd Annual Conference on Trace Substances in Environmental Health*, St. Louis, Missouri. May 23-26, 1988.
- Bernard A., Lauwerys R. 1992. Renal toxicity from hazardous chemicals in *Hazardous Materials Toxicology. In Clinical Principles of Environmental Health* (J.B. Sullivan, Jr, G.R. Krieger, Eds) pp. 163-167. Williams & Wilkins, Baltimore
- Crete, M., Potvin, F., Walsh, P., Benedetti, J., Lefebvre, M.A., Weber, J., Paillard, G., and Gagnon, J. 1987. Pattern of cadmium contamination in the liver and kidneys of moose and white-tailed deer in Quebec. *Sci Total Environ*, 66:45-53. Cited In: USGS, 2005.
- Crichton, V. and Paquet, P.C. 2000. Cadmium in Manitoba's wildlife. *Alces*, 36:205-216. Cited In: USGS, 2005.
- Eisler, R. 1985. *Cadmium Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review*. U.S. Fish and Wildlife Service, Washington, DC. Biological Report No 85(1.2).
- Farmer, A.A and A.M. Farmer. 2000 Concentrations of cadmium, lead and zinc in livestock feed and organs around a metal production centre in eastern Kazakhstan *The Science of the Total Environment* 257: 53. p60
- Flandysz, J. 1994. Some toxic and trace metals in big game hunted in the northern part of Poland in 1987-1991. *Sci Total Environ*, 141:59-73. Cited In: USGS, 2005.
- Frank, R., Suda, P., and Luyken, H. 1989. Cadmium levels in bovine liver and kidney from agricultural regions on and off the Canadian Shield, 1985-1988. *Bull Environ Contam Toxicol*, 43:737-741.
- Friberg L, Nordberg G.F., Vouk V.B. 1979. *Handbook on the toxicology of metals*. Elsevier, Amsterdam.
- Glooschenko V, Downes C, Frank R, Braun HE, Addison EM, Hickie J, 1988. Cadmium levels in Ontario moose and deer in relation to soil sensitivity to acid precipitation. *Sci Total Environ* 71: 173-86.
- Hoffman, D.J. Rattner B.A., Burton Jr G.A., Cairns J. 1995. *The Handbook of Ecotoxicology*. CRC Press.
- Jin, A. and Joseph-Quinn, K.M. 2003. Consumption guideline for cadmium in moose meat in northern British Columbia. *Circumpolar Health*, 169-173.

- Koh T., Bansemer P., Frensham A. 1998. A survey of the cadmium concentration in kidney, liver and muscle of South Australian cattle, *Australian Journal of Experimental Agriculture*, 38 (6): 535- 540
- Kottferova J, Korenekova B. 1995 The effect of emissions on heavy metals concentrations in cattle from the area of an industrial plant in Slovakia. *Arch Environ Contam Toxicol* 29:400–405.
- Kovalesky, A.L. 1984. The cadmium informativeness of various plant species. *Geo Chem Int*, 21:148-157. Cited In: Frank et al., 1989.
- Kreuzer, W., Sansoni, B., Kracke, W., and Wiszmath, P. 1976. Cadmium background content in meat, liver and kidney from cattle and its consequences to cadmium tolerance levels. *Chemosphere*, 4:231-240.
- López Alonso, M., Montana, F.P., Miranda, M., Castillo, C., Hernández, J., and Benedito, J.L. 2000. Cadmium and lead accumulation in cattle in NW Spain. *Vet Human Toxicol*, 45(3):128-130.
- McLaughlin. M. 2002. Bioavailability of Metals to Terrestrial Plants: In: Allen. H. (ED). *Bioavailability of Metals in Terrestrial Ecosystems: Importance of Partitioning for Bioavailability to Invertebrates, Microbes and Plants*. Pensacola FL: Society of Environmental Toxicology and Chemistry (SETAC)
- Miranda, M., López-Alonso, M., Castillo, C., Hernández, J., and Benedito, J.L. 2001. Cadmium levels in liver, kidney and meat in calves from Asturias (North Spain). *Eur Food Res Technol*, 212:426-430.
- Musante, C.L., Ellingwood, M.R., and Stilwell, D.E. 1993. Cadmium contamination of deer livers in Connecticut. *Bull Environ Contam Toxicol*, 51(6):833-846. Cited In: ATSDR, 1999.
- Parker, G.H. and Hamr.J. 2001. Metal levels in body tissues, forage and fecal pellets of elk (*Cervus elaphus*) living near the ore smelters at Sudbury, Ontario. *Environmental Pollution* 113: 347-355.
- Sample, B.E., Beauchamp, J.J., Efrogmson, R.A., Suter II, G.W. and Ashwood, T.L. 1998. Development and validation of bioaccumulation models for earthworms. ES/ER/TM-220. Oak Ridge National Laboratory, Oak Ridge, TN.
- Sample, B.E. and C.A. Arenal. 2001. Development of literature-based bioaccumulation models for terrestrial arthropods. Presented at the Society for Environmental Toxicology and Chemistry (SETAC) North American Annual Meeting, November, 2001.
- Scanlon, P.F., Morris, K.I., Clark, A.G., Fimreite, N., and Lierhagen, S. 1986. Cadmium in moose tissues: comparison of data from Maine, U.S.A. and from Telemark, Norway. *Alces*, 22:303-311. Cited In: USGS, 2005.
- Shilts, W.W. 1981. Sensitivity of bedrock to acid precipitation: modification by glacial processes. Geological Survey of Canada, Paper 81-14. Cited In: Frank et al., 1989.
- Shore, R. F. and Douben, P. E. T. 1994. Predicting ecotoxicological impacts of environmental contaminants on terrestrial small mammals. *Reviews of Environmental Contamination and Toxicology*, vol. 134: 6874
- Shore R.F. and B. Rattner A (eds). 2001. *Ecotoxicology of Wild Animals*. Wiley & Sons Ltd

