

Sudbury Area Risk Assessment Volume II

Appendix E:

Vegetable Garden Survey Data Report

EXECUTIVE SUMMARY

The city and surrounding area of Sudbury has been the site of more than 100 years of mining and smelting activity. The need to evaluate past and current impacts of smelting emissions on the health of local residents and the surrounding ecosystem resulted in the initiation of a Human Health (HHRA) and Ecological Risk Assessment (ERA) of the Greater Sudbury area. As part of the HHRA component of the study, 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 site-specific data on the range of concentrations of metals found in fruit and vegetables that comprise a portion of the dietary intake of local residents. For the purpose of the HHRA, six primary chemicals of concern (COC) have been identified, including arsenic, cobalt, copper, nickel, lead and selenium.

This document is a data report which outlines the methods and results used to select sites, sample, process, and analyze soil and produce for metal levels and other parameters. The results of the survey provide data that are specific to the Sudbury community and will be used as part of the exposure assessment component of the HHRA. The sampling locations were chosen to reflect a variety of soil metal concentrations, site types and soil conditions. This collection effort was not intended to be a comprehensive survey of the metal levels in vegetables and fruit in the Sudbury area but rather, was designed to provide site specific values to be used in the HHRA. Soil samples were collected at all sites in the same manner as they were collected during the 2001 Sudbury soil survey. It is rare for the total metal content of soil samples to correlate to the total metal content in plant material due to the many factors governing bioavailability of metals in soil. Consequently, no correlation analysis between soil and plant metal levels has been included in this report.

Produce samples and co-located soil samples were collected from gardens in private residences and commercial grow operations. A total of 89 sites were sampled, including: 64 residential properties; 15 commercial properties; and, 10 natural sites.

Soil samples (0-15 cm and 15-30 cm) were collected at all sites. The soil samples were submitted for physical and chemical analysis. Table E.1 provides the range of concentrations of the COC and the pH in the 0-15 cm soil layer. The Ministry of the Environment (MOE) Table A soil quality screening criteria are also provided for comparative purposes.

Table E.1 Range of COC concentration in garden soil samples (0-15 cm) µg/g dry wt.

MOE Table A Soil Screening Criteria ^(a)		Arsenic	Cobalt	Copper	Nickel	Lead	Selenium
		20	40	225	150	200	10
Residential (n = 70) ^(b)	pH = 5.1 - 7.9	<dl - 173	4 - 56	21 - 1170	31 - 1100	5.9 - 520	<dl - 11
Commercial (n = 24) ^(b)	pH = 4.2 - 7	<dl - 14.7	2.8 - 11	6 - 110	9 - 78	6.2 - 35	<dl - 2.1
Wild Plant Sites (n = 10)	pH = 4 - 5.2	5.7 - 36.5	3 - 15	38 - 440	38 - 400	10 - 79	<dl - 3.5

^(a) 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

^(b) At some sites more than one garden or field was sampled, so there are more soil samples than sites
<dl = below detection limit

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

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 E.1). The metal levels at commercial sites were generally quite low with just one sample that had concentrations above Table A. 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 – 15 cm) layer, reflecting that the soil layers are not mixed, and that atmospheric deposition is a possible source of the COC. The pH of the samples was variable: the mean pH at the residential sites was higher (6.7) than the commercial (5.6) or natural sites (4.6).

Produce was collected from the natural, commercial and residential sites. The natural sites were chosen on the basis of the availability of either wild blueberries or mushrooms. At the residential sites the minimum requirements per site were three vegetable types to include a representative 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 which included: 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. Table E.2 presents the range of concentrations of the COC ($\mu\text{g/g}$ wet weight) in a selection of the produce types collected.

Table E.2 Summary of Range of Concentrations of COC for a Selection of Produce ($\mu\text{g/g}$ w.w.)

Produce	n	Arsenic	Cobalt	Copper	Lead	Nickel	Selenium
Residential							
Beets	17	<dl	<dl - 0.046	0.595 - 1.691	<dl - 0.266	<dl - 1.169	<dl - 0.060
Carrots	16	<dl - 0.062	<dl - 0.044	0.250 - 0.787	0.030 - 0.277	0.061 - 2.512	<dl - 0.103
Cucumber	31	<dl - 0.039	<dl - 0.157	0.147 - 0.656	<dl - 0.101	0.035 - 2.705	<dl - 0.034
Lettuce	35	<dl - 0.142	<dl - 0.210	0.311 - 2.073	<dl - 0.180	0.088 - 2.960	<dl - 0.207
Onions	17	<dl - 0.025	<dl - 0.034	0.136 - 0.644	<dl - 0.583	0.116 - 2.364	<dl - 0.282
Potatoes	29	<dl	<dl - 0.089	0.754 - 2.424	<dl - 0.619	<dl - 2.030	<dl - 0.130
Tomatoes	46	<dl - 0.030	<dl - 0.091	0.148 - 0.770	<dl - 0.269	<dl - 1.843	<dl - 0.052
Zucchini	17	<dl - 0.016	<dl - 0.073	0.289 - 0.819	<dl - 0.727	0.047 - 1.888	<dl - 1.059
Commercial							
Cucumber	3	<dl - 0.012	<dl - 0.026	0.198 - 0.339	0.036 - 0.056	<dl - 0.930	<dl - 0.007
Potatoes	8	<dl	<dl - 0.102	0.826 - 1.519	<dl - 0.140	<dl - 1.580	<dl - 0.076
Strawberries	4	<dl	<dl	0.238 - 0.403	<dl	<dl - 0.432	<dl
Wild							
Blueberries	7	<dl	<dl	0.228 - 0.931	<dl - 0.095	0.264 - 1.034	<dl
Mushrooms	3	0.090 - 0.295	0.042 - 0.086	2.881 - 4.429	1.265 - 1.876	0.103 - 0.255	0.616 - 1.265

<dl = below detection limit

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

The COC concentrations were typically low in the produce samples as metals were below detection in a large portion of the samples. The concentration of As, Pb, Co and Se were not detected or low in the majority of produce samples. Cu and Ni were consistently the dominant metal in produce from all three site types. The highest concentration of all COC, except Co, was found in mushrooms which were collected only from natural sites. The quality control program revealed variability in the reported As levels in the produce samples. This variability increased the uncertainty surrounding the interpretation of As in vegetable samples. Further testing was initiated and the SARA Group concluded that the repeatability of the analysis of As in vegetables was low at concentration below $3 \mu\text{g/g}$ dry weight, as a result it is necessary to discuss these limitations when using this dataset. The QA/QC program revealed that the analysis of all other elements in both soil and produce was of a high quality.

For the purpose of data interpretation it is often desirable to be able to compare survey results with regulatory criteria or other guidelines. However, there is paucity of established criteria for metal levels in food items. Therefore, 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)
- Above-ground vegetables (*e.g.* cucumbers, lettuce, tomatoes, zucchini)
- Fruit (*e.g.* black currants, blackberries, blueberries, raspberries, strawberries)

Different consumption rates are assumed for each category.

The maximum metal concentrations ($\mu\text{g/g}$ wet weight) in each plant type 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 containing elevated arsenic, all plant metal concentrations were below the COC screening criteria. At the wild plant sites, all blueberry samples were below the screening criteria. The mushroom samples were below for all COC with the exception of arsenic.

The actual potential risk from the arsenic concentrations in the vegetables to human consumers is dependent upon several factors, including: arsenic species (inorganic vs. organic) in the produce; actual amounts of produce consumed; the analytical detection limits; and, safety factor of the screening criteria. The significance of these factors is discussed in the report.

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 risk to residents consuming produce and no risk was ever predicted from the metal concentrations in produce.

The site specific data generated from the vegetable garden survey will be incorporated in the exposure pathway model for the HHRA.

SUDBURY AREA RISK ASSESSMENT
VEGETABLE GARDEN SURVEY

TABLE OF CONTENTS

E-1.0 INTRODUCTION.....1
 E-1.1 Background1
 E-1.2 Study Objective2
 E-1.3 Site Selection.....2
 E-1.4 Quality Assurance.....2

E-2.0 METHODOLOGY5
 E-2.1 Study Sites.....5
 E-2.1.1 Pre-Site Visit/Phone Call 5
 E-2.1.2 Site Arrival 6
 E-2.1.3 Site Description..... 9
 E-2.2 Sampling10
 E-2.2.1 Soil 10
 E-2.2.2 Produce: Classification and Selection 12
 E-2.2.3 Produce: Collection 13
 E-2.3 Sample Preparation14
 E-2.3.1 Soil 14
 E-2.3.2 Produce..... 14
 E-2.4 Equipment Decontamination14
 E-2.4.1 Soil 14
 E-2.4.2 Produce..... 14
 E-2.5 Sample Handling.....15
 E-2.5.1 Sample Storage..... 15
 E-2.5.2 Sample Shipping 15
 E-2.5.3 Site and Sample Identification 19
 E-2.6 Soil Analysis.....23
 E-2.6.1 Soil Characterization..... 23
 E-2.6.2 Total Metals 24
 E-2.7 Fruit and Vegetable Sample Analysis25
 E-2.7.1 Sample Preparation 25
 E-2.7.2 Total Metals Analysis 26
 E-2.8 Quality Assurance and Quality Control26
 E-2.8.1 Data Recording and Documentation 27
 E-2.8.2 Data Validation 27
 E-2.8.3 Data Verification..... 27
 E-2.8.4 Data Handling and Transmission 30
 E-2.9 Data Screening30

E-3.0 RESULTS33

E-3.1 Sample Location and Schedule33

E-3.2 Number of Samples.....33

E-3.3 Soil Physical and Chemical Characteristics34

E-3.4 Soil Metal Concentrations.....37

 E-3.4.1 Arsenic 37

 E-3.4.2 Cobalt..... 38

 E-3.4.3 Copper..... 39

 E-3.4.4 Lead..... 39

 E-3.4.5 Nickel 40

 E-3.4.6 Selenium..... 41

E-3.5 Vegetable and Fruit Metal Concentrations41

 E-3.5.1 Residential Garden Vegetables and Fruits 42

 E-3.5.2 Commercial Vegetables and Fruits 43

 E-3.5.3 Wild Blueberries and Mushrooms..... 45

E-3.6 QC Results.....46

 E-3.6.1 Split Produce Samples..... 49

 E-3.6.2 Standard Reference Material..... 49

 E-3.6.3 Additional Analysis to Address Uncertainty Surrounding Arsenic Plant Tissue Concentrations..... 51

 E-3.6.4 QC Conclusions 53

E-3.7 Comparison of Soil Concentrations to Previous Sudbury Studies.....54

E-3.8 Comparison of Soil Concentrations to Soil Guidelines54

E-3.9 Comparison of Metal Concentrations in Produce to SARA Screening Criteria ...56

E-4.0 DISCUSSION60

E-4.1 Arsenic Forms61

E-4.2 Likely Form of Arsenic in the Samples.....62

E-4.3 Arsenic Levels in 2003 Samples Compared to Previous Studies64

E-5.0 SUMMARY AND CONCLUSIONS66

E-6.0 REFERENCES.....68

Tables

Table E2.1	Detection Limits for Soils ($\mu\text{g/g}$)	25
Table E2.2	Detection Limits for Plant Tissue ($\mu\text{g/g}$ dry weight).....	26
Table E2.3	Vegetable Garden Screening Levels ($\mu\text{g/g}$ wet weight).....	31
Table E3.1	Vegetable Type and Quantities for Residential Gardens.....	33
Table E3.2	Vegetable Type and Quantities for Commercial Sites	34
Table E3.3	Vegetable Type and Quantities for Wild Plant Sites	34
Table E3.4	Summary of Soil Physical and Chemical Properties in Residential Gardens.....	35
Table E3.5	Summary of Commercial Site Soil Physical and Chemical Properties	36
Table E3.6	Summary of Wild Plant Site Soil Physical and Chemical Properties.....	36
Table E3.7	Summary of Soil Textures for the Vegetable Garden Soils	37
Table E3.8	Summary of Arsenic Concentrations in Soil ($\mu\text{g/g}$ dry weight).....	38
Table E3.9	Summary of Cobalt Concentrations in Soil ($\mu\text{g/g}$ dry weight).....	38
Table E3.10	Summary of Copper Concentrations in Soil ($\mu\text{g/g}$ dry weight).....	39
Table E3.11	Summary of Lead Concentrations in Soil ($\mu\text{g/g}$ dry weight)	40
Table E3.12	Summary of Nickel Concentrations in Soil ($\mu\text{g/g}$ dry weight).....	40
Table E3.13	Summary of Selenium Concentrations in Soil ($\mu\text{g/g}$ dry weight).	41
Table E3.14	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Above-Ground Residential Vegetables (n = 179)	42
Table E3.15	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Below-Ground Residential Vegetables (n = 87).	43
Table E3.16	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Residential fruits (n = 6).....	43
Table E3.17	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Above-Ground Commercial Vegetables (n = 18)	44
Table E3.18	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Below-Ground Commercial Vegetables (n = 12).	44
Table E3.19	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Commercial Fruits (n = 6).	45
Table E3.20	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weights) in Wild Blueberries (n = 7).	45
Table E3.21	Summary of Metal Concentrations ($\mu\text{g/g}$, wet weights) in Wild Mushrooms (n = 3).....	46
Table E3.22	Summary of 0-15 cm Soil Field Duplicates	47
Table E3.23	Summary of Percent Difference between 15-30 cm soil field duplicates.....	48
Table E3.24	Mean Percent Difference and Percent Recovery for San Joaquin Soil SRM (n = 3 replicates)	50
Table E3.25	Mean Percent Difference and Percent Recovery for Spinach Leaf SRM (n = 3).....	51
Table E3.26	Range of COC Concentrations ($\mu\text{g/g}$) in Surface Soil from 2001 and 2003	54
Table E3.27	Soil Values Above Table A (absolute number and % of total).	55
Table E3.28	Soil values above Table F (absolute number and % of total).	56
Table E3.29	Calculation of Hazard Quotient (Q) for Above-Ground Vegetables.....	57
Table E3.30	Calculation of Hazard Quotient (Q) for Below-Ground Vegetables	57
Table E3.31	Calculation of Hazard Quotient (Q) for Fruits	58
Table E4.1	Distribution of Arsenic in SARA Vegetable Garden Samples, 2003	60

Figures

Figure E-2-1. Vegetable Garden Sampling Sites 7
Figure E-2-2. Soil Sample Collection at Residential and Commercial Sites 10
Figure E-2-3. Duplicate Soil Sample Collection at Residential and Commercial Sites 11
Figure E-2-4. Soil Sample Routine and QC Procedures 17
Figure E-2-5. Plant Tissue Routine and QC Procedure 21

**Sub Appendices
(on CD 2)**

Sub Appendix E-A Protocols
Sub Appendix E-B Landowner Consent Form
Sub Appendix E-C Easting and Northing Co-ordinates for Sample Sites
Sub Appendix E-D Photographs
Sub Appendix E-E Chain of Custody Forms
Sub Appendix E-F Analytical Methodology
Sub Appendix E-G Fruit and Vegetable Preparation
Sub Appendix E-H Vegetable Garden Survey Database
Sub Appendix E-I Vegetable Screening Criteria Calculation and Derivation of Values
Sub Appendix E-J Soil Physical and Chemical Results
Sub Appendix E-K Soil Metal Data
Sub Appendix E-L Fruit and Vegetable Metal Data for COC (wet and dry weights)
Sub Appendix E-M Laboratory Reports
Sub Appendix E-N Quality Control Results: Standard Reference Material SRM Reports, Laboratory Reports, QC Analysis and Additional Arsenic Analysis
Sub Appendix E-O Field Duplicate and Split Samples: Results Tables and QC Analysis
Sub Appendix E-P Summary of Arsenic Data From Deloro, Port Colborne, Gatchell and SARA

E-1.0 INTRODUCTION

E-1.1 Background

The Sudbury Basin is an area rich in mineral deposits, particularly the nickel and copper ores that have drawn people to the region for the past 125 years. Recent studies have identified areas in Sudbury with elevated metal levels in the soil. These areas are generally close to the historic smelting sites of Coniston, Falconbridge and Copper Cliff. Although these metals do occur naturally in all soils, the studies generally indicate higher levels in surface soil (the top 5 cm) as a result of local mining, smelting and refining operations.

In 2001, the Ontario Ministry of the Environment (MOE) released a report that identified concentrations of nickel, cobalt, copper and arsenic in the area exceeded the generic MOE soil quality guidelines. Under Ontario legislation, this triggers the need for more detailed study. Therefore, the MOE made two recommendations:

- That a more detailed soil study be undertaken to fill data gaps; and,
- That a human health and ecological risk assessment be undertaken.

Both Vale Inco (formerly Inco Limited) and Xstrata Nickel (formerly Falconbridge Limited) voluntarily accepted the recommendations and began working together to establish what is commonly referred to as “The Sudbury Soils Study”. The mining companies partnered with four other major stakeholders in Sudbury to oversee this rigorous study. The community partners are Vale Inco, Xstrata Nickel, the MOE, the Sudbury & District Health Unit, the City of Greater Sudbury, and Health Canada First Nations and Inuit Health Branch. These partners formed a Technical Committee to oversee the study.

The Human Health Risk Assessment (HHRA) in Sudbury will evaluate the possible risk from airborne particulate emissions of the chemicals of concern (COC) resulting from past and current smelting operations on Sudbury residents. The COC are nickel, copper, cobalt, arsenic, lead and selenium (referred to as “metals”). During the planning phase for the HHRA several data gaps were identified for Sudbury specific information. The lack of Sudbury specific data for locally grown vegetables and produce was identified as a significant area of uncertainty. The following document presents the results of a sampling program that was conducted in the summer of 2003 to address this uncertainty.

E-1.2 Study Objective

The Vegetable Garden Survey was intended to obtain site-specific data on the range of metal concentrations found in fruit and vegetables that comprise a portion of the dietary intake of the residents of the Greater Sudbury Area. The results of the survey will be used as part of the exposure assessment component of the on-going HHRA for the area.

