

SUDBURY AREA RISK ASSESSMENT

VOLUME II – CHAPTER 3 PHASE 2: SAMPLING AND ANALYSES TO FILL IDENTIFIED DATA GAPS

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3.0 PHASE 2: SAMPLING AND ANALYSES TO FILL IDENTIFIED DATA GAPS

The purpose of Phase 2 of the HHRA was to collect the necessary data to fill the information gaps identified in Phase 1 (if feasible) and to decrease the level of uncertainty in the risk assessment. Using Phase 1 findings as a guide, Phase 2 included the development of sampling plans, sample collection and analyses, review of the new sampling data and incorporation of new information into the spatial analysis or related databases. Based upon previous assessments and a review of the available data, the following issues were addressed in Phase 2:

- A comprehensive air monitoring program for the GSA;
- The bioavailability of COC in soil and dust media (*e.g.*, investigation of bioavailability/bioaccessibility in soil and dust for each COC using simulated stomach acid leach bioaccessibility test data);
- Speciation of COC in soil and air samples to enable species-specific exposure and toxicity issues to be addressed;
- Detailed dietary (*i.e.*, food consumption survey, including local fish and wild game) and behavioural data (*i.e.*, participation in gardening, hunting, and fishing activities) for each COI, particularly anglers and hunters, and the unique First Nations communities;
- Concentrations of COC in local fish and livestock;
- Concentrations of COC in private potable water sources;
- Concentrations of COC in indoor dust; and
- Concentrations of COC in garden produce.

An overview of the methodology and results for each of these studies is provided in the section below. Complete methodologies and data reports for each study can be found in the Appendices to this volume.



3.1 Air Monitoring Program

3.1.1 Overview of Program

Given the historic and ongoing atmospheric emissions from the two active smelting facilities within Sudbury, it is very important to have an accurate measure of airborne concentrations of the COC to which GSA residents are exposed. While some historic and ongoing ambient air monitoring data are available within the GSA, the MOE-regulatory monitoring stations maintained by the two companies are limited to specific geographical areas (*i.e.*, Copper Cliff, Falconbridge, and Sudbury Centre) and do not provide an adequate estimation of ambient conditions in all of the communities of interest. In addition, the routine monitoring programs did not include all the COC included in this risk assessment. This was a significant data gap for the HHRA. Given the necessity to evaluate all potential exposure pathways as part of the HHRA, an extensive air monitoring program was established to provide the necessary air data to the assessment. As such, the purpose of the air monitoring study was to collect samples of the air inhaled by residents of the Greater Sudbury area as part of the overall HHRA. The following section provides a summary of the methodology and results of the program. A more detailed report is provided in Appendix F.

The air monitoring network followed the National Air Pollution Surveillance Program (NAPS) six-day schedule between October, 2003 and September, 2004, inclusive. Three size fractions of particulate matter (PM) were collected on quartz fibre filters using high volume (approximately 1,630 m³ of air per day – termed "hi-vol") and low volume (approximately 24 m³ of air per day – termed "lo-vol") samplers. The three size fractions of PM sampled were:

- Respirable particulate matter less than 2.5 microns in diameter (PM_{2.5});
- Respirable particulate matter less than 10 microns in diameter (PM₁₀); and
- Total suspended particulate matter less than 44 microns in diameter (TSP).

These size fractions are relevant to the HHRA because they represent particulate matter that could be retained in the nose (TSP), upper lung (PM_{10}) and lower lung ($PM_{2.5}$). The particulate size considered to be of the most toxicological significance in the HHRA is PM_{10} (*i.e.*, this fraction was used as the primary inhalation component for the assessment modelling), while concentrations detected within the $PM_{2.5}$ size fraction also provide useful qualitative information to the assessment.



After the total mass of the particulate matter collected was determined by weighing the filters before and after sampling, the samples were analyzed for a suite of metals that included the six COC. Analytes included antimony, arsenic, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, molybdenum, nickel, selenium, sulphur, thallium, uranium, vanadium, and zinc. TSP, PM₁₀ and PM_{2.5} ratios were also determined, in an attempt to differentiate the sources of the samples collected (*i.e.*, smelting *versus* non-smelting operations in the Greater Sudbury Area, such as blown dust from tailings piles).

Ten monitoring sites were chosen for the air quality monitoring survey. These included two existing MOE sites (*i.e.*, Copper Cliff and Falconbridge/Edison), seven new sites within the Greater Sudbury area and one background site. An extensive site selection process was used by the SARA Group, and is described in detail in the Work Plan and Operations Manual section of the monitoring study report in Appendix F. The sites were primarily selected based on proximity to current and past smelter and mining operations and/or as a result of predicted impacts from these operations derived through dispersion modelling, and to represent exposure to residents in the different communities. Power, security, access, and unobstructed air flow to the site were some of the additional conditions considered when choosing site locations.

To establish representative ratios between the different size fractions, samples of all three size-fractions were collected as part of this study. However, it was not considered necessary to install three monitors (*i.e.*, one for each size fraction) at every sampling location. Rather, a plan was adopted to apply the ratios from the sites with three monitors to sites where only PM_{10} was measured, if considered statistically appropriate.

A list of the sites is provided in Table 3.1 below, with the actual locations shown on the map provided in Figure 3-1.

Site Location	Parameters Measured at Each Site ^a
Copper Cliff (Pumphouse on Nickel Street)	TSP, PM ₁₀ , PM _{2.5} and PM _{2.5} Partisol lovol
Falconbridge (Edison Building)	TSP, PM ₁₀ , PM _{2.5} and PM _{2.5} Partisol lovol
Sudbury Centre West (Travers Street, Catholic School Board yard)	TSP, PM ₁₀ and PM _{2.5}
Garson (Public Works Building yard)	TSP, PM ₁₀ and PM _{2.5}
Walden (Jesse Hamilton School, adjacent to SO ₂ monitor)	PM ₁₀
Coniston (on hill adjacent to Communication Tower)	PM ₁₀
Hanmer (Pumphouse on Notre Dame Road)	PM ₁₀
Sudbury Centre South (Algonquin Public School)	PM ₁₀
Skead (Bowland Bay Road, adjacent to SO ₂ monitor)	PM ₁₀
Windy Lake Provincial Park, Onaping (near works yard)	TSP, PM ₁₀ and PM _{2.5}

 Table 3.1
 Site Locations and Parameters for Air Quality Monitoring Network

At the laboratory, all of the air filters were cut into strips for analysis. Extra filter strips were cut from the MOE Copper Cliff and the Falconbridge/Edison samples and were distributed to the MOE and Xstrata Nickel laboratories for independent analysis. This procedure served as a partial quality assurance measure (*i.e.*, the comparison of results obtained from different laboratories for the same filter). Differences in analytical methodologies must be taken into consideration, as well as the possibility of uneven distribution of particulate matter over the surface of the filters caused by additional handling.

All sampling units were subject to a full calibration once every three months, or more often if required (*e.g.*, if equipment was replaced). The first calibration was performed in September, 2003, immediately after the units were installed at the sites. A second calibration was performed in December, 2003, a third one in March, 2004 one in July, 2004 and a final one at the end of the study in September, 2004. The MOE performed an audit on all of the units at the onset of the study, before any samples were collected. A second audit was performed in March (after six months of operation), and the last audit was performed at the conclusion of the study. All units were given a pass designation by the MOE at each auditing session (MOE certificates are available in Appendix F).

Laboratory analysis of the samples collected on the quartz filters included total particulate matter for the TSP, PM_{10} and $PM_{2.5}$ samples and a multi-metal scan. Some of the samples collected were also submitted for further metal speciation for COC identified during the screening phase of the HHRA process (Chapter 4, Section 4.1). This requirement for speciation was based upon the relative differences in respiratory toxicology of the various chemical species (*e.g.*, soluble *versus* insoluble forms). One blank filter was also submitted for analysis with every 10 sample filters, as a quality assurance measure.



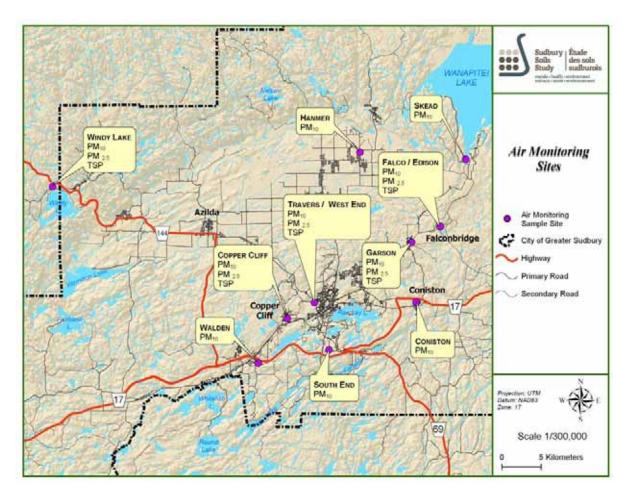


Figure 3-1 Air Monitoring Sites Selected for the Sudbury Soils Study

3.1.2 Study Results

Results of the air monitoring study for PM_{10} , $PM_{2.5}$, and TSP size fractions are presented in Tables 3.2 through 3.4, respectively. Statistics are provided for the arithmetic and geometric means, as well as the minimum and maximum COC concentrations detected at each monitoring location throughout the year long study period. For comparison purposes, MOE 24-hour ambient air quality criteria (AAQC) are provided for the relevant particulate matter fraction (*i.e.*, TSP, PM_{10} , or $PM_{2.5}$). However, it should be noted that these criteria are not used in the current assessment for any screening purpose or evaluation of risk. The AAQC were only provided to demonstrate the common regulatory benchmark used in the routine monitoring of these types of COC (*i.e.*, refer to the MOE annual monitoring reports).



Statistics			Sampled Parameter (µg/m ³)				
Statistics	PM ₁₀	Arsenic	Cobalt	Copper	Lead	Nickel	Selenium
24-Hour AAQC	50	0.3	0.1	50	0.5	2	10
Algonquin (56 samples tak					2	-	т
Arithmetic Mean	10.5	0.0025	0.0007	0.018	0.0062	0.010	0.0034
Geometric Mean	9.0	0.0021	0.0007	0.010	0.0002	0.0054	0.0033
Minimum	4.0	nd ^a	nd	0.0032	nd	nd	nd
Maximum	41.0	0.020	0.0026	0.073	0.032	0.062	0.013
95 UCLM	14.3	0.0040	0.00097	0.027	0.0096	0.017	0.0043
Number > AAQC	0	0.0010	0	0	0	0	0
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0018	0.0018	0.0062
% less than Det. Limit	0.00	89%	91%	0%	14%	18%	95%
Coniston (61 samples taken	•)		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		11/0	1070	, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
Arithmetic Mean	10.3	0.0022	0.0007	0.014	0.0064	0.0086	0.0032
Geometric Mean	8.6	0.0022	0.0007	0.014	0.0004	0.0080	0.0032
Minimum	3.0	nd	nd	0.0029	nd	nd	0.0031 nd
Maximum	41.4	0.0077	0.0045	0.0029	0.043	0.043	0.010
95 UCLM	14.2	0.0028	0.0043	0.019	0.043	0.043	0.0037
Number > AAQC	0	0.0028	0.0010	0.019	0.010	0.014	0.0037
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0018	0.0018	0.0061
% less than Det. Limit	0.00	89%	92%	0.0012	10%	15%	98%
	-1)	0970	9270	070	1070	1370	9870
Copper Cliff (60 samples to		0.0001	0.0017	0.064	0.015	0.040	0.0045
Arithmetic Mean	12.1	0.0031	0.0017	0.064	0.015	0.048	0.0045
Geometric Mean	10.1	0.0024	0.0012	0.041	0.0068	0.028	0.0037
Minimum	2.5	nd	nd	0.0061	nd	0.0020	nd
Maximum	43.4	0.023	0.0073	0.34	0.092	0.24	0.030
95 UCLM	16.2	0.0049	0.0025	0.10	0.026	0.076	0.0068
Number > AAQC	0	0	0	0	0	0	0
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0019	0.0019	0.0062
% less than Det. Limit		80%	50%	0%	13%	0%	87%
Falconbridge (61 samples t	·····						
Arithmetic Mean	9.1	0.0022	0.0016	0.023	0.0072	0.023	0.0032
Geometric Mean	6.7	0.0021	0.0012	0.018	0.0038	0.017	0.0032
Minimum	0.4	nd	nd	0.0029	nd	0.0028	nd
Maximum	44.7	0.0058	0.0097	0.084	0.054	0.10	0.0082
95 UCLM	13.4	0.0027	0.0024	0.031	0.013	0.033	0.0037
Number > AAQC	0	0	0	0	0	0	0
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0018	0.0018	0.0061
% less than Det. Limit		87%	48%	0%	26%	0%	97%
Garson (57 samples taken)							
Arithmetic Mean	12.4	0.0025	0.0010	0.027	0.0059	0.013	0.0035
Geometric Mean	10.1	0.0022	0.0008	0.022	0.0044	0.0074	0.0033
Minimum	2.6	nd	nd	nd	nd	nd	nd
Maximum	43.9	0.0082	0.0060	0.090	0.019	0.054	0.011
95 UCLM	17.0	0.003	0.0016	0.037	0.0084	0.021	0.0043
Number > AAQC	0	0	0	0	0	0	0
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0019	0.0019	0.0062
% less than Det. Limit		82%	79%	0%	14%	14%	95%

Table 3.2Results of PM10 Samples at each Monitoring Location (October 2003 to
September 2004)



Statistics			Sample	ed Paramete	$r (\mu g/m^3)$		
Statistics	PM ₁₀	Arsenic	Cobalt	Copper	Lead	Nickel	Selenium
24-Hour AAQC	50	0.3	0.1	50	0.5	2	10
Hanmer (56 samples taken)							<u>.</u>
Arithmetic Mean	11.6	0.0029	0.0006	0.047	0.0050	0.0057	0.0035
Geometric Mean	9.2	0.0022	0.0006	0.021	0.0028	0.0027	0.0033
Minimum	0.6	nd	nd	0.0024	nd	nd	nd
Maximum	41.5	0.036	0.0014	0.32	0.027	0.032	0.014
95 UCLM	16.1	0.0056	0.00068	0.082	0.0082	0.010	0.0046
Number > AAQC	0	0	0	0	0	0	0
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0019	0.0019	0.0062
% less than Det. Limit		88%	98%	0%	43%	43%	95%
Skead (61 samples taken)							,
Arithmetic Mean	9.8	0.0021	0.0008	0.015	0.0041	0.0068	0.0032
Geometric Mean	7.7	0.0021	0.0007	0.012	0.0011	0.0031	0.0032
Minimum	2.2	nd	nd	0.0012	nd	nd	nd
Maximum	47.4	0.0061	0.0027	0.047	0.033	0.051	0.0032
95 UCLM	14.0	0.0026	0.0010	0.021	0.0067	0.012	0.0032
Number > AAQC	0	0	0	0	0	0	0
Detection Limit	0.06	0.0039	0.0013	0.0013	0.0019	0.0019	0.0065
% less than Det. Limit	0.00	93%	90%	0%	33%	41%	100%
Sudbury Centre West (60 san	nnles taken)					1	1
Arithmetic Mean	18.5	0.0055	0.0070	0.13	0.020	0.11	0.0074
Geometric Mean	14.4	0.0035	0.0070	0.062	0.0095	0.033	0.0074
Minimum	4.2	nd	nd	0.002	nd	0.0021	nd
Maximum	84.9	0.028	0.065	1.1	0.13	0.87	0.081
95 UCLM	26.9	0.0089	0.005	0.24	0.035	0.21	0.001
Number > AAQC	20.5	0.0005	0.011	0	0.055	0.21	0.011
Detection Limit	0.07	0.0041	0.0014	0.0014	0.0020	0.0020	0.0068
% less than Det. Limit		67%	48%	0%	7%	0%	82%
Walden (61 samples taken)			10/0	0/0	//0	070	02/0
Arithmetic Mean	11.6	0.0024	0.0009	0.030	0.0075	0.011	0.0034
Geometric Mean	9.7	0.0021	0.0009	0.022	0.0075	0.0042	0.0033
Minimum	2.1	nd	nd	0.0059	nd	nd	nd
Maximum	45.7	0.0091	0.0049	0.24	0.056	0.088	0.011
95 UCLM	15.8	0.0031	0.00085	0.048	0.014	0.020	0.0040
Number > AAQC	0	0	0	0	0	0	0
Detection Limit	0.06	0.0039	0.0013	0.0013	0.0019	0.0019	0.0064
% less than Det. Limit	0.00	90%	84%	0%	34%	31%	97%
Windy Lake (54 samples take	<i>n</i>)						
Arithmetic Mean	10.7	0.0020	0.0006	0.023	0.0036	0.0039	0.0030
Geometric Mean	8.7	0.0020	0.0006	0.023	0.0030	0.0039	0.0030
Minimum	3.2	nd	nd	0.0079	0.0022 nd	nd	0.0030 nd
Maximum	58.4	0.0087	nd	0.0079	0.028	0.046	nd
95 UCLM	15.0	0.0026	0.0006	0.040	0.0063	0.0040	0.0032
Number > AAQC	13.0	0.0020	0.0000	0.028	0.0005	0.0087	0.0032
Detection Limit	0.06	0.0036	0.0012	0.0012	0.0018	0.0018	0.0061
% less than Det. Limit	0.00	94%	100%	0.0012	48%	57%	100%

Table 3.2Results of PM10 Samples at each Monitoring Location (October 2003 to
September 2004)

^a nd indicates a non-detect, or more specifically, the COC concentration was below the listed detected limit.



Statistics			Sample	ed Paramete	er (µg/m ³)		
Statistics	PM _{2.5}	Arsenic	Cobalt	Copper	Lead	Nickel	Seleniun
24-Hour AAQC	30	0.3	0.1	50	0.5	2	10
Copper Cliff (56 samples tal	3					1	
Arithmetic Mean	10.2	0.0029	0.0012	0.047	0.012	0.037	0.0040
Geometric Mean	8.7	0.0023	0.00012	0.047	0.0012	0.037	0.0040
Minimum	1.5	nd ^a	nd	0.0053	nd	nd	nd
Maximum	30.9	0.022	0.0073	0.0033	0.076	0.23	0.030
95 UCLM	13.6	0.022	0.0073	0.29	0.070	0.23	0.0062
Number > AAQC	13.0	0.0048	0.0020	0.000	0.021	0.005	0.0002
Detection Limit	0.06	0.0035	0.0012	0.0012	0.0018	0.0018	0.0059
% less than Det. Limit	0.00	80%	73%	0%	13%	2%	88%
	-1)	0070	1370	070	1370	2/0	0070
Falconbridge (58 samples to		0.0000	0.0000	0.011	0.0000	0.0000	0.0000
Arithmetic Mean	7.0	0.0020	0.0009	0.011	0.0082	0.0088	0.0032
Geometric Mean	5.1	0.0020	0.0008	0.0099	0.0038	0.0079	0.0032
Minimum	0.4	nd	nd	0.0041	nd	0.0032	nd
Maximum	34.8	0.0043	0.0042	0.033	0.095	0.024	0.0032
95 UCLM	10.5	0.0022	0.0013	0.014	0.017	0.011	0.0032
Number > AAQC	1	0	0	0	0	0	0
Detection Limit	0.06	0.0039	0.0013	0.0013	0.0019	0.0019	0.0064
% less than Det. Limit		97%	88%	0%	26%	0%	100%
Garson (60 samples taken)							
Arithmetic Mean	10.0	0.0021	0.0008	0.017	0.0046	0.0076	0.0031
Geometric Mean	8.3	0.0019	0.0007	0.014	0.0032	0.0040	0.0030
Minimum	1.3	nd	nd	0.0038	nd	nd	nd
Maximum	35.9	0.0068	0.0057	0.068	0.020	0.046	0.0086
95 UCLM	13.5	0.0026	0.0012	0.023	0.0068	0.013	0.0036
Number > AAQC	1	0	0	0	0	0	0
Detection Limit	0.06	0.0035	0.0012	0.0012	0.0017	0.0017	0.0058
% less than Det. Limit		90%	90%	0%	22%	22%	97%
Sudbury Centre West (59 sa	mples taken)						
Arithmetic Mean	12.0	0.0041	0.0022	0.046	0.015	0.033	0.0059
Geometric Mean	10.3	0.0030	0.0013	0.029	0.0076	0.014	0.0041
Minimum	3.4	nd	nd	0.0047	nd	nd	nd
Maximum	41.1	0.020	0.016	0.35	0.10	0.28	0.059
95 UCLM	16.1	0.0064	0.0037	0.078	0.026	0.062	0.011
Number > AAQC	2	0	0	0	0	0	0
Detection Limit	0.06	0.0038	0.0013	0.0013	0.0019	0.0019	0.0064
% less than Det. Limit		69%	54%	0%	12%	8%	85%
Windy Lake (60 samples tak	ken)					·	
Arithmetic Mean	8.3	nd	nd	0.026	0.0027	0.0019	nd
Geometric Mean	6.2	nd	nd	0.020	0.0027	0.0013	nd
Minimum	0.2	nd	nd	0.0068	nd	nd	nd
Maximum	66.3	nd	nd	0.14	0.012	0.016	nd
95 UCLM	13.2	nd	nd	0.038	0.0012	0.0032	nd
Number > AAQC	13.2	0	0	0.058	0.0040	0.0032	0
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0019	0.0019	0.0062
% less than Det. Limit	0.00	100%	100%	0.0012	53%	72%	100%

Table 3.3Results of PM2.5 Samples at each Monitoring Location (October 2003 to
September 2004)

^a nd indicates a non-detect, or more specifically, the COC concentration was below the listed detected limit.



Statistics			Sample	ed Paramete	$r (\mu g/m^3)$		
Statistics	TSP	Arsenic	Cobalt	Copper	Lead	Nickel	Selenium
24-Hour AAQC	120	0.3	0.1	50	0.5	2	10
Copper Cliff (60 samples ta	ken)						·
Arithmetic Mean	24.6	0.0040	0.0057	0.30	0.021	0.18	0.0052
Geometric Mean	20.9	0.0030	0.0043	0.24	0.012	0.13	0.0032
Minimum	5.9	nd ^a	nd	0.057	nd	0.022	nd
Maximum	82.0	0.032	0.021	1.1	0.12	0.80	0.038
95 UCLM	32.8	0.0065	0.0021	0.42	0.034	0.26	0.0083
Number > AAQC	0	0.0002	0	0	0.051	0.20	0.0005
Detection Limit	0.07	0.0041	0.0014	0.0014	0.0020	0.0020	0.0068
% less than Det. Limit		72%	10%	0%	2%	0%	85%
Falconbridge (58 samples to	nkon)	1270	10/0		270	0/0	
Arithmetic Mean	16.8	0.0025	0.0051	0.16	0.0091	0.059	0.0033
Geometric Mean	12.8	0.0023	0.0031	0.10	0.0091	0.039	0.0033
Minimum	3.1	nd	nd	0.016		0.0067	nd
Maximum	89.8	0.011	0.039	0.010	0.092	0.0007	0.010
95 UCLM	25.7	0.0011	0.0089	0.33	0.092	0.28	0.0040
Number > AAQC	0	0.0033	0.0089	0.23	0.017	0.095	0.0040
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0018	0.0018	0.0061
% less than Det. Limit	0.00	85%	14%	0.0012	24%	0.0010	95%
		0570	1470	070	2470	070	5570
Garson (60 samples taken)				·		-	
Arithmetic Mean	25.6	0.0025	0.0028	0.18	0.0074	0.045	0.0031
Geometric Mean	21.3	0.0021	0.0018	0.13	0.0056	0.035	0.0029
Minimum	6.9	nd	nd	0.019	nd	0.0065	nd
Maximum	81.9	0.0082	0.013	1.8	0.034	0.15	0.011
95 UCLM	35.0	0.0036	0.0044	0.30	0.011	0.064	0.0039
Number > AAQC	0	0	0	0	0	0	0
Detection Limit	0.05	0.0032	0.0011	0.0011	0.0016	0.0016	0.0054
% less than Det. Limit		80%	28%	0%	7%	0%	92%
Sudbury Centre West (59 sa	mples taken)						
Arithmetic Mean	40.5	0.0064	0.020	0.32	0.024	0.29	0.0067
Geometric Mean	31.5	0.0039	0.0080	0.20	0.013	0.13	0.0041
Minimum	10.0	nd	nd	0.030	0.0018	0.014	nd
Maximum	153.8	0.031	0.16	2.0	0.19	1.8	0.085
95 UCLM	57.9	0.011	0.036	0.53	0.042	0.53	0.014
Number > AAQC	2	0	2	0	0	0	0
Detection Limit	0.06	0.0035	0.0012	0.0012	0.0017	0.0017	0.0058
% less than Det. Limit		49%	8%	0%	0%	0%	80%
Windy Lake (61 samples tak	ken)						
Arithmetic Mean	16.0	nd	nd	0.19	0.0033	0.0048	nd
Geometric Mean	10.6	nd	nd	0.18	0.0023	0.0028	nd
Minimum	2.2	nd	nd	0.0591	nd	nd	nd
Maximum	147.3	0.0049	0.0026	0.68	0.017	0.049	nd
95 UCLM	27.2	0.0024	0.00079	0.25	0.0051	0.0088	0.0031
Number > AAQC	1	0	0	0	0	0	0
Detection Limit	0.06	0.0037	0.0012	0.0012	0.0019	0.0019	0.0062
% less than Det. Limit		95%	97%	0%	43%	31%	100%

Table 3.4Results of TSP Samples at each Monitoring Location (October 2003 to
September 2004)

^a nd indicates a non-detect, or more specifically, the COC concentration was below the listed detected limit.



3.1.2.1 Arsenic Concentrations

In general, arsenic levels across all size fractions were consistent at all of the monitoring sites, in most cases at or below the detection limits, even at the 75th percentile level. The exception to this was the Sudbury Centre West station, where there was a significant number of values in the range of 0.002 to 0.008 μ g/m3 (PM10 fraction). This is well above the detection limit but still at least two orders of magnitude lower than the AAQC level of 0.3 μ g/m3. The median value was at the detection limit, indicating that there were "non-detectable" levels measured during the majority of the sampling days at all stations. The highest 95th percentile level was measured at the Sudbury Centre West site, at a level that was three times greater than the levels at any of the other stations. As arsenic has not been widely sampled at monitoring stations around Ontario, no broad comparison can be made.