- Spierenburg, TH.J., de Graaf, G.J., Baars, B.J., Brus, D.H.J., Tielen M.J.M., and Arts, B.J. 1988. Cadmium, zinc, lead, and copper in livers and kidneys of cattle in the neighbourhood of zinc refineries. *Environ Monit Assess*, 11:107-114.
- Stansley, W., Roscoe, D.E., and Hazen, R.E. Cadmium contamination of deer livers in New Jersey, USA – Human health risk assessment. *Sci. Total Environ*, 107:71-82.
- Sutou, S., K. Yamamoto, H. Sendota, K. Tomomatsu, Y. Shimizu, and M. Sugiyama. 1980. Toxicity, fertility, teratogenicity, and dominant lethal tests in rats administered cadmium subchronically. I. Toxicity studies. *Ecotoxicol. Environ. Safety* 4:39–50.
- Tahvonen, R. and Kumpulainen, J. 1994. Lead and cadmium contents in pork, beef and chicken, and in pig and cow liver in Finland during 1991. *Food Addit Contam*, 11(4):415-426.
- US EPA (United States Environmental Protection Agency). 2003 (Revised 2005). Guidance for Developing Ecological Soil Screening Levels. Office of Solid Waste and Emergency Response. 1200 Pennsylvania Avenue, N.W. Washington, DC 20460. OSWER Directive 9285.7-55 November 2003 (Revised February 2005).
- US EPA (United States Environmental Protection Agency). 2001. Final Ecological Risk Assessment – Coeur d’Alene Basin Remedial Investigation/Feasibility Study. U.S. Environmental Protection Agency, Region 10. Prepared by: CH2M Hill and URS Corp. May, 2001.
- Vahteristo, L., Lyytikäinen, T., Venäläinen, E.-R., Eskola, M., Lindfors, E., Pohjanvirta, R., and Maijala, M. 2003. Cadmium intake of moose hunters in Finland from consumption of moose meat, liver and kidney. *Food Addit Contam*, 20(5):453-463.
- Wolkers H., Wensing, T. 1994. Heavy metal contamination in organs of red deer (*Cervus elaphus*) and wild boar (*Sus scrofa*) and the effect on some trace elements. *The Science of the Total Environment*. 144, 191-199.
- World Health Organization. 1992. Cadmium. Geneva, (Environmental Health Criteria, No.134).
- World Health Organization. 2000. Cadmium Copenhagen, Denmark, (Air Quality Guidelines - Second Edition)
- Wren, C. 1983. Literature Review of the Occurrence and Toxicity of Metals in Wild Animals (Publication Reference No. KN107-2-4609). Canadian Wildlife Service, Canada.

APPENDIX A

LOAELS USED IN ECO-SSL CALCULATIONS

Table A1 LOAEL data (values µg/g) from Eco-SSL for birds (US EPA, 2003)

	Bounded LOAEL	Bounded LOAEL minus 4 high values^a	Unbounded LOAEL	All LOAELs
	2.37	2.37	2.4	2.37
	2.37	2.37	3.71	2.37
	2.4	2.4	7.65	2.4
	21.1	3.3	10.4	21.1
	21.1	4.66	1.05	21.1
	7.08	3.44	4.26	7.08
	3.3	3.44	4.8	3.3
	4.66		4.9	4.66
	3.44		5.63	3.44
	3.44		9.57	3.44
	37.6		9.75	37.6
			12.2	2.4
			12.8	3.71
			13	7.65
			13.8	10.4
			14.7	1.05
				4.26
				4.8
				4.9
				5.63
				9.57
				9.75
				12.2
				12.8
				13
				13.8
				14.7
Sample size	11	7	16	27
Geomean	5.88	3.05 ^a	6.69	6.35
Min	2.37	2.37 ^a	1.05	1.05
Max	37.6	4.66	14.7	37.6