Vegetables and fruit were collected from home gardens, local growing operations and natural sites containing wild edible plants. Plant tissue samples were collected and prepared in a manner consistent with how they are normally harvested by residents consuming those garden or commercial growing operation produce, and then analyzed for total metal content. Soil samples were evaluated for total metal concentrations as well as various other soil and physical characteristics. Wild blueberries and mushrooms (as well as co-located soil samples) were also sampled as they are commonly consumed by residents of the Greater Sudbury Area.

E-1.3 Site Selection

The MOE conducted a Vegetable Garden Survey in 2001. Initial site selection for the SARA 2003 Vegetable Garden Survey was undertaken using the existing MOE participant list. Sites representing residential and commercial areas were selected by telephone interviews. Some geographical areas were not adequately represented using this approach, therefore members of the SARA group canvassed these areas to find additional properties.

Surveys were filled out by all potential participants. Residents were asked: whether they had a vegetable garden; and, if they consumed the produce grown from it. Selected participants grew at least one vegetable from each of the following groupings: leafy, root and fruit type vegetables.

Edible wild plant sites were chosen following discussions with local residents. Criteria for site selection included: represented a pre-determined area; be easily accessible; be commonly used; and, have sufficient berries or mushrooms to sample.

E-1.4 Quality Assurance

Quality assurance relates to a system of activities whose purpose is to provide data that meets a defined standard of quality. It consists of two separate but related activities: quality assurance (QA) and quality control (QC) (CCME, 1993). The QA process includes documentation of procedures, identification of critical points within the data collection activities that require monitoring by QC procedures, the level of

quality achieved, problems encountered, and corrective actions undertaken. The QA/QC program for the study is presented in detail in Protocol 10 provided in Sub Appendix E-A. The QA measures undertaken and the QC approach to the sampling, analysis and results are described throughout the methods and results sections of this report.

This page left blank intentionally.

E-2.0 METHODOLOGY

The following sections describe the methods used to select the study sites and collect and analyze the soil and produce samples. The associated QA/QC procedures are outlined. Detailed protocols are provided in Sub Appendix E-A.

E-2.1 Study Sites

This section describes the activities conducted by personnel prior to sampling. These activities include a pre-site visit as described in Section E-2.1.1, site arrival as described in Section E-2.1.2, and the background information collected at each site, as described in Section 0. The location of all sampling sites is shown in Figure E-2-1.

E-2.1.1 Pre-Site Visit/Phone Call

Residential and Commercial Sites

Before visiting a residential or commercial site for the first time, the landowner was contacted and the following factors established:

- Permission to sample at the site;
- A date and time of sampling;
- Access to the site, if the landowner was to be absent during the sampling time;
- The state of readiness/ripeness of produce to be sampled; and,
- The amount of produce the landowner would allow to be sampled.

Wild Plant Sites

Approximately three days to one week prior to sampling, the pre-determined wild berry and mushroom sites were visited in order to establish:

- The stage of development of the berries or mushrooms that were to be sampled and likely ideal time to harvest;
- Access to the site; and,
- The amount of produce available for sampling.

E-2.1.2 Site Arrival
Residential and Commercial Sites

Upon arrival at the site, field personnel made their presence known to the landowner. Field personnel did not enter the site without permission. On the first site visit, a consent form was signed by the landowner. One signed copy was left with the landowner and the other retained for the Study records. An example of the landowner consent form is provided in Sub Appendix E-B.

Wild Plant Sites

Permission was not required for wild plant sites. Upon arrival, field personnel parked their vehicle in a location that did not impede traffic and entered the wild plant site.

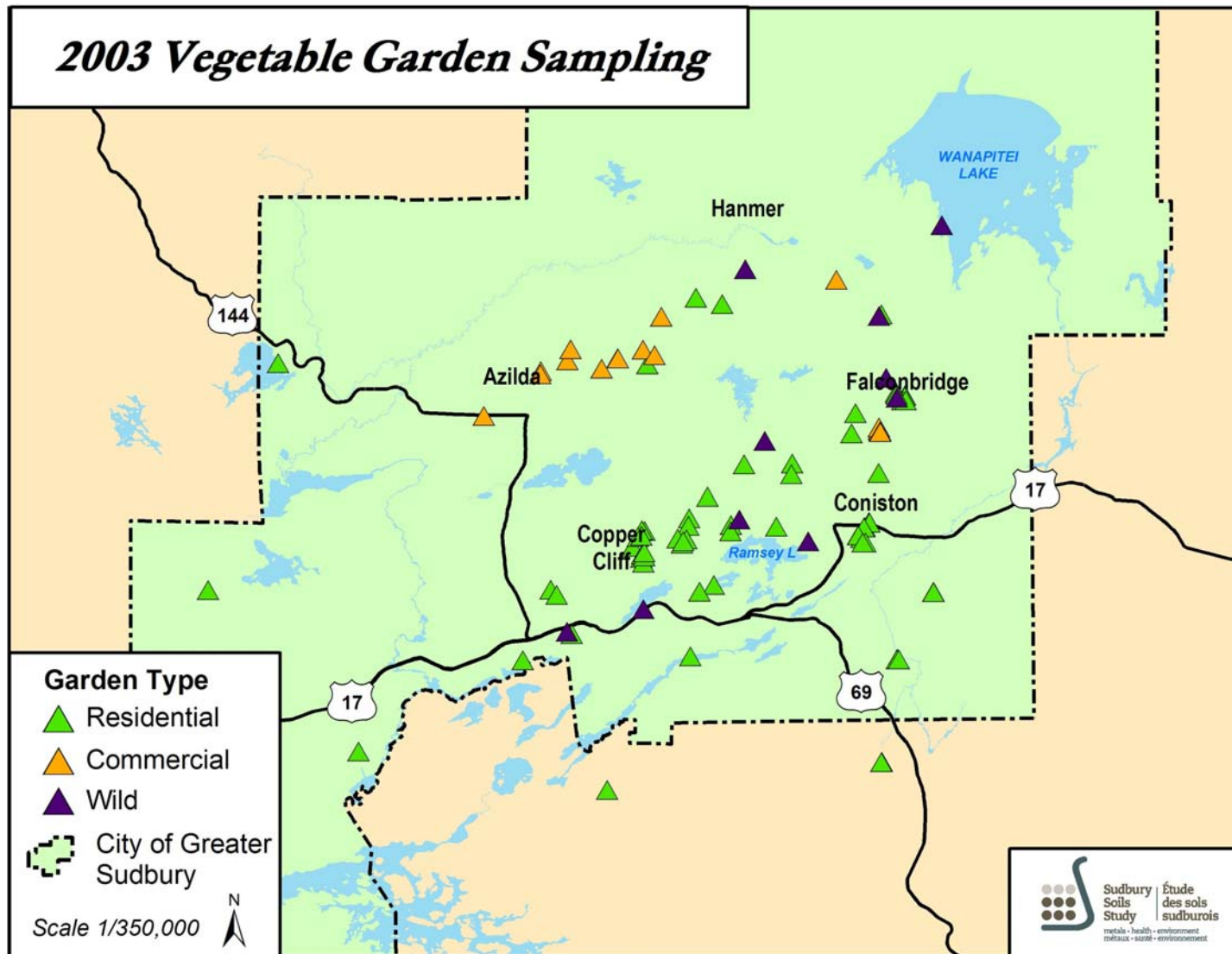


Figure E-2-1. Vegetable Garden Sampling Sites

This page left blank intentionally.

E-2.1.3 Site Description

During the first site visit the site was delineated and described. The boundaries of the sampling area were determined, based on either: the physical boundaries of the garden/plot/field at the commercial and residential sites; or, the abundance of berry bushes or mushrooms present and any physical boundaries of the landscape at the wild plant sites. For commercial and wild plant sites, a sampling area was chosen that was restricted to approximately 100 m² within a given plot or field, and was dictated by the profusion of berries or produce growing at the sites. Care was taken to choose the 100 m² sampling areas within a representative portion of the plot/field/vegetation, and to try to avoid edge effects, areas of noticeably wet or dry soil, roads, rail beds, and driveways, *etc.*

The location and details of the site were described during the initial site visit. Where applicable, the street address were recorded at each site. GPS coordinates were recorded during the first visit at each sampling area (*i.e.* individual garden/plot/field) (GPS Coordinates are provided in Sub Appendix E-C). GPS coordinates were taken from the NW and SE corners of each sampling area (*i.e.* garden) on a site, unless the garden(s) was less than 5 m², in which case the GPS coordinates were taken from the NW corner of the sampling area only.

Digital photographs (minimum of 4) were taken from each corner of the garden or sampling area. The photographs were identified by: sampling site, date, corner of garden photograph was taken from, and direction faced when photograph was taken (*e.g.* Site A, date, NE corner facing SE). All photographs are provided in Sub Appendix E-D.

A diagram of the site was drawn and recorded in the field book. This diagram included a directional north arrow, sampling area boundaries, photograph sites (and direction photograph taken), and any information of particular note (*i.e.* distance from driveway/road, unusual slopes, and tree cover). Anecdotal information was also noted in the field book at this time regarding, for example: site history; presence of animals; soil amendments (removal, additions, and cultivation); and, use of pesticide or commercial fertilizer (including the brand and application rate if known).

E-2.2 Sampling

Soil and produce sample were collected at all residential, commercial and wild plant sites. The objective of collecting samples for analysis was to obtain a small and informative portion that accurately reflects the sampling media. From the sampling phase until the analysis of the data, QA guidelines and principles were followed. The QA process included documentation of procedures, identification of critical points within the data collection activities, QC procedures, the level of quality achieved, problems encountered, and corrective actions undertaken. The following sections briefly describe the design, collection, sample preparation and equipment decontamination used for the sampling. Detailed protocols are provided in Sub Appendix E-A.

E-2.2.1 Soil

Composite soil samples consisting of 20 cores were collected from two depths: 0-15 cm and 15-30 cm (or to refusal). Soil samples were collected using an Oakfield™ sampler with a 12” stainless steel tube. At residential and commercial gardens a systematic sampling design (shown in Figure E-2-2) was applied. Samples were collected across a single sampling area in four alternating rows consisting of 5 sample sites per row. At wild sites the soil samples were taken from areas adjacent to plants from which berries or mushroom samples were collected. All soil samples from each sampling depth were placed into a Ziploc® plastic bag and stored until they could be air-dried, sieved and homogenized.

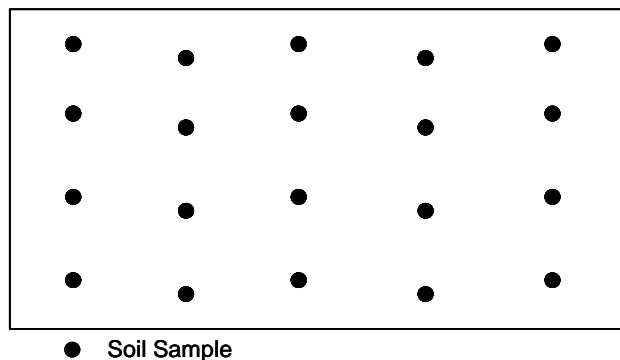


Figure E-2-2. Soil Sample Collection at Residential and Commercial Sites

Separate soil corers were used to collect the 0-15 and 15-30 cm soil cores. Before the corer was inserted into the soil, any surficial organic matter (*i.e.* leaves, stubble, weeds, grass) was removed by hand. The samples consisted of a composite of 20 cores. A detailed description of the sampling procedure is provided in Sub Appendix E-A.

In some instances, collecting soil samples to a 30 cm depth or even less was not possible due to the shallow nature of the soil. In such cases, only the 0-15 cm sample was taken and a record of the occurrence was noted in the field notebook. The sample was then placed into the sample bag with the other sub-samples as per normal.

Duplicate soil samples were collected at each sampling area (and per soil depth). Duplicates were collected within 10 cm of the original sample in the same sampling pattern (Figure E-2-3). The duplicate samples were air-dried, sieved, homogenized and archived until needed.

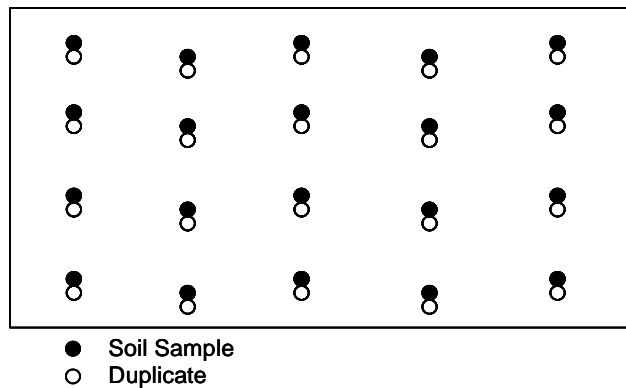


Figure E-2-3. Duplicate Soil Sample Collection at Residential and Commercial Sites

Notes:

- Wild plant sites were visited during times that were unlikely to be visited by the public (*i.e.*, during working hours) to minimize loss of berries and mushrooms available for sampling.
- For wild plant sites, berries/mushrooms and soil were collected at the same time.
- For commercial sites, soil and produce samples were collected at the same time, particularly if different fields/plots were sampled for different produce species.

E-2.2.2 Produce: Classification and Selection

Residential and Commercial Sites

At each residential and commercial site, a minimum of 3 and a maximum of 5 vegetable and/or fruit species were collected.

Minimum collection at a site consisted of 3 species, to include an example of: a below-ground crop such as a root or tuber vegetable; a leafy vegetable, and; an above-ground fruit vegetable. Collection depended on availability. For the three categories, listed in order of collection preference, examples of the types of vegetables collected are:

Below-ground crops:

- potatoes
- carrots
- onions
- beets
- radishes
- garlic

Leafy vegetable crops:

- lettuce (all kinds)
- Swiss chard
- spinach
- cabbage
- onions (greens)
- beet tops

Above-ground fruit vegetable crops:

- tomatoes (especially if not transplanted)
- cucumbers
- beans
- peas
- zucchini

If the residential garden also contained a berry crop, at least one berry species was collected. If more than one berry crop was present, the order of preference so as to maximise the number of samples of the same species as follows:

- strawberries
- raspberries
- blueberries
- other

It was not necessary to collect 5 species per site, however, if more than 3 species were available, 2 more species may have been collected if the other species included:

- A berry crop (as mentioned above), or;
- A species of interest to the study due to perceived sensitivity/longer potential exposure to the COC (such as peas, beans, garlic or rhubarb), or;
- A species that was of special interest to the landowner, and he/she specifically requested the inclusion of the species in the survey.

Samples of fruit from trees were not collected unless by specific request of the landowner, as mentioned above.

Wild Plant Sites

At each wild plant site, mushrooms and/or blueberries were collected.

E-2.2.3 Produce: Collection

Residential and Commercial Sites

Once the species to be collected were identified, the crop was inspected to ensure whether they were at the appropriate stage of development (ripeness) that would normally be harvested by the landowner. Ripeness was estimated prior to the site visit by the pre-site visit telephone call as mentioned above, however it was confirmed upon arrival at the site.

The produce was collected in a manner consistent with normal harvesting practices for that crop, and only the edible portions of each crop were collected. For above-ground leafy and fruit crops, stainless steel secateurs (clippers) were used to cut the edible portions of the crop from the non-edible portions; for berry crops the berries were gently removed by hand, and; for the below-ground crops, the edible portions were dug from the ground by hand.

Once harvested, the produce was placed into Ziploc® plastic bags and weighed with a Pesola® 2500 g scale, then placed into a cooler with ice packs. Where possible, 3 kg of produce was collected; however a minimum of 0.5 kg was acceptable. If less than 0.5 kg of produce was available for sampling, an alternate species was considered. If an alternate species was not available or not desirable, as much produce as possible was collected and the mass recorded. If more than one species was harvested at a site at one time, then the sampling tools were decontaminated before sampling a different species.

Wild Plant Sites

Upon arrival at the site, the berries were inspected to ensure that they were at the appropriate stage of development (ripeness) that would normally be harvested by the public. The berries were collected in a manner consistent with normal harvesting practices; only the edible portions of the berry crop were collected. The berries were gently removed by hand, placed into Ziploc® plastic bags or container, and weighed with a Pesola® 2500 g scale.

Mushrooms (stems and caps) were collected by hand, stored in Ziploc® plastic bags and weighed with the Pesola® 2500 g scale.

Once 0.5 kg to 3 kg of produce was collected, the Ziploc® bags/container was immediately placed into a cooler with ice packs. Where possible, 3 kg of produce were collected; however a minimum of 0.5 kg was acceptable.

E-2.3 Sample Preparation

E-2.3.1 Soil

Preliminary soil sample preparation was conducted in a laboratory at the Willet Green Miller Centre on the Laurentian University Campus. The samples were allowed to air dry and then were sieved through a 2 mm Nalgene® sieve into a Nalgene® receiving pan. Some samples were split for QA/QC analysis. This was achieved by scooping (using a plastic spoon) the soil from the sample into new, clean pre-labelled plastic bags.

E-2.3.2 Produce

Plant tissue samples were not washed or rinsed with the exception of the leafy vegetables. Leafy vegetables were rinsed with reverse osmosis water, and then dried with a lettuce spinner and clean paper towels. No produce was scrubbed or peeled prior to storage or shipment to the analytical laboratory.

E-2.4 Equipment Decontamination

E-2.4.1 Soil

The field equipment was decontaminated in the following manner. Once all of the soil samples were collected in a sampling area the soil corers and any other sampling equipment were thoroughly washed prior to sampling at another sampling area. To achieve this the sampling equipment was carefully wiped with a paper towel to remove excess soil, scrubbed with a brush and/or cloth using phosphate-free soap, rinsed with reverse osmosis water and hand-dried with clean paper towels. The laboratory equipment, such as the Nalgene® sieves and plastic spoons were thoroughly cleaned after each usage using phosphate free soap and rinsed with reverse osmosis water.