3.1.2.2 Cobalt Concentrations

Similar to arsenic, cobalt concentrations at the ten survey sites were very consistent throughout the duration of the survey. The highest concentrations were measured at the Sudbury Centre West station, followed by significantly lower, but still measurable, levels at Copper Cliff and Falconbridge. The great majority of cobalt concentrations were several orders of magnitude less than the 24-hour AAQC of 0.1 μ g/m³ for cobalt, with the exception of the absolute maximum concentration of 0.06 μ g/m³ (PM₁₀ fraction) measured at the Sudbury Centre West station, which approached but remained below the AAQC. As cobalt has not been widely sampled at monitoring stations around Ontario, no comparison values were available.

3.1.2.3 Copper Concentrations

Fairly low (compared to AAQC), but measurable levels of copper were measured at all of the ten monitoring stations. The highest levels were at the Sudbury Centre West station, followed by Copper Cliff and Hanmer. The other sites reported concentration distributions with 95th percentiles all less than $0.05 \ \mu g/m^3$. The highest 24-hour value for the year was $1.05 \ \mu g/m^3$ (PM₁₀ fraction) at the Sudbury Centre West station, which is well below the AAQC of 50 $\ \mu g/m^3$ for copper. As a point of comparison, the arithmetic mean of copper concentrations (PM₁₀) at monitoring stations throughout Ontario between 1998 and 2002 was $0.02 \ \mu g/m^3$ (MOE, 1998; 1999; 2000; 2001; 2002).



3.1.2.4 Lead Concentrations

Results of the year-long monitoring program indicate that, except for occasional excursions, all of the stations recorded consistently low levels of lead (compared to the AAQC). Occasional higher values were observed in Copper Cliff, where the highest 95th percentile value was measured, and the Sudbury Centre West station, which recorded the highest 75th percentile level. This would indicate that Copper Cliff experienced some relatively elevated values of lead, but not as often as the moderately high levels experienced at the Sudbury Centre West station. The 25th and 75th percentiles and median values were all below 0.025 μ g/m³ (PM₁₀ fraction). The highest single concentration of 0.13 μ g/m³ was measured at the Sudbury Centre West station. As a point of comparison, the arithmetic mean of lead concentrations (PM₁₀) at monitoring stations throughout Ontario between 1998 and 2002 was 0.01 μ g/m³ (MOE, 1998; 1999; 2000; 2001; 2002). All stations recorded concentrations well below the provincial AAQC level of 2.0 μ g/m³.

3.1.2.5 Nickel Concentrations

Fairly low levels of nickel were recorded at most stations (compared to the AAQC) with the exception of the Sudbury Centre West station, which reported considerably higher distributions than the other stations, and Copper Cliff, which was moderately higher than the other locations. The maximum single nickel concentration measured during the year was $0.87 \ \mu g/m^3$ (PM₁₀ fraction) at the Sudbury Centre West station. As a point of comparison, the arithmetic mean of nickel concentrations (PM₁₀) at monitoring stations throughout Ontario between 1998 and 2002 was $0.007 \ \mu g/m^3$ (MOE, 1998; 1999; 2000; 2001; 2002). All levels were below the 24-hour AAQC of 2.0 $\mu g/m^3$.

3.1.2.6 Selenium Concentrations

Selenium was essentially non-detectable, and was measured only very occasionally at levels above the detection limit. The Sudbury Centre West station recorded the highest single concentration during the year ($0.08 \ \mu g/m^3$ on the PM₁₀ fraction), whereas the other sites did not record much higher than the detection limit for most of the time. As selenium has not been widely sampled at monitoring stations around Ontario, no broad comparison value was available. All values were well below the 24-hour AAQC level of $10.0 \ \mu g/m^3$.



3.1.3 Additional Observations

Wind direction and speed were additional parameters recorded as part of the air monitoring study. Further analysis of these data provided some information on seasonal trends observed in the GSA during the study period (2003 to 2004) which is fairly consistent with the historical metereological data for the GSA presented in Section 2.1.1.2. To examine seasonal trends in wind direction in the GSA, the monitoring data was categorized into four seasons; winter (December through February), spring (March through May), summer (June through August), and fall (September through November).

During the winter months, the wind direction varied considerably with the predominant winds coming from the north and northwest (33%), and occasionally from the south and southwest (27%). Wind speed ranged between 7.8 and 23.3 km/hr with an average speed of 15.5 km/hr and the strongest winds coming from the northwest.

Winds were predominantly from the north (60%), including north-westerly and north-easterly winds, during the spring months, with some winds from the south and southwest (33.3%). Wind speed ranged from 8.4 to 23.4 km/hr, with an average speed of 16 km/hr.

During 50% of the summer recording days, winds were coming from the west and southwest, while 37.5% of the recordings showed winds from the north and northeast. The wind speed ranged from 4.3 to 18.8 km/hr during the summer months, with an average speed of 12 km/hr.

Winds came predominantly from the south (46.7%), including from the southeast and the southwest, during the fall, with occasional winds from the north and northwest (33.3%). The fastest and slowest wind speeds were recorded during the fall, with a range of 2.2 to 29.2 km/hr. The average wind speed during the fall was 12.2 km/hr.

A number of interesting observations can be made about the results presented in this report. The Sudbury Centre West station consistently recorded high concentrations of particulate matter and metals/metalloids. This site is situated close to a process waste pile, and these results emphasize the possible importance of fugitive emissions, (*i.e.*, the concentrations recorded at this station were greater than those measured at stations that were situated close to other industrial sources).

Windy Lake Provincial Park was established as a regional background (northern Ontario) station remote from direct influence of the smelters. Moderate levels of arsenic, copper and particulate matter were measured on occasion at this site. Interestingly, much of the particulate matter measured on these days



was observed to be pollen (filters were yellow rather than grey or brown), and seemed to be present in all of the particulate size fractions.

Higher than expected copper levels were recorded at the Hanmer site at the onset of this study, but these were reduced when the Wedding hi-vol monitor was replaced (due to mechanical reliability issues) with a newer (Tisch) model.

In some instances, the Falconbridge/Edison station recorded concentrations that were lower than those in less industrialized settings. This may have been due to local meteorology (this station was not consistently downwind of the sources at the Falconbridge smelter) or the fact that the monitoring site is located on a rooftop, which may have influenced the measurement capacity of the hi-vols.

3.1.4 Conclusions of the Air Study

In conclusion, relatively low levels of all metals/metalloids and particulate matter were measured in the 1,220 hi-vol samples collected from October, 2003 to September, 2004, inclusive. The air quality limits were exceeded only 14 times (five times for the AAQC, three times for the Interim AAQC and six times for the Canada-Wide Standard), with some of these exceedances attributed to natural sources.

Data from the survey were incorporated into the HHRA, representing the ambient air concentrations inhaled by residents of the various communities. Data from both Sudbury Centre West and Sudbury Centre South monitoring stations were used to represent exposure to residents of Sudbury Centre as a whole. Use of the Sudbury Centre West station to represent typical airborne concentrations for the entire Sudbury Centre COI would be a very conservative approach, given the proximity of this site to both the Copper Cliff smelter and the nearby slag piles and would likely over estimate actual exposure to the broader area.

Table 3.5 provides a summary of the PM_{10} air concentrations carried forward for use in the current HHRA. Further details on the use of these data are provided in Chapter 4 of this volume.

Table 3.5Summary of Ambient Air Concentrations (PM10) in the GSA (µg						
COI		COC	Min	Max	Mean ^a	95% UCLM
		As	0.0019	0.0077	0.0022	0.0024
		Со	0.0006	0.0045	0.0007	0.0009
Coniston		Cu	0.0029	0.0509	0.0142	0.0162
(n=61)		Ni	0.0009	0.0427	0.0086	0.0121
		Pb	0.0009	0.0424	0.0064	0.0080
		Se	0.0031	0.0100	0.0032	0.0034

Table 3.5Summary of Ambient Air Concentrations (PM10) in the GSA (µg/m³)								
COI	COC	Min	Max	Mean ^a	95% UCLM			
	As	0.0019	0.0229	0.0031	0.0050			
	Со	0.0006	0.0073	0.0017	0.0025			
Copper Cliff	Cu	0.0061	0.3426	0.0641	0.0809			
(n=60)	Ni	0.0020	0.2401	0.0476	0.0595			
	Pb	0.0009	0.0924	0.0145	0.0220			
	Se	0.0031	0.0301	0.0045	0.0055			
	As	0.0019	0.0058	0.0022	0.0024			
	Со	0.0006	0.0097	0.0016	0.0025			
Falconbridge	Cu	0.0029	0.0843	0.0227	0.0264			
(n=61)	Ni	0.0028	0.1027	0.0226	0.0280			
	Pb	0.0009	0.0539	0.0072	0.0152			
	Se	0.0031	0.0082	0.0032	0.0034			
	As	0.0018	0.0284	0.0041	0.0061			
	Со	0.0006	0.0648	0.0040	0.0097			
Sudbury Centre	Cu	0.0032	1.05	0.0771	0.17			
(n=116)	Ni	0.0009	0.87	0.0610	0.0947			
	Pb	0.0009	0.13	0.0133	0.0254			
	Se	0.00308	0.0808	0.00550	0.00924			
	As	0.0019	0.0357	0.0029	0.0056			
	Со	0.0006	0.0014	0.0006	0.0007			
Hanmer	Cu	0.0024	0.3242	0.0472	0.0992			
(n=56)	Ni	0.0009	0.0321	0.0057	0.0123			
	Pb	0.0009	0.0271	0.0050	0.0098			
	Se	0.0031	0.0135	0.0035	0.0040			

The arithmetic mean was used for the current statistical presentation.

3.2 Sudbury Locally-Grown Food Consumption Survey

A key set of information required in the HHRA is a profile of the various local foods that residents of the Greater Sudbury area consume annually and on a seasonal basis. To address this data gap, a food consumption survey was conducted by the SARA Group, with the resulting data considered as part of the exposure assessment.

The key research questions addressed by the survey were:

- 1. What types of local foods do residents consume?
- 2. What approximate quantities of local foods do residents consume?
- 3. What are the sources of local food consumed by residents?

The survey was designed to collect relatively detailed information on consumption patterns from population sub-groups predicted to have higher levels of local food consumption (*e.g.*, gardeners, hunters,



First Nations residents), and more generally, to obtain broad information from the general public. Respondents were asked to recall consumption of local foods over the past year. The detailed information was collected through in-person interviews with representatives from the higher consumption groups. The broader information was collected *via* a telephone interview with a random sample of representatives from Sudbury households.

The survey region for vegetables and fruit included those grown in the respondent's garden or a neighbour's garden, as well as local fruit and vegetables grown in the Greater Sudbury area (available at local markets and/or grocery stores). Local fish and game included species caught or hunted within a 100-kilometer radius of the Sudbury city core.

In-person interviews were conducted with members of Whitefish Lake First Nations, local gardeners, and local hunters and anglers following the recruitment process. Residents of the Whitefish Lake First Nations reserve were notified of the survey *via* notices in a local newsletter and announcements at community meetings. Gardeners who had participated in a previous component of the Study (*i.e.*, the Vegetable Garden Survey) were contacted to determine if they were willing to participate in the current component. This group is likely representative of a population that consumes a higher than average proportion of local vegetables and fruit. Finally, through interviews with representatives of the Sudbury Game and Fish Protective Association (an Ontario Federation of Anglers and Hunters member club), the study team determined that, in the winter months, one way to recruit local anglers and hunters was to target the ice-fishing community. The rationale presented by the representatives of the Association was that many people from the hunting and fishing community are involved in ice fishing. The interview team visited ice-fishing locations on local lakes to inform the sub-population of the survey.

Consumption statistics for the general population were gathered using telephone interviews. It is important to note that the survey used a self-reporting data collection methodology. While self-reporting methods are convenient for community-based surveys, some of the limitations include under or over-reporting, difficulties with recall, and social desirability with respect to responses.

Of particular importance in considering the limitations with this survey is the challenge involved in accurately reporting food consumption. Most respondents find it challenging to recall frequency of consumption, accurately estimate portion sizes, and few have accurate knowledge of where local fruits and vegetables are grown and harvested, if not from their own gardens. As a result, the data collected in this survey should not be considered as necessarily representative of local diets. Rather, it should be considered as suitable for providing estimate ranges required for the purposes of the HHRA. It should be



noted that the data provided in this report have not been validated using any other food consumption reporting techniques such as 24-hour diaries, in-home monitoring, or secondary recall.

3.2.1 Survey Respondent Profiles

3.2.1.1 Typical Sudbury Residents

For the telephone survey of the general population, interviewers contacted 1,470 households. Of the 1,470 households contacted, 426 households (29%) agreed to participate. The interviews collected household-level data as well as individual-level data for 1,226 individuals from the community.

The following interviews were conducted according to geographic areas:

- Sudbury, New Sudbury (n=105);
- Hanmer, Val Therese, Capreol, Val Caron (n=107);
- Falconbridge, Garson, Coniston (n=107); and
- Copper Cliff, Lively (n=107).

Respondents were asked about household members' participation in hunting, fishing and gardening. Results of the survey indicated that 48% did not participate in any hunting or fishing, while 22% participated in both hunting and fishing activities. Approximately one third of households (38%) reported that they plant a garden. When asked about source of local drinking water the majority of households (65.7%) reported to be on the municipal water supply (Appendix K, Figure 3-2). The second-most commonly reported water supply was bottled water (23%).

3.2.1.2 Whitefish Lake First Nations Residents

This portion of the food consumption study involved interviews with 71 households (65%) of the 110 households from the Whitefish Lake First Nations reserve. The interviewers collected household-level data as well as individual-level data for 218 individuals.

The study sampled a wide rage of respondents, spanning all ranges of age. With respect to gender distribution, the study collected interview data from 105 male and 113 female respondents. Respondents were asked about household members' participation in hunting, fishing and gardening. Almost all (85%) of the households reported that they had not planted a garden in the past 12 months. A large (77%) majority of households reported to either fish or hunt. When asked about source of local drinking water



the majority of households (78%) reported to be on the municipal water supply. Only a small minority (1%) of Whitefish Lake First Nations households reported well water as their primary source for drinking water.

3.2.1.3 Hunters and Anglers

Interviews were conducted with 29 households, representing 70 respondents. The interviews collected household data as well as individual-level data. The response group was comprised of 40 males and 30 females. Respondents were asked about household members' participation in hunting, fishing and gardening. A large majority of households (79%) reported that they both fish and hunt, while less than one quarter (21%) reported that they only fish. In response to questions about gardening activity more than half (55%) of the households reported to have planted a garden in the last 12 months.

When asked about source of local drinking water a large majority of households (72.4%) reported to be on the municipal water supply (Appendix K, Figure 5-3). Well and bottled water were equally reported as the second-most common water sources (10.3%) for the hunter and angler sub-group.

3.2.1.4 Gardeners

Interviews were conducted with 29 households, representing 65 respondents in the gardening sub-group. The interviews collected household data as well as individual-level data. The response group was comprised of 34 males and 29 females. Respondents were asked about household members' participation in hunting, fishing and gardening. Almost all households (92.7%) reported that they had planted a garden in the last 12 months. A large majority of households (75%) reported that they do not fish or hunt. When asked about source of local drinking water the majority of respondents (65.5%) reported to be on the municipal water supply (refer to Appendix K, Figure 6-2). Ground well water was reported as the second most common water source (17.2%) for the gardening sub-group.

3.2.2 Survey Results

Data representing consumption rates for specific food groups reported by each respondent group (see Appendix K for detailed survey results) were evaluated and compared to data presented in larger studies published in the scientific literature (as outlined in U.S. EPA, 1997). Results of this comparison provided food group-specific consumption rates, appropriate for GSA residents, for use in the HHRA. Refer to Chapter 4 for a further discussion of this issue, and Appendix K for the complete Local Food Consumption Survey Technical Report.



3.3 **COC** in the Sudbury Area Potable Water Supply

In addition to exposure related to food consumption, potential consumption of COC via potable drinking water is one of the primary exposure pathways for Sudbury residents. The majority of households in the GSA are serviced by a municipal water supply (see discussion in Chapter 4). These municipal water supplies all undergo routine monitoring, including chemical analyses for a suite of metals containing the COC under review in the current HHRA. However, one area of uncertainty in the HHRA is the concentration of metals in private wells and households drawing their potable water from surface water resources (*i.e.*, nearby lakes). To address this concern, a Drinking Water Survey was initiated in the fall of 2004.

Drinking water samples were collected from 94 residential properties, including both private wells drawing water from groundwater and residences drawing surface water from lakes. Where applicable, the results of the analysis were compared to provincial drinking water standards set out in the Safe Drinking Water Act of 2002 (no provincial drinking water standards have been established for cobalt, copper, or nickel). In the case of copper, the 1996 Canadian Drinking Water Quality Guideline was used for comparative purposes. The following table provides summary statistics for each COC for private water supplies in the GSA.

Table 3.6Drinking Water Survey Concentrations (µg/L)								
Potable Water Source	COC	Ontario Drinking Water Standard	Min	Max	Mean			
	As	25	1.00	23.00	2.37			
	Со	na	0.15	8.70	0.56			
Groundwater	Cu	1,000 ^b	0.25	216.00	45.14			
(n=76)	Ni	na	0.50	123.00	11.18			
	Pb	10	0.05	8.00	0.70			
	Se ^a	10	1.50	1.50	1.50			
	As ^a	25	1.00	1.00	1.00			
	Со	na	0.15	0.40	0.16			
Lake water	Cu	1,000 ^b	20.90	302.00	97.67			
(n=18)	Ni	na	9.96	126.00	56.77			
	Pb	10	0.20	5.00	1.46			
	Se ^a	10	1.50	1.50	1.50			

$I a D I \cup J \cup D I \cup D I \cup D \cup D \cup D \cup D \cup D \cup D \cup D$	Table 3.6	Drinking Water Survey Concer	ntrations (µg/L)
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n Number of samples analyzed.

All samples were below the minimum detection limit (MDL); arsenic MDL = $2.0 \mu g/L$, selenium MDL = $3.0 \mu g/L$.

1996 Canadian Drinking Water Guideline based on aesthetic water quality objective to minimize staining of laundry and plumbing fixtures.



Results of the survey indicated that concentrations of all COC in the water supplies surveyed were below their respective drinking water guidelines (where available). These data were also evaluated in comparison to the concentrations detected within the normal municipal water supplies for the various COI as part of the HHRA. Refer to Chapter 4 for a further discussion of this issue, and Appendix L for the complete Drinking Water Survey Report.

3.4 Bioavailability/Bioaccessibility

The ingestion of soils is often considered to be the major route of potential exposure to metals in humans (Sheppard *et al.*, 1995; Paustenbach, 2000). To effectively assess the dose of soil metals received by humans, the determination of bioavailability becomes an invaluable tool in risk assessment. The approach for oral bioavailability assessment of contaminants can typically be divided into four fundamental processes: i) the oral intake of soil/dust including metals; ii) bioaccessibility; iii) intestinal absorption; and, iv) metabolism in the liver/intestines (Oomen *et al.*, 2006; Sips *et al.*, 2001). Out of these processes that construct the basis of bioavailability, bioaccessibility testing is a key component. The inclusion of bioaccessibility testing as part of the assessment process allows for a more realistic estimate of the systemic exposure to metals from soil and dust ingestion than using generic assumptions such as those employed to derive soil guideline values (EAUK, 2005a).

3.4.1 Overview of Bioaccessibility

Oral bioaccessibility can be defined as the fraction of a substance that is released from the soil or dust matrix during digestion, thus making it soluble and available for absorption through the gastrointestinal tract (Defra and Environment Agency, 2002). In effect, this fraction represents the upper limit of bioavailability. Oral bioaccessibility only takes into account the direct ingestion of soil and dust and does not incorporate other routes of exposure such as skin and lungs. The bioaccessible fraction is the fraction of the substance of interest that is dissolved from soil into chyme, and represents the maximum fraction available for intestinal absorption (Ruby *et al.*, 1999; Sips *et al.*, 2001). The dissolved substance may be absorbed and transported across the intestinal wall into the blood or the lymphatic system. Once dissolved, some of the substance may precipitate in the intestine, be bound to other substances or undergo chemical transformation to an insoluble form. Any of the processes would lead to a portion of the substance remaining unavailable for absorption. Once distributed into the systemic circulation from the intestines or the liver, substances can ultimately start to exert systemic toxicity (Sips *et al.*, 2001). Thus, one can see the importance in assessing bioaccessibility as it will determine the amount of a soil- or dust-bound material that will actually become bioavailable to potentially exert effects in the body.



Bioavailability depends, in large measure, upon bioaccessibility. When bioaccessibility is low, oral bioavailability will also be low. Absolute oral bioavailability of soil-borne substances can be estimated on the basis of bioaccessibility in combination with the absorption and metabolism values from toxicological studies (Sips et al., 2001). Hence, the effectiveness of methods in determining the bioaccessibility of soil contaminants may dictate the overall conclusions of risk assessments.

Toxicity data employed in most risk assessments (*e.g.*, reference doses [RfDs] and cancer slope factors [CSFs]) are typically developed, in part, from toxicological studies using animals. These studies generally use a highly bioavailable chemical form (*e.g.*, soluble inorganic salts, *etc.*) and delivery media (*e.g.*, food, water, *etc.*) to ensure a high dose reaches the target tissue. As such, RfDs and CSFs do not inherently address the availability of compounds in other environmental media, such as soils and dust. It is, therefore, important that the bioavailability of the compound present in soil or dust, relative to bioavailability of the chemical species and delivery media used by the critical toxicological study (*i.e.*, the study used to develop either the RfD or CSF), be quantitatively supported.

Absolute bioavailability refers to the fraction or percentage of a compound that is ingested, inhaled or applied to the skin that is absorbed and reaches systemic circulation (Hrudey *et al.*, 1996). Relative bioavailability, as it pertains to risk assessment, has been defined as "*the difference in absorption of a compound from the environmental medium of concern (e.g., food, soil and/or water) versus the absorption from the vehicle (or medium) used in the toxicological study from which the toxicity-based reference value is derived"* (Kelly *et al.*, 2002).

Traditionally, *in vivo* studies (*i.e.*, animal studies) have been used to determine the relative bioavailability of metals; however, *in vivo* studies can have significant associated time and cost constraints (Ruby *et al.*, 1999). Therefore, more rapid and inexpensive *in vitro* extraction studies (designed to simulate the human stomach and intestinal system) have been developed to provide a reasonable, yet conservative, approximation of true bioavailability by assuming relative bioavailability is equal to bioaccessibility. *In vitro* extraction studies have been designed to simulate the human gastrointestinal tract (*e.g.*, pH, temperature, and chemical composition of solutions in both the stomach and small intestine, *etc.*) in order to assess the mobilization of compounds from soil during the digestion process.

Given the importance of evaluating the potential toxicity of soil and dust-bound COC to Sudbury residents, in-vitro bioaccessibility analyses were conducted. The objective of these analyses was to estimate the bioaccessible fractions of arsenic, copper, cobalt, lead, nickel, and selenium in Sudbury soil and dust samples. These results were then used to derive a relative absorption factor (RAF) for each COC.



An RAF based on a bioaccessibility evaluation is a simple quotient comparing the solubility of COC in soil and the exposure medium used to develop the RfD/CSF (*i.e.*, spiked food) in simulated digestive fluids. The RAF makes no assumptions about digestive differences between humans and other mammalian species, and is calculated as follows:

RAF= Bioaccessibility of Chemical in Soil Bioaccessibility of Chemical in Exposure Medium used to Develop the RfD

Many different in vitro test methods are available to measure bioaccessibility of inorganic compounds in soil. Oomen *et al.* (2002) evaluated five different types of in vitro digestion models for three different soil types, producing a wide range of bioaccessibility results. Although data on bioaccessibility of lead and arsenic in soil are available, limited data are available for other metals such as nickel, copper, zinc, cadmium, and chromium (DEPA, 2003). At this time, no single *in vitro* method has been universally accepted (DEPA, 2003).

It is important to note that oral bioaccessibility testing is only applicable to the soil and dust human exposure pathways, and not the food consumption pathways (EAUK, 2005a). While bioaccessibility testing may be a valuable addition to risk assessment practices, it is an evolving science and several uncertainties remain. Oral bioaccessibility results have been shown to vary considerably within and between contaminated sites. Therefore, it is prudent to only apply bioaccessibility data on a site-specific basis (EAUK, 2005a). Furthermore, bioaccessibility test results have been reported to be significantly affected by various factors such as physical-chemical properties of the contaminants (Dieter *et al.*, 1993; Freeman *et al.*, 1996; Gasser *et al.*, 1996; Ruby *et al.*, 1996; 1999), soil characteristics (Ruby *et al.*, 1993; 1996; 1999; Hamel *et al.*, 1998; 1999), the composition of digestive fluids (Guyton, 1991; Ruby *et al.*, 1992; Oomen *et al.*, 2000), and the presence of food constituents (Hack and Selenka, 1996). Hence, it is not realistic to propose a single value to represent the bioaccessibility of a given metal; site-specific values must be developed on a case-by-case basis. Table 3.7 provides an overview of bioaccessibility results for key COC, published in the primary literature, from a variety of different test methods and site-specific conditions.