^aValues were used in Eco-SSL re-calculation

Table A2 LOAEL data (values µg/g) from Eco-SSL for mammals (US EPA, 2003)

	Reproductive Bounded LOAELs	All Reproductive LOAELs	Growth Bounded LOAELs	Growth and Reproduction Bounded LOAELs^c
	15.6	15.6	1	15.6
	4.88	4.88	1	4.88
	10	10	1.6	10
	10	10	1.3	10
	2.28	2.28	4	2.28
	4.5	4.5	0.909	4.5
	40	10	1.2	10
	54	18.4	1.6	18.4
	10	0.661	7.7	1
	18.4	1.42	10	1
	75	1.45	5.2	1.6
		1.87	10.8	1.3
		2.14	6.13	4
		3.93	10.6	0.909
		4.61	10	1.2
		5.59	15.4	1.6
		5.82	12.1	7.7
		6.3	8.71	10
		7.28	15.2	5.2
		75	17.1	10.8
		40	44.4	6.13
		54	54	10.6
		236	85.9	10
			100	15.4
				12.1
				8.71
				15.2
				17.1
Min^a	2.28^b	0.661	0.909	0.909
Max^a	18.4	18.4	17.1	18.4
Geomean^a	7.85	4.45	4.59	5.35^b
n^a	8	19	20	28

^aShaded values excluded^bUsed in Eco-SSL re-calculation^chighest values removed

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 cadmium 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 B1.

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.

Table B1 A general scale¹ 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

¹ From Senter (1969).

Selection of Correlation Method

Two common methods of correlation analysis are Pearson's correlation and Spearman's rank correlation. The benefit of using Spearman's correlation analysis is that the data need not be parametric. 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 raw data. The ability of Spearman's rank correlation to determine the relationship between two variables without the assumptions of parametric data made it more desirable for this analysis.

Correlations Performed

Spearman's rank correlation was used to determine:

1. If there is a spatial link between concentration of cadmium and distance from the smelters (*i.e.* the closer one gets to the smelter, the higher the cadmium concentration); and,
2. If there is a similar distribution pattern in elevated levels of cadmium as that of other established COCs associated with smelter operations, indicating that elevated cadmium levels originate from smelter operations.

To perform Spearman's rank correlation test, the concentration of cadmium at a site and the distance that the collected soil was from each smelter was determined. The data for the other COCs at each site was also added and ranked, with the correlation coefficient determined. The tests were one-tailed and used a significance value of $\alpha = 0.01$. Vanadium was used in the second analysis as a control, as this metal is not associated with smelter operations and should therefore have no significant relationship with cadmium.

Analysis of Copper Cliff smelter:

The total number of samples (n) was 796, consisting of all samples at the 0 - 5 cm depth out to a radius of 10,000m from the Copper Cliff, Coniston and Falconbridge smelters. Samples with Cd < 1 $\mu\text{g/g}$ were included to produce a better correlation coefficient.

Correlation analysis 1: Cadmium levels and distance from Copper Cliff smelter.

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

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

Results

The correlation coefficient associated with distance and cadmium was -0.508, with a p value <0.01 (indicated by the "Sig. (1-tailed)" value) which implies a significant, negative correlation between cadmium and distance from smelter.

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

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

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

Results

The correlation coefficients associated with Cd and Cu, Ni, were all > 0.7 , with a p value < 0.01 , which implies a significant, positive correlation between Cd and Cu or Ni.

The correlation coefficient for Cd and V was 0.206, with a p value < 0.01 , indicating that the correlation was significant, but negligible between Cd and V.

Table B2 Summary of correlation analysis for Cd, Cu, Ni, V and distance, to a radius of 10,000m from the Copper Cliff Smelter

			Cd	DISTANCE	Cu	Ni	V
Spearman's rho	Cd	Correlation Coefficient	1	-0.508	0.752	0.755	0.206
		Sig. (1-tailed)	.	0	0	0	0
		N	796	796	796	796	796
	DISTANCE	Correlation Coefficient	-0.508	1	-0.603	-0.559	-0.077
		Sig. (1-tailed)	0	.	0	0	0.015
		N	796	798	796	796	796
	Cu	Correlation Coefficient	0.752	-0.603	1	0.984	0.223
		Sig. (1-tailed)	0	0	.	0	0
		N	796	796	796	796	796
	Ni	Correlation Coefficient	0.755	-0.559	0.984	1	0.212
		Sig. (1-tailed)	0	0	0	.	0
		N	796	796	796	796	796
	V	Correlation Coefficient	0.206	-0.077	0.223	0.212	1
		Sig. (1-tailed)	0	0.015	0	0	.
		N	796	796	796	796	796

Analysis of Coniston smelter:

Correlation analysis 1: Cadmium levels and distance from Coniston smelter.