E-2.4.2 Produce

Once all of the produce samples were collected at a site and/or sampling area, the sampling equipment was thoroughly washed using phosphate free soap and rinsed with reverse osmosis water prior to sampling at another site/sampling area.

E-2.5 Sample Handling

This section describes the storage, shipping, and identification of soil and produce samples taken from residential, commercial, and wild plant sites.

E-2.5.1 Sample Storage

Once sieved, homogenized, and split (if necessary), all soil samples were stored at room temperature until shipped. Duplicate samples for each site were archived at the offices of NAR Environmental, Sudbury.

Produce samples were shipped to the appropriate facility as quickly as possible after collection. If shipping was not possible that day, the vegetables were stored in a refrigerator until they could be shipped. The allowable waiting period was no longer than 3 days.

E-2.5.2 Sample Shipping

Soil

For the majority of the samples, composite soil samples (from the 0-15 cm soil depth) were sent to different analytical laboratories for a variety of analysis. The laboratories and the analysis they performed are detailed below and are summarized in Figure E-2-4.

- SGS Lakefield Research, Lakefield, Ontario (SGS LR)
 - 0-15 cm and 15-30 cm soil depths
 - Analysis: total metal analysis of a suite of metals and metalloids and moisture content
- University of Guelph Soil and Nutrient Laboratory (SNL)
 - 0-15 cm soil depth only
 - Analysis: soil fertility (pH, “plant available” magnesium, potassium, phosphorous, and nitrogen recommendations), particle size distribution, total, and carbon package (total, inorganic and organic carbon).

Chain-of-custody forms were sent with each soil sample shipment, which clearly indicated the samples contained within the shipment package, and the analysis to be conducted. A copy of the chain of custody forms are provided in Appendix E.

Samples were sent to each analytical laboratory via courier (in a sealed plastic cooler or another equally secure package at room temperature) for overnight delivery.

This page left blank intentionally.

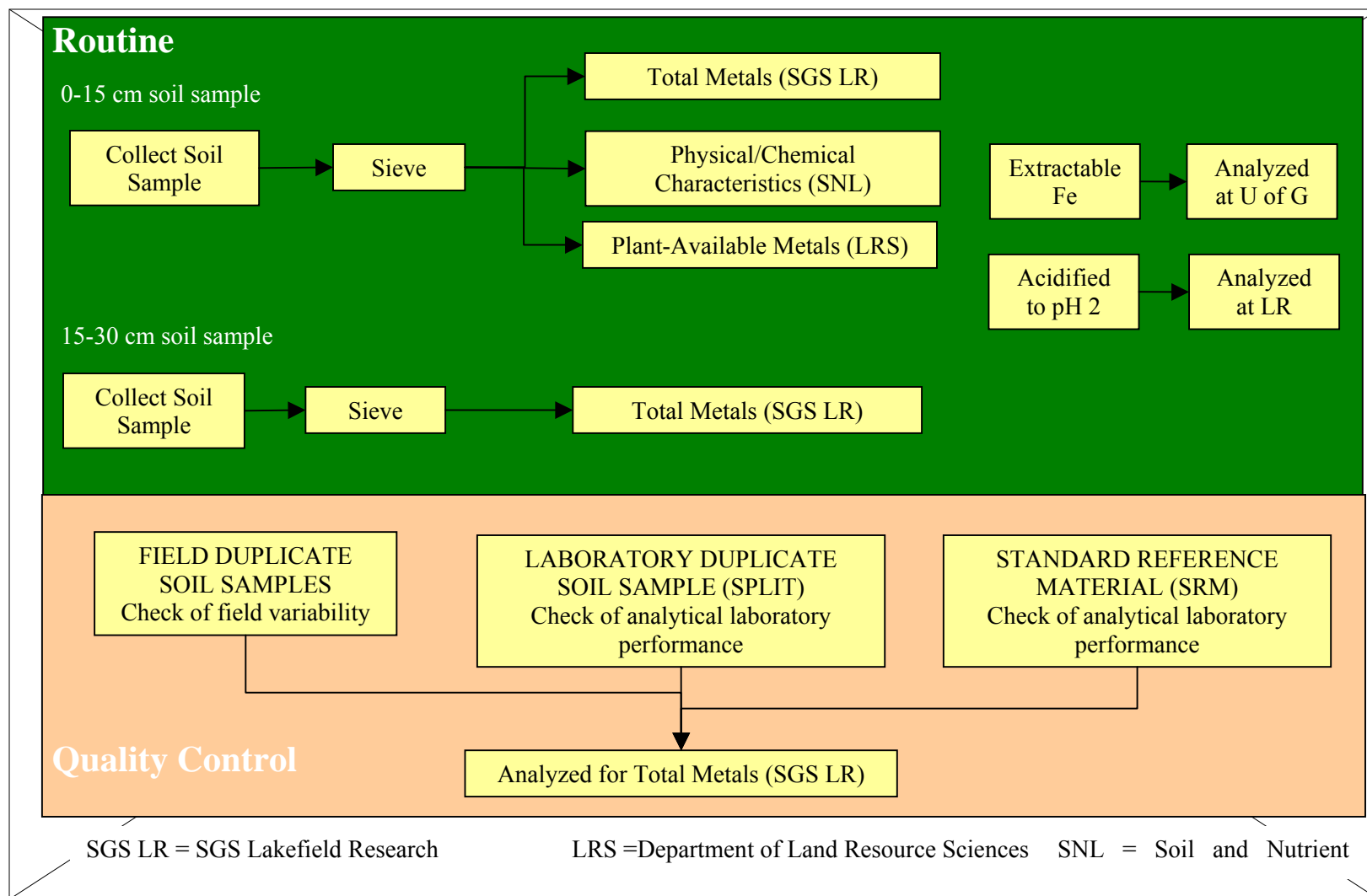


Figure E-2-4. Soil Sample Routine and QC Procedures

This page left blank intentionally.

Produce

All plant samples were shipped to the University of Guelph, Department of Land Resource Science (LRS), where they underwent preparation for analysis. Once the plant samples were prepared, they were shipped directly to SGS Lakefield Research (SGS LR) for total metal analysis. Figure E-2-5 shows a summary of the routine path to analysis of the produce samples and the QC samples.

Chain-of-custody forms were sent with each plant tissue sample shipment, which clearly indicated the samples contained within the shipment package, and the analysis to be conducted with each sample.

Samples were sent to the analytical laboratory via courier (in a plastic cooler with sufficient ice packs to maintain cooled temperatures) for overnight delivery. Samples were not sent on Fridays or just prior to holidays, as the integrity of the samples may have been compromised if they did not remain cooled. The Department of Land Resource Science was contacted at least a day prior to every shipment to ensure that the samples were processed in a timely manner.

E-2.5.3 Site and Sample Identification

The sites were identified with a site number and a letter which indicated whether they were residential (R), commercial (C) or wild site (B). If a site contained multiple plots or gardens the gardens were allocated a letter (A-C). For example, if site number 3 in the residential sampling area contained three gardens then the site would be labelled:

- 3- R:A; 3-R:B and 3-R:C

All soil samples were clearly identified with all relevant information, including site type, site number, date, duplicate, and soil depth. A full description can be found in Protocol 5: ‘Site and Sample Identification (Sub Appendix E-A). Duplicate samples were identified with the insertion of a “Dup” into the sample code.

All plant samples were clearly identified with all information, including vegetable/fruit type, site type, site number, date of collection and when applicable identified as a split. Split samples were identified by the insertion of as “S” into the sample code.

This page left blank intentionally

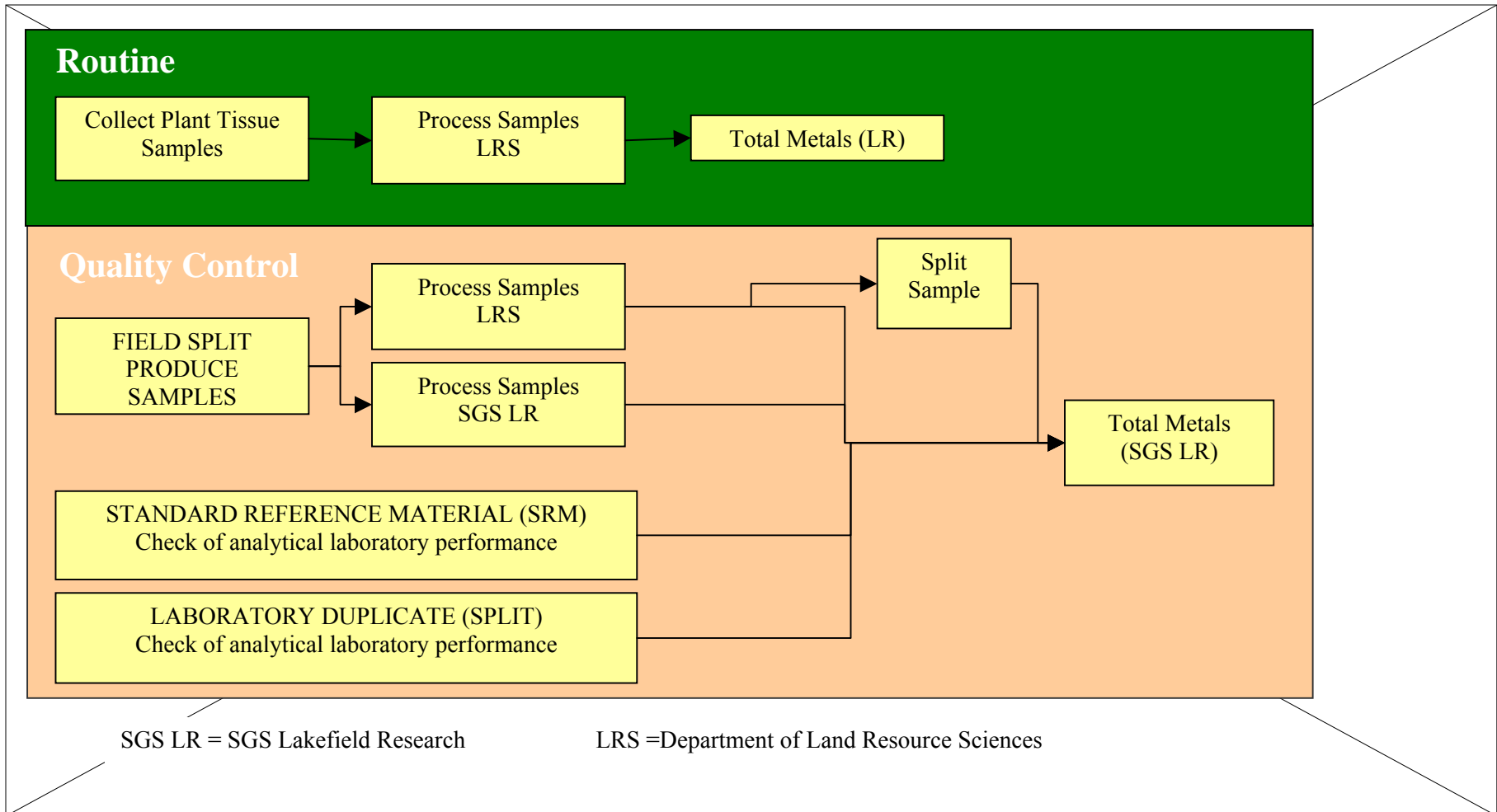


Figure E-2-5. Plant Tissue Routine and QC Procedure

This page left blank intentionally.

E-2.6 Soil Analysis

All soil samples were analyzed for total metal content, pH, fertility (nitrogen, potassium and phosphorous), total, organic and inorganic carbon. The physical aspects of the surface soil were characterized including: particle size, bulk density and moisture. A summary of the methods used to determine the physical and chemical analysis on the soil are presented in Sub Appendix E-F.

E-2.6.1 Soil Characterization

Particle size distribution, calcium carbonate equivalence, total, inorganic and organic carbon (C), phosphorus (P), potassium (K), magnesium (Mg) and pH were determined at the Soil and Nutrient Laboratory (SNL) at the University of Guelph. For all tests, samples were dried at 350°C and sieved through 2 mm sieve prior to analysis.

Total, inorganic and organic carbon analysis was conducted using a LECO SC444 (dry combustion) (for details on methodology refer to Tissen and Moir, 1993). For inorganic C, a sample was first ashed overnight at 475°C in a muffle furnace. Organic C was determined by subtracting inorganic C from total C. Particle size distribution was completed using the pipette method as described in Sheldrick and Wang, 1993.

The analysis for P, K, Mg and pH were completed as per the Ontario Ministry and Agriculture and Food (OMAF) methodologies for accredited soil testing in Ontario. P was determined using a sodium bicarbonate extraction followed by automated colourimetric determination as described in Schoneau and Karamanos, 1993. K and Mg were determined according to Bates and Richards, 1993. This method uses an ammonium acetate extraction followed by flame AAS determination. pH was determined using the slurry method which involves a saturated paste in deionized water (Hendershot *et al.*, 1993). Buffer was completed on samples which had a pH less than 6 and this was completed using the SMP (Shoemaker *et al.*, 1961) single-buffer method.

Bulk Density and Moisture Content Samples

Soil bulk density is a measurement to aid in determining soil structure, total pore space and the degree of packing of the soil particles. Bulk density samples were collected at all sampling sites. Moisture content of the soil was also determined from this sample. The comprehensive protocol for the bulk density sample collection is provided in Sub Appendix E-A and is briefly described below.

Using a 5 cm deep ring (radius = 4.75 cm), two bulk density samples were collected from every sampling area (garden/field/plot) in the following manner. In a representative location within a sampling area, a bulk density sampler (ring) and a “dummy” ring were placed on the soil. These rings were tapped into place using a rubber mallet and a piece of wood. The soil in the first ring was trimmed without compression and the contents placed into a Ziploc® bag. If the soil to be sampled was rocky or shallow, a smaller 2.5 cm wide bulk density sampler (r = 4.96 cm) was used.

In the laboratory, the soil was placed into an aluminium weigh boat dried and weighed. The percent moisture content of the soil was determined by using the following equation:

$$\% \text{ moisture} = \frac{(\text{wet mass of the soil (g)} - \text{dry mass of the soil (g)})}{\text{wet mass of the soil (g)}}$$

The volume of the bulk density ring was equivalent to the volume of the soil sample, and was determined by using the following equation:

$$\text{Volume of bulk density ring (cm}^3\text{)} = \pi r^2 \times \text{height}$$

Where r is the radius of the bulk density ring.

The bulk density of the soil sample was measured by using the following equation:

$$\text{Bulk density (g/cm}^3\text{)} = \frac{\text{mass of dry soil (g)}}{\text{Volume of the bulk density ring (cm}^3\text{)}}$$

E-2.6.2 Total Metals

All of the samples were sent to SGS Lakefield Scientific for metals analysis. The samples were digested following US EPA 3051B-digestion protocol which provides a measure of environmentally recoverable metals. Briefly the method is as follows: 0.5 g of sample were heated to 170°C under 200 p.s.i. in nitric acid. The resulting sample was then diluted to 50 mL and submitted for instrument analysis 6010B (ICP-OES) and 6020 (ICP-MS). Arsenic levels were determined using hydride generation due to chlorine influence produced from the digestion method.

All samples were analyzed for the same parameters selected in the 2001 survey (MOE, 2003). The detection limit for each element is shown in Table E2.1. The detection limit presented is the lower limit of concentration of a substance that must be present before the method is considered to provide quantitative results (SGS Lakefield, R. Irwin, personal communication).

Table E2.1 Detection Limits for Soils ($\mu\text{g/g}$)

Element	DL	Element	DL
Aluminium	2.5	Lead	0.2
Arsenic	0.5	Magnesium	1
Barium	1	Manganese	2
Boron	2.5	Molybdenum	1
Cadmium	0.8	Nickel	1
Cobalt	1	Selenium	0.5
Copper	1	Strontium	0.2
Chromium	1	Titanium	3
Iron	5	Vanadium	0.9
Potassium	5	Zinc	2.5

E-2.7 Fruit and Vegetable Sample Analysis

The produce samples were analyzed for total metal content. A brief description of the preparation and analysis is provided in the following sections.

E-2.7.1 Sample Preparation

All samples of fruit and vegetables were sent to the LRS for processing and preparation. The plant samples were cleaned as per a realistic “worst-case exposure scenario”. For instance, below-ground crops were scrubbed rather than peeled and blueberries were unwashed. The moisture content of all tissue was determined so that all measurements of total metals content could be presented on both a dry weight and wet weight basis (procedure for the conversion is provided in Appendix A: Protocol 9 QA/QC).

Finally the plant tissue was oven-dried and ground. Sub Appendix E-G shows the specific process each plant species underwent through preparation.

E-2.7.2 Total Metals Analysis

The produce samples were sent to SGS LR for analysis of total metals. A comprehensive list of the method used to analyze each element is provided in Sub Appendix E-F. Tissue digestions were performed using high pressure microwave digestion and nitric acid. The samples were digested by adding 0.25g of dried and homogenized sample using 5 mL concentrated nitric acid in a high-pressure microwave digestion system. The digestion occurred at 1000 p.s.i. and 260°C. The resulting sample was then diluted to 50 mL and submitted for instrument analysis 6010B (ICP-OES) and 6020 (ICP-MS).

The detection limits for metals in plant tissue are presented in Table E2.2. The levels presented represent the lower limit of concentration of a substance that must be present before the method is considered to provide quantitative results (SGS Lakefield, R. Irwin, personal communication).

**Table E2.2 Detection Limits for Plant Tissue
(µg/g dry weight)**

Element	DL	Element	DL
Aluminium	2.5	Lead	0.5
Antimony	0.2	Magnesium	0.5
Arsenic	0.2	Manganese	2
Barium	0.5	Molybdenum	0.2
Boron	2.5	Nickel	0.5
Cadmium	0.8	Selenium	0.2
Calcium	10	Strontium	0.5
Cobalt	1	Titanium	3
Copper	0.5	Vanadium	0.5
Chromium	0.5	Zinc	1
Iron	1		

E-2.8 Quality Assurance and Quality Control

The QA/QC approach used included assessment of the following areas:

- Data recording and documentation;
- Data validation: this deals with an assessment of the completeness, correctness and representativeness of the data;
- Date verification: this includes checking that all the data are present and correct;
- Data handling: this includes data rounding and treatment of significant figures;
- Data transmission; and,
- Data evaluation: this includes interpretation and laboratory reporting.