Chemical	Value	e (%)	Medium	Method	Source of Chemical	Reference	
	Mean ± SD	Range					
	48.0 ± 3.0^{a}	41.0 - 48.0 ^b	Gastric phase	U.S. Pharmacopeia methodology for extraction. Total extractable metal digestion procedure followed	NIST Montana SRM 2710 (Control)	Hamel et al., 1998	
	13 ± 3.0^{a}	4.5 - 25.0 ^b		modified EPA method 3051. Analysis performed using ICPMS	New Jersey, Jersey City composite soil		
	66.0 ± 8.0	-	Gastric + intestinal	Using mass-balance and soil	NIST Montana SRM 2710 (Control)		
	34.0 ± 14.0	-	phase	recapture analytical methods	Slag material in Jersey City, USA	Hamel et al., 1999	
	41.0 ± 2.0	-	pilase	recapture anarytical methods	Residential soil in Jersey City, USA		
	59.0 ± 2.0	-		SBET method (BGS), United	NIST Montana SRM 2710 (Control)		
	50.0 ± 0.2	-	Gastric Phase	Kingdom	Flanders		
	11.0 ± 2.0	-		Kiiiguoiii	Oker 11		
50.0 ± 1.0 44.0 ± 3.0 18.0 ± 3.0 41.2 ± 2.0 30.0 ± 1.0 11.0 ± 1.0 59.0 ± 1.0	50.0 ± 1.0	-			NIST Montana SRM 2710 (Control)	Oomen <i>et al.</i> , 2002	
	44.0 ± 3.0	-		DIN method (RUB), Germany	Flanders		
	18.0 ± 3.0	-		· · · -	Oker 11		
	41.2 ± 2.0	-			NIST Montana SRM 2710 (Control)		
	30.0 ± 1.0	-	Gastric + intestinal	DIN method-without whole milk	Flanders		
	11.0 ± 1.0	-	phase	powder (RUB), Germany	Oker 11		
		-			NIST Montana SRM 2710 (Control)		
	95.0 ± 10.0	-		In vitro digestion model (RIVM),	Flanders		
Arsenic (As)	19.0 ± 1.0	-		Netherlands	Oker 11		
	10.0 ± 0.4	-	Gastric + intestinal	SHIME method (Lab MET/Vito)	NIST Montana SRM 2710 (Control)		
	6.0 ± 0.5	-			Flanders	Oomen <i>et al.</i> , 200	
	1.0 ± 0.02	-	phase	Belgium	Oker 11		
	50.0 ± 1.0	-	Gastric + Intestinal		NIST Montana SRM 2710 (Control)		
52.0 ± 1.0	52.0 ± 1.0	-	phase (3 sections:	TIM method (TNO) Nutrition,	Flanders		
	15.0 ± 3.0	-	duodenum, jejunum, and ileum)	Netherlands	Oker 11		
	24.8	-	Gastric phase	Invitro Gastrointestinal method			
	21.9	-	Intestinal phase	(IVG)			
23.0	23.0	-	Gastric+ intestinal phase	IVG with adsorption ^c	Arsenic contaminated soil, excluding calcine ^d	Rodriguez and Basta 1999	
	18.3	-	Gastric phase	Physiologically based			
	12.5	-	Intestinal phase	Extraction test (PBET)			
	50.0 ^m	50.0 - 50.0	• • •	PBET (PH 1.3)	Composite residential soil from		
	32.0 ^m	30.0 - 34.0		PBET (PH 2.5)	Anaconda (ARS-I)		
	44.0 ^m	44.0 - 44.0	Tute at a 1 al a	PBET (PH 1.3)	Composite residential soil from	D 1 (1 100)	
	31.0 ^m	20.0 - 32.0	Intestinal phase	PBET (PH 2.5)	Anaconda (ARS-II)	Ruby et al., 1996	
	34.0 ^m	32.0 -36.0		PBET (PH 2.5)	Composite house dust sample from Anaconda (AHD-I)		

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Chemical	Value	e (%)	Medium	Method	Source of Chemical	Reference	
	Mean ± SD	Range					
	11.0 ± 3.5^{a}	11.0 -14.0 ^b	Gastric phase	U.S. Pharmacopeia methodology for extraction. Total extractable metal digestion procedure followed modified EPA method 3051. Analysis performed using ICPMS	NIST Montana SRM 2710 (Control)	Hamel <i>et al.</i> , 1998	
Nickel (Ni) $ \begin{array}{r} 34.0 \pm 14.0^{a} \\ \underline{34.0^{e}} \\ \underline{2.0^{e}} \\ \underline{5.0^{e}} \\ \underline{44.0^{e}} \\ \end{array} $	34.0 ± 14.0^{a}	$13.0 - 40.0^{b}$		U.S. Pharmacopeia methodology for extraction. Total extractable metal digestion procedure followed modified EPA method 3051. Analysis performed using ICPMS	New Jersey, Jersey City composite soil	Hamel et al., 1998	
	4.0 ^e	-	Gastric phase		Top Soil, particle size <53µm		
	2.0 ^e	-			Top Soil, particle size 53 – 100 μm		
		-		Simulated stomach acid digestion	Top Soil, particle size 100-500 μm	Rasmussen, 2004	
		-		procedure ^f	Urban house dust<53µm		
	30.0 ^e	-			Urban house dust 53 - 100µm		
31.0 ^e		-			Suburban house dust <100µm		
	19 ⁱ	$7.6 - 28^{j}$	Not reported	Solubility in an acidic leachate	30 soil samples from the OMOE risk assessment of Port Colborne	Richardson et al., 2006	
64.8 ± 9.4 12.1 ± 8.2 34.0 ± 7.5^{a} 46 ± 16^{a} Lead (Pb) 62.0 ± 1.0 70.0 ± 11.0 39.0 ± 14.0 69.0	64.8 ± 9.4	52.4 - 77.2	Gastric phase	Using modified method (Mass- balance and soil recapture) of Hamel et al., 1999; Ellickson et al.,	House dusts from carpets of urban homes.	Yu <i>et al.</i> , 2006	
	12.1 ± 8.2	4.9 - 32.1	Intestinal phase	2001,2002; Ruby et al., 1992, 1993,1996			
	34.0 ± 7.5^{a}	$29.0 - 46.0^{b}$	Gastric phase	U.S. Pharmacopeia methodology for extraction. Total extractable metal digestion procedure followed	NIST Montana SRM 2710 (Control)	Hamel <i>et al.</i> , 1998	
	46 ± 16^{a}	$22 - 58^{b}$		modified EPA method 3051. Analysis performed using ICPMS	New Jersey, Jersey City composite soil		
	62.0 ± 1.0	-			NIST Montana SRM 2710 (Control)		
	70.0 ± 11.0	-	Gastric + intestinal phase	Using mass-balance and soil recapture analytical methods	Contaminated soil from Bunker- Hill, ID, USA	Hamel et al., 1999	
	39.0 ± 14.0	-	phase	recupture analytical methods	Slag material in Jersey City, USA		
	69.0	-			Residential soil in Jersey City, USA		
	90.0 ± 2.0	-		ODET = 4(DCO) Usite 1	NIST Montana SRM 2710 (Control)		
	91.0 ± 2.0	-	Gastric Phase	SBET method (BGS), United	Flanders		
	56.0 ± 4.0	-		Kingdom	Oker 11	Oomen et al., 200	
	68.0 ± 2.0	-	Gastric + intestinal	DIN method (RUB), Germany	NIST Montana SRM 2710 (Control)		

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Chemical	Value (%)		Medium	Method	Source of Chemical	Reference	
	Mean ± SD	Range					
	40.0 ± 2.0	-		DIN method (RUB), Germany	Flanders		
	23.0 ± 1.0	-		Dirv method (ROD), Germany	Oker 11		
	46.0 ± 2.0	-			NIST Montana SRM 2710 (Control)		
	31.0 ± 3.0	-	_	DIN method-without whole milk	Flanders		
	16.0 ± 2.0	-	- Gastric + intestinal	powder (RUB), Germany	Oker 11		
	11.0 ± 2.0	-	phase		NIST Montana SRM 2710 (Control)		
	66.0 ± 9.0	-	- phase	In vitro digestion model (RIVM),	Flanders	.1	
	29.0 ± 2.0	-		Netherlands	Oker 11	Oomen et al., 2002	
	3.0 ± 0.3	-		~~~~	NIST Montana SRM 2710 (Control)		
	4.0 ± 1.0	-		SHIME method (Lab MET/Vito)	Flanders		
	1.0 ± 0.1	-	- Belgium		Oker 11		
	17.0 ± 3.0	_	Gastric + Intestinal		NIST Montana SRM 2710 (Control)		
		-	phase (3 sections:	TIM method (TNO) Nutrition,	Flanders		
	4.0 ± 1.0 - and ileum)		Netherlands	Oker 11			
13.0 ^e 15.0 ^e	-			Top Soil, particle size <53µm			
	-			Top Soil, particle size 53 – 100 μm			
	29.0 ^e	-	Gastric phase	Simulated stomach acid digestion procedure ^f	Top Soil, particle size 100-500 μm	Deam	
Lead (Pb)	74.0 ^e	-			Urban house dust<53µm	Rasmussen, 200	
	55.0 ^e	-			Urban house dust 53 - 100µm		
	60.0 ^e	-			Suburban house dust <100µm		
	23.0	0.70 - 36.3	Gastric phase	In vitro Gastrointestinal method			
	0.56	0.02 - 1.16	Intestinal phase	(IVG) with dough ^g	Contaminated soil	Schroder et al., 200	
	32.2	1.40 - 64.4	Gastric phase	In vitro Gastrointestinal method	Containinated Soli		
	1.06	0.03 - 3.23	Intestinal phase	(IVG) without dough ^g			
	9.5 ^k	5.0 - 9.9	Gastric phase	PBET (PH 1.3)		1	
	4.6 ¹	1.0 - 3.6	Intestinal phase				
	3.8 ^k	2.7 - 3.8	Gastric phase	PBET (PH 2.5)	Composite mine waste materials from		
	2.7 ¹	0.94 - 1.2	Intestinal phase	· · · · · · · · · · · · · · · · · · ·	Butte, MT (BMW-I)		
	1.3 ^k	1.1 - 1.3	Gastric phase	PBET (PH 4.0)			
	-	0.48 - 1.84	Intestinal phase			Ruby <i>et al.</i> , 1996	
	35.0 ^k	22.0 - 35.0	Gastric phase	PBET (PH 1.3)		Kuby et al., 1990	
	8.3 ¹	4.0 - 4.0	Intestinal phase	· · · ·	Composite mine waste materials from		
	13.0 ^k	6.0 - 13.0	Gastric phase	PBET (PH 2.5)	Butte, MT (BMW-II)		
	9.80 ¹	3.0 - 13.0	Intestinal phase				
	70.0 ^k	58.0 - 70.0	Gastric phase	PBET (PH 1.3)	Composite residential soil from Bartlesville (BVS)		

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Chemical	l Value (%)		Medium	Method	Source of Chemical	Reference
	Mean ± SD	Range				
	29.0	12.0 - 70.0	Intestinal phase	PBET (PH 1.3)	Composite residential soil from	
	26.0 ^k	22.0 - 26.0	Gastric phase	PBET (PH 3.0)	Bartlesville (BVS)	
	29.0 ¹	11.0 - 26.0	Intestinal phase	rbei (rn 3.0)		
	83.0 ^k	72.0 - 83.0	Gastric phase	PBET (PH 1.3)		oil from Salt
	54.0 ¹	25.0 - 83.0	Intestinal phase	rbei (rn 1.3)	Composite residential soil from Salt	
	22.0 ^k	11.0 - 22.0	Gastric phase	PBET (PH 2.5)	Lake City (SCS)	
	18.0 ¹	7.0 - 8.0	Intestinal phase	rBEI (FH 2.3)		
	16.0	12.0 -16.0	Gastric phase	PBET (PH 1.3)		
Lead (Pb)	3.0	1.2 – 1.7	Intestinal phase	rbei (rn 1.3)	Composite tailings sample from	Ruby et al., 1996
	8.0	6.8 - 8.0	Gastric phase	PBET (PH 2.5)	Copperton (CT-1)	,
	0.6	0.2 - 0.3	Intestinal phase	FBE1 (FH 2.3)		
	10.0	8.0 - 10.0	Gastric phase	PBET (PH 1.3)		
	1.1	0.4 - 0.7	Intestinal phase	rbei (rn 1.3)	Composite tailings sample from	
	6.0	4.0 - 6.0	Gastric phase	PBET (PH 2.5)	Copperton (CT-2)	
	2.1	0.7 - 1.0	Intestinal phase	rbei (rn 2.3)		
	49.0	39.0 -49.0	Gastric phase	DDET (DU 1 2)		
	14.0 5.0 - 8.0 Intestinal phase PBET (PH 1.3)	Г D E1 (ГП 1.3)	Composite stream channel sample			
	24.0	22.0 - 24.0	Gastric phase	PBET (PH 2.5)	from Bingham (CT-3)	
	17.0	7.0 - 7.0	Intestinal phase			

^a Values recorded at the 1000:1 liquid(gastric fluid) to solid ratio, because authors stated that 1000:1 ratio provided the most representative extractability for most metals.

^b Range represent values recorded at various liquid to solid ratios (100:1 to 5000:1)

^c Incorporated iron hydroxide gel in an in vitro procedure to stimulate intestinal absorption, results showed statistical resemblance to in vivo bioaccessibility test results

^d Reported values that were similar to the results of the *in vivo* method of assessing bioaccessibility

Results presented as relative bioavailability factors calculated by expressing the migratable metal content as a percentage of the total metal content for each sample medium
 Originally developed for toy safety.

^g A dosing vehicle (wet feed) equivalent to the amount of gastric extraction solution.

^h Authors claim that The PBET method of extraction which do not used food in the extraction to mimic fasting conditions, has been correlated with relative bioavailavle Pb as estimated by two animal models (weanling rats and swine). The authors also claim that the IVG method is an accurate predictor of relative bioavailable As in contaminated soils and waste materials as estimated by a juvenile swine model while utilizing food in the extraction procedure.

ⁱ Bioavailability adjustment factor for oral intake of Ni in soil

^j Bioaccessibility was measured using two methods(not stated), bioaccessibility value expressed as a percent of the total Ni contained in each soil sample.

^k Data presented as **relative** bioaccessibility (*bioaccessibility of Pb from the test substrate was corrected for the recovery of a soluble Pb spike*) based on gastric phase bioaccessibility data from PBET, the range represent the range of bioaccessibility data from the gastric phase based on time.

¹ Data presented as **relative** bioaccessibility based on intestinal phase bioaccessibility data from PBET, the range represent the range of bioaccessibility data from the intestinal phase based on time.

^m Data presented as **relative** bioaccessibility (*calculated as average soluble As mass in small intestinal simulation divided by total As mass in the reaction vessel, corrected for recovery of soluble As spike in small intestinal simulation*) based on intestinal phase bioaccessibility data from PBET, the range represent the range of bioaccessibility data from the intestinal phase based on time.



The biggest uncertainly in any *in vitro* bioaccessibility test is knowing how closely the values relate to human bioavailability. No *in vitro* method can recreate the physiological process of the human gastrointestinal tract, the presence of food, and the effect of microbial communities perfectly (Smith and Rawlins, 1998). Standardized soil reference material and bioaccessibility methods may improve human bioaccessibility data. In the absence of human bioaccessibility data, the best validation of the *in vitro* results has been done using *in vivo* studies in rats and pigs (Sips *et al.*, 2001).

Bioaccessibility does not only vary between substances, it also varies from site to site and between the compositions of different contaminants (EAUK, 2005b). As observed in Table 3.7, the bioaccessibility of nickel, lead, and arsenic varied greatly in different geographical locations. Geological differences between land uses will affect the properties of metals within the soil as well (EAUK, 2005b). For example, the addition of phosphates or organic matter in soil will desorb non-bioaccessibile metals bound to iron oxides and convert them into bioaccessible forms (EAUK, 2005b).

Another uncertainty regarding bioaccessibility is the comparability of the *in vitro* results within and between laboratories (EAUK, 2005b), which are based on such factors as differences in procedures (e.g. source of glassware, solvents, reagents, etc., preparation prior to bioaccessibility testing, instrumentation calibration, etc.). Human error will also contribute to inter- and intra-laboratory differences in results. There is no single method suitable for all metals, since such a method would need to satisfy the key requirements such as simulation of the human gastrointestinal conditions, simplicity and cost effectiveness (Danish EPA, 2003).

3.4.2 Approach for Bioaccessibility Testing in this Study

Following a thorough review of the available literature, a two-phase bioaccessibility protocol (*i.e.*, simulating both gastric and intestinal phases of absorption) adapted from the standard operating procedure (SOP) developed by the Solubility/Bioavailability Research Consortium (SBRC) (Ruby *et al.*, 1999) was initially selected to estimate the bioaccessibility of all COC in Sudbury area outdoor soils and indoor dust (Golder, 2005). It should be noted that this study employed an *in vitro* procedure to determine bioaccessibility of the COC in Sudbury soils and dust. To our knowledge, published *in vivo* validation of this method has only been conducted for lead and arsenic.



3.4.2.1 **Round One Analyses**

Soil and dust collected as part of the Indoor Dust Study was utilized for the bioaccessibility study. In this first round of analyses, 87 soil samples and 10 dust samples were subjected to the bioaccessibility testing. Table 3.8 outlines the number of samples tested from each of the communities. Sample specific results are included as Appendix D of the Golder (2005) bioaccessibility study.

Chemical	Sample ID number				
Chemical	Soil	Dust			
Coniston	515, 516, 524, 525, 526, 547, 552, 553, 554, 557, 530, 561, 564, 567, 569, 574, 599, 605, 606	515			
Copper Cliff	504, 505, 506, 509, 510, 511, 512, 521, 530, 533, 566, 579, 580, 584, 585, 586, 588, 593, 602, 607	504, 584, 602			
Falconbridge	501, 502, 507, 514, 517, 518, 519, 522, 523, 528, 529, 532, 534, 568, 571, 573, 577, 581, 597, 598, 613	521, 523, 534			
Hanmer	542, 546, 559, 562, 572, 594, 600, 601, 611, 612	600			
Sudbury Centre	513, 520, 531, 541, 550, 551, 563, 565, 570, 582, 589, 590, 591, 592, 596, 608, 648	550, 582			

f Call Tabla 3.8 C .. D: •1 •1• 1 D . 4 T c ъ T

Results of the bioaccessibility testing indicated that either the 95% upper confidence limit on the mean (95% UCLM) or the regression equation could be used to estimate bioaccessibility in soil samples for arsenic, cobalt, lead and nickel, although the regression correlation is weak. However, a statisticallysignificant regression relationship between metal soil concentration and bioaccessibility did not exist for copper or selenium. After examination of the regression lines, goodness of fit, and 95% UCLM estimates, it was decided that a conservative point estimate (*i.e.*, 95% UCLM) be used for risk assessment purposes.

In the case of dust, a statistically-significant regression relationship between metal dust concentration and bioaccessibility did not exist for arsenic, copper, lead or nickel. As a result, the upper 95% UCLM is recommended as a conservative measure of bioaccessibility in house dust for these COC. Selenium in house dust was below the MDL, and thus 100% bioavailability was conservatively assumed. For cobalt detected in house dust, either the upper 95% UCLM or the regression relationship could be used for estimating bioaccessibility. The latter (i.e., 95% UCLM) was chosen as a conservative estimate of bioaccessibility.



Table 3.9 provides the results of the bioaccessibility testing conducted for each of the COC in both the soil and dust test media in round one.

Chemical	Bioaccess	ibility (%)
Chemical	Soil	Dust
Arsenic	41	3.7
Cobalt	26	2.4
Copper	64	4.6
Lead	16	3.4
Nickel	42	2
Selenium	27	100

Table 3.9 Su	mmary of Round One	Bioaccessibility Results
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Spiked rat chow was also subjected to the bioaccessibility assay and an overall bioaccessibility of 94.7% was observed. This was used in the RAF determination for nickel.

The study was modified from the originally proposed one-stage (*i.e.*, stomach) test to the more biologically realistic two-stage (gastro-intestinal) analyses. This modification was made following preliminary analysis of ten soil samples from the GSA. The preliminary study resolved several issues and provided a sound scientific basis for moving forward with the two stage analysis. Complications seen previously by JWEL (2003) with glycine and nickel did not appear to be factors in this study. Previous researchers found that at higher pHs, such as those used in the intestinal extraction phase, nickel complexed with glycine, increasing the measured bioaccessibility. As part of the current study, Golder Associates tested the bioaccessibility of ten samples during the gastric extraction and the gastric and intestinal extraction phases to determine if a difference in bioaccessibility would be observed for all six metals. The bioaccessibility for all metals was similar in both the gastric extraction and the gastric plus intestinal extraction, with the exception of lead. Lead had a reduced bioaccessibility in the gastric and intestinal phase relative to the gastric phase alone. This is presumably the result of the interaction of lead with organic matter and/or the precipitation of lead as the pH increases in the intestinal phase, making it less bioaccessible. This is a physiologically relevant phenomenon that should not be discounted. The acidic gastric phase is likely the key chemical event responsible for the extraction of metals/chemicals from the soil matrix, but once released, chemicals whose solubilities are sensitive to pH would nevertheless be subject to precipitation chemistry on particle surfaces during passage through the entire gastrointestinal tract.



The modelling of absorption is extremely complex, and variable depending on many factors (the chemical species; dietary state (fed *vs.* fasting); the type and amount of macronutrients and micronutrients concurrently consumed; the presence of competing ions such as Ca^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} ; binding capacity and precipitating ability of complexing agents in food such as phosphate, phytates, proteins, citric acid *etc.*, and in the chyme and exocrine secretions including enzymes, bile salts, bicarbonate as the main buffering agent, mucin and other proteins, mucus); physiologic factors such as gastric and intestinal motility (*i.e.*, residence time), uptake mechanisms; development stage and age of the receptor, and the presence/absence of disease). Since bioavailability is variable and complex, the intended purpose of this study was to adjust for the difference in bioaccessibility between exposure medium (soil) relative to the exposure medium used in the key toxicological study (spiked rat chow for nickel). The significance of this decision has been examined as part of the sensitivity analysis conducted as part of Chapter 7.

The results of the study demonstrate a clear difference between soil and dust bioaccessibility estimates. There were no methodological or physiological issues that would explain the difference. The supposition was that the higher organic content of dust as compared to soil (20 to 34% *vs.* 4%) (Rasmussen, 2004) results in greater binding of metals in dust as compared to soil. Tessier sequential leach results support this supposition (see Section 3.5). A comparison of the Tessier leach results for several pairs of soil and dust samples indicated that in the dust samples there was a relatively larger proportion of nickel in the "organic" phase (see Figures 3-2).

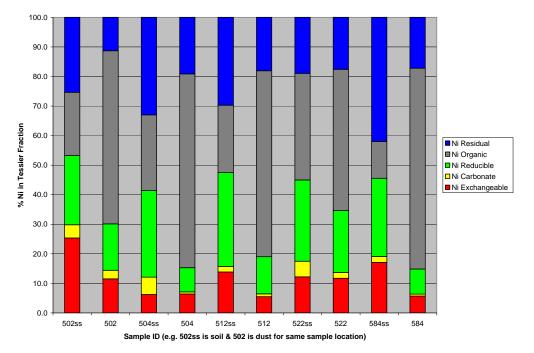


Figure 3-2 Nickel in Tessier Extracts of Matching Soil and Dust Samples (% values)



Furthermore, Yu *et al.* (2006) found a significantly lower bioaccessibility for intestinal extraction of lead in vacuumed house dust for particle size fractions <75 μ m versus larger particle size fractions up to 250 μ m. Based on preliminary range-finding done as part of the dust study (Appendix M), it was found that there was virtually no dust greater than 60 μ m in the samples collected from the GSA. As indicated below, Yu *et al.* found that, for the <75, 75 to 150, and 150 to 250 μ m fractions, bioaccessibilities for lead were as follows: 9.4 ± 4.2 %, 17.1± 7.2; and 16.2 ± 8.0, respectively (mean and 95% CL 2-sided). The results for the <75 μ m fraction were similar to those found for this study.

Literature was consulted to examine evidence of a similar phenomenon in other studies. Metal bioaccessibility values determined in this study for soils were consistent with values published by other researchers (Golder, 2005). However, it should be noted that given the site-specific nature of bioaccessibility, published values range substantially for all metals, so this comparison does not provide an indication of the reliability of the results of this study. The dust bioaccessibilities determined in this study are lower than values published by other researchers (Rasmussen (2004) and Yu *et al.* (2006)); this is likely due to site-specific differences in dust, including differences in the amount of organic matter, as well as differences in the bioaccessibility methods. Unfortunately, there is a paucity of data available regarding the bioaccessibility of metals from house dust. Results of the two studies which were identified are provided in Table 3.10.

14510 0110						
	Ras	mussen (2004))	Yu <i>et al.</i> (2006)		
COC	<53 μm (urban)	53-100 μm (urban)	<100 µm (suburban)	<75 μm	75-150 μm	150-250 μm
Ni	44%	30%	31%	9.4 ± 4.2 %	17.1±7.2%	$16.2 \pm 8.0\%$
Pb	74%	55%	60%	-	-	-

Table 3.10	Bioaccessibility of Metals in House Dust
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Due to comments and recommendations provided by the IERP and Technical Committee, a second round of analyses were conducted to obtain additional information on both phases of extraction (*i.e.*, gastric and gastric+intestinal), as well as to confirm the validity of the bioaccessibility noted for dust samples during the round one analyses.



3.4.2.2 Round Two Analyses

Soil and dust collected as part of the Indoor Dust Study were again utilized for the second round of bioaccessibility analyses. Table 3.11 outlines number of samples tested from each community. Samples not previously analysed in Round One were selected based upon the available range of concentrations and coverage throughout each of the COI.

For the Round Two analyses, the soil and dust samples were divided and submitted for analysis to Golder and to Dr. John Drexler's laboratory at the University of Colorado, as recommended by the IERP. In total, 40 soil samples (unsieved), 25 dust samples (sieved) and 2 reference samples were sent to Dr. Drexler, while splits of all 40 soil samples were sent to Golder, and only 10 of the dust samples had sufficient material to split for two parallel analyses. As such, all 25 dust samples were analyzed by Drexler, while a subset of 10 dust samples were analyzed by Golder (those analyzed by both labs are denoted in **bold** in the table below). Neither laboratory was informed of the other independent analysis.

Testing	resting						
Chemical	Sample ID number						
	Soil	Dust					
Coniston	525, 526, 552, 553, 554, 560, 561, 593, 599	524, 547 , 564 , 574					
Copper Cliff	506, 511, 512, 516, 521, 530, 533, 566, 584, 602, 607	510, 521, 530, 602, 616					
Falconbridge	501, 502, 514, 517, 519, 522, 523, 529, 534, 581	514, 518, 522, 529, 605 , 617					
Hanmer	-	572, 612, 615					
Sudbury Centre	513, 520, 531, 541, 551, 563, 565, 570, 582, 596	541, 610, 614 , 618 , 619 , 620, 621					
Note: Splits of dust samples de samples were only sent to	noted in bold were sent to both Drexle o Drexler's lab.	er and Golder labs. Otherwise,					

Table 3.11Summary of Soil and Dust Locations for Round Two Bioaccessibility
Testing

It is important to note that both Golder and Drexler use similar *in vitro* methods to establish bioaccessibility, with small changes in the overall methodology. One key difference is that Golder provides bioaccessibility results for both phases (*i.e.*, gastric and gastric + intestinal), while Drexler only provides results for the gastric phase.

Table 3.12 provides the results of the Round Two bioaccessibility analyses on soil and dust samples for both gastric and gastric+intestinal phases, where available.