Null Hypothesis H_{o1} : There is no correlation between cadmium concentration and distance from the Coniston smelter.

Alternate Hypothesis H_{a1} : There is a correlation between cadmium concentration and distance from the Coniston smelter.

Results

The correlation coefficient associated with distance and cadmium was 0.233 with a p value <0.01 , which implies a significant, moderate correlation between cadmium and distance from the smelter.

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

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

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

Results

The correlation coefficients associated with Se and As, Co, Cu, Ni, Pb were all > 0.6 with a p value <0.01 . Therefore, H_{o2} was rejected and it was concluded that there was a high, positive correlation between cadmium and the other established COCs associated with smelter operation.

The correlation coefficient for V was 0.102 with a p value <0.01 indicating that there was a significant, negligible correlation between Cd and V.

Complete results of the statistical analysis are found in Table B3.

Table B3 Summary of correlation analysis for Cd, Cu, Ni, V and distance, to a radius of 10,000m from the Coniston Smelter

		Cd	DISTANCE	Cu	Ni	V	
Spearman's rho	Cd	Correlation Coefficient	1	0.233	0.688	0.707	0.102
		Sig. (1-tailed)	.	0	0	0	0.006
		N	618	618	618	618	618
	DISTANCE	Correlation Coefficient	0.233	1	0.127	0.115	0.193
		Sig. (1-tailed)	0	.	0.001	0.002	0
		N	618	618	618	618	618
	Cu	Correlation Coefficient	0.688	0.127	1	0.980	0.098
		Sig. (1-tailed)	0	0.001	.	0	0.007
		N	618	618	618	618	618
	Ni	Correlation Coefficient	0.707	0.115	0.980	1	0.076
		Sig. (1-tailed)	0	0.002	0	.	0.030
		N	618	618	618	618	618
	V	Correlation Coefficient	0.102	0.193	0.098	0.076	1
		Sig. (1-tailed)	0.06	0	0.007	0.030	.
		N	618	618	618	618	618

Analysis of Falconbridge smelter:

Correlation analysis 1: Cadmium concentration and distance from Falconbridge smelter.

Null Hypothesis H_{01} : There is no correlation between cadmium concentration and distance from the Falconbridge smelter.

Alternate Hypothesis H_{a1} : There is a correlation between cadmium concentration and distance from the Falconbridge smelter.

Results

The correlation coefficient associated with distance and cadmium was -0.488 with a p value <0.01 which implies a significant, negative correlation between cadmium and distance from the Falconbridge smelter.

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

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

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

Results

The correlation coefficients associated with Cd and As, Co, Cu, Ni, Pb were all > 0.8 with a p value < 0.01 which implies a significant, positive correlation between Cd and As, Co, Cu, Ni, and Pb.

The correlation coefficient for V was 0.211 with a p value < 0.01 indicating that there was a significant but negligible correlation between Cd and V. Complete results of the statistical analysis are found in Table B4.

Table B4 Summary of correlation analysis for Cd, Cu, Ni, V and distance, out to a radius of 10,000m from the Falconbridge Smelter

			Cd	Cu	Ni	V	DISTANCE
Spearman's rho	Cd	Correlation Coefficient	1	0.814	0.831	.211	-0.488
		Sig. (1-tailed)	.	0	0	0	0
		N	360	360	360	360	360
	Cu	Correlation Coefficient	0.814	1	0.980	0.225	-0.409
		Sig. (1-tailed)	0	.	0	0	0
		N	360	360	360	360	360
	Ni	Correlation Coefficient	0.831	0.980	1	0.212	-0.415
		Sig. (1-tailed)	0	0	.	0	0
		N	360	360	360	360	360
	V	Correlation Coefficient	0.211	0.225	0.212	1	-0.247
		Sig. (1-tailed)	0	0	0	.	0
		N	360	360	360	360	360
	DISTANCE	Correlation Coefficient	-0.488	-0.409	-0.415	-0.247	1
		Sig. (1-tailed)	0	0	0	0	.
		N	360	360	360	360	360

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

- 1) There is a relationship between cadmium concentration and distance from the Copper Cliff smelter - the closer one gets to the smelter, the higher the concentration of cadmium in the soil.
- 2) Cadmium follows the same trend as the other already established COCs, which increase in concentration as the distance to the smelter decreases, therefore indicating a link between the presence of elevated levels of cadmium and smelter operation.