E-2.8.1 Data Recording and Documentation

The data recording and documentation involved with the sampling process have been discussed in the relevant sections and include: chain of custody forms (provided in Sub Appendix E-E), sample progress sheets and field books.

E-2.8.2 Data Validation

The data validation procedures included the assessment of unusual events that occurred either during sampling or analysis, correction of transmittal errors, temporal continuity, a procedure for flagging anomalous data and sample consistency checks.

E-2.8.3 Data Verification

Data verification was undertaken in a number of ways. The presence of all samples was established by cross checking soil and produce samples collected against the chain of custody records. In order to determine variability and uncertainty introduced from the sampling approach, field duplicate samples (soils only) and field split samples (plant tissue only) were collected. The correctness of the analysis was assessed through the analysis of Standard Reference Material (SRM), the collection of field duplicate or split samples. The QC procedures were summarized in Figure E-2-4 (soils) and Figure E-2-5 (produce) and are discussed in greater detail in Protocol 9 (Sub Appendix E-A) and below.

The total metal analysis of the soil and tissue samples was undertaken at SGS LR. This is a laboratory accredited by the Standards Council of Canada (SCC), in co-operation with the Canadian Association for Environmental Analytical Laboratories (CAEAL), for analysis of total metals. The laboratory operates under an internationally recognized quality standard, which consists of a documented quality system. As part of the laboratory's comprehensive validation program, the following checks are made: accuracy, short and long-term precision, Limit of Detection, Limit of Quantification, linearity, and estimation of uncertainty of measurement. As part of the internal validation process of the laboratory's performance split samples (plant tissue and soil) were analyzed for total metal content. The results of the internal laboratory comprehensive validation are available upon request.

Field Duplicate Soil Samples

Soils are characterized by several types of variation; they are not a homogeneous mass, but a rather heterogeneous body of material (CCME, 1993). To determine whether the sampling methods used produced a sample which was representative of the area being sampled duplicate samples of soil were collected at all sites and were submitted for analysis at 10% of the sites. The purpose of analyzing duplicate samples was to obtain an estimate of the variability of the soil physical and chemical characteristics, as well as metal levels, within a sampling site. From both soil sampling depths, 10% of all field duplicate samples were randomly chosen, prepared and handled in a manner identical to that of the original samples. These field duplicate samples were analyzed for total metal content (SGS LR), soil pH, particle size distribution, total, organic and inorganic carbon content and “plant-available” Mg, K, P and N fertilizer recommendations (University of Guelph, SNL).

Field Split Plant Tissue Samples

It is impossible to produce a true duplicate when dealing with plant tissue, consequently plant split samples were collected at 10% of the sites. The aim of collecting these samples was to gain an understanding of the variability of total metal concentrations in the produce collected and to determine whether any contamination was being introduced during routine plant tissue processing. The following procedure was used to collect these split samples:

- At 10% of the commercial sites, 3 designated species had double the amount of plant samples collected (*i.e.* up to 6 kg). The three designated species were potatoes, tomatoes, and cucumbers;
- At 10% of the residential sites, 5 designated species had double the amount of plant samples collected. The five designated species were potatoes, tomatoes, cucumbers, beets, and lettuce; and,
- At 10% of the wild plant sites, 1 designated species had double the amount of plant samples collected. The designated species was blueberries.

The split tissue samples were sent to LRS and to SGS LR. The portion sent to LRS, was treated as a routine sample: it was prepared in the manner of all other study tissues. Once processed, this portion was split again and both parts were sent to SGS LR for analysis of total metals. This provided a check of the variability between the analytical techniques used to assess the plant tissue.

The portion sent to SGS LR was prepared in-house using the same protocol as LRS. It was then digested and analyzed in the routine manner for total metals. The purpose of this parallel preparation was to determine whether any contamination was introduced during the processing phase.

Standard Reference Material

The SARA Group purchased standard reference material (SRM) to determine the variability related to the performance of the determination of metals in the soil and produce samples. The SRMs were purchased from the National Institute of Standards and Technology and consisted of spinach leaves and San Joaquin soil. These samples were sent in triplicate to SGS LR for the analysis of total metals.

Approach Used to Determine the Variation in QC Sample Results

The following section outlines the approach that was used to determine the variation in the sampling approach used. The field split and duplicate samples were tabulated together and compared.

The first comparison made was the percentage deviation. This value was determined using the following equation:

$$\text{Percentage deviation (\%)} = \frac{(\text{value of duplicate/split sample} - \text{value of original sample}) \times 100}{(\text{value of duplicate/split sample} + \text{value of original sample})/2}$$

A value of 30% deviation between samples is usually deemed acceptable for within laboratory variability between like samples. This value has been used previously to determine variability (Jacques Whitford Environmental Limited, 2002). This level of reproducibility is expected for internal laboratory split samples and this was the level of accuracy achieved by SGS LR between split samples which had undergone the same processing, extraction and analysis. A percentage deviation in this range between field duplicate samples and field split samples can be unobtainably low. Despite this, the 30% deviation limit was used to determine field splits and duplicates which required more attention to determine whether the results were comparable. A summary of the decisions related to the treatment of the QC data is summarised below:

All matched duplicates and splits with a percentage deviation greater than 30% were highlighted in the spreadsheet and flagged for further investigation.

The flagged values were compared to the minimum analytical detection limit (MDL). If the flagged values were marginally above the detection limit this often accounted for the elevated percentage difference. For each analyte the laboratory produces an internal method validation report. Within these reports the laboratory reports a confidence interval range. If the values related to the increased level of

percentage deviation fell within the analysis range (usually 3 x the limit of quantification) then the deviation was attributed to analytical “noise”. For example a value of 0.2 and 0.3 are 100% different from each other. If the confidence interval produced through the laboratories method validation process shows that the MDL values can range from 0.1 to 0.4 then it would appear that the percentage deviation was attributable to analytical noise and not an inconsistency in sampling approach.

Any comparative values with an increased percentage deviation which was not explained by examining the MDL were flagged and investigated further.

The soil results were compared to the MOE Table F to determine whether the concentrations detected were within the range of background metal concentrations. The rationale for this approach is that soils are not a homogeneous mass and some level of natural variation exists. If both of the compared values fell within the range of concentrations reported to be background levels then the variation was attributed to the heterogeneous nature of soil and not to an error in the sampling approach.

Next, the occurrence of elevated percentage deviations within a sample pair was investigated to determine whether one of the matched pair was consistently elevated over the other. For example, were all metal levels reported for one sample elevated over the other sample? If greater than 80% of the measured parameters did not agree then the samples were resubmitted for analysis.

This QC approach allows any variation in the sampling approach to be addressed and ensures that the quality of the data used is high.

E-2.8.4 Data Handling and Transmission

All data was entered into Excel spreadsheets and triple checked by separate persons to alleviate transmission errors. Where possible the data was received from the laboratory in an Excel format so that actual transmission was not duplicated. Data was reported to 3 significant figures. When whole numbers were required levels reported below the detection limit were entered as half of the MDL value.

E-2.9 Data Screening

For the purpose of data interpretation it is desirable to be able to compare results with regulatory criteria or other guidelines. In the case of the total metal levels in soil, well established screening criteria have been developed by the MOE (*Guidelines for Contaminated Sites in Ontario*, 1997). Similar guidance values have not been developed for produce vegetables or fruit. A literature search was conducted which revealed that there is a paucity of vegetable-specific screening criteria available from any regulatory

agency. Despite this, it was considered necessary to determine whether the levels of COC (As, Co, Cu, Pb, Ni and Se) in the vegetables collected in Sudbury posed an immediate potential human health risk to residents who were consuming them. 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)
- Above-ground vegetables (*e.g.* cucumbers, lettuce, tomatoes, zucchini)
- Fruit (*e.g.* black currants, blackberries, blueberries, raspberries, strawberries)
- Wild mushrooms (the above-ground vegetable criteria were used)

Different consumption rates are assumed for the different categories. Table E2.3 summarizes the screening criteria for metal levels in vegetables that were developed by the SARA Group. These levels are indicative of an extremely safe scenario and are based on a one in a million increase in risk of systemic disease to a resident whose diet is comprised of 10% home garden sources for the entire growing season.

Table E2.3 Vegetable Garden Screening Levels (µg/g wet weight).

Category	Nickel	Lead	Cobalt	Copper	Selenium	Arsenic ^{nc}	Arsenic ^c
Below-ground Vegetables	9.0	0.8	9.0	18.0	2.3	0.1	0.01
Above-ground Vegetables	13.3	1.2	13.3	26.6	3.3	0.2	0.01
Fruit	10.1	0.9	10.1	20.3	2.5	0.2	0.01

nc = non cancer risk

c = cancer risk

The screening values provided in Table E2.3 address both the systemic (non-cancer) and cancer approach; for this reason there are two screening values for arsenic.

The derivation of the specific values used in calculating the screening criterion (µg/g) for each COC is shown in more detail in Sub Appendix E-I. Screening criteria were calculated using the following equation:

$$\text{Screening criterion } (\mu\text{g/g}) = \frac{\text{RfD/RSD } (\mu\text{g/kg/day}) \times \text{bodyweight (kg)}}{\text{Consumption rate (g/day)} \times \text{Amortization factor} \times \text{Allocation factor}}$$

Chemicals that give rise to toxic endpoints other than cancer and gene mutations are referred to as systemic toxicants because of their effects on the function of various organ systems. The majority of the COC, with the exception of arsenic, are not known to be carcinogenic via the ingestion pathway. The reference dose (RfD) is the maximum allowable daily dose of a toxicant that causes systemic effects, the RfD is available for all of the COC. Oral RfDs are based on the assumption that thresholds exist for certain toxic effects. In general, the RfD is an estimate (with uncertainty spanning an order of magnitude) of a daily exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a lifetime. RfDs can be derived to address the non-carcinogenic health effects of a substance that is also a carcinogen (such as arsenic). The oral RfDs used in the calculations for the vegetable screening levels are provided in Sub Appendix E-I.

When a chemical is considered carcinogenic, an oral slope factor is used to determine the calculated Risk Specific Dose (RSD). The slope factor is the result of the application of a low-dose extrapolation procedure and is presented as the risk (mg/kg) per day. In the case of arsenic, the US Environmental Protection Agency (EPA) slope factor was derived from literature documenting an increase in lung cancer mortality observed in multiple human populations which were exposed primarily through inhalation, increased mortality from multiple internal organ cancers (liver, kidney, lung, and bladder), and an increased incidence of skin cancer observed in populations consuming drinking water high in inorganic arsenic. The slope factor that was used in the calculation of the cancer arsenic screening level is provided in Sub Appendix E-I.

The method used to compare the measured values to the screening values and to produce a preliminary estimate of hazard was calculated by the Quotient Method and is shown in the following equation:

$$Q = \frac{\text{Measured Concentration in Produce}}{\text{Screening Value}}$$

If the Q value is >1 then the value indicates that the concentration in at least one vegetable from the category exceeded the screening criterion value. If the Q <1 then it indicates that all collected vegetables for the category were below the criterion value. Therefore, no immediate risk is estimated and the produce category does not require further evaluation at this stage of the study

E-3.0 RESULTS

E-3.1 Sample Location and Schedule

In total, 64 residential gardens were sampled along with 15 commercial and 10 wild plant sites. Sub Appendix E-C provides the easting and northing coordinates for all areas sampled in the vegetable garden survey. All produce samples were collected between June and September, 2003.

E-3.2 Number of Samples

Soil samples were collected at two depths: 0-15 cm and 15-30 cm. At the 0-15 cm depth, 104 samples were collected, where 70 were collected from residential gardens, 24 from commercial fields and 10 from wild plant sites. At the 15-30 cm depth, 100 samples were collected, 70 samples from residential gardens, 24 from commercial fields and 6 from wild plant sites.

Table E3.1 summarizes the vegetable types and quantities collected from the residential gardens, while Table E3.2 and Table E3.3 summarize the commercial and wild plant sites, respectively. A total of 272 vegetables and fruits were analyzed for total metal content from residential gardens in the Sudbury area (Table 3.1).

Table E3.1 Vegetable Type and Quantities for Residential Gardens

Sample Type	Total Sampled	Sample Type	Total Sampled
Beans	8	Lettuce	35
Beet Tops	6	Onion Tops	6
Beets	17	Onions	17
Black Currents	1	Parsley	1
Black Berries	1	Peas	2
Cabbage	2	Peppers	1
Carrots	16	Potatoes	29
Celery	1	Radicchio	2
Chives	3	Radishes	3
Corn	1	Raspberries	3
Cucumbers	31	Rhubarb	7
Currents	1	Squash	5
Eggplant	1	Swiss chard	5
Garlic	2	Tomatoes	44
Horseradish	1	Turnip	2
Lambs quarters	1	Zucchini	17

A total of 34 vegetables and fruits were analyzed for total metal content from commercial sites in the Sudbury area.

Table E3.2 Vegetable Type and Quantities for Commercial Sites

Sample Produce	Total Sampled
Beets	1
Broccoli	1
Cabbage	3
Cucumbers	3
Green Beans	1
Lettuce	2
Onions	1
Potatoes	8
Raspberries	2
Squash	3
Strawberries	4
Tomatoes	2
Turnip	2
Zucchini	1

A total of 10 blueberries or mushroom samples were collected from the 10 wild plant sites. None of the wild sites contained both blueberries and mushrooms as they grow under different conditions.

Table E3.3 Vegetable Type and Quantities for Wild Plant Sites

Sample Produce	Total Sampled
Blueberries	7
Mushrooms	3

E-3.3 Soil Physical and Chemical Characteristics

The 0-15 cm layer of the vegetable garden soils were analyzed for inorganic, organic and total carbon, as well as particle size distribution, pH, calcium carbonate equivalence, bulk density, and fertility (details found in Sub Appendix E-F). The results of the analysis are contained in Sub Appendix E-J, and are summarized in the following sections for residential soils (Table E3.4), commercial soils (Table E3.5) and wild plant sites (Table E3.6). The soil textures for all sites are presented together in Table E3.7.

In the residential soils (Table E3.4), pH ranged from 5.1 to 7.9, where the mean pH was 6.7. These values are typically higher than those found in the natural environment and would suggest the addition of liming amendments. Total carbon ranged from 1.37 to 22.7% dry soil, while organic and inorganic carbon ranged from 1.37 – 22.51%, and 0 – 1.27 % dry soil, respectively. Magnesium, phosphorous and potassium all ranged widely in the residential soil indicating the different fertility practices of the residents of Sudbury. Bulk density varied from 0.46 to 1.32 g/cm³, with an average of 0.886 g/cm³. This variance shows the heterogeneous nature of the garden soils, and difference in the degree of compaction.

Table E3.4 Summary of Soil Physical and Chemical Properties in Residential Gardens

Parameter	Units	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence of Mean	Upper 95th Percentile
pH	pH	70	5.1-7.9	6.7	0.6	0.14	7.4
Inorganic Carbon	% dry	70	0-1.27	0.3	0.3	0.06	0.71
Organic Carbon	% dry	70	1.37-22.51	5.6	3.8	0.90	11.0
Total Carbon	% dry	70	1.37-22.7	5.9	3.8	0.91	11.3
Magnesium	mg/L soil	70	122-697	294.6	108.1	26.0	460.2
Phosphorous	mg/L soil	70	13-266	92.2	62.2	14.8	199.9
Potassium	mg/L soil	70	30-916	233.8	154.4	36.8	460.6
Bulk Density	g/cm ³	69 ^(a)	0.5-1.3	0.9	0.2	0.05	1.22

^(a) one bulk density not collected

Table E3.5 summarizes the chemical and physical properties of the commercial soils. Soil pH ranged from 4.2 to 7.0 with a mean value of 5.59. Total carbon ranged from 1.16 to 3.72% dry soil, while organic and inorganic carbon varied between 1.16 – 3.72% and 0 – 0.07% dry soil, respectively. Once again magnesium, phosphorous and potassium values varied widely throughout the different soils, where mean values were 133.04, 50.04 and 148.63 mg/L soil, respectively. Bulk density ranged from 0.83 to 1.33 g/cm³.

Table E3.5 Summary of Commercial Site Soil Physical and Chemical Properties

Parameter	Units	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence of Mean	Upper 95th Percentile
PH	pH	24	4.2-7	5.6	0.10	0.40	6.9
Inorganic Carbon	% dry	24	0-0.07	0.005	0.02	0.007	0.04
Organic Carbon	% dry	24	1.16-3.7	2.2	0.60	0.23	2.9
Total Carbon	% dry	24	1.16-3.7	2.2	0.6	0.23	2.9
Magnesium	mg/L soil	24	32-308	133.0	85.0	33.9	282.9
Phosphorous	mg/L soil	24	12-139	50.0	33.5	14.14	119.7
Potassium	mg/L soil	24	31-322	148.6	75.8	32.01	294.8
Bulk Density	g/cm ³	23 ^(a)	0.8-1.3	1.1	0.1	0.06	1.3

^(a) one bulk density not collected

Ten soils were sampled as part of the wild plant sites (Table E3.6), where the pH ranged from 4 to 5.2 with a mean value of 4.61. Total carbon varied from 1.09 to 21.3% dry soil with organic and inorganic carbon values of 1.09 – 21.3%, and 0 – 0.09% dry soil, respectively. Mean magnesium, phosphorous and potassium values were 22.1, 18.1 and 45.9 mg/L of soil. Bulk density was taken for nine of the ten sites and ranged from 0.13 to 1.28 g/cm³.