		Gastric	Gastric + Intestinal			
COC	GOLI	DER 2007	DREX	LER 2007	GOLI	DER 2007
	Mean	95UCLM	Mean	95UCLM	Mean	95UCLM
<u> </u>		SC	DIL SAMP	LES	-	-
Arsenic	24	26	31	39	30	33
Cobalt	26	28	26	28	23	25
Copper	50	54	69	74	61	65
Lead	62	66	69	78	14	16
Nickel	35	39	40	44	35	38
Selenium	7	12	15	26	21	33
		DU	IST SAMP	LES		
Arsenic	39	43	41	45	41	45
Cobalt	28	32	28	30	32	38
Copper	44	50	46	49	58	67
Lead	79	83	83	95	18	21
Nickel	32	36	29	31	37	43
Selenium	24	NC ¹	43	67	0	NC

In the case of most of the COC evaluated in the current assessment, bioaccessibility provides a reasonably conservative approximation of the overall bioavailability. In fact, results of round two of the bioaccessibility analyses indicate for most of the COC, there is little difference in bioaccessibility between the gastric and gastric+intestinal phases. The one exception to this is lead, which shows considerably higher bioaccessibility if one considers only the gastric phase of absorption as representative of lead's bioaccessibility in the gastrointestinal tract.

While the gastrointestinal absorption of lead (and all chemicals for that matter) in humans occurs in two organs: the stomach (gastric phase), and the small intestine (intestinal phase), only the gastric phase has been validated for *in vitro* bioaccessibility testing for lead and only the gastric phase bioaccessibility results for lead are considered acceptable by many regulatory authorities (including Health Canada, U.S. EPA, and MOE). This is somewhat counter-intuitive as research has shown that for metals the actual absorption occurs in the small intestine, with very small to negligible amounts being absorbed in the stomach (Mushak, 1991). While lead and probably most other metals will certainly be solubilized at stomach pH, it is important to remember that solubilization does not necessarily equal uptake.



An issue that results from this regulatory policy on the use of bioaccessibility data in HHRA is that sitespecific HHRA which utilize only gastric phase soil bioaccessibility data for lead can generate remedial objectives that are lower than regulatory human health-based soil quality guidelines (SQGhh) for lead. Thus, while agencies such as CCME, MOEE and U.S. EPA endorse SQGhh for lead that include 140, 200, 400, and 1000 mg Pb/kg soil, detailed site-specific HHRA that rely only on gastric phase soil bioaccessibility can generate remedial objectives for lead in soil that are less than these generic SQGhh values. This situation is counter-intuitive as the more refined and site-specific one gets in an HHRA, the remedial objectives tend to be higher than generic SQGhh, as the generic values are designed to be highly conservative and protective of human health under the majority of common exposure conditions. Sitespecific remedial objectives are almost always higher than generic SQGhh as they incorporate detailed site-specific information, and do not need to rely on the same degree of conservatism as the generic SQGhh.

While bioaccessibility provides one aspect of the potential uptake of a particular COC, a variety of other factors can affect the overall bioavailability of lead, including:

- GI absorption is dependent on soluble forms of lead; insoluble forms are very poorly absorbed;
- GI absorption is higher in children than in adults (*i.e.*, 40-50% of ingested lead absorbed in children *versus* 3-10% of ingested lead absorbed in adults); data are limited for older children and adolescents;
- GI absorption increases markedly if subjects are fasted;
- Nutritional status also influences GI absorption of lead (*e.g.*, most well characterized influences are Fe and Ca; Fe- and Ca-deficient subjects absorb greater amounts of lead than non-deficient subjects);
- Lead absorption may increase during pregnancy;
- Gastrointestinal absorption of inorganic lead occurs primarily in the duodenum (Mushak, 1991); exact mechanisms of absorption are unknown and may involve active transport and/or diffusion through intestinal epithelial cells or between cells, and may involve ionized lead (Pb⁺²) and/or inorganic or organic complexes of lead;
- WHO documents on lead report that 50% of soluble lead is absorbed in the small intestine;



- Saturable mechanisms of absorption have been inferred from measurements of net flux kinetics of lead in the *in situ* perfused mouse intestine, the *in situ* ligated chicken intestine, and in *in vitro* isolated segments of rat intestine; by analogy to other divalent cations, saturable transport mechanisms for lead may exist within the mucosal and serosal membranes and within the intestinal epithelial cell;
- Numerous observations of nonlinear relationships between PbB concentration and lead intake in humans suggest the existence of a saturable absorption mechanism or some other capacity-limited process in the distribution of lead in humans; where the percentage of ingested lead that is absorbed may decrease with increasing rate of lead intake; however, still no firm basis for discerning if the gastrointestinal absorption of lead is limited by dose - the dose at which absorption becomes appreciably limited in humans is not known;
- This saturation observation can be seen in the curvilinear dose-response relationships between lead dose and PbB, where the increment in PbB per unit of intake decreases with increasing PbB;
- Lead intake-blood lead relationships also vary with age as a result of age-dependency of gastrointestinal absorption of lead, and vary with diet and nutritional status (Mushak 1991);
- In immature swine that received oral doses of lead in soil, lead dose-blood lead relationships were nonlinear (curvilinear); however, dose-tissue lead relationships for bone, kidney, and liver were linear. The same pattern (nonlinearity for blood lead and linearity for tissues) was observed in swine administered lead acetate intravenously (Casteel et al. 1997). This raises the question of whether there is an effect of dose on absorption or on some other aspect of the biokinetics of lead;
- Rat studies with lead acetate also suggest a capacity-limited process at the level of the intestinal epithelium;
- The U.S. EPA IEUBK model assumes that GI absorption of lead is the sum of a capacity limited process and unlimited process; fractional absorption is decreased at high intake levels (>5 mg/kg/day); and
- PbB levels are linked to both external intakes and interactions with lead that deposits in bone tissue (*i.e.*, resorption, formation processes can increase or decrease PbB independently of external exposures, depending on age and physiological status, such as pregnancy, menopause, osteoporosis, prolonged immobility).



As such, while the bioaccessibility of lead is certainly an important factor, there are a variety of other factors which impact upon the bioavailability of lead and the ultimate potential of the exposure to lead to adverse effects. The gastrointestinal absorption of lead varies depending on a number of factors including speciation, solubility, particle size (if lead is in a matrix like food or soil), the exposure medium (*e.g.*, food, water, soil), and the age and physiological state of the exposed animal (*e.g.*, fasting or fed, nutritional status, pregnancy status, *etc.*).

The results of the bioaccessibility study indicates that as much as 78% of the lead present in GSA soils becomes solubilized (*i.e.*, is available for absorption) in the gastric phase of the study. Similary, 95% of the lead present in dust collected from the GSA becomes solubilized in the gastric phase of the bioaccessibility study. Drexler and Brattin (2007) have related relative *in vivo* bioavailability (RBA) and *in vitro* bioaccessibility (IVBA) estimates from a large dataset of lead-contaminated soils and wastes. A highly significant correlation coefficient between the two sets of data was found and the following linear regression equation relating the two derived:

RBA = 0.878 * IVBA - 0.028

This equation allows an estimate of RBA when only IVBA is known. In the current study, the IVBA estimates for lead (78% for soil and 95% for dust) results in estimates for soil RBA of 66% and dust RBA of 83%. These values were utilized in the current assessment.

Also noteworthy following the second round of analysis were the differences between the Round 1 and Round 2 dust results. No mathematical or methodological error could be identified to explain the different results, although it is suspected that a laboratory dilution error explains the lower results from Round 1. Due to the consistency between the Golder Round 2 and Drexler results for dust, the more conservative Round 2 results were utilized for this study.

3.4.3 Recommended Relative Absorption Factors

As noted previously, a RAF based on a bioaccessibility evaluation is a simple quotient comparing the solubility of contaminants in soil and the exposure medium used to develop the RfD/CSF (*i.e.*, spiked food) in simulated digestive fluids. Table 3.13 provides the recommended RAFs for each of the COC used in the current human health risk assessment for the GSA.

Chemical	Relative Absorption Factor (RAF)						
Chemical	Soil	Dust					
Arsenic	39	45					
Cobalt	28	30					
Copper	74	49					
Copper Lead ^a Nickel ^b	66	83					
Nickel ^b	42	30					
Selenium	26	67					

Table 3.13 Summary of Recommended Relative Absorption Factors (RAF)

^a The RAF for lead in soil and dust has been adjusted based on the Drexler and Brattin (2007) regression equation.

^b The bioaccessibility of nickel in soil and dust has been adjusted by the bioaccessibility of nickel in spiked rat chow (media used in TRV development).

The complete bioaccessibility report, including each analytical report, can be viewed in Appendix J, and a discussion of the application of these bioaccessibility values is provided in Chapter 4 of this volume. It is important to keep the purpose of the bioaccessibility study in context. The purpose of the study was to estimate the relative difference in bioaccessibility between metals in soil and dust from the GSA, and those used in the toxicological studies used to derive the TRVs utilized in the HHRA. The study was not intended to measure the absolute bioavailability of metals in soil and dust from the GSA. Since the results of the study are used in a relative manner, these uncertainties are not expected to significantly affect the results or conclusions of the HHRA.

3.5 Speciation of the COC

The geological history of the Sudbury basin and the highly mineralized nature of the area, will have significant implications on the form in which many of the COC will be available for potential exposure. Potential exposures related to natural deposits *versus* those arising from smelting and processing activities are likely to be different in structure. For example, nickel may be present in the environment in a variety of forms including: metallic nickel; water soluble forms of nickel (like nickel sulphate); sulphidic nickel (including nickel subsulphide); and various oxides of nickel (including nickel oxide and complex oxides). However, studies of emissions from metallurgical processes such as those employed by Vale Inco and Xstrata Nickel have demonstrated that oxidic, sulfidic and soluble forms of nickel tend to be the predominate forms present, particularly when considering emissions from historic operations. The process of determining the actual form of metal COC present within a given sample matrix is typically referred to as *speciation*.



The MOE, as part of their recent information draft on the development of air standards for nickel and its compounds (MOE, 2004), provided a table of species-specific measurements of nickel compounds in ambient air in Ontario and other locations throughout the world (see Table 3.14 below). It provides a good indication of the nickel species typically observed under a variety of environment conditions and industrial emission profiles.

For the purpose of the Sudbury Soils Study, a detailed review of the available information and literature on relevant speciation techniques was conducted. A preliminary draft of this report was provided to the Technical Committee for discussion in the fall of 2004. This was followed by a technical meeting on November 3, 2004, to discuss how speciation should be addressed in the current study.



Type of Location	Location	Total Ni Species (ng/m)	Soluble Ni Species ^a (%)	Sulphidic Ni Species (%)	Metallic Ni Species (%)	Oxidic Ni Species (%)	Comments
Urban background	Dortmund, Germany	7.4	22.4%	8.3%	18.6%	50.7%	24 hr TSP samples; 4 samples, mean;
Industrial, Near Steel Mill [°]	Dortmund, Germany	11.9	42.1%	4.5%	7.4%	46%	24 hr TSP samples; 8 samples, mean;
Industrial, Near Utility Boiler	Florida, U.S.	1010 Elemental Ni	>95% is NiSO ₄ and NiFe ₂ O ₃ ^e	No Ni ₃ S ₂ found			9hr TSP sample
f Urban	Toronto, Windsor, Ontario	41	72% NiSO ₄	n/d	n/d	18% NiO 8% Ni(OH) ₂	Four 24 hr PM ₁₀ samples, mean; 1998 -2000;
Industrial (Petroleum Refinery)	Sarnia, Ontario	157	58% $NiSO_4$	n/d	n/d	20% NiO 23% Ni(OH) ₂	Four 24 hr PM ₁₀ samples, mean; 1998 -1999;
Industrial (Steel Manuf.)	Hamilton Ontario	90	57% NiSO ₄	n/d	n/d	27% NiO 17% Ni(OH) ₂	Two 24 hr PM ₁₀ samples, mean; 1999;
Industrial (Active Ni smelting & refinery)	Sudbury, Copper Cliff, Ontario	612	60% NiSO ₄	n/d	3% Ni	31% NiO 12% Ni(OH) ₂	Three 24 hr PM ₁₀ samples, mean; 2000;
Industrial (Previous Ni refinery) ^g	Port Colborne, Ontario	60	85% NiSO ₄	n/d	n/d	6% NiO 9% Ni(OH) ₂	Four 24 hr PM ₁₀ samples, mean; 2001-02;

Table 3.14 Species-Specific Measurements of Nickel Compounds in Ambient Air (MOE, 2004)

^a This is the % of a particular nickel compound or species from the total nickel species present in air. These percentages may not add up exactly to 100% due to rounding and merging of sample results.

^b EC, 2000 p. 24; Füchtjohann *et al.*, 2001. Method does not identify individual nickel compounds (*e.g.*, soluble fraction includes all nickel salts - sulphate and chloride; sulphidic fraction primarily consists of nickel sulphides but does not separate nickel subsulphide from nickel sulphide).

^c Steel factory with blast furnaces, within a distance of about 1 to 2 km.

^d Utility (400 MW)-scale combustion system burning no. 6 fuel oil (Galbreath *et al.*, 2000).

^e Data is semi-quantitative but specific nickel species identified; the proportion of NiSO4 relative to NiFe2O3 much greater than in the utility's fly ash.

^f Specific nickel species identified and quantitated. Analytical standards included in the speciation were: Ni metal, Nickel sulphide (NiS), nickel disulphide (NiS2), nickel subsulphide (NiS2), nickel sulphate (NiSO4), nickel oxide (NiO), and nickel hydroxide [Ni(OH)2] (Lamoureux, 2003).

^g Current precious metal recovery operations.

During that meeting, and subsequent discussions, it was agreed that:

- Speciation of nickel is the priority for the Human Health Risk Assessment (HHRA);
- Metal speciation is not necessary for the Ecological Risk Assessment;



- Speciation of nickel in soil and air samples is considered the priority from an exposure pathway perspective;
- Speciation may be carried out on samples of indoor dust if sufficient material is available and it is considered necessary;
- Total metal (metalloid) concentrations will be used to assess human health risks and ecological risks for COC other than nickel;
- A weight-of-evidence approach to speciation will be employed;
- The recommended primary analytical methodology for sample speciation is the modified Tessier sequential leach extraction;
- The secondary method involving a bulk analysis using a soil trace mineral search technique (also termed QemSCAN) will be performed on approximately 10% of the samples to verify results of the leach extraction procedure; and
- Samples will be submitted for QA/QC purposes that may include Certified Reference Material (if available), split samples or round robin testing. However, it is recognized that speciation analysis is not a common commercially available procedure.

Based upon these recommendations, the following "weight-of-evidence" analytical approach was conducted for air filter, soil, and dust samples collected during Phase II of the HHRA (see relevant sections in this chapter):

- 1. All selected samples were analyzed using a modified Tessier sequential leach extraction technique, which quantifies the mass fraction of each COC within the sample which leaches out in sequentially more aggressive digestion procedures; and
- All dust and air filter samples were analyzed using mineralogical analyses, such as soil trace mineral search techniques and soil bulk mineralogical analyses (*i.e.*, using a scanning electron microscopy). A subset of the soil samples analysed using the sequential leach extraction (approximately 10%) were also analysed using these mineralogical techniques.

The results of these analyses, and subsequent follow up analyses, are summarized in the following section. A revised draft of the initial speciation methodology used by the SARA Group, as well as the actual analytical report by SGS Lakefield Research Ltd. (SGS), are provided in Appendix I.



3.5.1 Sequential Leach Analysis

Sequential leach analysis is a long-standing, documented analytical technique used to predict metal associations in soils. The chemical models that provide the rationale for these methods have been based on equilibrium reactions, or on empirical determinations from wet chemical methods that rely on the sequential extraction of various phases (Tessier *et al.*, 1979; Tessier and Campbell, 1988; Gaillard *et al.*, 2001; Fernádez Espinosa *et al.*, 2002).

However, it should be noted that wet extraction procedures have presented serious challenges for analyses of samples in matrices other than aquatic sediments or soils. Thermodynamic equilibrium is rarely achieved in natural systems and consequently the predictive power of generalized speciation techniques applied to soil or sediments remains poor (Gaillard *et al.*, 2001). Sequential extraction protocols are also prone to artifacts (Tipping *et al.*, 1985) and require careful evaluation and calibration before being used on a specific sample (Tessier and Campbell, 1988; Profumo *et al.*, 2003). Further discussion of these uncertainties is provided in Appendix I.

The sequential extraction procedure of Tessier *et al.* (1979) was adopted for the present study with one modification to omit an easily reducible step and generate a reducible fraction in a single aggressive stage (see Step 3). The method and nominally defined speciation fractions are outlined in Table 3.15.

Definition	Fraction Sought	Method Used				
<i>Fraction 1</i> Exchangeable	Metals bound by sorption/desorption processes. Readily bioavailable.	1 M MgCl ₂ shaken for 1 hr at neutral pH				
<i>Fraction 2</i> Carbonate-hosted	COC bound to carbonate. Bioavailable subsequent to degradation/dissolution of carbonate.	Residue from 1 leached with sodium acetate (NaOAc) adjusted to pH 5 with acetic acid (HOAc) to completion.				
<i>Fraction 3</i> Reducible ^a	Bound to Fe-Mn-Oxides. Complete free Fe-oxide dissolution evaluated.	Residue from 2 leached with 0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAc at 96°C.				
<i>Fraction 4</i> Organic-bound or Oxidizable	Bound to organic matter.	Residue from 3 leached with $30\% v/v H_2O_2$. 0.02 M HNO ₃ , 85° C. 3.2 M NH ₄ Ac ($20\% v/v HNO_3$) added, shaken for 3 min.				
<i>Fraction 5</i> Residual	Nitric-acid soluble species. Excludes silicate-bound and thus inert/stable/benign COC	Residue from 4 leached with $25\% \text{ v/v}$ HNO heated to dryness. Then leached in $10\% \text{ v/v}$ HNO ₃ .				

Table 3.15Tessier Leach Fractions and Methodology

^a A combined leach, rather than two steps usually separating an easily and moderately reducible fraction. (*e.g.*, easily reducible targets Mn-Oxides.)

These analyses were conducted by the Analytical Services department of SGS Lakefield Research Ltd. Further details on the approach are provided in the full speciation report found in Appendix I.

3.5.2 Mineralogical Procedure

The mineralogical analyses were carried out by scanning electron microscopy (SEM) using a Leo 440 SEM combined with energy dispersive X-ray spectrometry (EDS) and equipped with both a secondary electron and back-scattered electron detector.

Mineralogical analysis of soils is typically conducted in two phases: 1) trace mineral analysis, and, 2) bulk mineral analysis. These vastly different objectives require different methodologies. The trace mineral analysis involves detailed, systematic, high magnification scanning of polished grain mounts prepared from soil size fractions, with the COC-bearing phases characterized by elemental composition, particle size and association (Stanley and Laflamme, 1998). Bulk mineral analysis involves X-ray diffraction and scanning electron microscopy to characterize mineral weight percent particle size, calculated chemistry and elemental/mineral associations (Jambor and Blowes, 1998). It is important to note that mineralogical analyses, while very useful techniques, do have a number of methodological limitations (some of which can be observed in the results for this study).



These analyses were conducted by the Mineral Technologies Department of SGS Lakefield Research Limited. Further details on the approach and its limitations are provided in the full speciation report found in Appendix I.

3.5.3 Sample Selection

Table 3.16 outlines the number of samples in each of the three media types which were evaluated using these two analyses in the weight-of-evidence approach.

Table 5.10 Number of Samples Analyzed using each Speciation Technique	Table 3.16	Number of Samples Analyzed using each Speciation Technique
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Analytical Technique	Total Samples Analyzed							
Analytical Teeninque	Soil	Air Filter	Dust					
Sequential leach	84	10	25					
Mineralogical analyses	10	10	25					

3.5.3.1 Soil Samples

A total of 84 soil samples were analyzed using the sequential leach technique, including 19 samples from Copper Cliff, 21 samples from Falconbridge, 18 samples from Coniston, 16 samples from Sudbury Centre, and 10 samples from Hanmer. These samples were splits of the residential soil samples taken as part of the Indoor Dust Survey (see Section 3.6 for a review of the Indoor Dust Survey, and Appendix M for the full Indoor Dust Survey report). Of these 84 samples, 10 were selected for additional mineralogical analyses using the SEM (four from Falconbridge, three from Copper Cliff, and three from Coniston). These particular samples were selected for the additional analyses by SEM due to their locations in the three original smelting communities and the presence of elevated nickel concentrations detected in the samples.

3.5.3.2 Air Filters

A total of 10 air filters were selected for evaluation by both sequential leach and SEM analyses. Due to the very low concentrations of all metals, including nickel, detected in samples taken throughout the entire air monitoring program (refer to Section 3.1 for an overview of the program results, and Appendix F for the City of Greater Sudbury Air Monitoring Program report), to ensure sufficient material for the speciation analyses, air filters from the day demonstrating the highest particulate and nickel concentrations were selected. A review of the monitoring data indicated that June 8th, 2004, consistently demonstrated the highest concentrations across all monitoring locations.



To evaluate potential differences in COC speciation between the key communities of interest, PM_{10} filters from the Copper Cliff, Sudbury Centre West, Hanmer, and Windy Lake stations on June 8th, 2004, were selected. To evaluate the potential differences in COC speciation at different size fractions, the $PM_{2.5}$ filters from the Copper Cliff, Sudbury Centre West, and Windy Lake stations for the same date were also submitted (only PM_{10} sampling was conducted at the Hanmer location, so a $PM_{2.5}$ filter was unavailable).

Metal concentrations detected at the Sudbury Centre West monitoring locations were consistently higher than those observed at other monitoring locations. Concentrations at this particular location appeared to be influenced by wind direction. As demonstrated in Figure 3-3, wind direction on June 8th was out of the south-west, blowing across the Vale Inco Copper Cliff facility and nearby waste piles toward the Sudbury Centre West monitoring station. As noted previously, the location chosen for this particular monitoring site was intended to assess potential impacts on air quality from both of these sources.

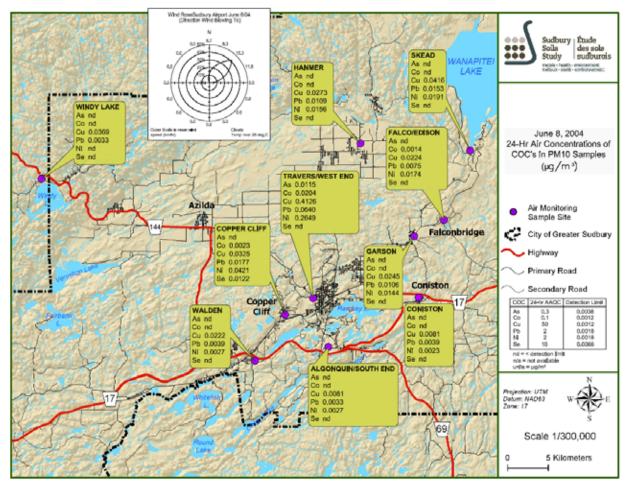


Figure 3-3 Windrose depicting Wind Direction and COC Concentrations at each Air Monitoring Location for June 8th, 2004



To evaluate whether the speciation of COC, and nickel in particular, differ when the wind was not approaching from this direction, an additional PM_{10} filter was submitted from the Sudbury Centre West location from September 24, 2004. As demonstrated in Figure 3-4, wind direction on September 24th, 2004, was out of the South-Southwest, likely resulting in minimal contribution from the Inco Copper Cliff facility and nearby slag piles. While particulate concentrations on this day were not considerably less than those observed on June 8th (*i.e.*, 45.3 *versus* 69.7 µg/m³), measured concentrations of the COC were generally much lower (*i.e.*, nickel concentrations of 0.058 *versus* 0.265 µg/m³). Therefore, this additional filter was selected for analyses to determine whether the species of COC measured on this particular day differed from those on June 8th.

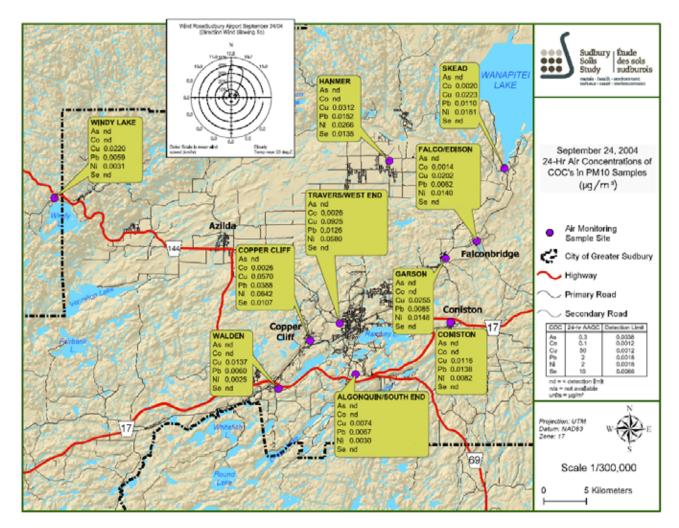


Figure 3-4 Windrose depicting Wind Direction and COC Concentrations at each Air Monitoring Location for September 24th, 2004



3.5.3.3 Indoor Dust Samples

A total of 25 indoor dust samples were selected for evaluation by both sequential leach and SEM analyses. These included four from Falconbridge, seven from Copper Cliff, four from Sudbury Centre, five from Coniston and three from Hanmer. As with the soil samples, these samples were from the indoor dust samples taken as part of the Indoor Dust Survey (see Section 3.6 for a review of the Indoor Dust Survey and Appendix M for the full Indoor Dust Survey report). These particular samples were selected for speciation analyses due to their locations in the various COI, and due to the presence of elevated COC concentrations, in particular nickel in the samples.

3.5.4 Results of Initial Speciation Analyses

The following sections provide the results of the speciation analyses conducted using both the sequential leach technique and the SEM analyses. Refer to Appendix I of this volume for the complete speciation analytical report from SGS.

3.5.4.1 Sequential Leach Analyses Results

Tables 3.17, 3.18 and 3.19 provide the results of the sequential leach analyses conducted on the soil, air filter, and indoor dust samples, respectively, gathered as part of the Sudbury Soils Study.

In the case of the soil samples, the results indicated the speciation "fingerprint" (*i.e.*, the breakdown of percentages in each leaching step) was generally consistent across the samples taken from each COI. When evaluating the air filter samples, the results indicated the speciation fingerprint did vary from sample to sample. This variability appears to be particularly evident with respect to the fractions that were extracted in the exchangeable and organic phases. This is likely due to the presence of exchangeable metals which have been coated by an organic layer, preventing their quantification prior to the organic extraction step. Finally, the speciation fingerprints for the indoor dust samples were also very similar across the various COI. However, a slight difference was observed in those samples taken from Sudbury Centre residences when compared to those from the other COI, particularly with respect to the fraction leaching out in the organic leach step. In the case of the Sudbury Centre samples, it appears that more of the various COC were leached out in the steps prior to the organic step (particularly during the reducible step). However, there is no obvious explanation for this minor difference.