Table E3.6 Summary of Wild Plant Site Soil Physical and Chemical Properties

Parameter	Units	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence of Mean	Upper 95th Percentile
PH	pH	10	4-5.2	4.61	0.32	0.201	5.02
Inorganic Carbon	% dry	10	0-0.09	0.001	0.03	0.019	0.07
Organic Carbon	% dry	10	1.09-21.3	5.85	5.91	3.66	15.03
Total Carbon	% dry	10	1.09-21.3	5.87	5.91	3.66	15.03
Magnesium	mg/L soil	10	5-58.0	22.1	14.86	9.21	48.10
Phosphorous	mg/L soil	10	9-42.0	18.1	11.33	7.02	38.85
Potassium	mg/L soil	10	16-68	45.9	17.46	10.85	67.55
Bulk Density	g/cm ³	10	0.13-1.28	0.57	0.44	0.29	1.24

Table E3.7 summarizes the soil textures of all soil samples collected during the vegetable garden study. The majority of the soils collected from the residential sites were either fine sandy loam (n=15), loam (n=20) or silt loam (n=23). At the commercial sites half of the soils were silt loam textures (12), while the other 12 soils fell under the categories of fine sandy loam (2), loam (1), loamy fine sand (3), silt (5) and very fine sandy loam (1). The soils from the wild sites varied from silt loam (n=4) to loamy fine sand (n=2), loamy sand (n=2).

Table E3.7 Summary of Soil Textures for the Vegetable Garden Soils

Soil Type	Total Sampled	Clay Loam	Fine Sandy Loam	Loam	Loamy Fine Sand	Loamy Sand	Sandy Loam	Silt	Silt Loam	Silty Clay Loam	Very Fine Sandy Loam
Residential	70	1	15	20	1	0	2	1	23	2	3
Commercial	24	0	2	1	3	0	0	5	12	0	1
Wild Plant	10	0	0	1	2	2	0	0	4	0	1

E-3.4 Soil Metal Concentrations

Sub Appendix E-K contains the full analytical results of the metal concentrations measured in the soil samples collected during the vegetable garden survey. In the following sections, the concentrations of COC in the soil samples are presented and discussed.

E-3.4.1 Arsenic

Table E3.8 summarizes the arsenic concentrations in the vegetable garden soils. In the residential soils, arsenic concentrations varied from below detection to 173 µg/g in the 0 – 15 cm layer, and below detection to 136 µg/g in the 15 – 30 cm layer. The mean concentrations for the two layers were 13.51 and 13.35 µg/g respectively.

The commercial soils had lower arsenic concentrations, which varied from below detection to 14.7 µg/g in the 0 – 15 cm layer, and below detection to 10.6 µg/g in the 15 – 30 cm layer. Mean concentrations were found to be 5.10 and 4.56 µg/g respectively.

The wild plant sites had arsenic concentrations of 5.7 to 36.5 µg/g in the 0 – 15 cm layer and 2.4 to 14.1 µg/g in the 15 – 30 cm layer. Mean concentrations were 18 and 6.13 µg/g respectively in the two layers.

Table E3.8 Summary of Arsenic Concentrations in Soil ($\mu\text{g/g}$ dry weight)

	Depth (cm)	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence on Mean	Upper 95th Percentile
Residential	0-15	70	<dl-173	13.64	23.91	5.61	34.86
	15-30	70	<dl-136	13.44	20.71	4.79	35.84
Commercial	0-15	24	<dl-14.7	5.10	3.30	1.32	9.30
	15-30	24	<dl-10.6	4.56	2.66	1.06	8.71
Wild Plant	0-15	10	5.7-36.5	18.00	10.05	6.23	33.58
	15-30	6 ^(a)	2.4-14.1	6.13	4.28	3.42	12.08

^(a) Four 15-30 cm samples were not collected

dl = Detection Limit

Approximate detection limit for As = 0.5 $\mu\text{g/g}$ dry weight

E-3.4.2 Cobalt

Table E3.9 shows that cobalt concentrations in the top 15 cm of residential soils ranged from 4 to 56 $\mu\text{g/g}$ with a mean of 12.6 $\mu\text{g/g}$. In the 15 – 30 cm layer concentrations varied from 3.8 to 40 $\mu\text{g/g}$ with a mean of 11.78 $\mu\text{g/g}$. The commercial soils had relatively lower concentrations with a range of 2.8 – 11 $\mu\text{g/g}$ in the 0 – 15 cm layer and 3 – 12 $\mu\text{g/g}$ in the 15 – 30 cm layer. The mean cobalt concentrations were 5.29 and 5.47 $\mu\text{g/g}$ in the respective layers.

The wild plant sites had similar concentrations to the commercial soils with a range of 3 – 15 $\mu\text{g/g}$ in the 0 – 15 cm layer and 4 – 7 $\mu\text{g/g}$ in the 15 – 30 cm layer. Mean values were 9.35 and 6 $\mu\text{g/g}$ in the two layers, respectively.

Table E3.9 Summary of Cobalt Concentrations in Soil ($\mu\text{g/g}$ dry weight)

	Depth (cm)	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence on Mean	Upper 95th Percentile
Residential	0-15	70	4.0-56	12.60	9.90	2.34	31.00
	15-30	70	3.8-40	11.78	8.02	1.86	28.00
Commercial	0-15	24	2.8-11	5.29	1.91	0.76	8.85
	15-30	24	3.0-12	5.47	2.33	0.93	9.85
Wild Plant	0-15	10	3.0-15	9.35	3.88	2.40	15.00
	15-30	6 ^(a)	4.0-7	6.00	1.26	1.01	7.00

^a Four 15-30 cm samples were not collected

Approximate detection limit for Co = 1 $\mu\text{g/g}$ dry weight

E-3.4.3 Copper

Copper concentrations ranged from 21 to 1170 µg/g (Table E3.10) in the 0 -15 cm layer of the residential soil, where the mean concentration was 200.1 µg/g. In the 15 – 30 cm depth, the concentrations varied from 16 to 1200 µg/g with a mean of 170.54 µg/g. At the commercial sites the concentration in the 0 – 15 cm layer was 6 to 110 µg/g and in the 15 – 30 cm layer the range was 8 to 110 µg/g. Mean concentrations were found to be 29.25 µg/g for the 0 – 15 cm range and 29.88 µg/g for the 15 – 30 cm depth.

At the wild plant sites, concentrations ranged between 38 and 440 µg/g in the 0 – 15 cm layer, and 9 to 91 µg/g in the 15 – 30 cm depth. Mean concentrations were 215.6 µg/g and 54.83 µg/g, respectively for the two depths.

Table E3.10 Summary of Copper Concentrations in Soil (µg/g dry weight)

	Depth (cm)	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence on Mean	Upper 95th Percentile
Residential	0-15	70	21-1170	200.10	254.12	59.96	808.00
	15-30	70	16-1200	170.54	204.06	47.47	545.00
Commercial	0-15	24	6-110	29.25	22.58	9.03	70.20
	15-30	24	8-110	29.88	24.67	9.87	84.45
Wild Plant	0-15	10	38-440	215.60	127.83	79.23	413.00
	15-30	6 ^(a)	9.0-91	54.83	36.04	28.84	90.75

^(a) Four 15-30 cm samples were not collected

Approximate detection limit for Cu = 1 µg/g dry weight

E-3.4.4 Lead

Table E3.11 summarizes the lead concentrations found in the three sample types. For the residential soil, lead concentrations ranged from 5.9 to 520 µg/g in the 0 – 15 cm layer, and 4.3 to 310 µg/g in the 15 – 30 cm layer. The mean concentrations were 51.36 µg/g and 37.61 µg/g, respectively. In the commercial soil, concentrations were lower and varied from 6.2 to 35 µg/g in the 0 – 15 cm layer, and 5.5 to 44 µg/g in the 15 – 30 cm layer. As a result the mean concentrations were lower and were 10.31 µg/g and 9.49 µg/g for the two depths. The wild plant site soils had concentrations that ranged from 10 to 79 µg/g in the top 15 cm and 3.8 to 12 µg/g in the lower. The mean concentrations were 33.2 µg/g for the 0 – 15 cm layer and 7.07 µg/g for the 15 – 30 cm layer.

Table E3.11 Summary of Lead Concentrations in Soil ($\mu\text{g/g}$ dry weight)

	Depth (cm)	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence on Mean	Upper 95th Percentile
Residential	0-15	70	5.9-520	51.36	90.44	21.34	171.00
	15-30	70	4.3-310	37.61	49.93	11.61	120.00
Commercial	0-15	24	6.2-35	10.31	5.67	2.27	14.85
	15-30	24	5.5-44	9.49	7.55	3.02	11.00
Wild Plant	0-15	10	10.0-79	33.20	23.54	14.59	70.00
	15-30	6 ^(a)	3.8-12	7.07	2.94	2.36	11.18

^(a) Four 15-30 cm samples were not collected
 Approximate detection limit for Pb = 0.2 $\mu\text{g/g}$ dry weight

E-3.4.5 Nickel

Residential soil nickel concentrations ranged from 31 to 1100 $\mu\text{g/g}$ in the 0 – 15cm layer and from 22 to 1000 $\mu\text{g/g}$ in the 15 – 30 cm layer (Table E3.12). Mean concentrations were 218.03 $\mu\text{g/g}$ for the first 15 cm and 183.42 $\mu\text{g/g}$ for the second layer. Commercial soil nickel varied from 9 to 78 $\mu\text{g/g}$ in the top 15 cm and from 13 to 160 $\mu\text{g/g}$ in the 15 – 30 cm layer. The means for the two layers were 38.38 $\mu\text{g/g}$ and 39.25 $\mu\text{g/g}$, respectively. The wild plant site soils ranged from 38 to 400 $\mu\text{g/g}$ in the 0 – 15 cm layer and from 20 to 66 $\mu\text{g/g}$ in the 15 – 30 cm layer. The mean concentrations were 185.70 $\mu\text{g/g}$ and 43.67 $\mu\text{g/g}$, respectively.

Table E3.12 Summary of Nickel Concentrations in Soil ($\mu\text{g/g}$ dry weight)

	Depth (cm)	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence on Mean	Upper 95th Percentile
Residential	0-15	70	31-1100	218.03	250.65	59.14	782.00
	15-30	70	22-1000	183.42	185.45	43.14	560.00
Commercial	0-15	24	9.0-78	38.38	17.20	6.88	68.90
	15-30	24	13-160	39.25	29.27	11.71	78.00
Wild Plant	0-15	10	38-400	185.70	123.14	76.32	373.00
	15-30	6 ^(a)	20-66	43.67	19.02	15.22	65.75

^(a) Four 15-30 cm samples were not collected
 Approximate detection limit for Ni = 1 $\mu\text{g/g}$ dry weight

E-3.4.6 Selenium

Selenium concentrations ranged from below detection to 11 µg/g in the 0 – 15 cm of the residential soils (Table E3.13). In the 15 – 30 cm layer the concentrations ranged from below detection to 13 µg/g. Means of 1.95 µg/g and 1.96 µg/g were observed for the two respective layers. In the commercial soils, concentrations ranged from below detection to 2.1 µg/g in the top 15 cm, and below detection to 2.2 µg/g in the 15 – 30 cm layer. The mean concentrations for the commercial soil were 0.94 µg/g and 0.96 µg/g for the 0 -15 cm and 15 – 30 cm layers respectively. The wild plant site soils had similar concentrations with ranges of below detection to 3.5 µg/g in the 0 – 15 cm layer and below detection to 1.1 µg/g in the 15 – 30 cm layer.

Table E3.13 Summary of Selenium Concentrations in Soil (µg/g dry weight).

	Depth (cm)	Total Sampled (n)	Range	Mean	Standard Deviation	95% Confidence on Mean	Upper 95th Percentile
Residential	0-15	70	<dl-11	1.95	1.78	0.42	4.83
	15-30	70	<dl-13	1.96	2.08	0.48	4.96
Commercial	0-15	24	<dl-2.1	0.94	0.56	0.22	1.92
	15-30	24	<dl-2.2	0.96	0.62	0.25	1.93
Wild Plant	0-15	10	<dl-3.5	2.41	0.87	0.54	3.50
	15-30	6 ^(a)	<dl-1.10	0.95	0.21	0.17	1.09

^(a) Four 15-30 cm samples were not collected

dl = Detection Limit

Approximate detection limit for Se = 0.5 µg/g dry weight

E-3.5 Vegetable and Fruit Metal Concentrations

An electronic database containing the total metal concentrations in vegetables and fruit collected during the vegetable garden survey is provided in Sub Appendix E-H. The data are summarized (wet and dry weight) in Sub Appendix E-L.

Sections E-3.5.1 through E-3.5.3 describe the vegetable and fruit metal results. The results are presented from the various sampling areas (residential, commercial and wild sites) and are split into the different produce categories (above-ground vegetables, below ground vegetables and fruit) which were determined by the developed vegetable screening criteria. A description of these categories was provided earlier in Section 1.9. Only the wet weight concentrations are discussed in detail in this report. The wet weight values are most relevant for human consumption and are the values used in the HHRA.

There is a degree of uncertainty surrounding the arsenic levels in the produce as a result of the achievable detection limits, a discussion of these issues are provided in Section 6.6.4. The arsenic results obtained are presented but must only be used with full knowledge of the analytical limitations.

E-3.5.1 Residential Garden Vegetables and Fruits

Table E3.14 summarizes the above-ground vegetable metal concentrations for the residential sites. Arsenic concentrations ranged from 0.0055 to 0.142 $\mu\text{g/g}$ with a mean of 0.026 $\mu\text{g/g}$. Cobalt concentrations were found in the same range and varied from 0.007 to 0.364 $\mu\text{g/g}$, where the mean was 0.0449 $\mu\text{g/g}$. Copper and nickel had higher concentrations and ranged from 0.147 to 2.54 $\mu\text{g/g}$ for copper and from 0.035 to 5.28 $\mu\text{g/g}$ for nickel. Mean concentrations were 0.59 $\mu\text{g/g}$ and 0.781 $\mu\text{g/g}$ respectively. Lead concentrations ranged from 0.008 to 0.73 $\mu\text{g/g}$, while selenium concentrations were in the range of 0.004 to 1.6 $\mu\text{g/g}$.

Table E3.14 Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Above-Ground Residential Vegetables (n = 179)

	As	Co	Cu	Ni	Pb	Se
Range	0.0055-0.142	0.007-0.364	0.147-2.54	0.035-5.28	0.008-0.73	0.004-1.6
Mean	0.026	0.0449	0.59	0.781	0.0804	0.087
Standard Deviation	0.0241	0.055	0.441	0.883	0.103	0.223
95% Confidence on mean	0.00352	0.00803	0.0645	0.129	0.0151	0.0325
Upper 95th Percentile	0.687	0.136	1.43	2.56	0.271	0.361
Approximate detection limits $\mu\text{g/g}$ dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.						

Below-ground residential vegetables metal concentrations are summarized in Table E3.15. The concentrations for arsenic and cobalt were lower than those found in above-ground vegetables. For example, the maximum arsenic concentration was 0.0712 $\mu\text{g/g}$, as opposed to the above-ground value of 0.142 $\mu\text{g/g}$. Copper, nickel, lead and selenium concentrations were comparable to those found in the above ground vegetables where the means for the below ground vegetables were 0.915 $\mu\text{g/g}$, 0.784 $\mu\text{g/g}$, 0.112 $\mu\text{g/g}$ and 0.104 $\mu\text{g/g}$, respectively. The mean cobalt concentration was 0.0608 $\mu\text{g/g}$, which is higher than the corresponding above-ground concentration.

Table E3.15 Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Below-Ground Residential Vegetables (n = 87).

	As	Co	Cu	Ni	Pb	Se
Range	0.0198-0.0712	0.0187-0.164	0.136-2.42	0.0609-4.93	0.0176-0.674	0.0109-1.682
Mean	0.0369	0.0608	0.915	0.784	0.112	0.104
Standard Deviation	0.0186	0.0456	0.489	0.771	0.131	0.287
95% Confidence on mean	0.00395	0.0097	0.104	0.164	0.0279	0.0611
Upper 95th Percentile	0.0676	0.15	1.78	2.31	0.278	0.191

Approximate detection limits $\mu\text{g/g}$ dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.

Residential fruits had the lowest metal concentrations of the three area groupings (Table E3.16), where arsenic and cobalt concentrations were below detection for all samples and only one sample had a detectable selenium concentration (0.0582 $\mu\text{g/g}$). Copper, nickel and lead concentrations were in the ranges of 0.433 to 0.903 $\mu\text{g/g}$; 0.402 to 2.986 $\mu\text{g/g}$ and 0.0263 to 0.0813 $\mu\text{g/g}$, respectively.

Table E3.16 Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Residential fruits (n = 6).

	As	Co	Cu	Ni	Pb	Se
Range	<dl	<dl	0.433-0.903	0.402-2.986	0.0263-0.0813	0.0582
Mean	<dl	<dl	0.694	1.624	0.0516	0.0582
Standard Deviation	na	na	0.187	0.923	0.0278	na
95% Confidence on mean	na	na	0.149	0.739	0.0222	na
Upper 95th Percentile	na	na	0.895	2.931	0.0779	na

dl = Detection limit

na = Not Applicable

Approximate detection limits $\mu\text{g/g}$ dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.

E-3.5.2 Commercial Vegetables and Fruits

Metal concentrations in above ground commercial vegetables (Table E3.17) were generally lower than levels in residential above ground vegetables (Table E3.14). For example, copper had a maximum concentration of 2.54 $\mu\text{g/g}$ in the residential vegetables, and only 0.905 $\mu\text{g/g}$ in the commercial vegetables. The maximum concentrations of arsenic, cobalt, nickel, lead and selenium were 0.0289 $\mu\text{g/g}$, 0.199 $\mu\text{g/g}$, 3.909 $\mu\text{g/g}$, 0.518 $\mu\text{g/g}$, and below detection, respectively.

Table E3.17 Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Above-Ground Commercial Vegetables (n = 18)

	As	Co	Cu	Ni	Pb	Se
Range	0.006-0.0289	0.018-0.199	0.2-0.905	0.081-3.909	0.036-0.518	<dl
Mean	0.0186	0.053	0.458	1.255	0.127	<dl
Standard Deviation	0.010	0.051	0.234	1.067	0.135	na
95% Confidence on mean	0.045	0.0234	0.108	0.493	0.0623	na
Upper 95th Percentile	0.0283	0.0554	0.749	2.26	0.252	na

dl = Detection limit

na = Not Applicable

Approximate detection limits $\mu\text{g/g}$ dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.

Below-ground commercial vegetables, like the above-ground commercial vegetables, had concentrations that were less than the corresponding residential vegetables. Table E3.18 shows that the maximum concentrations of cobalt, copper, nickel, lead and selenium were 0.102 $\mu\text{g/g}$, 1.52 $\mu\text{g/g}$, 1.76 $\mu\text{g/g}$, 0.139 $\mu\text{g/g}$, and 0.0759 $\mu\text{g/g}$ respectively, where arsenic concentrations were below detection limits. The mean value for arsenic was below detection; cobalt: 0.0616 $\mu\text{g/g}$; copper: 0.983 $\mu\text{g/g}$; nickel: 0.988 $\mu\text{g/g}$; lead: 0.0928 $\mu\text{g/g}$ and selenium: 0.0591 $\mu\text{g/g}$.

Table E3.18 Summary of Metal Concentrations ($\mu\text{g/g}$, wet weight) in Below-Ground Commercial Vegetables (n = 12).

	As	Co	Cu	Ni	Pb	Se
Range	<dl	0.0419-0.102	0.320-1.52	0.379-1.76	0.0587-0.139	0.0422-0.0759
Mean	<dl	0.0616	0.983	0.988	0.0928	0.0591
Standard Deviation	na	0.0245	0.376	0.539	0.0318	0.0238
95% Confidence on mean	na	0.0196	0.301	0.431	0.0254	0.0191
Upper 95th Percentile	na	0.0939	1.427	1.69	0.133	0.0742

dl = Detection limit

na = Not Applicable

Approximate detection limits $\mu\text{g/g}$ dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.

Table E3.19 shows that similar to the residential gardens, the fruits had the lowest metal concentrations of the three plant types from commercial sites. Again, only copper and nickel levels were above the detection limits. The maximum concentrations of copper and nickel found in the residential fruits were

0.569 µg/g and 1.199 µg/g respectively, with mean concentrations of 0.377 µg/g for copper and 0.436 µg/g for nickel.

Table E3.19 Summary of Metal Concentrations (µg/g, wet weight) in Commercial Fruits (n = 6).

	As	Co	Cu	Ni	Pb	Se
Range	<dl	<dl	0.238-0.569	0.0645-1.199	<dl	<dl
Mean	<dl	<dl	0.377	0.436	<dl	<dl
Standard Deviation	na	na	0.115	0.448	na	na
95% Confidence on mean	na	na	0.0923	0.358	na	na
Upper 95th Percentile	na	na	0.53	1.045	na	na

dl = Detection limit

na = Not Applicable

Approximate detection limits µg/g dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.

E-3.5.3 Wild Blueberries and Mushrooms

Wild blueberries had concentrations of arsenic, cobalt and selenium that were below detection limits (Table E3.20), with only one sample with a detectable lead value of 0.1 µg/g. Copper and nickel concentrations ranged from 0.2 to 0.7 µg/g and 0.3 to 0.6 µg/g, respectively. The concentration for both copper and nickel was 0.4 µg/g.

Table E3.20 Summary of Metal Concentrations (µg/g, wet weights) in Wild Blueberries (n = 7).

	As	Co	Cu	Ni	Pb	Se
Range	<dl	<dl	0.2-0.7	0.3-0.6	<dl-0.1	<dl
Mean	<dl	<dl	0.4	0.4	<dl	<dl
Standard Deviation	na	na	0.169	0.119	na	na
95% Confidence on mean	na	na	0.135	0.095	na	na
Upper 95th Percentile	na	na	0.664	0.589	na	na

dl = Detection limit

na = Not Applicable

Approximate detection limits µg/g dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.

Table E3.21 summarizes the metal concentrations found in wild mushrooms. The metal concentrations were among some of the highest values measured in the study, however, only three samples were collected. Arsenic ranged from 0.0898 to 0.295 $\mu\text{g/g}$, where the mean was 0.184 $\mu\text{g/g}$. The maximum cobalt concentration was 0.0856 $\mu\text{g/g}$, with a mean of 0.0627 $\mu\text{g/g}$. Copper and nickel had mean concentrations of 3.407 $\mu\text{g/g}$ and 1.475 $\mu\text{g/g}$ respectively. Lead concentrations were similar to arsenic, where the mean value was 0.161 $\mu\text{g/g}$. Selenium concentrations ranged from 0.616 to 1.265 $\mu\text{g/g}$.

Table E3.21 Summary of Metal Concentrations ($\mu\text{g/g}$, wet weights) in Wild Mushrooms (n = 3).

	As	Co	Cu	Ni	Pb	Se
Range	0.0898-0.295	0.0422-0.0856	2.881-4.429	1.264-1.876	0.103-0.244	0.616-1.265
Mean	0.184	0.0627	3.407	1.475	0.161	0.984
Standard Deviation	0.103	0.0218	0.885	0.347	0.017	0.333
95% Confidence on mean	0.117	0.0247	1.002	0.393	0.0924	0.377
Upper 95th Percentile	0.282	0.083	4.248	1.817	0.242	1.246

Approximate detection limits $\mu\text{g/g}$ dry weight As: 0.2, Co: 0.2, Cu: 0.5, Ni: 0.5, Pb: 0.5, Se: 0.2.

E-3.6 QC Results

Numerous QA/QC procedures, as described in Sub Appendix E-N, were undertaken to ensure the quality of the data from the vegetable garden study. The QC samples including: internal laboratory split sample analysis; SRMs; field duplicates (soil) and field split (produce) samples were analyzed to determine the degree of variability. The QC performed by each of the laboratories is contained within the individual reports, or is available from the laboratory. Each of the laboratories used undertook a vigorous internal QC regime to ensure there is confidence in the quality of the analysis provided. To assess the degree of variability arising from the sampling methods the relative percentage deviation (RPD) between the soil samples and the produce samples was assessed. The procedure used and an explanation of the approach to analyzing this variation is provided in Section 2.8.3. The results of this analysis are provided in the following sections for the COC, the complete results for all elements analysed are provided in Sub Appendix E-N and Sub Appendix E-O.

Field Duplicate Soil Samples

Field duplicates were taken for all soil samples, but only submitted for analysis for 10% of all samples. The following sections present the results of a comparison between original and duplicate samples for the COC. The results show that the level of variability between the paired samples was within acceptable range.

0-15 cm Soil Samples

For the 0-15 cm soil layer a total of 11 duplicate samples were submitted for analysis of total metals. Table E3.22 shows the RPD for each of the six COC between the paired duplicate samples submitted for the 0-15 cm soil layer.

Table E3.22 Summary of 0-15 cm Soil Field Duplicates

Metal	As	Co	Cu	Ni	Pb	Se
Number of samples <20% difference	9	10	10	10	9	5
Number of samples 20-30% difference	0	1	1	1	1	3
Number of samples >30% difference	2	0	0	0	1	3
Total sample size (n)	11	11	11	11	11	11
Percentage of values <30%	81.0%	100.0%	100.0%	100.0%	90.9%	72.7%

The RPD analysis confirmed that the paired field duplicate samples were all within an acceptable range of variability. This information allows confidence to be placed in the analysis of the metal levels in the 0-15 cm soil samples. The details involved with this analysis are discussed in the following sections.

The RPD for cobalt, copper and nickel percent differences were all below 30%, while arsenic had two pairs and lead had one pair of samples that had a percent difference above 30%. Selenium values tended to differ by a larger degree, due to the fact that selenium concentrations were near detection limits and, therefore, more difficult to duplicate.

The treatment of percent difference values from the QAQC approach developed for the Port Colborne risk assessment (Jacques Whitford Environmental Limited, 2002) were followed for this study. This approach involves excluding any values less than three times the MDL from QAQC process with the rationale that these values are variable due to the limits of instrument sensitivity. Using this approach two original/duplicate sample pairs containing arsenic concentrations (MDL = 5 µg/g) with percent differences greater than 30%, and three samples with selenium concentrations (MDL = 0.5 µg/g) were no

longer a cause for concern in the QC analysis. The single sample pair containing lead (no MDL available) with a percent difference of 40% (30 and 45 µg/g) is sufficiently below the Table F value of 120 µg/g, and can, therefore, be considered to represent acceptable variability.

15-30 cm Soil Samples

The RPD between the paired duplicate samples for the 15-30 cm soils are summarized in Table E3.23. The majority of the sample pairs had an RPD which was below 30%. Specifically: arsenic had 80% of the sample pairs with a RPD below 30%; lead and selenium had 90% of the sample pairs with a RPD below 30% and cobalt, copper and nickel had an RPD below 30% for all samples. Following the QAQC protocol from Port Colbourne study, (excluding any values <3xMDL from QA/QC) the two original and duplicate pairs containing As >30% (MDL=5 µg/g) were excluded from further concern in the QC analysis. This left a single original and duplicate pair which contained a RPD of cobalt which was marginally in excess at 37.6% (concentrations of 8.2 µg/g, 12 µg/g) (no MDL available). This value was much lower than the Table F value for Co (21 µg/g). The single original and duplicate pair which contained a percent difference in copper of 43.1% (concentrations of 110 µg/g, 71 µg/g) (no MDL available) was close to the Table F value for Cu (85 µg/g). The single original and duplicate pair containing a percent difference in nickel of 56.4% (concentrations of 28 µg/g, 50 µg/g) (no MDL available) was close to the Table F value for Ni (43 µg/g). The two original and duplicate pairs containing a percent difference in lead of 46.2% and 40% (concentrations of 10 µg/g, 16 µg/g and 42 µg/g, 28 µg/g) (no MDL available) was much lower than the Table F value for Pb (120 µg/g). The two original and duplicate pair pairs containing a percent difference in selenium of 111.1% and 62.1% (concentrations of 2.1 µg/g, 0.6 µg/g and 1.9 µg/g, 1 µg/g) (MDL=0.5) was close to the Table F value for Se (1.9 µg/g).

Table E3.23 Summary of Percent Difference between 15-30 cm soil field duplicates

Metal	As	Co	Cu	Ni	Pb	Se
Number of samples <20% difference	5	8	7	7	8	7
Number of samples 20-30% difference	3	1	2	2	0	1
Number of samples >30% difference	2	1	1	1	2	2
Total sample size (n)	10	10	10	10	10	10
Percentage of values <30%	70.0%	90.0%	90.0%	90.0%	80.0%	80.0%

E-3.6.1 Split Produce Samples

As described in the methods section, the split produce samples were used to determine the variability between split samples which were treated identically (processed at LRS and analyzed at SGS LR) and samples which were processed at different laboratories but digested and analyzed at the same laboratory. The first scenario is testing the variability in the analytical method and the second is testing the variability introduced during the processing.

Variability in Analytical Method

A comparison of the split produce samples which were processed at LRS and analyzed at SGS LR were compared to determine the variability in the analytical method. The analysis percent difference between these samples is shown in Sub Appendix E-O. This analysis shows the amount of variability in the results as a result of the analytical method is low and confirms that the analytical method preformed well.

Variability in Processing

Half of the split produce sample was processed at SGS LR and half processed was processed at LRS. The purpose of this was to assess whether the processing procedure was introducing any metal contamination. If present, the contamination would likely appear as a single contaminant consistently elevated in all paired samples. The comparison of the split samples that underwent differing processing revealed that there were no inconsistencies or anomalous values in the paired samples. The processing phase did not introduce any additional metal contamination to the samples.

E-3.6.2 Standard Reference Material**San Joaquin Soil**

A summary of the results for the soil SRM analyzed for quality assurance purposes are presented in Table E3.24 and the detailed analysis is shown in Sub Appendix E-N. The soil SRM used was San Joaquin Soil (Standard Reference Material 2709, certificate provided in Sub Appendix E-N), which was submitted for analysis in triplicate to SGS Lakefield. The mean percent difference between the triplicates for each of the COC was below 30% showing that the analytical technique produced little variability between triplicate samples.

The percent of each metal recovered was determined by comparing the certified metal levels in the SRM with the analyzed levels. The mean percent recoveries for each of the COC are shown in Table E3.24. The amount of material recovered varied between 63.5% for Pb to 75.9% for As.

Table E3.24 Mean Percent Difference and Percent Recovery for San Joaquin Soil SRM (n = 3 replicates)

Metal	As	Co	Cu	Ni	Pb	Se
Mean percent difference	4.6%	2.7%	2.7%	2.2%	0.0%	5.8%
Mean percent recovery	75.9%	71.3%	72.6%	70.1%	63.5%	72.2%

Spinach Leaves

The spinach leaves SRM (Standard Reference Material 1570a, certificate provided in Sub Appendix E-N) were analyzed in triplicate by SGS Lakefield. The spinach SRM results revealed with the exception of arsenic the analysis of the COC in plant tissue produced results which were within the range expected, these results are discussed in more detail below and are presented in Table E3.25. When the SRM results were first received from SGS (CA 10499-MAY05, received July 25, 2005, report available in Sub Appendix E-N), the arsenic levels reported were variable and much higher than the arsenic value certified to be contained in the sample. The amount of arsenic certified to be in the sample (0.068 µg/g dry weight) is in fact below the minimum detection limit reported by the laboratory (0.2 µg/g dry weight). The laboratory was immediately contacted and the samples were reanalyzed for arsenic. The reissued results showed all samples to be below the detection limit for arsenic (report CA10388-JUL05, received July 29, 2005). This analysis cast a certain level of uncertainty over the reliability of the arsenic analysis in the vegetable samples. A description of the uncertainty surrounding the arsenic levels is discussed in greater detail in the section 3.6.4 along with additional steps taken by the SARA Group to reduce and address this uncertainty. In the following section the results of the QC analysis determining the percent difference between the triplicate spinach samples and the percent recovery of the COC were calculated using the reissued arsenic values.

The results for the plant tissue SRM analyzed for quality assurance purposes are presented in Table E3.25.

Table E3.25 Mean Percent Difference and Percent Recovery for Spinach Leaf SRM (n = 3)

Metal	As	Co	Cu	Ni	Pb	Se
Mean percent difference	0.0%	5.8%	0.0%	9.3%	16.1%	< MDL
Mean percent recovery	< MDL	92.9%	< MDL	99.7%	no CRM value	< MDL

The analysis shows the percent difference between the triplicate samples was low for the elements which had certified values the recovery of metals was within a satisfactory range.

E-3.6.3 Additional Analysis to Address Uncertainty Surrounding Arsenic Plant Tissue Concentrations

As described in the previous section the analysis of the spinach SRM produced anomalous results in terms of the concentration of arsenic reported. The laboratory was alerted to the problem and the explanation provided was that the anomalous reading had occurred because hydride analysis had been used to determine the arsenic levels rather than ICP-MS. In soils it is necessary to use hydride analysis at low concentrations because chlorine from the extraction interferes with the analysis, in plant tissue hydride analysis is not necessary and ICP-MS can be utilized. The CRM samples had been submitted with the request that total metal analysis be completed. No specific analytical approach was requested. This is the same request that accompanied all vegetable garden samples submitted. The laboratory assured the SARA Group that hydride analysis had not been used to determine the arsenic levels of the previously submitted vegetable garden samples. The laboratory reanalyzed the samples and all results for the triplicate CRM returned with the arsenic levels which were below the level of detection.

Although the reanalysis of the samples produced satisfactory results once the laboratory was alerted to the problem, a level of uncertainty now surrounded the arsenic levels reported in the plant tissue samples. To alleviate this uncertainty eight vegetable tissue samples from the 2003 Vegetable Garden Study which had previously been reported to contain levels of arsenic were split, relabelled and submitted for total metal analysis. These samples were split so some were submitted as duplicates and others were triplicates. All were relabelled so that the laboratory was not aware that they had previously analyzed these samples. The laboratory had no knowledge of what the previous reported arsenic levels in the samples were or that they were analyzing duplicates/triplicate samples.

The results from this analysis are presented Sub Appendix E-N. The laboratory report (CA10449-JUL05) refers to “Ground Plant Tissue 1-15”, these samples codes are not related to the original code allocated to the plant tissue sample during the 2003 Vegetable Garden Study. Table N.3 shows which samples were analyzed and presents the arsenic results in comparison to the original arsenic values obtained in 2003. QC analysis was performed on these samples as described in the following section.

Assessing the variability between the 2005 values

To ascertain whether the duplicate and triplicate samples submitted in 2005 had an acceptable level of variability the percent difference of the paired and triplicate samples were determined. Five samples were submitted in duplicate and one was submitted in triplicate. To achieve this: the homogenized vegetable mater was mixed and two (duplicate) or three (triplicate) aliquots were placed in new ziplock bags. The results of the percent difference analysis are shown in Table N-4. The results show that 2 of the 5 samples submitted in duplicate had a percent difference above 30%. A percent difference of this magnitude is not considered acceptable and the level of variability can be considered too high. For the sample submitted in triplicate two of the comparisons had a percent difference which was greater than 30% and the remaining comparison differed by 28%. These results indicate that the plant tissue reanalyzed in 2005 for arsenic did not achieve a satisfactory level of repeatability between split samples.

Assessing the variability between the 2003 and 2005 values

To ascertain whether the 2003 values were similar to the 2005 values the percent difference was calculated. These results are presented in Table N-5. The results show that out of 15 samples submitted for analysis 8 had a percent difference from the original value which was greater than 30%. This analysis showed that for the results obtained in 2005 less than half of the values were within the range previously reported in 2003. The 2005 analysis produced results which were generally lower than the results obtained in 2003.