Leach Fractions	OVERALL (84 samples)	Copper Cliff (19 samples)	Falconbridge (21 samples)	Coniston (18 samples)	Sudbury (16 samples)	Hanmer (10 samples)
Arsenic	2.8%	1.0%	4.9%	1.2%	1.2%	2.0%
As Exchangeable	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
As Carbonate	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
As Reducible	32.2%	37.5%	30.8%	24.0%	54.3%	50.0%
As Organic	65.4%	62.5%	66.1%	76.0%	45.7%	50.0%
Cobalt	3.1%	1.8%	3.7%	3.6%	4.9%	8.5%
Co Exchangeable	3.1%	2.7%	4.5%	1.0%	0.3%	0.0%
Co Carbonate	0.6%	0.1%	0.9%	0.4%	0.1%	0.0%
Co Reducible	31.7%	36.1%	30.5%	32.9%	30.4%	21.6%
Co Organic	34.5%	24.3%	40.9%	30.9%	26.9%	30.6%
Co Residual	30.1%	36.8%	23.2%	34.8%	42.3%	47.8%
Copper	42.7%	50.2%	39.2%	34.4%	40.5%	25.7%
Cu Exchangeable	0.9%	1.2%	0.6%	0.4%	0.8%	0.0%
Cu Carbonate	4.5%	6.3%	2.8%	4.8%	2.6%	0.5%
Cu Reducible	24.3%	34.7%	13.1%	24.9%	27.0%	14.7%
Cu Organic	62.9%	52.8%	73.5%	62.5%	61.5%	74.0%
Cu Residual	7.5%	4.9%	10.0%	7.5%	8.0%	10.7%
Lead	6.7%	7.5%	4.2%	10.7%	10.5%	20.9%
Pb Exchangeable	0.7%	0.8%	0.4%	0.3%	2.0%	0.0%
Pb Carbonate	5.0%	4.2%	3.5%	6.8%	6.7%	11.6%
Pb Reducible	34.8%	30.8%	30.1%	48.6%	42.4%	34.0%
Pb Organic	50.2%	57.2%	57.6%	35.1%	32.9%	29.1%
Pb Residual	9.3%	6.9%	8.4%	9.2%	16.0%	25.2%
Nickel	44.7%	39.5%	48.1%	50.1%	42.9%	42.9%
Ni Exchangeable	13.0%	13.6%	14.1%	9.2%	9.6%	3.8%
Ni Carbonate	3.8%	3.2%	4.2%	5.3%	2.3%	0.3%
Ni Reducible	30.0%	26.4%	30.4%	38.7%	28.7%	30.6%
Ni Organic	27.4%	20.2%	33.1%	26.6%	21.1%	25.9%
Ni Residual	25.9%	36.6%	18.2%	20.2%	38.4%	39.4%
Selenium	0.03%	0.09%	0.00%	0.00%	0.00%	0.00%
Se Exchangeable	0.0%	0.0%	-	-	_	_
Se Carbonate	0.0%	0.0%	-	-	_	-
Se Reducible	0.0%	0.0%	-	-	-	-
Se Organic	100.0%	100.0%	-	-	-	-
Se Residual	0.0%	0.0%	_	_	_	-

Table 3.17	Results of Sequential Leach Analyses in Sudbury Soils (SGS, 2005)
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Note: Bolded and shaded values for the specific COC are the percentage of all COC represented by that particular COC (*i.e.*, 1% of the metals detected in Copper Cliff soil samples were arsenic, while the remainder of the rows depict the percentage of that particular COC which was extracted at each leaching step (*i.e.*, 26.4% of the nickel in Copper Cliff soil samples leached out in the reducible step.

"-" indicates that particulate COC was not detected in any of the samples for that COI.



Table 3.18	Res	ults of Sequ	ential Leach	Analyse	es in Sud	bury Air Fi	lters (SGS	5, 2005)				
			PM ₁₀	Air Filter	8				P	M _{2.5} Air Filters	8	
Leach Fractions	All PM ₁₀ Samples	Copper Cliff (June 8 th)	Falconbridge (June 8 th)		Sudbury (June 8 th)		Sudbury (Sept 24 th)	All PM _{2.5} Samples	Copper Cliff (June 8 th)	Falconbridge (June 8 th)	Sudbury (June 8 th)	Windy Lake (June 8 th)
Arsenic	1.8%	2.4%	2.4%	1.4%	2.2%	0.0%	0.0%	1.7%	2.0%	2.9%	1.8%	0.0%
As Exchangeable	26.3%	52.6%	100.0%	41.6%	17.6%	-	-	52.1%	100.0%	100.0%	31.8%	_
As Carbonate	0.0%	0.0%	0.0%	0.0%	0.0%	-	-	0.0%	0.0%	0.0%	0.0%	_
As Reducible	14.5%	0.0%	0.0%	0.0%	18.4%	-	-	14.9%	0.0%	0.0%	21.2%	_
As Organic	59.2%	47.4%	0.0%	58.4%	64.0%	_	-	33.0%	0.0%	0.0%	47.0%	_
As Residual	0.0%	0.0%	0.0%	0.0%	0.0%	_	-	0.0%	0.0%	0.0%	0.0%	_
Cobalt	2.6%	3.1%	4.1%	2.2%	2.7%	1.9%	1.6%	2.5%	3.0%	4.4%	2.3%	2.0%
Co Exchangeable	21.4%	41.0%	59.7%	27.1%	14.5%	43.2%	17.9%	40.6%	68.1%	66.7%	25.4%	51.6%
Co Carbonate	4.1%	5.0%	6.9%	7.6%	2.4%	11.4%	9.5%	8.9%	12.8%	10.4%	5.3%	22.6%
Co Reducible	13.1%	6.0%	5.6%	5.1%	15.2%	0.0%	25.0%	10.8%	0.0%	4.2%	16.9%	0.0%
Co Organic	44.2%	37.0%	22.2%	38.1%	52.8%	25.0%	0.0%	28.6%	19.1%	12.5%	37.6%	12.9%
Co Residual	17.2%	11.0%	5.6%	22.0%	15.2%	20.5%	47.6%	11.1%	0.0%	6.2%	14.8%	12.9%
Copper	54.9%	34.1%	35.6%	70.1%	54.8%	68.7%	53.8%	49.0%	36.5%	30.2%	50.5%	66.8%
Cu Exchangeable	34.6%	27.8%	39.9%	73.9%	24.9%	39.4%	42.6%	29.5%	53.6%	31.4%	25.2%	33.0%
Cu Carbonate	4.8%	4.6%	11.0%	2.5%	4.6%	7.9%	6.4%	6.0%	10.0%	7.9%	4.3%	9.8%
Cu Reducible	2.2%	6.9%	6.9%	1.9%	0.8%	6.5%	6.5%	10.6%	4.7%	10.0%	12.6%	6.4%
Cu Organic	41.7%	48.7%	33.2%	14.1%	54.2%	28.8%	6.3%	39.4%	21.4%	35.6%	44.9%	28.8%
Cu Residual	16.6%	12.0%	9.1%	7.6%	15.6%	17.4%	38.1%	14.4%	10.3%	15.1%	13.0%	21.9%
Lead	6.9%	11.2%	9.6%	7.2%	6.2%	7.4%	6.7%	13.3%	15.2%	12.0%	14.0%	8.2%
Pb Exchangeable	53.6%	60.9%	61.8%	58.0%	53.0%	41.8%	46.9%	67.3%	74.8%	58.3%	70.3%	35.4%
Pb Carbonate	13.7%	13.0%	14.1%	11.6%	13.5%	10.6%	18.9%	11.8%	10.3%	10.6%	12.0%	14.6%
Pb Reducible	9.4%	12.2%	10.0%	7.2%	7.8%	8.2%	18.3%	7.1%	5.8%	10.6%	5.8%	16.9%
Pb Organic	14.7%	10.8%	8.8%	14.2%	17.9%	22.4%	0.3%	8.7%	5.4%	12.1%	8.2%	16.2%
Pb Residual	8.6%	3.0%	5.3%	9.0%	7.8%	17.1%	15.6%	5.1%	3.7%	8.3%	3.7%	16.9%



Table 3.18	Res	ults of Seque	ential Leach	Analyse	es in Sud	bury Air Fi	lters (SGS	5, 2005)				Gittere		
			PM ₁₀ .	Air Filter	s			PM _{2.5} Air Filters						
Leach Fractions	All PM ₁₀ Samples	Copper Cliff (June 8 th)	Falconbridge (June 8 th)		Sudbury (June 8 th)	•	Sudbury (Sept 24 th)	All PM _{2.5} Samples	Copper Cliff (June 8 th)	Falconbridge (June 8 th)	Sudbury (June 8 th)	Windy Lake (June 8 th)		
Nickel	29.6%	33.7%	25.0%	13.1%	32.8%	9.5%	33.8%	22.7%	18.8%	23.1%	26.3%	7.3%		
Ni Exchangeable	22.7%	29.4%	27.2%	13.5%	22.5%	5.9%	23.8%	20.0%	23.2%	19.8%	20.6%	0.0%		
Ni Carbonate	4.3%	3.9%	17.2%	5.7%	3.3%	5.9%	6.2%	8.9%	15.4%	36.8%	4.4%	17.4%		
Ni Reducible	4.4%	3.9%	5.4%	2.4%	3.8%	0.9%	8.9%	7.3%	4.4%	4.3%	8.2%	4.3%		
Ni Organic	41.4%	46.2%	35.6%	40.6%	48.4%	30.6%	0.0%	43.3%	38.6%	29.2%	46.9%	16.5%		
Ni Residual	27.3%	16.4%	14.5%	37.8%	21.9%	56.6%	61.1%	20.5%	18.5%	9.9%	19.8%	61.7%		
Selenium	4.2%	15.5%	23.3%	6.0%	1.3%	12.5%	4.1%	10.8%	24.5%	27.4%	5.0%	15.8%		
Se Exchangeable	17.1%	16.0%	26.8%	15.6%	14.3%	10.3%	18.2%	14.7%	17.9%	16.7%	7.1%	20.0%		
Se Carbonate	14.4%	20.0%	14.6%	28.1%	0.0%	0.0%	27.3%	8.8%	7.7%	10.0%	14.3%	0.0%		
Se Reducible	18.5%	16.0%	14.6%	21.9%	16.7%	20.7%	27.3%	19.1%	17.9%	23.3%	11.9%	28.0%		
Se Organic	31.5%	38.0%	22.0%	21.9%	45.2%	27.6%	27.3%	27.2%	30.8%	16.7%	31.0%	28.0%		
Se Residual	18.5%	10.0%	22.0%	12.5%	23.8%	41.4%	0.0%	30.1%	25.6%	33.3%	35.7%	24.0%		

Note: Bolded and shaded values for the specific COC are the percentage of all COC represented by that particular COC (*i.e.*, 2.4% of the metals detected in Copper Cliff air filter were arsenic, while the remainder of the rows depict the percentage of that particular COC which was extracted at each leaching step (*i.e.*, 46.2% of the nickel in Copper Cliff air filter leached out in the organic step.

"-" indicates that particulate COC was not detected in any of the samples for that COI.

Leach Fraction	All Dust Samples (24 samples)	Sudbury (4 samples)	Falconbridge (5 samples)	Copper Cliff (7 samples)	Coniston (5 samples)	Hanmer (3 samples)
Arsenic	1.2%	1.1%	1.5%	1.2%	1.1%	2.3%
As Exchangeable	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
As Carbonate	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
As Reducible	18.6%	33.3%	13.5%	20.3%	17.4%	10.7%
As Organic	79.6%	66.7%	86.5%	77.7%	78.7%	89.3%
As Residual	1.8%	0.0%	0.0%	2.0%	3.8%	0.0%
Cobalt	2.2%	1.8%	3.8%	2.4%	1.3%	1.9%
Co Exchangeable	4.1%	14.4%	5.0%	2.2%	3.0%	10.4%
Co Carbonate	0.7%	0.3%	1.2%	0.4%	1.0%	0.0%
Co Reducible	16.8%	25.8%	22.2%	12.0%	17.3%	20.4%
Co Organic	52.9%	36.8%	44.6%	57.3%	59.9%	50.4%
Co Residual	25.5%	22.7%	27.0%	28.1%	18.7%	18.7%
Copper	47.2%	52.7%	52.3%	39.3%	52.9%	55.2%
Cu Exchangeable	8.3%	20.3%	15.5%	5.7%	3.8%	12.7%
Cu Carbonate	1.2%	2.9%	0.7%	1.0%	1.0%	1.5%
Cu Reducible	5.7%	15.9%	6.2%	3.9%	4.4%	7.4%
Cu Organic	81.6%	58.6%	75.5%	86.1%	86.6%	76.4%
Cu Residual	3.2%	2.2%	2.0%	3.2%	4.1%	1.9%
Lead	15.5%	17.6%	8.2%	21.7%	10.6%	13.4%
Pb Exchangeable	6.2%	14.6%	15.2%	2.2%	7.5%	23.4%
Pb Carbonate	16.9%	16.4%	11.8%	17.2%	19.7%	6.6%
Pb Reducible	40.7%	43.8%	36.7%	40.5%	41.9%	37.3%
Pb Organic	34.4%	22.8%	34.5%	38.2%	29.3%	29.9%
Pb Residual	1.8%	2.4%	1.6%	1.8%	1.5%	2.8%
Nickel	33.7%	26.2%	34.0%	35.3%	34.1%	26.9%
Ni Exchangeable	6.9%	20.5%	10.0%	6.4%	3.3%	8.5%
Ni Carbonate	1.5%	2.7%	1.8%	1.3%	1.4%	1.7%
Ni Reducible	13.8%	14.1%	20.5%	12.9%	11.5%	14.9%
Ni Organic	61.7%	45.1%	54.1%	62.0%	68.7%	58.8%
Ni Residual	16.1%	17.6%	13.5%	17.4%	15.1%	16.2%
Selenium	0.2%	0.7%	0.4%	0.1%	0.03%	0.2%
Se Exchangeable	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Se Carbonate	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Se Reducible	74.0%	75.7%	100.0%	33.3%	100.0%	100.0%
Se Organic	18.7%	0.0%	0.0%	66.7%	0.0%	0.0%
Se Residual	7.3%	24.3%	0.0%	0.0%	0.0%	0.0%

Table 3.19Results of Sequential Leach Analyses in Sudbury Indoor Dust (SGS, 2005)

Note: Bolded and shaded values for the specific COC are the percentage of all COC represented by that particular COC (*i.e.*, 1.5% of the metals detected in the Falconbridge dust samples were arsenic, while the remainder of the rows depict the percentage of that particular COC which was extracted at each leaching step (*i.e.*, 54.1% of the nickel in Falconbridge dust samples leached out in the organic step.

"-" indicates that particulate COC was not detected in any of the samples for that COI.



3.5.4.2 SEM Analyses Results

Tables 3.20, 3.21 and 3.22 provide the results of the SEM analyses conducted on the soil, air filter, and indoor dust samples, respectively, gathered as part of the Sudbury Soils Study. For each form of the COC detected, mineralogists at SGS provided a probable origin based upon their observations.

Results of the SEM analyses indicated considerable variability between and within COI for all media types evaluated. Most of the COC species detected likely originated from an industrial source, such as smelting and refining.

Soil

In the case of lead, the predominant form detected was anglesite (*i.e.*, lead sulphate), an emission from smelting/refining sources. With the exception of one sample taken in Coniston, galena (a natural leadbearing ore) represented little to none of the total lead present. Very little arsenic was present in any of the soil samples, even in the town of Falconbridge. Those samples that did have arsenic were in the form of arsenopyrite or enargite, both forms naturally present in rock ores. Copper was present in a variety of forms in the soils gathered around Sudbury. The predominant forms observed were chalcopyrite (a natural ore) and a copper alloy. Interestingly, brass (copper-zinc alloy) was detected in most of the soil samples, likely due to contamination from domestic or other industrial sources. The predominant forms of nickel present in all soils throughout Sudbury were oxides of nickel related to smelting and refining emissions. Pentlandite, a natural ore form of nickel, was also present in most samples, though at lesser amounts. Stainless steel was also observed in a number of the samples, likely due to contamination from domestic sources. No nickel subsulphide (Ni₃S₂) was detected in any of the soil samples taken throughout Sudbury.

Air Filters

In the case of lead, like the soil samples, the predominant form detected in the air filters sampled throughout Sudbury was anglesite. No obvious forms of arsenic were detected in any of the air filter samples analyzed for metal speciation. Unlike soil, the predominant form of copper observed in the air filters was chalcopyrite, with copper matte (a smelting product) as a lesser form found in most of the samples. While the predominant forms of nickel found in soil samples were various oxides of nickel, interestingly enough, the predominant form found in all air samples (both PM_{10} and $PM_{2.5}$) was the natural ore form of pentlandite. However, SGS identified small amounts of nickel subsulphide (*i.e.*,



nickel matte) in two of the PM_{10} air filters (*i.e.*, Copper Cliff and Sudbury) and one of the $PM_{2.5}$ air filters (*i.e.*, Copper Cliff).

Dust Samples

In the case of lead, as with the soil and air filter samples, the predominant form detected in dust samples was anglesite. Arsenic was detected in less than half of the dust samples, with highest number of detections in samples taken from residences in the Town of Falconbridge. The form of arsenic detected was typically arsenopyrite, though one sample did identify arsenic oxide (a smelter emission) as a major component present. The predominant forms of copper present in the dust samples were copper matte (Cu₂S) and copper sulphate, both smelting/refining emission products. Not surprisingly, copper metal and brass were also detected in most of the dust samples, likely arising from domestic sources around the home. Finally, a variety of different forms of nickel were detected in dusts from homes throughout Sudbury. While pentlandite and various oxides of nickel were the predominant forms identified, small amounts of nickel subsulphide (Ni₃S₂, also called heazlewoodite) were identified in a number of dust samples taken from the various COI. One sample in Hanmer even demonstrated the presence of Ni₃S₂. This finding is unexpected given the relatively long distance between Hanmer and any of the three smelters, and may be indicative of historic impacts or alternate sources of the Ni₃S₂ material. Not surprisingly, stainless steel was detected in many of the dust samples, likely arising from domestic sources around the home.



Table 3.20Results of SEM Analyses of Relevant COC in Sudbury Soils (SGS, 2005)

				Perce	ntages of (COC Speci	ies in Sudl	oury Soil S	amples		
Speciated COC	Probable Origin		Falcor	ıbridge		(Copper Cl	iff		Coniston	
		1	2	3	4	1	2	3	1	2	3
Lead		19.9%	1.07%	3.26%	0.57%	3.43%	3.07%	13.2%	1.35%	0.47%	0.13%
Anglesite (Pb-S-O)	Smelter Fumes	62.3%	100.0%	74.0%	84.1%	50.0%	63.9%	88.6%	80.1%	51.8%	100.0%
Pb-SS (Pb-Sb-Ag)	Ore/Refining	37.7%	0.0%	21.6%	15.9%	50.0%	36.1%	4.7%	19.9%	6.9%	0.0%
Galena (PbS)	Ore	0.0%	0.0%	4.4%	0.0%	0.0%	0.0%	6.7%	0.0%	41.3%	0.0%
Arsenic		4.84%	0.00%	0.00%	0.15%	0.56%	0.00%	0.00%	0.00%	0.00%	0.83%
Arsenopyrite (FeAsS)	Ore	100.0%	-	-	0.0%	100.0%	-	-	-	-	100.0%
Enargite ($Cu_{12}Sb_3S_{13}$)	Ore	0.0%	-	-	100.0%	0.0%	-	-	-	-	0.0%
Copper		28.7%	12.4%	64.6%	40.2%	2.4%	7.3%	12.0%	4.5%	7.8%	3.2%
Chalcopyrite (CuFeS ₂)	Ore	86.2%	90.0%	24.2%	0.0%	100.0%	0.0%	0.0%	69.4%	3.8%	80.1%
Cu Matte (Cu ₂ S)	Matte	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	14.0%	0.0%	0.0%
Cu Alloy (Cu)	Refining	0.0%	10.0%	75.2%	4.5%	0.0%	30.9%	0.0%	0.0%	92.9%	0.0%
Cu Oxide (Cu-O)	Refining	6.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Fe-Cu Oxide (Fe-Cu-O)	Refining	0.0%	0.0%	0.0%	94.2%	0.0%	16.6%	0.0%	0.0%	3.2%	0.0%
Cu-Slag (Cu-Fe-Mg-Si-O)	Refining/Smelter	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	28.7%	0.0%	0.0%	0.0%
Brass (Cu-Zn)	Domestic	6.9%	0.0%	0.6%	1.3%	0.0%	52.5%	71.3%	16.6%	0.0%	19.9%
Nickel		46.6%	86.5%	32.2%	59.1%	93.6%	89.6%	74.8%	94.1%	91.7%	95.8%
Pentlandite (Fe ₅ Ni ₄ S ₈)	Ore	11.3%	54.1%	2.2%	0.3%	7.7%	0.0%	0.0%	33.7%	0.7%	2.2%
Fe-Ni-Cu Alloy (Fe-Ni-Cu)	Refining	0.0%	4.3%	0.0%	0.2%	0.0%	0.0%	10.4%	0.0%	15.1%	1.9%
Ni-Fe-Co Alloy (Ni-Fe-Co)	Refining	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	17.0%
Ni-Fe- Alloy (Ni-Fe)	Refining	22.2%	7.2%	17.1%	0.0%	4.8%	0.0%	31.8%	7.6%	60.2%	0.0%
Ni-Co Oxide (Ni-Co-O)	Refining	0.0%	0.0%	0.0%	0.0%	6.1%	7.7%	0.0%	0.0%	0.0%	0.0%
Ni-Fe-Oxide (Ni-Fe-O)	Refining	66.5%	26.6%	80.7%	83.5%	81.4%	85.3%	0.0%	39.7%	1.2%	76.4%
Ni-Cu-Fe Oxide (Ni-Cu-Fe-O)	Refining	0.0%	0.0%	0.0%	15.5%	0.0%	4.0%	35.8%	19.0%	22.7%	2.5%
Ni-Fe Sulphate (Ni-Fe-S-O)	Refining	0.0%	0.0%	0.0%	0.0%	0.0%	3.0%	0.0%	0.0%	0.0%	0.0%
Ni Slag	Refining/Smelter	0.0%	7.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Stainless Steel	Miscellaneous	0.0%	0.0%	0.0%	0.5%	0.0%	0.0%	22.1%	0.0%	0.1%	0.0%

Note: Bolded and shaded values for the specific COC are the percentage of the total metals represented by that particular COC (*i.e.*, 19.9% of the metals detected in Falconbridge sample #1 were lead, while the remainder of the rows depict the percentage that the given species represents for that particular COC (*i.e.*, 66.5% of the nickel in Falconbridge sample #1 was classified as an oxide of nickel).



				PM ₁₀ Air F	ilters			PM _{2.5} Air Filters				
Speciated COC	Probable Origin	Copper Cliff (June 8 th)	Falconbridge (June 8 th)	Hanmer	Sudbury (June 8 th)	Windy Lake (June 8 th)	Sudbury (Sept 24 th)	Copper Cliff (June 8 th)	Falconbridge (June 8 th)	Sudbury (June 8 th)	Windy Lake (June 8 th)	
Lead		24.6%	54.2%	4.77%	7.44%	22.8%	10.6%	2.30%	14.2%	1.31%	62.6%	
Anglesite (Pb,S,O)	Emissions	100.0%	100.0%	100.0%	100.0%	89.2%	12.1%	100.0%	100.0%	100.0%	86.1%	
Galena (Pb,S)	Ore	0.0%	0.0%	0.0%	0.0%	10.8%	0.0%	0.0%	0.0%	0.0%	0.0%	
Lead Alloy (Pb, Sn)	Ore/PGM- Residue	0.0%	0.0%	0.0%	0.0%	0.0%	87.9%	0.0%	0.0%	0.0%	0.0%	
Pb-Pd Alloy (Pb,Pd)	Ore/PGM- Residue	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	13.9%	
Copper		27.9%	10.7%	67.8%	52.6%	60.0%	56.4%	35.1%	22.6%	52.2%	21.0%	
Chalcopyrite (Cu,Fe,S)	Ore	32.6%	70.6%	23.3%	45.6%	56.6%	71.4%	91.8%	47.8%	42.1%	7.1%	
Cu Matte (Cu,S)	Matte	67.4%	0.0%	29.9%	54.4%	1.4%	28.6%	8.2%	37.4%	50.2%	47.5%	
Cu Sulphate (Cu,S,O)	Refining	0.0%	0.0%	45.3%	0.0%	0.0%	0.0%	0.0%	1.2%	0.0%	8.9%	
Cu Oxide (Cu,O)	Refining	0.0%	29.4%	1.5%	0.0%	11.7%	0.0%	0.0%	2.2%	7.7%	0.0%	
Cu metal (Cu)	Refining	0.0%	0.0%	0.0%	0.0%	10.0%	0.0%	0.0%	11.4%	0.0%	0.0%	
Cu-Sb Oxide (Cu,Sb,O)	Refining	0.0%	0.0%	0.0%	0.0%	0.8%	0.0%	0.0%	0.0%	0.0%	0.0%	
Brass (Cu,Zn)	Domestic/refining	0.0%	0.0%	0.0%	0.0%	19.4%	0.0%	0.0%	0.0%	0.0%	0.0%	
Argentotennantite (Ag,Sb,Cu,S)	Ore/PGM- Residue	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	33.8%	
Ag-Cu Alloy (Ag,Cu)	Ore/PGM- Residue	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.6%	
Nickel		47.5%	35.0%	27.3%	39.9%	17.3%	33.0%	62.6%	41.5%	46.4%	15.9%	
Pentlandite (Ni,Fe,S)	Ore	48.3%	60.3%	67.5%	38.8%	72.7%	69.3%	37.3%	56.0%	81.4%	73.4%	
Co-Pentlandite (Co,Ni,Fe,S)	Ore	3.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Millerite (Ni~S)	Ore	0.0%	0.0%	0.7%	0.5%	0.0%	24.3%	1.5%	9.4%	3.5%	0.0%	
Pyrrhotite (Fe,S>Ni)	Ore	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	2.5%	
Ni-Arsenide (Ni,As,S)	Ore	2.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Ni Oxide (Ni,O)	Refining	0.0%	31.9%	31.5%	1.7%	10.5%	4.9%	40.2%	6.3%	15.0%	6.9%	
Fe/Mn/Ni Oxide (Fe,Mn,Ni,O)	Refining	15.3%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	
Ni-Co Oxide (Ni,Co,O)	Refining	7.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	



Fable 3.21Results of SEM Analyses of Relevant COC in Sudbury Air Filters (SGS, 2005)											
				PM _{2.5} Air Filters							
Speciated COC	Probable Origin	Copper Cliff (June 8 th)	Falconbridge (June 8 th)	Hanmer (June 8 th)	Sudbury (June 8 th)	Windy Lake (June 8 th)	Sudbury (Sept 24 th)	Copper Cliff (June 8 th)	Falconbridge (June 8 th)	Sudbury (June 8 th)	Windy Lake (June 8 th)
Ni Matte (Ni ₃ S ₂)	Matte	17.6%	0.0%	0.0%	27.5%	0.0%	0.0%	1.2%	0.0%	0.0%	0.0%
Ni Sulphate (Ni,S,O)	Refining	5.2%	7.8%	0.3%	31.4%	16.8%	1.5%	3.2%	2.0%	0.0%	10.5%
Ni/Co Sulphate (Ni,Co,S,O)	Refining	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	11.4%	0.0%	0.0%
Ni Slag (Ni< <fe,mg,si)< td=""><td>Matte/Smelting</td><td>0.0%</td><td>0.0%</td><td>0.0%</td><td>0.0%</td><td>0.0%</td><td>0.0%</td><td>0.0%</td><td>14.8%</td><td>0.0%</td><td>0.0%</td></fe,mg,si)<>	Matte/Smelting	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	14.8%	0.0%	0.0%
Stainless Steel (Fe,Cr,Ni)	Miscellaneous	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	16.7%	0.0%	0.0%	6.6%

Note: Bolded and shaded values for the specific COC are the percentage of the total metals represented by that particular COC (*i.e.*, 24.6% of the metals detected in the Copper Cliff PM₁₀ air filter were identified as lead, while the remainder of the rows depict the percentage that the given species represents for that particular COC (*i.e.*, 48.3% of the nickel in the Copper Cliff PM₁₀ was classified as pentlandite).