Conclusions from the additional arsenic analysis

Following this additional arsenic analysis in plant tissue, the uncertainty surrounding the arsenic levels obtained from the plant tissue analysis which was first raised following the analysis of the spinach CRM sample was increased rather than decreased.

The SARA Group concluded from this additional analysis that arsenic levels which exceeded 3 µg/g appeared to remain at this level (sample 32-R Lettuce) but that other results which were previously between 1 and 2µg/g were variable and sometimes reported as below detection (0.2 µg/g).

The laboratory was contacted with these concerns over the variability associated with the arsenic analysis. The laboratory response was as follows:

“Almost all of the issues are due to the low levels that we are analyzing and the amplification of the analytical uncertainty inherent in the analysis. Our detection limits are based on the point at which statistically we can see the difference between background noise and an analytical signal. The actual calculations that we have adopted are from the MISA guidelines. Small changes in instrument baseline, have a “large” effect on the final result. The false positive results of the original hydride generation (SARA insert: this refers to the CRM spinach sample) were caused by this issue. Hydride analysis does work well for soil digestions because of the presence of chloride, which is an interference for As and Se by MS. However its baseline is not as stable as ICP-MS, which leads to higher detection limits. Plant tissue can be run by MS because no chloride is used in the sample digestion.”

It is clear from this exercise that there is uncertainty surrounding the analysis of arsenic at levels below 3 µg/g in the vegetable tissue. Some of the samples which were reported to contain arsenic may in fact not contain arsenic at levels which are as high as those reported. For the HHRA the 2003 arsenic values (which are the highest and indicative of a worst case scenario approach) have been incorporated. This analysis shows that the arsenic values in the plant tissue samples are variable and must only be used in full knowledge of the analytical shortcomings.

E-3.6.4 QC Conclusions

The internal laboratory QC confirmed that the quality of the analytical results were high and confidence can be placed in all analysis, with the exception of arsenic in plants tissue. Overall, the QC analysis showed that:

- There was good agreement between the analytical results for both the field duplicate soil samples and split produce samples;
- The processing phase did not introduce any metal contamination to the samples although it did increase the variability between the split produce samples;

- The SRM results of the soil and spinach leaves confirmed that the analytical method performed within the expected range for all certified elements with the exception of arsenic in spinach;
- The reanalysis of plant tissue that had previously been reported to contain arsenic confirmed that for levels below 3 µg/g analytical uncertainty is elevated. Levels in this range can be incorporated but the uncertainty surrounding them must be addressed and discussed in all analysis in which they are used.

Thus, all data generated during the vegetable garden study can be considered acceptable for use in the HHRA.

E-3.7 Comparison of Soil Concentrations to Previous Sudbury Studies

The overall aim of the vegetable garden survey was to establish and collect produce at sites which had a variety of soil metal concentrations and soil types. In order to determine whether this aim was achieved, the metal concentrations obtained during the survey were compared to the concentrations of the COC obtained during the 2001 Sudbury Soil Survey. Table E3.26 shows the range and mean concentration of COC in soil collected during the 2001 survey compared to the levels found during the Vegetable Garden Survey. The rationale for this comparison was to determine whether the soil metal concentrations measured for the COC were in the range of previous soil collections in Sudbury.

Table E3.26 Range of COC Concentrations (µg/g) in Surface Soil from 2001 and 2003

	As	Co	Cu	Ni	Pb	Se
2001 Soils Survey (n = 1932)	2.5-400	2-160	5.9-5600	11-3649	1-410	0.5-36
Vegetable Garden Survey (n = 104)	0.6-173	2.8-56	6-1170	9-1100	3.8-520	0.5-13

This comparison shows that the concentrations of COC in the soil samples collected are within the range of the soil samples collected during the 2001 survey. The produce samples collected were grown in soils which contained a range of soil COC concentrations which are representative of the Sudbury region.

E-3.8 Comparison of Soil Concentrations to Soil Guidelines

For comparative purposes the garden soil metal concentrations were compared to Table A (Table E3.27) from the MOE's *Guideline for Use at Contaminated Sites in Ontario* (MOE 1997). When the pH was 5 or less, Table F (Table E3.28) which contains values which are considered generic Ontario background levels and are based on the Ontario typical metal levels ranges for soils (MOE 1993) were used.

In the residential soils at the 0-15 cm depth, all soils had pH values above 5, so the metal concentrations were compared to the Table A criteria only (Table E3.27). Arsenic, cobalt, lead and selenium, concentrations were on average below Table A, where less than 15% of samples exceeded the criteria. Concentrations of nickel and copper were higher than the other COC, where 43% of sites had values above Table A, but were below the maximum Sudbury Area concentrations as reported in the MOE 2001 study (see Table E3.26 for comparison).

Of the twenty-four commercial soils sampled for the vegetable study, 17 sites had soil pHs that were above 5. All these sites had soil concentrations below the respective Table A value. Only one wild plant site had a soil pH value above 5, where the only soil criterion that was exceeded was arsenic. Site 10-B had an arsenic concentration of 36.50 µg/g, while the provincial Table A guideline is 20 µg/g.

Table E3.27 Soil Values Above Table A (absolute number and % of total).

MOE Table A Criteria				20		40		225		200		150		10	
				Arsenic		Cobalt		Copper		Lead		Nickel		Selenium	
	Depth (cm)	Total n	Soils above pH 5	n	%	n	%	n	%	n	%	n	%	n	%
Residential	0-15	70	70	8	11	2	3	15	21	3	4	30	43	1	1
Commercial	0-15	24	17	0	0	0	0	0	0	0	0	0	0	0	0
Wild Plant	0-15	10	1	1	50	0	0	0	0	0	0	0	0	0	0

Seven commercial sites had soil pH values that were below 5 (Table E3.28). Of the six COC, only copper and nickel concentrations exceeded Table F, where one site had a copper concentration above 85 µg/g, and 4 sites had nickel concentrations above 43 µg/g. The wild plant sites were acidic soils, as 9 out of the 10 sites had pH values below 5. Within these 9 sites, the arsenic Table F value (17 µg/g) was exceeded at 2 sites, copper (85 µg/g) at 8 sites, nickel (43 µg/g) at 8 sites and selenium Table F value (1.9 µg/g) was exceeded at 6 sites.

Table E3.28 Soil values above Table F (absolute number and % of total).

MOE Table F Criteria				17		21		85		120		43		1.9	
				Arsenic		Cobalt		Copper		Lead		Nickel		Selenium	
	Depth (cm)	Total n	Soils below pH 5	n	%	n	%	n	%	n	%	n	%	n	%
Commercial	0-15	24	7	0	0	0	0	1	14	0	0	4	57	0	0
Wild Plant	0-15	10	9	2	22	0	0	8	89	0	0	8	89	6	67

E-3.9 Comparison of Metal Concentrations in Produce to SARA Screening Criteria

The maximum metal concentrations ($\mu\text{g/g}$ wet weight) in each plant type category were compared to the data screening levels developed by the SARA Group and summarized in Table E2.3. The method used to compare the measured values to the screening values and to produce a preliminary estimate of hazard was calculated using the Quotient Method. As described previously, if the Q value is >1 then the value indicates that the concentration in at least one vegetable from the category exceeded the screening criterion value and if the $Q < 1$ then it indicates that all vegetables for the category collected were below the criterion value. If the $Q < 1$ then no risk is estimated and the produce category was not subject to further evaluation at this stage of the study. In the following tables any Q value >1 has been shaded. For all categories only one screening value was developed, the exception to this is arsenic which has a cancer and a non-cancer screening value.

Table E3.29 compares the maximum concentration of each of the COC found in the above ground-vegetable category to the relevant screening criterion to determine the Q value. The results show that for all COC, with the exception of arsenic, the maximum concentration of the above-ground vegetables were below the screening criterion. The majority of the concentrations in above-ground vegetables were well below the screening criterion. In the case of arsenic the screening criterion for both the systemic and cancer evaluation is exceeded. It is important to note that this maximum value applies to mushrooms collected at the wild plant sites. If mushrooms are excluded there is only one sample (lettuce) out of all above-ground vegetables which exceeds the screening criteria. Therefore, elevated arsenic levels were not considered a widespread problem in above-ground.

Table E3.29 Calculation of Hazard Quotient (Q) for Above-Ground Vegetables

Parameter		Screening Level ^(a)	Maximum Concentration ^(b)	Q
Arsenic	C	0.01	0.295	29.5
	NC	0.20	0.295	1.475
Cobalt		13.31	0.364	0.03
Copper		26.62	4.429	0.17
Nickel		13.31	5.278	0.40
Lead		1.23	0.727	0.59
Selenium		3.33	1.68	0.50

^(a) Screening levels ($\mu\text{g/g ww}$) from Table E2.3

^(b) Maximum concentrations ($\mu\text{g/g ww}$) for this produce group

C = Cancer Risk

NC = Non-cancer Risk

Table E3.30 summarizes the maximum concentration of each of the COC found in the below-ground vegetable category and compares this value to the relevant screening criterion. These values were compared to the screening criterion to determine the Q. The results show that for all COC, with the exception of arsenic, the maximum concentration of the below-ground vegetables were below the screening criterion. The majority of the concentrations in below-ground vegetables were well below the screening criterion. In the case of arsenic only the screening criterion for the cancer evaluation was exceeded.

Table E3.30 Calculation of Hazard Quotient (Q) for Below-Ground Vegetables

Parameter		Screening Level ^(a)	Maximum Concentration ^(b)	Q
Arsenic	C	0.01	0.07	7
	NC	0.14	0.07	0.5
Cobalt		9.01	0.164	0.02
Copper		18.02	2.42	0.13
Nickel		9.01	4.93	0.55
Lead		0.83	0.619	0.75
Selenium		2.25	0.4	0.18

^(a) Screening levels ($\mu\text{g/g ww}$) from Table E2.3

^(b) Maximum concentrations ($\mu\text{g/g ww}$) for this plant group

Table E3.31 compares the maximum concentration of each of the COC found in the fruit category and to the relevant screening criterion to determine the Q value. The results show that for all COC the maximum concentrations found in the fruits were below the screening criterion.

Table E3.31 Calculation of Hazard Quotient (Q) for Fruits

Parameter		Screening Level ^(a)	Maximum Concentration ^(b)	Q
Arsenic	C	0.01	<dl	0
	NC	0.15	<dl	0
Cobalt		10.12	0.06	0.006
Copper		20.25	0.93	0.05
Nickel		10.12	0.06	0.006
Lead		0.94	0.10	0.10
Selenium		2.53	0.06	0.02

^(c) Screening levels (µg/g ww) from Table E2.3

^(d) Maximum concentrations (µg/g ww) for this plant group

This page left blank intentionally.

E-4.0 DISCUSSION

As discussed in the previous section the only COC in produce that exceeded the screening levels was arsenic. The quality control program revealed that the arsenic analysis in plant tissue was variable and subject to a great deal of uncertainty. In the screening analysis, the arsenic cancer value was exceeded for both the below- and above-ground vegetables. The arsenic non-cancer screening value was exceeded for above-ground vegetables only. The actual potential risk from the arsenic concentrations in the vegetables to human consumers is dependent upon several factors, including:

- Arsenic species (inorganic vs. organic) in the produce;
- Actual amounts of produce consumed; and,
- Safety factor of the screening criteria.

The method detection limit (MDL) for arsenic in vegetables collected by the SARA Group in 2003 was 0.2µg/g dry weight. The moisture content was determined for all samples so that the dry weight concentration could be converted into the more commonly used wet weight concentration. Arsenic levels were below the MDL for the majority of vegetable samples. However, values at or near the MDL might exceed the screening criteria for arsenic, which were intentionally low to be as protective as possible. A summary of the distribution of arsenic above and below the MDL for all vegetables (residential, commercial and wild plant) collected in each screening category is presented in Table E4.1. All vegetable arsenic data are provided in Sub Appendix E-K.

Table E4.1 Distribution of Arsenic in SARA Vegetable Garden Samples, 2003

Category	Total Number of Samples	Samples With Arsenic Below Detection Limit	Samples With Arsenic Above Detection Limit	Percentage of the Total with Arsenic Above the Detection Limit (%)
Below-Ground	99	90	9	9
Fruit	19	19	0	0
Above-Ground	198	128	70	35
Mushroom	3	0	3	100

Table E4.1 reveals that only a small proportion of the samples collected actually contained detectable amounts of arsenic. In below-ground vegetables a total of 99 samples were collected, of which 90 had no detectable levels of arsenic and only 9 samples (9%) contained detectable arsenic. There was no arsenic

detected in any fruit samples. In the above-ground vegetable category a total of 198 samples were collected of which 128 had no detectable arsenic and 70 (35%) contained measurable amounts. Of these 70 samples the only produce type which exceeded the non-cancer screening criteria for arsenic (0.20 µg/g wet weight) was wild mushrooms (n=3), which exceeded the screening criteria level in all samples and contained a maximum concentration of 0.30 µg/g wet weight. Some of the above-ground samples were reanalyzed for arsenic in 2005 (see section 3.6.4 for full discussion) as blind, split samples and a great deal of variability in the arsenic concentration was found. This analysis revealed a high level of uncertainty surrounding arsenic in plant tissue at levels which were below 3 µg/g dry weight.

Another difficulty encountered in determining whether residents are at risk from arsenic in their produce is the fact that the arsenic concentration obtained in the screening criterion is extremely low and incorporates several conservative assumptions. The arsenic cancer screening level is so low that in fact any detected level of arsenic could, in most cases mean that the sample exceeded the criterion. This is because the MDL for arsenic is 0.2 µg/g dry weight; depending upon the moisture content of the individual sample, this is approximately equivalent to 0.01 µg/g wet weight. The cancer screening value is therefore identical to the MDL for arsenic. As the MDL is equal to the screening value, the presence of any measurable amount of arsenic in the samples is potentially an issue, and warrants further investigation. The arsenic issues in the vegetables collected by the SARA Group can be summarized as:

- Wild mushrooms have levels of arsenic which are above the preliminary non-cancer and cancer screening criteria;
- The MDL for arsenic is the same as cancer screening value so the presence of any measurable amount means that the criterion is exceeded.

Because arsenic occurred above the screening level in very few produce samples (*ie.*, only 4 of 306), the very conservative screening level used, and uncertainty with the arsenic analytical results, no immediate risk to Sudbury residents was predicted. These data were used for further detailed evaluation in the HHRA.

E-4.1 Arsenic Forms

Evaluation of the metal 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 samples were below for all COC with the exception of arsenic.

Arsenic has been identified in a small portion of the collected samples to exist at concentrations which exceed the screening criterion. As already mentioned one reason for this is that the conservative cancer screening level is very close to the MDL for arsenic thus any detectable concentration of arsenic in a sample could be problematic. In order to properly assess whether the arsenic concentrations measured are a likely health risk to residents consuming the mushrooms, the only produce sample that consistently showed elevated concentrations, a review of arsenic in vegetables in both the published and grey literature was undertaken. The following section discusses arsenic and its potential forms in vegetable material, and then compares the results from Sudbury with other similar studies.

Arsenic is both a naturally occurring substance and a common contaminant at hazardous waste sites in Canada, the United States and a variety of countries in Europe. Its toxicological potential depends largely upon its chemical form and bioavailability.

Four main species of arsenic have been determined in the water/soil/plant system (Sohrin *et al.*, 1997). These are:

- Arsenate [As_v] [H₂AsO₄⁻ and HAsO₄²⁻]- inorganic
- Arsenite [As_{III}] [As(OH)₃] – inorganic
- Methylarsonic acid [CH₃AsO(OH)₂; MMAA] – organic
- Dimethylarsinic acid [(CH₃)₂AsO(OH)₂; DMAA] – organic

The inorganic arsenate form is considered the most significant from a toxicological perspective. The arsenate form is thermodynamically stable under aerobic conditions, as the result of the dissociation of one or two protons at natural soil solution pH values. Arsenate is a chemical analogue of phosphate and may interfere with oxidative phosphorylation (Terwelle and Slater, 1967). Arsenite is a neutral species at natural pH values and inhibits the activity of enzymes by binding to thiol groups. Methylarsonic acid and dimethylarsinic acid also form anions in soil but are much less toxic when compared to the inorganic complexes (Sohrin *et al.*, 1997).

E-4.2 Likely Form of Arsenic in the Samples

Peer-reviewed literature sources were reviewed by the SARA Group to find studies that have addressed the issue of arsenic bioavailability to plants, or have determined through speciation analysis the form of

arsenic occurring in various vegetable species. A summary of the findings in soil and plants are presented in the following sections.

In soil, the inorganic species (arsenate) is the most common form (Turpeinen *et al.*, 2003). The concentration of available arsenic is dependent on a variety of soil properties, including:

- soil iron and aluminum hydroxide content;
- clay content;
- redox potential; and,
- soil pH

Iron and aluminum oxides adsorb anionic arsenic species well in acidic soils, whereas calcium oxides in alkaline soils do to a lesser extent. Alexander (2000) found that the minute pores (<100 nm) on the surface of oxides and clays play an important role in sorption as they localize arsenic inside the pores and decrease its bioavailability. Anionic arsenic species are in general more available to plants grown in alkaline than acid soils (Helgesen and Larsen, 1998).

Arsenic is not essential for plants, and does not appear to be involved in specific metabolic reactions when present at low concentrations (Liebig, 1966). At elevated concentrations, arsenic has been reported to interfere with metabolic processes and to inhibit plant growth, leading to death in extreme cases (Marin *et al.*, 1993).

In below-ground vegetables (such as the root crops carrot and turnip) and in leafy vegetables, the majority of arsenic tended to be in its inorganic form. For example, Boharia *et al.* (2002) studied arsenic concentrations in a variety of produce types (rice, potatoes, carrots, cabbage, and shallots) grown in contaminated field sites in Indonesia. The study looked at four species of arsenic: arsenite (As^{III}), arsenate (As^{V}), monomethylarsonate (MMAA), and dimethylarsinate (DMAA) and found that As^{V} was the major species (59-95% of total arsenic) in samples. On average, carrots (As^{V} and As^{III}) and cabbage (As^{V}) contained 71% and 70%, respectively, inorganic arsenic of total arsenic.