Speciated	Probable		Fa	lconbrid	lge		Copper Cliff			Coniston						Sudi	oury	Hanmer							
COC	Origin	1	2	3	4	5	1	2	3	4	5	6	7	1	2	3	4	5	1	2	3	4	1	2	3
Lead	-	14.2%	3.3%	5.7%	16.0%	21.6%	3.1%	12.7%	67.1%	3.7%	30.0%	28.9%	44.9%	2.4%	67.3%	50.5%	22.3%	0.9%	49.0%	62.6%	12.8%	26.9%	14.3%	6.7%	19.0%
Anglesite (PbSO ₄)	Smelting/Refining	100.0%	100.0%	100.0%	100.0%	83.8%	100.0%	83.9%	100.0%	100.0%	90.5%	100.0%	100.0%	100.0%	94.8%	70.1%	62.4%	100.0%	100.0%	63.0%	94.9%	93.5%	76.7%	100.0%	100.0%
Pb-Sn	Domestic	0.0%	0.0%	0.0%	0.0%	16.2%	0.0%	0.0%	0.0%	0.0%	9.5%	0.0%	0.0%	0.0%	5.2%	25.0%	37.6%	0.0%	0.0%	37.0%	5.1%	6.5%	23.3%	0.0%	0.0%
Pb-Cl	Smelting/Refining	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Pb/Te/Se	Smelting/Refining	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	16.1%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	4.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Arsenic		12.9%	4.5%	0.0%	1.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	7.7%	0.0%	0.0%	12.6%	0.0%	0.0%	0.0%	1.8%	0.0%	6.0%	0.0%	16.1%	52.8%
Arsenopyrite (FeAsS)	Ore	100.0%	100.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	100.0%	100.0%
As Oxide	Smelter emission	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Copper		21.1%	54.6%	62.2%	32.3%	77.5%	23.7%	25.1%	3.2%	59.8%	42.2%	13.8%	24.4%	52.6%	25.0%	25.9%	20.4%	69.3%	33.1%	27.2%	47.5%	2.4%	19.2%	31.9%	14.8%
Tetrahedrite (Cu-Sb-S)	Ore	0.0%	0.0%	0.0%	2.4%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	47.1%	0.0%	0.0%
Chalcopyrite (Cu-Fe-S)	Ore	67.9%	0.0%	0.0%	47.5%	0.0%	0.0%	0.0%	54.2%	0.0%	0.0%	24.5%	64.5%	1.7%	0.0%	0.0%	0.0%	26.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Cu matte (Cu ₂ S)	Smelter/matte	32.1%	41.5%	59.1%	43.4%	0.0%	1.5%	39.3%	0.0%	56.2%	61.8%	1.8%	6.6%	66.3%	0.0%	0.0%	0.0%	38.3%	43.3%	17.7%	15.4%	100.0%	12.3%	0.0%	0.0%
Cu sulphate (Cu-S-O)	Refining	0.0%	43.5%	40.9%	0.0%	1.8%	98.5%	26.1%	0.0%	24.3%	24.4%	37.6%	15.2%	10.4%	22.0%	40.7%	20.1%	34.9%	35.3%	37.6%	1.1%	0.0%	6.0%	16.5%	4.2%
Cu Oxide (CuO)	Refining	0.0%	9.2%	0.0%	0.0%	44.7%	0.0%	5.7%	45.8%	3.0%	1.7%	36.1%	0.0%	21.5%	78.0%	14.7%	54.0%	0.5%	0.0%	0.0%	1.5%	0.0%	0.0%	22.6%	75.4%
Cu metal (Cu)	Refining	0.0%	0.0%	0.0%	0.0%	53.5%	0.0%	14.6%	0.0%	12.6%	0.0%	0.0%	1.1%	0.0%	0.0%	15.1%	0.0%	0.0%	0.0%	0.0%	64.2%	0.0%	0.0%	1.3%	1.9%
Brass (Cu >Zn)	Domestic/Other	0.0%	5.8%	0.0%	6.8%	0.0%	0.0%	14.3%	0.0%	4.0%	12.1%	0.0%	12.7%	0.0%	0.0%	29.5%	25.8%	0.0%	21.3%	44.7%	17.8%	0.0%	34.6%	59.7%	18.5%
Nickel		51.9%	37.7%	32.1%	50.0%	0.9%	73.2%	62.1%	29.7%	36.5%	27.8%	57.3%	23.0%	45.0%	7.6%	11.0%	57.3%	29.8%	17.9%	8.4%	39.7%	64.6%	66.5%	45.4%	13.4%
Pentlandite (Fe-Ni-Sulphide)	Ore	12.8%	5.3%	67.8%	16.9%	0.0%	0.0%	0.0%	91.2%	0.0%	0.0%	26.5%	11.3%	0.0%	0.0%	4.3%	0.0%	0.0%	0.0%	0.0%	0.0%	71.3%	0.0%	0.0%	0.0%
Millerite (NiS)	Ore	9.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	19.5%	1.9%	12.2%	0.0%	0.0%	0.0%	30.0%	0.0%	0.0%	0.0%	0.0%	0.0%	13.5%	0.0%
Heazlewoodite (Ni ₃ S ₂)	Smelter/matte	26.7%	3.7%	28.2%	11.0%	0.0%	36.0%	35.0%	8.8%	39.3%	0.0%	0.0%	59.1%	48.1%	0.0%	0.0%	0.0%	55.0%	0.0%	23.4%	93.5%	28.7%	0.0%	6.7%	0.0%
Ni Sulphate	Refining	0.0%	45.9%	2.9%	32.9%	0.0%	3.1%	23.8%	0.0%	46.5%	0.0%	27.1%	0.0%	8.0%	53.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.3%	0.0%	0.0%	22.4%	0.0%
Ni Oxide (NiO)	Refining	33.4%	14.1%	0.0%	39.2%	100.0%	24.0%	28.8%	0.0%	12.1%	100.0%	12.0%	10.4%	31.6%	46.4%	0.0%	0.0%	15.0%	100.0%	0.0%	6.2%	0.0%	3.3%	57.3%	66.0%
Ni-Co-Oxide	Refining	0.0%	17.7%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Ni metal	Refining	0.0%	0.0%	0.0%	0.0%	0.0%	36.9%	12.4%	0.0%	2.1%	0.0%	0.0%	7.9%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	43.1%	0.0%	0.0%	77.2%	0.0%	0.0%
Stainless Steel	Miscellaneous	17.5%	13.3%	1.2%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	14.9%	9.3%	0.0%	0.0%	95.7%	100.0%	0.0%	0.0%	33.4%	0.0%	0.0%	19.5%	0.0%	34.0%



3.5.5 Requirement for Supplemental Analyses

Results of the initial SEM analyses indicated that some of the air filters and dust samples likely contained small amounts of nickel subsulphide (Ni_3S_2). It is important to understand that nickel subsulphide differs in toxicity and mode of action from nickel oxide, the form of nickel typically found in the highest quantities within most media sampled in Sudbury (both nickel subsulphide and nickel oxide are considered smelter emission products). In fact, nickel subsulphide is more toxic *via* inhalation than nickel oxide, and raises a number of additional issues which must be addressed in the HHRA.

However, due to the small amounts of material present in the air filters, the small particle size, and limitations of the SEM equipment used in the speciation analyses (*i.e.*, the SEM beam size was too coarse to properly identify the ultra small particles on some of the air filter mounts), there was some question as to whether these nickel species were indeed Ni₃S₂ or a similar looking form (such as millerite, a natural ore form of nickel). Therefore, to confirm the identification of Ni₃S₂ in both the air filter and dust samples, the SARA Group contracted Dr. Frank Ford, a senior research mineralogist for Vale Inco Ltd. and a known expert in nickel smelter emission products, to meet with the mineralogists at SGS and examine their samples under the SEM. Dr. Ford reported that SGS used appropriate techniques and agreed with the identification of Ni₃S₂ in the dust samples. However, due to the small particulate size and equipment limitations, he could not positively identify the species in the air filters as Ni₃S₂ (*i.e.*, there was a 50:50 chance it was something else, such as millerite or a metallic nickel with a sulphate coating). Dr. Ford's report is also provided in Appendix I of this volume.

As a result of this information, additional analyses were undertaken to provide supplemental data on the potential speciation of nickel in both air and dust samples.

3.5.6 Additional SEM Analyses

To address the issues raised in the initial set of speciation work, additional SEM work was conducted by SGS. Based upon the results of these additional SEM analyses, a subsequent additional round of analyses was conducted, in parallel with XAFS analyses on the same samples, to further clarify the speciation fingerprint.



3.5.6.1 Additional SEM Analyses - Round 1

To attempt to confirm the presence of Ni_3S_2 in air samples taken from the Copper Cliff region of Sudbury, two TSP air filters collected on the same date as the previously analysed PM_{10} and $PM_{2.5}$ filters were analyzed by SEM: one from the Copper Cliff station, and the other from the Sudbury Centre West station representing Sudbury Centre. These two were the only stations where the potential presence of Ni_3S_2 in the analyzed PM_{10} filters was indicated. It was hoped that the larger particle sizes available in the TSP filters would better facilitate identification of any Ni_3S_2 present in the samples, as well as better clarify potential sources (*i.e.*, the Copper Cliff facility or the nearby slag piles).

Results of these additional analyses are provided in Table 3.23.

		TSP Air	Filters		
Speciated COC	Probable Origin	Copper Cliff (June 8 th)	Sudbury (June 8 th)		
Lead		3.5%	4.6%		
Anglesite (Pb,S,O)	Emissions	100%	69.6%		
Pb/Sn Alloy (Pb-Sn)	Domestic	-	30.4%		
Copper		43.7%	54.5%		
Chalcopyrite (Cu,Fe,S)	Ore	49.9%	51.0%		
Cu Matte (Cu,S)	Matte	20.8%	49.0%		
Cu Sulphate (Cu,S,O)	Refining	-	-		
Cu Oxide (Cu,O)	Refining	-	-		
Cu metal (Cu)	Refining	-	-		
Brass (Cu,Zn)	Domestic/refining	-	-		
Nickel		52.7%	34.9%		
Pentlandite (Ni,Fe,S)	Ore	59.8%	56.7%		
Millerite (Ni~S)	Ore	9.1%	25.8%		
Ni Subsulphide (Ni ₃ S ₂)	Matte	4.0%	-		
Ni Sulphate (Ni,S,O)	Refining	2.3%	8.9%		
Ni Oxide (Ni,O)	Refining	24.9%	8.6%		

Table 3.23Results of Additional SEM Analyses of Relevant COC in Sudbury Air Filters
(SGS, 2005)

Note: Bolded and shaded values for the specific COC are the percentage of the total metals represented by that particular COC (*i.e.*, 1.5% of the metals detected in the Falconbridge dust samples were arsenic, while the remainder of the rows depict the percentage of that particular COC which was extracted at each leaching step (*i.e.*, 54.1% of the nickel in Falconbridge dust samples leached out in the organic step. -" indicates that particulate COC was not detected in any of the samples for that COI.

^a Trace amounts of zinc ore (approximately 5.4% of total minerals) were also found in the Sudbury Center West TSP air filter, which was not included in this table, as it was not one of the assessed COC.



Results of the follow-up analyses of the TSP filters for both the Copper Cliff and Sudbury Centre West stations indicated a similar speciation breakdown as that observed for the PM_{10} (4.0%) filters. However, only the TSP air filter from the Copper Cliff monitoring station captured any Ni_3S_2 . No Ni_3S_2 was detected at the Sudbury Centre West station representing the Sudbury Centre COI.

3.5.6.2 Additional SEM Analyses - Round 2

One of the primary issues arising from the previous round of analytical work was whether wind direction played a role in the "fingerprint" of the nickel species present in air filters surrounding the Sudbury Centre West monitoring station. To address that, five new PM_{10} filters from the Sudbury Centre West monitoring station were submitted to SGS for further SEM speciation analyses. These samples were taken at different times of the year, and corresponded to differing wind directions: January 4th – wind blowing from north; March 10th – from south-southwest; July 2nd – from north and east; September 30th – from south-southwest; and, November 29th – from west and north. In addition to these air filter analyses, two indoor dust samples previously identified as containing nickel subsulphide by SGS were reanalyzed by SGS using a polished section investigation (as recommended in the previous task force meetings).

Table 3.24 provides the results of this second round of SEM analyses, focusing specifically on the forms of nickel identified within the air filter (see Appendix I for the full analytical report).



West S	tation Air Filters	(SGS, 200)6)			
Nickel Species	Particles (N)	Area (μm²)	Area %	Relative Mass %	Contained % Ni	Normalized Ni ratios (%)
November 29, 2003 (wind	from west and north)				
Pentlandite	18	339	62.0	53.2	34.2	35.7
Ni-Subsulphide	2	44	8.0	8.0	73.3	11.5
Ni-Oxide	7	164	30.0	34.3	78.6	52.9
Ni-Sulphate	-	0	0.0	0.0	22.3	0.0
January 4, 2004 (wind fr	om the north)					
Pentlandite	-	0	0.0	0.0	34.2	0.0
Ni-Subsulphide	-	0	0.0	0.0	73.3	0.0
Ni-Oxide	-	0	0.0	0.0	78.6	0.0
Ni-Sulphate	30	178	100.0	35.4	22.3	100.0
March 10, 2004 (wind fro	om the south-southwe	st)				
Pentlandite	5	284	59.0	50.7	34.2	60.3
Ni-Subsulphide	3	15	3.1	3.1	73.3	7.9
Ni-Oxide	7	36	7.5	8.6	78.6	23.4
Ni-Sulphate	13	146	30.4	10.7	22.3	8.3
July 2, 2004 (wind from the	he north and east)					
Pentlandite	11	122	48.0	41.3	34.2	61.2
Ni-Subsulphide	-	0	0.0	0.0	73.3	0.0
Ni-Oxide	4	15	5.9	6.8	78.6	23.1
Ni-Sulphate	13	117	46.1	16.3	22.3	15.8
September 30, 2004 (wind	l from south-southwe	st)				
Pentlandite	2	8	0.9	0.8	34.2	0.3
Ni-Subsulphide	14	118.38	13.2	13.1	73.3	11.0
Ni-Oxide	5	770	85.9	98.4	78.6	88.7
Ni-Sulphate	-	0	0.0	0.0	22.3	0.0

Table 3.24Results of Additional SEM Analyses of Nickel Species at Sudbury Centre
West Station Air Filters (SGS, 2006)

The results in the normalized nickel ratios confirm previous analytical results, showing that nickel oxide and pentlandite (*i.e.*, iron nickel sulphide – an important nickel ore) are the two predominant species of nickel found in these air filters, regardless of wind direction. However, the presence of nickel subsulphide was only noted in three of the five air filters. In fact, nickel subsulphide was only identified in those filters taken on days when the wind blew from a western direction across the Vale Inco Copper Cliff facility to the Sudbury Centre West monitoring station. When the wind blew from an easterly direction, no nickel subsulphide was detected. Results of this analytical work also indicated that, where nickel subsulphide was identified as being present, it only made up between 7.9 and 11.5% of the total nickel species present in the filters.



Results of the subsequent SEM analyses of the two residential dust samples by polished section confirmed the previous identification of nickel subsulphide in the two dust samples (see Table 3.25 below). As with the air filter samples, the predominant nickel species identified in the dust samples were nickel oxide and pentlandite, with the ratios of each Ni species fairly consistent between the two dust samples taken from completely different regions of the GSA. Of particular note, nickel subsulphide made up between 1.6 and 1.8% of the total nickel species present within these samples.

	ilts of Additional S t Samples (SGS, 20		yses of Nicl	kel Species	in Two Res	sidential
Nickel Species	Particles (N)	Area (μm²)	Area %	Relative Mass %	Contained % Ni	Normalized Ni ratios (%)
Sudbury Centre Reside	ntial Dust Sample					
Pentlandite	8	392.2	23.3	24.8	34.2	14.4
Ni-Subsulphide	1	19.4	1.2	1.5	73.3	1.8
Ni-Oxide	4	697.7	41.4	58.8	78.6	78.2
Ni-Sulphate	4	573.4	34.1	14.9	22.3	5.6
Copper Cliff Residentia	al Dust Sample					
Pentlandite	8	768	50.1	43.0	34.2	24.8
Ni-Subsulphide	1	20.3	1.3	1.3	73.3	1.6
Ni-Oxide	5	743.9	48.6	55.7	78.6	73.6
Ni-Sulphate	0	0	0.0	0.0	22.3	0.0

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3.5.7 **Analyses using XAFS Techniques**

The second set of analyses involved contracting Dr. Jeffrey Cutler of Canadian Light Source (CLS) Laboratories in Saskatoon to conduct X-Ray absorption fluorescence spectroscopy (XAFS) speciation analyses using their synchrotron light beam to determine all phases of nickel (including Ni₃S₂) present in select air filter samples. This technique is able to evaluate the K shell absorption spectrum of the sample to determine the various species of both nickel and sulphur present. Ouantification and description of the differences observed at these absorption edges allows the characterization of chemical species in the environmental sample, specifically the form of nickel compound present. Further information on XAFS speciation techniques are provided in the methodological overview document included in Appendix I of this volume.

Parallel to the analyses conducted by CLS, the MOE requested a number of air filters corresponding to days of high particulate and nickel concentration from various monitoring locations (different from those submitted to CLS) and contracted Dr. Marc Lamoureux of EnviroAnalytix Services to conduct XAFS analyses on these samples.



A total of six samples were submitted to CLS for further evaluation of nickel speciation by XAFS techniques:

- Splits of the PM₁₀ filters that previously indicated possible Ni₃S₂ from the Copper Cliff and Sudbury Centre West stations (two separate samples);
- Splits of the TSP filters for the Copper Cliff and Sudbury Centre West stations analyzed by SGS as part of the follow-up SEM analysis (two separate samples);
- A dust sample from a home in Copper Cliff which indicated the presence of Ni₃S₂, to allow for potential comparisons between air and dust speciation patterns (one sample); and,
- An air filter taken as part of routine monitoring by the MOE in Toronto, Ontario, to demonstrate typical nickel species present in an urban area without a smelting/refining point source.

Results of this analyses (see Appendix I for the complete report) indicated the following:

- The majority of the sulphur present in the air filters is in sulphate form;
- Only the TSP and PM₁₀ filters from the Sudbury Centre West station showed the presence of sulphide. The Copper Cliff station did not show any sulphide present;
- Analyses of the sulphide present in the Sudbury Centre West station samples (11 to 16% of total) indicates it more closely resembles nickel sulphide than nickel subsulphide; and,
- No nickel subsulphide was present in the dust sample analyzed.

Furthermore, the results of the MOE-sponsored XANES analyses by Dr. Lamoureaux mirrored the results of the CLS analyses, indicating the absence of nickel subsulphide in any of the analysed air filters, and showing a similar pattern of nickel species as observed in the CLS XANES analyses (see Appendix I for Dr. Lamoureux's report).

3.5.7.1 Additional XAFS Analyses - Round 2

As noted previously, one of the primary issues arising from the previous round of analytical work was whether wind direction played a role in the "fingerprint" of the nickel species present in air filters surrounding the Sudbury Centre West monitoring station. As with the second round of SEM analyses, the same five PM_{10} filters from the Sudbury Centre West monitoring station were submitted to CLS for



further XAFS analyses. In addition to these air filters, six indoor dust samples, previously identified as containing nickel subsulphide by SGS, were submitted to CLS for XAFS analyses.

The nickel K-edge XANES spectra for both the air filter and dust samples are provided in Table 3.26 based upon the best linear combination fit.

Dust Sample	s (CLS, 2006)					
Analyzed Sample		Linear Combina	tion Fits (weight %)			
Analyzeu Sample	Ni-Oxide	Ni-Sulfide	Ni-Subsulphide	Ni-Sulphate		
Air Filter Samples		-				
November 29, 2003 (wind from west and north)	41	27	0	32		
January 4, 2004 (wind from the north)	100	0	0	0		
March 10, 2004 (wind from the south-southwest)	50	0	0	50		
July 2, 2004 (wind from the north and east)	87	0	0	13		
September 30, 2004 (wind from south-southwest)	93	0	0	7		
Residential Dust Samples						
Falconbridge Residence	35	35	0	29		
Falconbridge Residence	22	54	0	24		
Sudbury Centre Residence	23	0	0	27		
Hanmer Residence	68	32	0	0		
Copper Cliff Residence	25	40	0	35		
Copper Cliff Residence	40	0	0	60		

Table 3.26Results of XAFS Analyses of Nickel Species in Air Filter and Residential
Dust Samples (CLS, 2006)

As noted in Table 3.26, nickel subsulphide was not detected in any of the air filter or residential dust samples. Following an additional speciation Task Force meeting to discuss these results, further clarification was obtained from CLS as to the potential method detection limit for nickel subsulphide using this approach. In response, Jeff Warner of CLS made the following statement:

"In the first report to Cantox [dated: November 23, 2005] we looked at mixtures of NiS and NiSO₄ [Table 4, Figures 6 and 8]. Figure 8 in that report puts the detection limit in that matrix at 7%. This agrees well with most of our work of this type which generally puts the analysis detection limit between 5 to 10%. We have achieved, in cases where we have good supplementary information on the samples, accuracies of ~3%."

Additional discussions of these issues are provided in Appendix I of this report.



3.5.8 Additional Speciation Work

In conjunction with a second round of bioaccessibility analyses, five outdoor soil samples and nine indoor dust samples were submitted for Electron Microprobe Analysis (EMPA) at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder (LEGS, 2007). This analyses was conducted using an electron microprobe (*i.e.*, JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and the Geller, dQuant data processing system. It is important to note, that due to limitations on available quantities of materials, these were not the same soil and dust samples that were tested in previous rounds of speciation analyses.

This round of speciation analysis focused primarily on arsenic, lead and nickel elements present within the soil or dust samples, and provided a detailed percentage breakdown of the specific species in relation to the overall mass of COC. Table 3.27 and 3.28 provide a composition breakdown by COC form on the five outdoor soil samples and nine indoor dust samples, respectively.

Results of the EMPA speciation appear to indicate a similar pattern as that observed in the previous rounds of speciation analyses. However, one set of observations in the current analyses does provide potential information for future risk management decision making. As noted previously, the primary form of lead identified by SGS Lakefield was in the form of anglesite (*i.e.*, lead sulphate), which is known to be an emission from smelting/refining sources. However, SGS did indicate that a major proportion of lead present in their limited number of samples could not be accounted for mineralogically, and pointed to other potential forms such as lead carbonate (refer to their detailed report in Appendix I). SGS suggested that more sophisticated techniques or methods could be applied to attempt to better isolate the forms present. However, as this was not a requirement of the risk assessment, it was not undertaken at that time.

However, results of the EMPA speciation work indicated that a significant percentage of the lead present in some of the dust samples analyses was in the form of cerussite (*i.e.*, lead carbonate). This form of lead was detected in most of the dust samples analysed (but none of the soil samples), and typically ranged between approximately 20 and 85% of the total lead present in the sample. This is of some risk management significance because cerussite, or "white lead", is a key ingredient in lead-based paints.



Table 3.27	-	cies Pe GS, 20		age Re	sults f	rom E	MPA	Specia	ation o	f Resi	dentia	l Outd	oor So	oil San	nples		
Form		Soil 1			Soil 2			Soil 3			Soil 4		Soil 5				
	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni		
Anglesite																	
Cerussite																	
Chalcopyrite				0	0	0.25				0	0	0.14					
CrMO																	
Cr-Ni metal	0	0	2.86														
CuMO					c		0										
FeCr metal			-		•	•	9			6	-	¢					
FeOOH	89.47	63.49	3.01	90.83	90.43	5.45	95.04	62.91	4.49	97.43	88.37	6.06	87.31	2.47	4.34		
FeS ₂	0	0.36	0.2	0	0.99	0.68	0	2.29	1.85	0	1.7	1.32	0	0.01	0.12		
FeSiO ₂	8.28	29.6	4.27	0.72	3.6	0.66	2.67	8.91	1.94	0.22	1.01	0.21	8.49	1.21	6.48		
FeSO ₄							0	0.51	0.43	0	2.51	2.01					
MnOOH	0.55	5.64	0.53	0.19	2.68	0.32	Ö			•				-			
Native Lead							0	24.97	0								
Ni metal													0	0	5.93		
NiFeO	0.9	0.23	4.22	5.62	2.02	47.16	1.59	0.38	10.47	1	1	[4.08	0.04	28.37		
NiMCISO ₄		-						¢									
NiMO	0.8	0.04	1.8	2.64	0.18	10.53	0.7	0.03	0	1.87	0.12	7.74	0.12	0	0.39		
NiMS		-													-8		
NiMSO ₄															-		
NiO	0	0	76.38	0	0	9.43				0	0	3.08	0	0	49.32		
NiP	-																
NiS															-		
NiSO ₄	Ì			0	0.1	3.7			Ì	0	0.01	0.24			1		
Paint		-									-				.5		
PbCrO ₄	1			<u> </u>	<u> </u>					İ	1	İ			1		
PbMO		-															
PbMSO ₄																	
PbTiO ₂	İ								<u> </u>	İ		İ			Ì		
PbO																	
PbSiO ₄										1			0	96.27	0		
Pentlandite	0	0	5.08	0	0	21.83	0	0	80.82	0	0	79.19	0	0	5.04		
Phosphate							c			0.48	6.29	0.01					
Plumbobarite	Ī										-				1		
Slag	0	0.63	1.66														
ZnMO														<u> </u>			

Table 3.2	8	Speci	ies Pe	ercen	tage	Resu	ılts fr	om H	EMP	A Spe	eciati	on of	f Resi	ident	ial Ir	ndoor	· Dus	t San	nples	(LE	GS, 2	2007)					
Form		Dust 1			Dust 2			Dust 3	6		Dust 4	ļ		Dust 5			Dust 6	í		Dust 7	'		Dust 8			Dust 9	,
	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni	As	Pb	Ni
Anglesite	0	59.78	0																								
Cerussite	0	21.32	0	0	56.14	0				0	74.32	0	0	85.72	0	0	67.4	0	0	71.3	0	0	68.08	0			
Chalcopyrite																						0	0	0.02	0	0	0.01
CrMO																						0	0.63	2.06			
Cr-Ni metal	0	0	12.56																								
CuMO							0	0	6.81				0	0	7.36	0	0	1.97	0	0	1.2				0	0	0.71
FeCr metal																0	0.01	0.34	0	0.06	0.46	-	-				
FeOOH	41.3	11.53	5.2	4.47	1.15	2.25	6.19	6.13	2.54	64.07	16.94	3.67	17.47	4.33	2.88	71.62	0.55	0.59	13.01	6.36	0.83	91.98	17.15	0.93	95.23	7.02	3.75
FeS ₂	0	0.07	0.38	0	0.1	2.14	0	0.25	1.18	0	0.1	0.25	0	0.16	1.24	0	0.15	1.86	0	0.63	0.93	0	1.86	1.15	0	0.52	3.18
FeSiO ₂				0.58	0.75	4.46	0.02	0.09	0.12	0.43	0.57	0.38	0.48	0.6	1.21	1.99	0.08	0.25	0.54	1.33	0.53	2.38	2.23	0.37	2.07	0.77	1.25
FeSO ₄	0	0.05	0.28				0	0.08	0.37	0	0.3	0.77	0	0.2	1.53	0	0.01	0.12	0	0.05	0.07	0	0.33	0.21	0	0.21	1.29
MnOOH																											
Native Lead											¢																
Ni metal	0	0	6.21	0	0	5.97	0	0	10.89							0	0	8.61	0	0	7.99	0	0	56.11	0	0	18.78
NiFeO							0.03	0.01	1.96	0.62	0.06	4.96				11.18	0.03	12.79	0.35	0.06	3.13	2.05	0.14	2.91	1.55	0.04	8.52
NiMCISO ₄							-				¢					9.41	0.04	2.53						6			
NiMO	1.35	0.03	11.3		F		0.68	0.05	18.63	<u>.</u>			0.89	0.02	9.72	5.8	0	3.16	0.22	0.01	0.94	2.5	0.03	1.69	1.15	0.01	3
NiMS					[1						0.7	1.63	2.93		ĺ				
NiMSO ₄		1			Î	<u> </u>		1	İ		ĺ	İ		İ		İ		ĺ			Ì	1.1	0.12	0.37	ĺ		
NiO	0	0	4.77	0	0	25.77	0	0	30.48	0	0	11.64	0	0	10.6	0	0	33.06	0	0	25.68	0	0	15.18	0	0	29.48
NiP	0	0	10.27	0	0	7.52		ĺ	1	1	1	1	1			1					ĺ		1	1	Í		
NiS	0	0	13.76	0	0	33.04	0	0	16.51	0	0	68.3	0	0	17.47	0	0	11.92	0	0	40.75	0	0	3.98	0	0	7.42
NiSO ₄	0	0.08	21.45	0	0	1.23		1	-																		
Paint				0	0.88	0	-						0	3			-}				¢		5		0		
PbCrO ₄				0	26.86	0	-														¢						
РЬМО	57.35	7.14	0	94.31	10.86	0	92.17	40.73	0	34.14	4.03	0	81.16	8.98	0				85.19	18.58	0						
PbMSO ₄				0.65	1.4	0																					
PbTiO ₂				0	1.85	0	-														¢			e			
PbO										7						0	31.31	0							0	78.15	0
PbSiO ₄							0	39.75	0														5		0	12.06	0
Pentlandite	0	0	13.82	0	0	17.63	0	0	10.41	0	0	10.03	0	0	47.99	0	0	22.08	0	0	14.58	0	0	15	0	0	22.55
Phosphate					ā		0.91	12.92	0.12	0.74	2.82	0.01					ē		0	0	0						
Plumbobarite										0	0.86	0	-			0	0.41	0				0	9.42	0	-		
Slag								- 								0	0.01	0.72			è				0	0	0.03
ZnMO					Ī		1		1	3		1				İ		Ī					7	·	0	1.21	0.01



3.5.9 Discussions and Conclusions

Results of the speciation analyses conducted on the soil, air filter, and dust samples taken throughout the GSA indicate emissions from smelting and refining sources have impacted each of the sample media.

The following are some key discussion points arising out of the speciation exercises:

- The speciation fingerprint noted in the Tessier leach analyses indicated similar species were present in each of the COI throughout the GSA. In particular, the arsenic species found were similar across the GSA, including those found in Falconbridge;
- Nickel and copper were the two predominant COC detected in most of the samples;
- Oxidic nickel appears to be ubiquitous throughout each of the COI, in each of the sample media, and in soil and dust samples, in particular;
- Obvious lead paint flakes were not observed by SEM analyses in any of the media, including dust samples taken from residences throughout the GSA;
- A form of lead carbonate called "cerussite" was detected by EMPA speciation in a number of indoor residential dust samples analysed, but no soil samples. Cerussite, or "white lead", is known to be a key ingredient in lead-based paints;
- The highest particulate matter and COC concentrations were detected at the Sudbury Centre West monitoring location, likely resulting from not only emissions from the Vale Inco Copper Cliff facility, but fugitive dusts blowing off of the Copper Cliff facility property;
- The species present in dust samples appear to be similar to those observed in air filters, indicating that the metals present within the dust likely originated from airborne emission sources, rather than being tracked in from outdoor soil sources;
- Much of the species present in the air filters appears to be coated by an organic carbonaceous layer. This protects the metal species within, as indicated in the results of Tessier leach analyses, where a significant fraction leaches out in the organic leach step;
- Nickel subsulphide (Ni₃S₂) was detected in a number of indoor dust samples taken throughout the GSA. Follow-up analyses indicated that it appears to be limited to less than 2% of the total nickel species present within a given dust sample; and

2



Nickel subsulphide was detected in a small number of air filters taken from the Sudbury Centre West monitoring station, but only on those days when the wind was blowing eastward across the Vale Inco Copper Cliff facilities. Based upon the results of the follow-up SEM and XAFS analyses, it would appear that a reasonable upper-bound estimate for the amount of nickel subsulphide present would be approximately 10% of the total nickel species in airborne particulate, under these conditions.

Air quality around the Sudbury Centre West monitoring station, and to a lesser extent the Copper Cliff monitoring station, appear to be strongly influenced by fugitive dusts arising from the Vale Inco Copper Cliff facility. When the wind is blowing across the facility, one particular nickel species "fingerprint" is evident, including the limited presence of nickel subsulphide. However, when the wind is blowing from the opposite direction (*i.e.*, not across the facility property), a different nickel species "fingerprint" is present, absent of any nickel subsulphide.

Based upon the results of the follow-up SEM and XAFS analyses, the following conservative estimates of these two specific nickel species "fingerprints" were established for use in the current assessment:

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Table 3.29 Summary of Proposed Nickel Species Fingerprints									
Nickel Species	Typical Ambient Fingerprint	Copper Cliff Facility Impacted Fingerprint							
Nickel Oxide	80%	75%							
Nickel Sulphide	10%	10%							
Nickel Subsulphide	0%	10%							
Nickel Sulphate	10%	5%							

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These conservatively estimated fingerprints were coupled with annual wind direction data collected from the GSA to evaluate the overall exposures to airborne nickel particulate throughout the Sudbury area. However, it is important to note that these hypothetical ambient air quality "fingerprints" are based upon only one year of ambient air monitoring data and a very small number of speciated air samples, and as such should be interpreted with caution.



3.6 Evaluation of Indoor Dust Level

One of the most important pathways to consider for the current HHRA is potential exposures to the COC in indoor dust within Sudbury homes. The Vale Inco and Xstrata Nickel smelters release atmospheric emissions containing chemicals and particulate matter, including the COC. Gradually, wet and dry deposition causes the COC to settle onto local soils and other surfaces. Both the settled material and the airborne chemicals may be transferred into residential homes *via* human and local meteorological activity.

Outdoor yard soil can be transported indoors on clothing or shoes of humans or by animals, and combines with other sources to form household dust (U.S. EPA Region VIII, 2001). Studies have reported that between 20 and 30% of indoor contamination comes from outdoor soil sources (Rutz *et al.*, 1997). Exposure to concentrations of COC present in indoor environments is an important pathway of exposure for human health, especially for children.

During the problem formulation phase of the HHRA, it was recognized that there was no information on the concentrations of the COC in indoor dust in Sudbury. Therefore, an indoor dust survey was developed to fill this significant data gap. The primary objectives of this survey were as follows:

- Measure concentrations of COC in indoor dust in the Greater Sudbury area (GSA);
- Measure concentrations of the COC in co-located outdoor soil samples to identify a relationship (if any) between indoor dust and outdoor soil concentrations;
- Compare the data collected in Sudbury with other information and relationships reported in the literature;
- If a relationship exists between COC concentrations in outdoor soil and indoor dust, use this relationship to predict indoor dust levels in indoor living spaces over the range of COC levels reported in the 2001 soil survey; and
- Generate data that can be utilized to estimate human exposure to COC in indoor environments in the HHRA.

Homes and schools from five regions throughout the GSA were selected for sampling. The five areas represent the primary Communities of Interest (COI) identified for the HHRA. A total of 91 homes participated in the survey, including: Copper Cliff (20); Coniston (20); Falconbridge (21); Sudbury Centre (19); and, Hanmer (11). Analyses of 86 indoor dust samples were completed, as five of samples were not able to be analysed. Soil samples from 86 of these residential properties sampled for indoor dust



were also evaluated in the current assessment. All dust and soil samples were analysed for a total of twenty elements. However, the study focused on the indoor dust and outdoor soil concentrations of the six COC being evaluated as part of the HHRA (*i.e.*, arsenic, cobalt, copper, lead, nickel and selenium).

Dust was collected using a high volume surface vacuum sampler (*i.e.*, an HVS3) by vacuuming a composite of at least three 1 metre² carpeted areas in each home. Sample areas were selected from high-traffic locations and areas most frequented by children (*e.g.*, floor areas in front of the main television, in a child's bedroom, in a playroom or family recreation room). Each sample area was measured using meter sticks and marked on the carpet/rug with tape. Concurrent surface soil samples (*i.e.*, a composite grid in the front yard) were also collected at each house to assist in evaluating the potential relationship between indoor dust and outdoor soils.

Tables 3.30 and 3.31 provide summaries of mean indoor dust and outdoor soil concentrations, respectively, from each community.

Community			INDOOR	R DUST (μg/	(g)	
	Arsenic	Cobalt	Copper	Lead	Nickel	Selenium
Coniston $(n = 19)$	19.65	32.16	916.21	202.31	768.47	2.57
Copper Cliff $(n = 19)$	27.32	70.10	1307.90	379.24	1543.68	10.52
Falconbridge $(n = 21)$	32.06	101.12	624.19	132.38	781.57	2.28
Hanmer $(n = 10)$	15.56	17.86	374.90	94.20	297.40	1.76
Sudbury Centre ($n = 17$)	14.80	29.68	662.29	107.66	428.00	4.08
Total Residential Dataset $(n = 86)$	22.94	55.23	818.30	193.04	820.86	4.46

Using $\frac{1}{2}$ minimum detection limit for all non-detect samples (< 0.8 μ g/g).

Table 3.31Summary of Mean Outdoor Yard Soil Concentrations by Community of
Interest

Community	YARD SOIL (µg/g)							
Community	Arsenic	Cobalt	Copper	Lead	Nickel	Selenium ^a		
Coniston $(n = 19)$	7.26	11.56	166.63	37.82	212.88	0.69		
Copper Cliff ($n = 18$)	15.36	28.99	1,047.83	88.09	610.39	5.76		
Falconbridge $(n = 21)$	100.05	61.20	1,065.23	93.26	1,130.29	3.36		
Hanmer (n = 11)	3.06	4.24	31.52	10.61	38.32	0.4 ^b		
Sudbury Centre $(n = 17)$	6.54	8.98	141.54	27.20	121.09	1.05		
Total Residential Dataset $(n = 86)$	30.93	25.89	548.25	56.30	479.62	2.44		

^a Using ½ minimum detection limit (MDL) for all non-detect samples (< 0.8 μg/g).
 ^b All samples were < MDL.



Results of the residential survey indicated that the concentrations of the COC in dust and soil differed between the five COI, which is consistent with the 2001 Soil Study. For example, arsenic levels in soil and dust tended to be higher in the Town of Falconbridge relative to the other communities examined. In dust, the levels of Cu, Pb and Ni were higher in Copper Cliff compared with the other communities. In all cases, COC concentrations were lowest in soil and dust samples obtained from Hanmer. This finding was expected considering that Hamner is located furthest from point source (*i.e.*, smelter) emissions of the COC. Furthermore, air dispersion modeling demonstrated little deposition in the Hanmer area.

Lead concentration trends in dust do not appear as consistent as those for the other COC, suggesting that an alternate source of lead may be present in some homes. Based on conservative screening criteria used in the study, several homes in the GSA exceed the U.S. EPA (U.S. EPA Region VIII, 2001) regulatory standard of 40 μ g lead/ft² of floor (including carpet), and were referred to the Sudbury & District Health Unit (SDHU). Following a review of the study data, the SDHU and Medical Officer of Health concluded that there was a very low, if any, potential for health risk expected from the lead levels detected in homes across the GSA. As such, preliminary analyses of these data indicated no cause for immediate concern for any of the COC, and the data underwent further analyses as part of the HHRA.

Indoor dust was also collected from eight elementary schools in the Rainbow District School Board, across the GSA: five in the core of the City of Greater Sudbury; one in Hanmer; one in Copper Cliff; and, one in Garson, which is attended by children living in Falconbridge.

Table 3.32 Concentrations of Metals in Indoor Dust from Elementary Schools						ools
Parameter	Arsenic (µg/g)	Cobalt (µg/g)	Copper (µg/g)	Lead (µg/g)	Nickel (µg/g)	Selenium (µg/g)
ALL SCHOOLS (n=	-8)					
Min	6.6	13.6	119.0	54.0	138.0	1.6
Max	17.4	45.1	600.0	100.0	700.0	8.4
Mean	10.9	28.8	391.1	78.3	464.7	4.8
Standard Deviation	3.9	9.4	171.6	17.6	198.7	2.4

Preliminary analyses of these data indicated no cause for immediate concern on the part of members of the Study Technical Committee, including the SDHU.

Concentration ratio (CR) values can be defined as the concentration of a specific metal observed in indoor dust (μ g/g) divided by the concentration observed in co-located yard soil. CR values were calculated for each site, the results of which have been summarized in Table 3.33.



Table 3.33	Summary Statistics of Residential Concentration Ratio (CR) ^a Values									
Variable	Mean	Std Dev	Std. Error	Ν	Minimum	Maximum	Median	Skewness		
Arsenic	2.89	3.31	0.370	80	0.055	17.33	1.61	2.29		
Cobalt	3.27	2.50	0.279	80	0.318	10.61	2.56	1.30		
Copper	0.28	0.27	0.030	80	0.021	1.18	0.186	1.43		
Lead	5.95	6.40	0.713	80	0.326	42.76	4.68	3.10		
Nickel	4.26	5.60	0.626	80	1.50	32.41	2.22	3.18		
^a CR value define	ed as [indoor dust	µg/g] / [yard	d soil μg/g]					•		

With the exception of copper, all median CR values (n=80) were greater than 1.0. This indicates that indoor dust COC levels were 2.8 to 5.9 times higher than corresponding soil levels. However, these data also indicate that the CR values do not remain constant over a large range of yard soil concentrations. For example, as the concentrations of COC in outdoor yard soil increase, CR values decrease, suggesting that indoor dust concentrations do not simply increase (in a linear fashion) with increasing soil COC concentrations.

Linear regression equations (based on the naturally log transformed data) were developed for each COC, describing indoor dust concentrations as a function of co-located outdoor yard soil concentrations. Table 3.34 provides the linear regression equations (*i.e.*, *ln*-transformed) which provided the best-fit based upon the paired outdoor soil and indoor dust concentration sets obtained from this study. Visual examination of the residuals indicated that linear regressions using the raw data resulted in a violation of at least one of the classical assumptions; as a result, data were transformed using the natural logarithm. Refer to Appendix M for a detailed discussion regarding the rationale used to transform these data, as well as summary statistics (*e.g.*, minimums, maximums, *etc.*) representing the dataset.

СОС	Equation (ln[indoor dust] = B ₀ ±SE × ln[soil] + C±SE)	R ²	P model fit	Ν
Arsenic	$\ln[\text{indoor dust}] = 0.22 \pm 0.06 \times \ln[\text{soil}] + 2.27 \pm 0.15$	0.148	0.0004	79
Cobalt	$\ln[\text{indoor dust}] = 0.57 \pm 0.07 \times \ln[\text{soil}] + 2.09 \pm 0.21$	0.441	< 0.0001	81
Copper	$\ln[\text{indoor dust}] = 0.21 \pm 0.05 \times \ln[\text{soil}] + 5.22 \pm 0.26$	0.203	< 0.0001	81
Lead	$\ln[\text{indoor dust}] = 0.26 \pm 0.06 \times \ln[\text{soil}] + 3.82 \pm 0.23$	0.182	< 0.0001	80
Nickel	$\ln[\text{indoor dust}] = 0.36 \pm 0.06 \times \ln[\text{soil}] + 4.32 \pm 0.33$	0.317	< 0.0001	82

Table 3.34 Summary of Best Fit Linear Regression Equations for Each COC



It is important to note that the slope of the best fit linear regression line and the mean CR value for any COC are not equivalent. The slope of the regression line was determined by the method of least squares and represents the rate of change (over a specific concentration range) in the indoor dust level as a function of yard soil concentration, while CR values are defined as the concentration of metal in indoor dust (μ g/g) divided by the concentration observed in co-located yard soil (μ g/g). The R² value represents the proportion of variance observed in indoor dust levels that could be explained by co-located yard soil concentrations, the P model fit represents the significance level of the relationship (a p-value <0.05 was considered statically significant) and N represents the number of sample included in each analysis.

Statistically, outdoor soil could not account for a large percentage of the variance observed in indoor dust concentrations. The regression models presented in Table 3.34 were able to explain approximately 15 to 44% of the variation observed in indoor dust concentrations. Levels of cobalt and nickel in yard soils explained approximately 32 and 44% of the variance observed in indoor dust levels, respectively. The variation observed in arsenic, copper and lead dust levels were explained by co-located outdoor soil levels to a lesser extent. That said, all regression equations were statistically significant and considered appropriate for the development of Sudbury-specific dust-to-soil relationships. It is noted that although these regression models are linear in fashion, they are based on ln-transformed data and, therefore, when plotted on a non-log scale (as provided in Figure 4-1 of Appendix M), the relationship become non-linear. Only linear functions were explored in the current assessment.

Additional analyses were conducted to evaluate whether the age of the residence had any impact on indoor dust levels. While significant correlations between the two were observed for lead and cobalt, these correlations were very weak with R^2 values of 0.18 and 0.44, respectively (see Table 3.34). The multiple regression analysis for lead and cobalt (*i.e.*, the addition of a second explanatory variable, house age) did not explain any additional variance in the dependent variable (*i.e.*, the indoor house dust concentration). In both cases, the age coefficient was not significantly different from zero and was removed from the model during the backward elimination process. Based on this preliminary examination, age was not considered a significant explanatory variable.

Based upon the results of the indoor dust survey, statistically significant regression equations were used to characterize Sudbury-specific indoor dust-to-outdoor soil relationships for each of the COC. Although the R^2 values for a number of COC were poor, it was decided that the use of linear regression models were more appropriate than using concentration ratio (CR) values. As illustrated in Appendix M, CR values do not remain constant over a large range of yard soil concentrations and, therefore, at higher COC



concentrations in soil, CR values tend to grossly over-estimate corresponding indoor dust levels relative to those predicted using the linear regression models. Further information on this process can be found in the indoor dust survey report in Appendix M.

3.7 Levels of COC in Locally Grown Produce

To address a key identified data gap in the HHRA, a vegetable garden survey was conducted by the SARA Group from May to October, 2003. The purpose of the vegetable garden survey was to obtain sitespecific data on the range of concentrations of metals found in fruit and vegetables that comprise a portion of the dietary intake of the residents in the Greater Sudbury Area. The results of the survey provided data that was specific to the Sudbury community and was used as part of the exposure assessment component of the HHRA.

Produce samples and co-located soil samples were collected from gardens in private residences as well as from commercial grow operations. A total of 89 sites were sampled, which included: 64 residential properties; 15 commercial properties; and, 10 natural sites. The sampling locations were chosen to reflect a variety of soil metal concentrations, site types and soil types.

Soil samples were collected at all sites at depths of 0 to 15 cm and 15 to 30 cm. The soil samples were submitted for physical and chemical analysis. The following summary table shows the range of concentrations of the COC and the pH in the 0 to 15 cm soil layer. These values are presented with the Ministry of the Environment (MOE) Table A screening criterion levels for comparative purposes.

Table 5.55	weight	entrations (of COC in	garden som s	amples (0-	-15 cm) μg/	g ary
	A Soil Screening	Arsenic	Cobalt	Copper	Nickel	Lead	Selenium
Cr	iteria ^a	20	40	225	150	200	10
Residential $(n = 70)^{b}$	pH = 5.1 to 7.9	<dl -="" 173<="" td=""><td>4 to 56</td><td>21 to 1,170</td><td>31 to 1,100</td><td>5.9 to 520</td><td><dl -="" 11<="" td=""></dl></td></dl>	4 to 56	21 to 1,170	31 to 1,100	5.9 to 520	<dl -="" 11<="" td=""></dl>

Table 3.35	Range of concentrations of COC in garden soil samples (0-15 cm) µg/g dry
	weight

Ontario Ministry of the Environment Table A (surface soil for residential land use for a potable groundwater condition) in Guideline for Contaminated Sites in Ontario, 1997.

2.8 to 11

3 to 15

6 to 110

38 to 440

9 to 78

38 to 400

6.2 to 35

10 to 79

b At some sites more than one garden or field was sampled, so there are more soil samples than sites.

<dl - 14.7

5.7 to 36.5

dl = detection limit

Commercial

 $(n = 24)^{b}$ Wild Plant Sites

(n = 10)

pH = 4.2 to 7

pH = 4 to 5.2

<dl - 2.1

<dl - 3.5



The concentrations of metals (particularly Cu and Ni) were generally higher in residential and natural soils compared to commercial soils. At some of the residential and natural sites, the concentration of metals in the soil exceeded the MOE Table A criterion (Table 3.35). The metal levels at commercial sites were generally quite low with just one sample that had concentrations above Table A values. At the residential and commercial sites there was little difference in the concentration of the COC with depth, suggesting that the soils are well mixed. At the natural sites the concentration of metals was elevated in the upper 0 to 15 cm layer, reflecting that the soil layers are not effectively mixed and that atmospheric deposition is a likely source of the COC. The pH of the samples was variable with the mean pH at the residential sites higher (pH=6.7) than either the commercial (pH=5.6) or natural sites (pH=4.6).

Produce was collected from the natural, commercial and residential sites. The natural sites were chosen on the basis of availability of either wild blueberries or mushrooms. At the residential sites, the minimum requirements per site were three vegetable types to include an example of: a below-ground crop (*e.g.*, carrot), a leafy vegetable (*e.g.*, lettuce), and an above-ground vegetable (*e.g.*, tomato). From the residential sites, the predominant samples collected were beets, carrots, cucumbers, lettuce, onions, potatoes, tomatoes, and zucchini. At the commercial sites, a sample of all available produce was collected. From the commercial sites, the predominant samples collected were potatoes, strawberries, cabbage, cucumbers, and squash. The plant tissue samples were collected and prepared in a manner consistent with how they would normally be harvested and prepared by residents consuming the food items. The produce samples were analyzed for total metal content by ICP-MS (the results were converted from dry weight values to wet weight values using the approach detailed in Appendix E sub-Appendix A, Protocol 9). Table 3.36 presents the range of concentrations of the COC (μ g/g wet weight) in a selection of the produce types collected.



Draduaa	Produce n		Cobalt	Copper	Lead	Nickel	Selenium
rrouuce	n			<u>+</u> +	t weight)	I	2
Residential							
Beets	17	<mdl< td=""><td>< mdl - 0.046</td><td>0.595 to 1.691</td><td>< mdl - 0.266</td><td>< mdl - 1.169</td><td>< mdl - 0.060</td></mdl<>	< mdl - 0.046	0.595 to 1.691	< mdl - 0.266	< mdl - 1.169	< mdl - 0.060
Carrots	16	< mdl - 0.062	< mdl - 0.044	0.250 to 0.787	0.030 to 0.277	0.061 to 2.512	< mdl - 0.103
Cucumber	31	< mdl - 0.039	< mdl - 0. 157	0.147 to 0.656	< mdl - 0.101	0.035 to 2.705	< mdl - 0.034
Lettuce	35	< mdl - 0.142	< mdl - 0.210	0.311 to 2.073	< mdl - 0.180	0.088 to 2.960	< mdl - 0.207
Onions	17	< mdl - 0.025	< mdl - 0.034	0.136 to 0.644	< mdl - 0.583	0.116 to 2.364	< mdl - 0.282
Potatoes	29	< mdl	< mdl - 0.089	0.754 to 2.424	< mdl - 0.619	< mdl - 2.030	< mdl - 0.130
Tomatoes	46	< mdl - 0.030	< mdl - 0.091	0.148 to 0.770	< mdl - 0.269	< mdl - 1.843	< mdl - 0.052
Zucchini	17	< mdl - 0.016	< mdl - 0.073	0.289 to 0.819	< mdl - 0.727	0.047 to 1.888	< mdl - 1.059
Commercial							
Cucumber	3	< mdl - 0.012	< mdl - 0.026	0.198 to 0.339	0.036 to 0.056	< mdl - 0.930	< mdl - 0.007
Potatoes	8	< mdl	< mdl - 0.102	0.826 to 1.519	<dl -="" 0.140<="" td=""><td>< mdl - 1.580</td><td>< mdl - 0.076</td></dl>	< mdl - 1.580	< mdl - 0.076
Strawberries	4	< mdl	< mdl	0.238 to 0.403	<dl< td=""><td>< mdl - 0.432</td><td>< mdl</td></dl<>	< mdl - 0.432	< mdl
Wild		_	-		_	-	_
Blueberries	7	< mdl	< mdl	0.228 to 0.931	< mdl - 0.095	0.264 to 1.034	< mdl
Mushrooms	3	0.090 - 0.295	0.042 to 0.086	2.881 to 4.429	1.265 to 1.876	0.103 to 0.255	0.616 to 1.265

Table 3.36 Summary of Range of Concentrations of COC for a Selection of

Samples collected summer <mdl = below minimum detection limit

Minimum Detection Limit ($\mu g/g \, d.w.$): As = 0.2, Co = 0.2, Cu = 0.5, Pb = 0.5, Ni = 0.5, Se = 0.2

Analytical results indicated that the COC concentrations were typically low in the produce samples as many of the values were below the minimum detection limits. Concentrations of As, Pb, Co and Se were either low or not detected at all in the majority of produce samples. Cu and Ni were consistently the dominant metals found in produce from all three site types. The exception was wild mushrooms which had elevated concentrations of As, Se and Pb relative to the other sample types. The highest concentration of Cu was found in mushrooms from natural sites.

For the purpose of data interpretation it is desirable to be able to compare results with regulatory criteria or other guidelines. Due to the paucity of established criteria, screening values based on human health considerations were developed by the SARA Group using the following categories:

- Below-ground vegetables (*e.g.*, carrots, beets, onions, potatoes); ٠
- Above-ground vegetables (e.g., cucumbers, lettuce, tomatoes, zucchini); and •
- Fruit (*e.g.*, black currants, blackberries, blueberries, raspberries, strawberries).



Different consumption rates were assumed for each of the different categories. Under the RME scenario (see Appendix B), 10.6, 23.3, and 5.3% of the total root vegetable, other vegetable and fruit intake rates were assigned to "local" sources, respectively. Of the fraction of fruits and vegetables that were considered to be derived from local sources, 25% of these were assumed to be derived from home gardens (at specific COI), while the remaining 75% were assumed to be from local agriculture (*i.e.*, all COI within the study area). These levels were indicative of an extremely safe scenario and were based on a acceptable risk level related to the consumption of local fruits and vegetables.

The method used to compare the measured values to the screening values and produce a preliminary estimate of hazard was calculated by the quotient (Q) method (*i.e.*, concentration detected within the fruit or vegetable divided by the corresponding screening value). If the Q value was >1, then the concentration in at least one vegetable from the category exceeded the screening criterion value; if Q was <1, then all vegetables for the category collected were below the criterion value.

The maximum metal concentrations (μ g/g wet weight) in each plant category were compared to the data screening levels developed by the SARA Group. Evaluation of the data for the residential and commercial vegetables and fruits showed that with the exception of one lettuce sample, all plant metal concentrations were below the determined COC screening criteria. At the wild plant sites, all blueberry samples were below the screening criteria. The mushroom COC concentrations were below the screening criteria for all COC but arsenic.

The actual potential risk from the arsenic concentrations in the vegetables to human consumers is dependent upon several factors, including arsenic species (inorganic *versus* organic) in the produce, actual amounts of produce consumed, the analytical detection limits, and uncertainty factor of the screening criteria. The significance of theses factors are discussed in detail in the 2003 Vegetable Garden report (see Appendix E).

The range of arsenic concentrations in the various produce types for this study were compared to the same vegetable types from previous studies conducted in Sudbury and other parts of Ontario. The ranges for all of the studies were very similar. Some of these previous studies evaluated potential risks to residents consuming produce and no risk was ever predicted from the metal concentrations in produce.



Concentrations measured during the survey were used to establish exposure point concentrations (EPCs) for produce in each of the COI using the 95% UCLM (on the arithmetic sample mean). Tables 3.37, 3.38, and 3.39 provide a complete summary of the vegetable and fruit concentrations evaluated in the current assessment.

It should be noted that during the survey the Vale Inco Copper Cliff facility was shut down because of a two-month strike between May 23rd and September 4th, 2003. During this time, due to the facility shutdown, no additional atmospheric inputs from the Vale Inco stack were released. The potential impact of this event on the results of the survey, as it pertains to the objectives of the Sudbury Soils Study, is discussed further in the uncertainty section.



COI	COC	Min	Max	Mean (arithmetic)	95% UCLM
	As	0.003	0.058	0.012	0.017
	Со	0.003	0.047	0.012	0.021
Coniston	Cu	0.193	1.226	0.457	0.540
(n=31)	Ni	0.013	2.170	0.418	0.568
	Pb	0.003	0.418	0.065	0.095
	Se	0.003	0.095	0.015	0.030
	As	0.003	0.109	0.019	0.037
	Со	0.003	0.364	0.027	0.132
Copper Cliff	Cu	0.239	2.392	0.734	0.916
(n=34)	Ni	0.192	5.278	1.448	1.810
	Pb	0.004	0.633	0.077	0.133
	Se	0.004	1.607	0.130	0.684
	As	0.004	0.142	0.021	0.125
Falconbridge (n=13)	Со	0.017	0.210	0.073	0.112
	Cu	0.176	1.459	0.568	0.751
	Ni	0.462	2.960	1.596	2.044
	Pb	0.005	0.069	0.028	0.038
	Se	0.004	0.043	0.012	0.027
	As	0.003	0.069	0.014	0.016
	Со	0.003	0.111	0.015	0.027
Sudbury Centre	Cu	0.147	2.535	0.645	0.750
(n=61)	Ni	0.035	4.316	0.605	0.750
	Pb	0.006	0.727	0.075	0.094
	Se	0.003	0.207	0.024	0.059
	As	0.003	0.016	0.007	0.011
	Со	0.003	0.012	0.005	0.007
Hanmer	Cu	0.163	0.732	0.338	0.465
(n=8)	Ni	0.037	0.420	0.185	0.280
	Pb	0.007	0.126	0.027	0.089
	Se	0.003	0.012	0.006	0.008
	As	0.003	0.142	0.014	0.019
	Со	0.003	0.364	0.021	0.038
Local	Cu	0.147	2.535	0.578	0.710
(n=198)	Ni	0.013	5.278	0.801	1.076
	Pb	0.003	0.727	0.066	0.078
	Se	0.002	1.607	0.037	0.100

Summary of COC Concentrations in Above ground Vegetables (ug/g wet wt) Table 3 37

Note: Samples collected summer 2003.

n = Number of samples analyzed.

Minimum Detection Limit ($\mu g/g d.w.$): As = 0.2, Co = 0.2, Cu = 0.5, Pb = 0.5, Ni = 0.5, Se = 0.2



Table 3.38 S	Summary of CO	C Concentration	ons in Below	Ground Vegetabl	les (µg/g wet wt.)
COI	СОС	Min	Max	Mean (arithmetic)	95% UCLM
	As	0.009	0.022	0.015	0.016
	Со	0.009	0.071	0.015	0.024
Coniston	Cu	0.221	1.358	0.675	0.810
(n=18)	Ni	0.120	1.219	0.432	0.564
	Pb	0.016	0.619	0.131	0.262
	Se	0.009	0.065	0.023	0.029
	As	0.005	0.042	0.016	0.021
	Со	0.005	0.042	0.014	0.019
Copper Cliff	Cu	0.136	2.424	0.950	1.235
(n=15)	Ni	0.245	2.512	1.384	1.689
	Pb	0.014	0.266	0.089	0.132
	Se	0.005	1.683	0.198	0.424
	As	0.012	0.071	0.039	0.059
	Со	0.033	0.164	0.068	0.130
Falconbridge	Cu	0.464	1.400	0.900	1.181
(n=6)	Ni	1.132	4.932	2.126	3.732
	Pb	0.022	0.279	0.142	0.228
	Se	0.008	0.022	0.012	0.016
	As	0.008	0.033	0.016	0.018
	Со	0.008	0.024	0.015	0.017
Sudbury Centre	Cu	0.280	2.375	0.966	1.143
(n=25)	Ni	0.023	1.691	0.555	0.788
	Pb	0.012	0.107	0.050	0.075
	Se	0.008	0.091	0.023	0.040
	As	0.016	0.100	0.058	0.100
	Со	0.016	0.100	0.058	0.100
Hanmer ^a	Cu	0.868	1.085	0.977	1.085
(n=2)	Ni	0.243	0.309	0.276	0.309
	Pb	0.040	0.250	0.145	0.250
	Se	0.032	0.100	0.066	0.100
	As	0.005	0.100	0.018	0.020
	Со	0.005	0.164	0.025	0.037
Local	Cu	0.136	2.424	0.916	0.996
(n=98)	Ni	0.023	4.932	0.779	0.914
	Pb	0.012	0.674	0.092	0.105
	Se	0.005	1.683	0.051	0.128

Note: Samples collected summer 2003.

n Number of samples analyzed.

^a 95% UCLM values were unable to be calculated due to the small sample size. Maximum values were used as surrogates for 95% ULCM value.

Minimum Detection Limit (μ g/g d.w.): As = 0.2, Co = 0.2, Cu = 0.5, Pb = 0.5, Ni = 0.5, Se = 0.2



(FB	g wet will				
Food Type	COC	Min	Max	Mean (arithmetic)	95% UCLM
	As	0.012	0.019	0.015	0.019
	Со	0.012	0.019	0.015	0.019
Fruits	Cu	0.552	0.903	0.739	0.903 ^a
(n=4)	Ni	0.403	2.986	1.461	2.749
	Pb	0.019	0.047	0.033	0.046
	Se	0.012	0.058	0.025	0.058 ^a
	As	0.009	0.019	0.013	0.014
	Со	0.009	0.061	0.017	0.035
Local Fruits (n=12)	Cu	0.238	0.903	0.535	0.651
	Ni	0.026	2.986	0.996	1.489
	Pb	0.015	0.081	0.033	0.042
	Se	0.009	0.058	0.016	0.024
	As	0.006	0.016	0.013	0.016 ^a
	Со	0.006	0.016	0.013	0.016 ^a
Wild Blueberries	Cu	0.228	0.931	0.501	0.680
(n=7)	Ni	0.264	1.034	0.522	0.706
	Pb	0.006	0.095	0.040	0.074
	Se	0.006	0.016	0.013	0.016

Table 3.39Summary of COC Concentrations in Fruits and Wild Blueberries
(µg/g wet wt.)

Note: Samples collected summer 2003.

n Number of samples analyzed.

^a Recommended 95% UCLM value is greater than the maximum value due to the small sample size. Maximum value was used as surrogate for 95% ULCM value.

Minimum Detection Limit (μ g/g d.w.): As = 0.2, Co = 0.2, Cu = 0.5, Pb = 0.5, Ni = 0.5, Se = 0.2

Further details on the results of this survey can be viewed in the 2003 Vegetable Garden Survey report located in Appendix E.



3.8 Levels of COC in Local Fish and Livestock

A key data gap identified during the problem formulation step of the HHRA was the lack of COC concentration data for local fish and livestock from the GSA. To address these issues, a local fish survey and a local livestock survey were conducted to provide data for the HHRA. The following two sections provide a summary of each survey and the results utilized in the assessment.

3.8.1 Local Fish Survey

The local fish survey was intended to obtain site-specific data on the range of metal concentrations found in a variety of fish species typically caught by anglers in the GSA. This study was integrated with other programs on local Sudbury lakes being undertaken by the Cooperative Freshwater Ecology Unit at Laurentian University. There were two primary objectives for conducting this study:

- To measure metal concentrations in the edible portions of fish tissue being consumed by local anglers; and
- To provide metal concentrations in forage fish and predatory fish species for the ecological aquatic problem formulation.

Fish for tissue analysis were collected from lakes in the Sudbury area by the Freshwater Co-op Unit of Laurentian University, under contract from the Sudbury Soils Study. A total of eight lakes were selected and sampled by the Freshwater Co-op Unit: Ashigami, Crooked, Long, Massey, McFarlane, Ramsey, Vermillion and Whitson. These specific lakes were chosen based upon proximity to the smelters, urban populations and the predator-prey assemblages; four lakes with walleye and yellow perch (*Perca flavescens*) (Ashigami, Massey, Ramsey, Whitson) and four lakes with walleye, yellow perch and lake herring (*Coregonus artedii*) (Crooked, Long, McFarlane, Vermillion). All of the eight lakes are known to have a moderate amount of recreational fishing activity. The fish from these lakes generate important information for the HHRA because some are in close proximity to the smelters, represent lakes with the highest metal concentrations and local Sudbury residents' fish and consume the fish from these lakes. The locations of the eight lakes are shown in Figure 3-5.



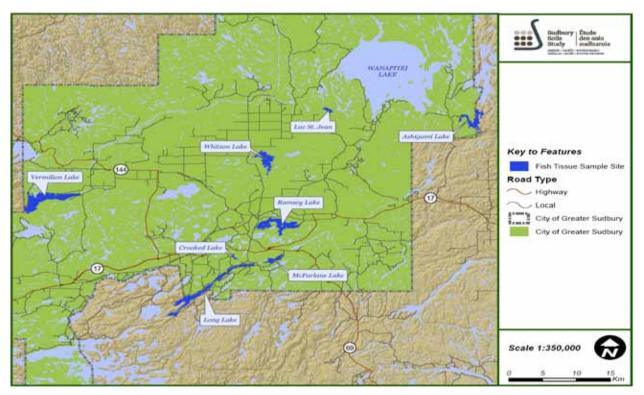


Figure 3-5 Fish Tissue Sampling Sites

Both Nordic and Fall Walleye Index Netting (FWIN) netting methods were used for sample collection, as both are standard Ontario Ministry of Natural Resources (MNR) methods for the collection of biological information to support management of a percid fishery dominated by walleye. Sampling was conducted between July, 2nd and October 30th, 2003.

A total of 211 fish muscle tissue samples were submitted for metal analysis. Some samples submitted for metal analysis were a composite of fish (10 or more). As such, the total number of fish used for sampling was 327. Walleye, yellow perch and lake herring made up the majority of the samples submitted for metal analysis, while five samples included spottail shiner, golden shiner and trout perch. However, for the purpose of the HHRA, only those fish species that are typically consumed by humans (*i.e.*, perch and walleye) were considered (*i.e.*, non-forage fish). It should be noted that trout or bass are not present in the majority of these lakes, and were not captured during the sampling program. These lakes are primarily considered walleye/yellow perch communities.

Table 3.40 provides summary statistics for the results of the fish tissue sampling used in the HHRA.



COC	Min	Max	Mean (arithmetic)	95% UCLM
Arsenic	0.004	0.657	0.074	0.111
Cobalt	0.001	0.137	0.015	0.019
Copper	0.083	4.980	0.357	0.521
Lead	0.004	2.600	0.225	0.301
Nickel	0.003	0.200	0.023	0.032
Selenium	0.295	4.470	1.642	1.957

Table 3.40	COC Concentrations Measured in Fish (Perch and Walleye) Muscle
	Tissues in the GSA (µg/g wet weight)

For the purpose of the current HHRA, mean and 95% UCLM values were used to represent the concentration of each COC within fish tissues potentially consumed by Sudbury residents. The complete methodology and dataset, including QA/QC results, are present in the Metal Levels in Fish Tissues from Sudbury Lakes – Data Report in Appendix G.

3.8.2 **Livestock Survey**

The Livestock Survey was intended to obtain site-specific data on the range of metal concentrations found in the tissue of beef cattle raised in the Sudbury Area. The majority of these animals are raised and consumed within the local area, possibly comprising a portion of the dietary intake of the residents of the Greater Sudbury Area. The results of the survey are intended to provide data that are specific to the Sudbury community and that can be used as part of the exposure assessment component of the HHRA. As a result, tissue samples were collected in a manner consistent with how they are normally collected by residents consuming this dietary source, and then analyzed for metal content.

It should be noted that information about sheep farming in the Sudbury region was obtained from the 2001 Census which confirmed that sheep are farmed in the Sudbury area (*i.e.*, there were four local farms reported with sheep in the Greater Sudbury area). However, sheep tissue was not collected as part of the livestock survey as it was concluded that cattle were the predominant domestic meat animal being consumed in the region.

Samples were collected by Professor Glenn Parker of Laurentian University from ten beef cattle raised in the GSA. These animals were destined for slaughter for private consumption and ranged in age from nine months to two years. A complete history of the animal was collected from the person submitting the animal for processing, including age, sex, breed, location where it was raised and pastured, location where

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the winter hay fed to the animal was grown, and any information on supplementary feeds used (if any). Figure 3-6 shows the locations of each sampled animal.

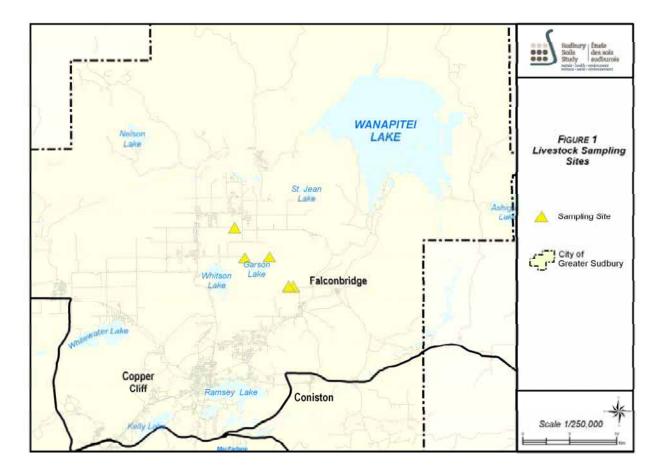


Figure 3-6 Location of livestock sampling sites in the Greater Sudbury Area

A 10 gram sample was collected from each animal under the direction of Dr. Glenn Parker. Samples of kidney, liver and muscle were collected using stainless steel cutting instruments, based on the following where possible:

- Kidney was a composite of both the medulla and the cortex;
- Liver was taken from the left lobe; and
- Muscle was taken from the left cheek.



Each sample was equally split into two five-gram portions, with one portion submitted for metal analysis at Testmark Laboratories in Sudbury, and the other portion archived for future possible analyses. Duplicate samples were also collected from three animals that had all tissue types available for collection. The moisture content of each tissue was also determined by Laurentian University (fresh samples after collection) and Testmark Laboratories (thawed samples prior to analyses).

Once received by Testmark, 1.0 to 1.7 grams of each sample was first chopped and then blended. Samples were then prepared by microwave digestion. All collected samples were analyzed for the following suite of metals and metalloids using ICP/MS:

- Aluminum
- Antimony
- Arsenic
- Barium
- Boron
- Cadmium
- Chromium

- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Molybdenum

- Nickel
- Selenium
- Strontium
- Titanium
- Vanadium
- Zinc

Results of analyses for COC are presented in the Table 3.41 below. All values are reported as wet weight mean concentrations. In cases where concentrations were below laboratory detection, one half of the detectable limit has been substituted as the concentration for those samples for statistical purposes.

Table 3.41	Concentrations of COC in Tissue Samples (µg/g wet weight) from Beef Cattle
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Statistics	Arsenic	Cobalt	Copper	Lead	Nickel	Selenium			
Kidney Tissue Samples (n=6)									
Mean	0.065	0.021	3.52	0.03	0.07	1.47			
95% UCLM	0.074	0.029	4.01	0.04	0.09	1.71			
Min	0.05	0.01	2.94	0.03	0.04	1.15			
Max	0.08	0.04	4.42	0.05	0.11	1.89			
Liver Tissue Samples (n=8)									
Mean	0.04	0.08	43.24	0.016	0.04	0.26			
95% UCLM	0.05	0.17	50.90	0.023	0.05	0.34			
Min	0.001	0.03	24.03	0.01	0.01	0.15			
Max	0.06	0.37	55.95	0.03	0.07	0.43			
Muscle Tissue Samples (n=10)									
Mean	0.04	0.0056	1.42	0.0057	0.06	0.17			
95% UCLM	0.06	0.011	1.84	0.0088	0.14	0.22			
Min	0.00	0.00	0.53	0.00217	0.00217	0.06			
Max	0.12	0.02	2.09	0.01	0.44	0.35			



Metal or metalloid levels varied among tissues. For example, the concentration of copper was markedly higher in liver followed by kidney, then muscle. In contrast, levels were generally higher in kidney tissue for arsenic, lead, nickel and selenium. The levels of all elements were generally lowest in muscle, which represents the most significant tissue from a human consumption perspective.

Results of livestock sampling in the GSA indicated that COC levels in local livestock were generally similar to those found elsewhere in Ontario. The complete methodology and dataset, including QA/QC results, are present in the Livestock Survey Report in Appendix H.

3.9 Falconbridge Urinary Arsenic Study

In response to community concerns over elevated levels of arsenic in soil on some residential properties within the community of Falconbridge, Xstrata Nickel (then Falconbridge Ltd.) commissioned the SARA Group to conduct an Arsenic Exposure Study. Representatives from Falconbridge Ltd. and the research team worked with the Falconbridge Citizens' Committee to ensure that the study addressed the proper questions, and that the results would be useful to the community. While not directly part of the Sudbury Soils Study, the results of this study provided a unique dataset for use in the current HHRA. The following section provides an overview of this study. The full detailed report can be found in Appendix N of this volume.

Community residents were consulted to identify primary concerns and to provide feedback on the objectives of the study. The research team then developed the study methodology to address two specific questions that were deemed to be most important by residents:

- 1) Do Falconbridge residents have higher urinary arsenic levels than residents living in a comparison area with lower levels of arsenic in their soil?
- 2) What health risks relative to other communities are associated with the urinary arsenic levels of Falconbridge residents?

To address these questions, the research team developed a methodology that combined both the analysis of first morning void urine samples, and interviews that captured lifestyle information pertaining to potential arsenic exposure. The study was comparative in nature, meaning that the main questions above were addressed by comparing Falconbridge with a similar community with lower soil arsenic



concentrations. Hanmer was selected as the comparison community as it was nearby and had similar characteristics to the Town of Falconbridge, but had significantly lower levels of arsenic in the soil. As well, the study used results from previous studies conducted in Ontario and Canada to make additional comparisons.

Discussions with the residents of Falconbridge began in the summer and fall of 2003. Dialogue continued as the study was designed during the winter of 2004. Sampling took place in September and early October, 2004 after the period of summer exposure to uncovered soils. All current Falconbridge residents were invited to participate in the study. The research team also randomly recruited a similar number of families from the comparison community of Hanmer to participate.

The data collection process employed in Hanmer was identical to the one used in Falconbridge. Initially, potential participants were sent a letter indicating that a member of the study team would visit their house to provide sample of the consent form, and to explain the study process. If they were willing to participate in the study, an appointment was scheduled.

At the appointment time, the study team walked the participants through the consent/assent forms in detail, had the participants sign them, and then conducted an in-home interview with the adults of the household. At the conclusion of the interview, each family was left a urine sampling kit with instructions. The study team then picked up the sample the following morning. Sample collection and interviewing occurred between early September and mid-October, 2004. Samples were processed and shipped to London Health Sciences Trace Elements Laboratory at the University of Western Ontario. All samples were analyzed for creatinine, total arsenic and inorganic arsenic and its major metabolites (*i.e.*, monomethylarsonic acid - MMA and dimethylarsinic acid – DMA).

A total of 273 households in the Town of Falconbridge were invited to participate in the study, of which 148 (54%) agreed. Overall, information was collected for 393 participants in the interview portion of the study and, of these, 369 participants provided a urine sample. In Hanmer, out of the 360 households approached, 129 (36%) agreed to participate in the study. Interviews captured information on 335 respondents and 321 participants provided urine samples.

Results of the study indicated that Falconbridge residents' urinary arsenic levels were very similar to those in the comparison community of Hanmer. With respect to *inorganic arsenic*, the type of arsenic most closely associated with health effects, the average levels in each community were nearly identical. Falconbridge residents had a mean level of 7.1 μ g/L and a median level of 6.0 μ g/L in comparison with



Hanmer residents who had a mean level of 7.2 μ g/L and a median level of 6.0 μ g/L. Approximately 80% of the urine samples in each community had an inorganic arsenic level below 10 μ g/L, and approximately 2 to 3% of samples in each community were at or above 20 μ g/L. Between the communities, there were no statistical differences overall or by various age groups.

With respect to *total arsenic* (both organic and inorganic forms), the communities again demonstrated similar distributions of urinary arsenic levels. The median level among Falconbridge residents was 8.9 μ g/L compared to 9.7 μ g/L for Hanmer residents. The mean levels were 21.2 μ g/L for Falconbridge residents compared to 14.1 μ g/L for Hanmer residents. There were two extreme outliers measured in the Falconbridge community that had a strong impact on the mean, but limited impact on the median as a measure of central tendency. The distribution is positively skewed with over 80% of the samples at levels below 20 μ g/L.

Approximately 2 to 3% of samples in each community were at or above 100 μ g/L. Statistical comparisons (non-parametric – Mann Whitney U) that were less influenced by extreme outliers indicated that there was not a statistically significant difference between the two communities. The statistical comparisons that tested the difference between means (independent t-test) found that Falconbridge residents had statistically higher average levels of total arsenic when compared to Hanmer residents.

In summary, for the form of arsenic that is most generally accepted to be a health concern for humans (inorganic arsenic), the two communities have nearly identical average levels.

Results of the survey also indicated that arsenic intakes for Falconbridge and Hanmer residents on average were within the typical daily intake of arsenic by Canadians; and therefore, are not at any increased risk from arsenic exposure compared to other Canadians in general. Health risks associated with urinary arsenic levels for Falconbridge residents would be similar to those in the comparison community of Hanmer. The median levels in Falconbridge are within the lower portion of the range estimated for typical daily intake of arsenic by Canadians (Health Canada).

Results of the survey were incorporated in the weight-of-evidence approach used to characterize overall health risks related to exposures of GSA residents to environmental concentrations of arsenic. The full Arsenic Exposure Study report can be reviewed in Appendix N.



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