In another study, Helgesen and Larsen (1998) looked at the bioavailability and speciation of arsenic in carrots and concluded that a level of 20 $\mu\text{g As/g}$ soil was a safe level to prevent unacceptable intake of inorganic arsenic.

Carbonell-Barrachina *et al.* (1999) looked at arsenic toxicity and accumulation in turnips and found that the chemical form of arsenic has more a more important effect on phytotoxicity than arsenic levels in

solution for turnips. This study found that in turnips, the arsenic tissue uptake followed the trend: $As^V > As^{III} > DMAA > MMAA$. The arsenic accumulated mainly in roots (75% of total arsenic), with low quantities translocated to shoots (25%).

In the SARA study, the highest concentration of arsenic was found in wild mushrooms, which exceeded both the cancer and non-cancer arsenic screening criteria levels. Slejkovec *et al.* (1997) studied arsenic uptake and speciation in different species of wild mushrooms and found that the pattern of arsenic compound uptake differs greatly among mushroom species. In contrast to all other vegetable species mentioned, where the majority of arsenic was in the more toxic inorganic form, in mushrooms arsenobetaine (AB) – a non-toxic organic compound, was the most common metabolite encountered in the 41 samples. Only nine of the 41 species studied did not contain this metabolite. The species of mushroom collected at the wild study sites during the Vegetable Garden Survey was not quantified so direct comparisons to this study are not possible however, this evidence suggests that although arsenic concentrations in mushrooms may be elevated, and that higher arsenic concentrations are accumulated in comparison to other vegetable species, most mushroom species are able to detoxify inorganic arsenic by converting it to the less harmful AB compound.

E-4.3 Arsenic Levels in 2003 Samples Compared to Previous Studies

Two previous vegetable garden surveys have been conducted in the Sudbury area. The MOE collected vegetable samples in 1994 in the Gatchell area, and again in 2001 in the areas around smelter sites.

Elsewhere in Ontario, vegetables have been collected in Port Colborne and Deloro and analyzed for metals. In Port Colborne, only a small number of vegetable samples were collected. During the Deloro study, specific vegetable garden plots were planted in soils of varying metal concentrations.

The Tables in Sub Appendix E-P present the range (in both wet and dry weight $\mu\text{g/g}$ where available) of arsenic found in samples from these four studies in comparison to the range of arsenic in vegetables and fruit from the current SARA study. The results are split into tables for all vegetables types (above-, below-ground and fruit). Data are grouped by produce species for comparative purposes. The results from the SARA study and the MOE 1994 collection are presented as both wet weight and dry weight, as a moisture value was determined for each sample. In the MOE 2001 study, produce is presented as dry weight only. The results from Port Colborne were available as dry weight and extrapolated wet weight. Moisture content was not determined during the Port Colborne study, however a conversion factor was used in the HHRA report to determine wet weight concentrations.

Deloro is a region where arsenic has been detected at higher concentrations in soils (mean value 49 µg/g) than exist in the soils collected during the vegetable garden survey in Sudbury (mean value residential 13.5 µg/g; commercial 5.10 µg/g; and, wild 18 µg/g). Levels of uptake of arsenic into plants was small and indicated that arsenic in Deloro soil was not readily available. The levels in the Deloro vegetables were comparable or greater than the levels found in vegetables from the SARA vegetable study. A risk evaluation of the arsenic levels in vegetables collected in Deloro concluded that no human health risk existed from consumption of these vegetables to residents of the region (MOE, 1999).

The comparison of arsenic concentrations from the various studies confirms that the arsenic concentrations in samples collected by the SARA Group in the Sudbury area are similar to previous studies conducted in this region and other parts of Ontario.

E-5.0 SUMMARY AND CONCLUSIONS

Total metal concentrations as well as other pertinent physical and chemical characteristics were measured in soil from 70 residential gardens, 24 commercial farms and 10 wild plant sites in the Sudbury area. Produce consisting of fruit, above-ground and below-ground vegetables were collected from the sites and analyzed for total metal content.

Soil:

- Metal concentrations in garden soils were similar to levels reported for surface soils in the 2001 Sudbury Soil Survey, showing that the areas selected for the Vegetable Garden sampling sites were indicative of the Sudbury region.
- Metal levels were generally higher in residential soils compared with commercial farms or wild sites.
- The levels of all COC (As, Co, Cu, Pb, Ni and Se) exceeded MOE Table A criterion at a proportion of the sites.
- Metal levels in the surface layer (0-15 cm) and deeper soils (15-30 cm) were similar in residential and commercial gardens, likely as a result of tilling and soil mixing. At the wild plant sites, COC levels were higher in the surface soil layers suggesting atmospheric deposition as a primary source, and that the soil layers were not disturbed.

Produce:

- Concentrations of Cu, Pb and Se were higher in below-ground vegetables than in above-ground vegetables. For the other COC the levels were comparable between the two categories.
- Five of the COC were present in produce at concentrations well below the screening criteria developed for the vegetable garden survey. The exception was As which exceeded the screening criteria in a few samples.
- The health screening criteria developed for the vegetable garden survey were developed only as an interim screening tool before the entire HHRA could be finalized. The risk estimates provided in the complete HHRA report should be consulted for estimated health risks related to the COC. [MGI]

E-6.0 REFERENCES

- Alexander, M. (2000) Aging, bioavailability and overestimation of risk from environmental pollutants. *Environmental Science and Technology* 34, 4259-4265.
- Bates, T.E. and Richards, J.E. 1993. Available potassium. Pages 59-64 in M.R. Carter , Ed. *Soil sampling and methods of analysis*. Canadian Society of Soil Science.
- Boharia, Y., G. Lobosb, H. Pinochetb, F. Pannierc, A. Astruc and M. Potin-Gautierc. (2002) Speciation of arsenic in plants by HPLC-HG-AFS: extraction optimisation on CRM materials and application to cultivated samples. *Journal of Environmental Monitoring* 4, 596-602.
- Canadian (Canadian Council of Ministers of the Environment). 1993. *Guidance manual on Sampling, Analysis and Data Management for Contaminated Sites. Volume 1: Main Report*. Winnipeg Manitoba. CCME EPC-NCS62E.
- Cantox Environmental Inc. 1999. *Deloro Village Exposure Assessment and Health Risk Characterization for Arsenic and Other Metals. Part 5 – Human Health Risk Assessment – Deloro Village*. Cantox Environmental Inc. (CEI), Mississauga, ON.
- Carbonell-Barrachina, A, F. Burlo, D. Valero, E. Lopez, D. Mart3nynez-Romero, and F. Mart3nynez-Sanchez. (1999) Arsenic toxicity and accumulation in turnip as affected by arsenic chemical speciation. *Journal of Agricultural and Food Chemistry* 47, 2288-2294.
- Evans, L.J. and W.G. Wilson. 1985. Extractable Fe, Al Si and C in B horizons of podzolic and brunisolic soils from Ontario. *Canadian Journal of Soil Science* 65, 489-496.
- Helgesen, H. and E.H. Larsen (1998) Bioavailability and speciation of arsenic in carrots grown in contaminated soil. *Analyst* 123, 791-796.
- Hendershot, W.H., Lalonde, H. and Duquette, M. 1993. Soil reaction and exchangeable acidity. Pages 141-146 in M.R. Carter , Ed. *Soil sampling and methods of analysis*. Canadian Society of Soil Science.
- Liebig, G.F., Jr. Arsenic. In *Diagnostic Criteria for Plants and Soils*; Chapman, H.D., Ed.; University of California, Division of Agricultural Sciences: Riverside, CA, 1966; pp 13-23.
- Jacques Whitford Environmental Limited. 2002. *Port Colborne Community Based Risk Assessment – Ecological Risk Assessment. Quality Assurance/Quality Control Protocol*
- Marin, A.R., S.R. Pezeshki, P.H. Masscheleyn and H.S. Choi (1993) Effect of dimethylarsenic acid (DMAA) on growth, tissue arsenic and photosynthesis of rice plants. *Journal of Plant Nutrition* 16, 865-880.
- O'Connor Associates. 1997. *Compendium of Canadian Human Exposure Factors for Risk Assessment*. O'Connor Associates Environmental Inc. and G. Mark Richardson, Ottawa, ON.
- Ontario Ministry of Environment and Energy, November (1994). *Assessments of Potential Health Risks of Backyard Vegetable Consumption in the Gatchell Area, Sudbury*. November 1994.
- Ontario Ministry of Environment. 1997. *Guideline for Use at Contaminated Sites in Ontario*. Ontario Ministry of the Environment (MOE). Revised February 1997.
- Ontario Ministry of Environment (1999). *The Deloro Village Environmental Health Risk Study Summary Report*. July 1999.

- Schoneau, J.J. and Karamanos, R.E. 1993. Sodium bicarbonate extractable P, K and N. Pages 51- 58 in in M.R. Carter , Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.
- Sheldrick, B.H. and Wang, C. 1993. Particle Size Distribution. Pages 499-511 in M.R. Carter , Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.
- Shoemaker, H.E., McLean E.O. and Pratt. P.F. 1961. Buffer methods for determining lime requirements of soils with appreciable amounts of extractable aluminum. Soil Sci. Soc. Amer. Proc. 25:274-277.
- Slejkovec, Z., A.R. Byrne, T. Stijve, W. Goessler and K.J. Irgolic (1997) Arsenic compounds in higher fungi. Applied Organometallic Chemistry 11, 673-682.
- Sohrin, Y., M Matsui, M. Kawashima, M. Hojo and H Hasegawa (1997) Arsenic biogeochemistry affected by eutrophication in Lake Biwa, Japan. Environmental Science and Technology 31, 2712-2720.
- Terwelle, H.F. and E.C. Slater (1967) Uncoupling of respiratory-chain phosphorylation by arsenate. Biochemica et Biophysica Acta 143, 1-17.
- Tiessen H and Moir, J.O. 1993 . Total and organic carbon. Pages 187-199 in M.R. Carter\, Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.
- Turpeinen, R., M. Virta and M. Haggblom (2003) Analysis of arsenic bioavailability in contaminated soils. Environmental Toxicology and Chemistry 22, 1-6.
- Tran, T.S. and van Lierop, W. 1993. Lime requirement. Pages 109-113 in M.R. Carter , Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.

SUB APPENDIX E-A

PROTOCOLS

(CD 2)

SUB APPENDIX E-B
LANDOWNER CONSENT FORM
(CD 2)

SUB APPENDIX E-C

EASTING AND NORTHING
CO-ORDINATES FOR SAMPLE SITES

(CD 2)

SUB APPENDIX E-D

PHOTOGRAPHS

(CD 2)

SUB APPENDIX E-E
CHAIN OF CUSTODY FORMS
(CD 2)

SUB APPENDIX E-F
ANALYTICAL METHODOLOGY
(CD 2)

Analytical Methodology for Soil Physical and Chemical Properties tested at Soil and Nutrient Laboratory, University of Guelph

For all tests, samples were dried at 35 degrees C and sieved through 2 mm sieve prior to analysis.

Total, inorganic and organic carbon:

C analysis was conducted using a LECO SC444 (dry combustion). For inorganic C, a sample was first ashed overnight at 475°C in a muffle furnace. Organic C was determined by subtracting inorganic C from Total C.

Tiessen, H. and Moir, J.O. 1993. Total and organic carbon. Pages 187-199 in M.R. Carter, Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.

Particle Size Distribution:

PSD analysis was done using the pipette method.

Sheldrick, B.H. and Wang, C.1993. Particle Size Distribution. Pages 499-511 in M.R. Carter, Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.

Phosphorous (P)

Sodium bicarbonate extraction followed by automated colourimetric determination.

Schoneau, J.J. and Karamanos, R.E.1993. Sodium bicarbonate extractable P, K and N. Pages 51- 58 in in M.R. Carter, Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.

Potassium (K), Magnesium (Mg)

Ammonium acetate extraction followed by flame AAS determination.

Bates, T.E. and Richards, J.E. 1993. Available potassium. Pages 59-64 in M.R. Carter, Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.

pH

Saturated paste using water.

Hendershot, W.H., Lalande, H. and Duquette, M. 1993. Soil reaction and exchangeable acidity. Pages 141-146 in M.R. Carter, Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.

and, if Buffer pH was done (pH <6.0):

Buffer pH

SMP single-buffer method.

Tran, T.S. and van Lierop, W. 1993. Lime requirement. Pages 109-113 in M.R. Carter, Ed. Soil sampling and methods of analysis. Canadian Society of Soil Science.

Note that P, K, Mg and pH are as per the OMAF methodologies for accredited soil testing in Ontario.

SUB APPENDIX E-G
FRUIT AND VEGETABLE PREPARATION
(CD 2)

SUB APPENDIX E-H
VEGETABLE GARDEN SURVEY DATABASE
(CD 2)

SUB APPENDIX E-I

VEGETABLE SCREENING CRITERIA CALCULATION AND DERIVATION OF VALUES

(CD 2)

Vegetable Screening Criteria Calculation and Derivation of Values

The equation used to derive the screening criteria values was:

$$\text{Screening criteria } (\mu\text{g/g}) = \frac{\text{RfD/RSD } (\mu\text{g/kg/day}) \times \text{bodyweight (kg)}}{\text{consumption rate (g/day)} \times \text{amortization factor} \times \text{allocation factor}}$$

The results for the screening criteria were calculated for each COC for infant, toddler, teenager and adult. The minimum value for each category (most protective) was used as the vegetable screening criterion value. Each of the values used in this equation are described in more detail below.

RfD Value

Chemicals that give rise to toxic endpoints other than cancer and gene mutations are often referred to as systemic toxicants because of their effects on the function of various organ systems. The majority of the COC, with the exception of arsenic, are not known to be carcinogens. The maximum allowable daily dose of toxicants that cause systemic effects has been calculated for all of the COC and is referred to as a reference dose (RfD). The oral Reference Dose (RfD) is based on the assumption that thresholds exist for certain toxic effects. In general, the RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. RfDs can be derived to address the noncarcinogenic health effects of a substance that is also a carcinogen (such as arsenic). The oral RfDs used in the equations were:

- Arsenic (nc) 0.3 $\mu\text{g/kg/day}$
- Nickel 20 $\mu\text{g/kg/day}$
- Lead 1.85 $\mu\text{g/kg/day}$
- Cobalt 20 $\mu\text{g/kg/day}$
- Copper 40 $\mu\text{g/kg/day}$
- Selenium 5 $\mu\text{g/kg/day}$

RSD Value

When a chemical is considered carcinogenic, an oral slope factor is used in calculations to determine the calculated Risk Specific Dose (RSD). The slope factor is the result of application of a low-dose extrapolation procedure and is presented as the risk (mg/kg) per day. In the case of arsenic, the EPA slope factor was derived from literature documenting an increased lung cancer mortality observed in multiple

human populations exposed primarily through inhalation, increased mortality from multiple internal organ cancers (liver, kidney, lung, and bladder) and an increased incidence of skin cancer observed in populations consuming drinking water high in inorganic arsenic.

The oral slope factor used in the equation was 0.0015 µg/kg/day. This value was divided by 0.000001 to determine a RSD with a 1 in a million risk factor.

Bodyweight

The average Canadian body weight at different life stages is shown in Table E-I-1 and was obtained from O'Connor Associates (1997).

Table E-I.1 Average Canadian Body Weight (kg) at Different Life Stages (years)

	Infant	Toddler	Child	Teen	Adult
Years (years)	0.5	4.5	7	18	50
Body weight (kg)	8.2	16.5	32.9	59.7	70.7

Consumption Rate

The total consumption rate for each of the age groups is shown in Table 2 and was obtained from O'Connor Associates (1997) and CEI (1999).

Table E-I.2 Average Canadian Consumption Levels (g/day wet weight) of Vegetables at Different Life Stages

	Infant	Toddler	Child	Teen	Adult
Backyard root veggies	-	7.326	10.58	14.06	11.618
Backyard other veggies	-	4.958	7.252	8.88	9.398
'Backyard' fruit	3.24	2.322	7.236	6.966	6.615

The total consumption was multiplied by the fraction of the diet which would be obtained from a home vegetable garden (7.4%) or from home garden fruit (2.7%) (CEI, 1999) to determine the average consumption for each age bracket of vegetables and fruit from the home garden.

Amortization Factor

Amortization factor was calculated in a different manner for the cancer and the non-cancer screening values. For non-cancer screening values amortization was calculated as years/years = 1. For the cancer screening value (arsenic) amortization was calculated as years/lifetime.

The years value is the life stage (*e.g.* 0.5 for infant, 4.5 for toddler, 7 for child). The lifetime value used was 70 years.

Allocation Factor

The allocation factor was set at 20%. For screening purposes, and criteria derivation, the MOE recommend application of a 20% source allocation factor. The factor allocates a portion of an individual's total exposure to any single exposure pathway (MOE, 1997).

SUB APPENDIX E-J

SOIL PHYSICAL AND CHEMICAL RESULTS

(CD 2)

SUB APPENDIX E-K

SOIL METAL DATA

(CD 2)

SUB APPENDIX E-L

**FRUIT AND VEGETABLE METAL DATA FOR COC
(WET AND DRY WEIGHTS)**

(CD 2)

SUB APPENDIX E-M
LABORATORY REPORTS
(CD 2)

SUB APPENDIX E-N

**QUALITY CONTROL RESULTS:
STANDARD REFERENCE MATERIAL
SRM REPORTS, LABORATORY REPORTS, QC ANALYSIS AND ADDITIONAL
ARSENIC ANALYSIS**

(CD 2)

SUB APPENDIX E-O

**FIELD DUPLICATE AND SPLIT SAMPLES:
RESULTS TABLES AND QC ANALYSIS**

(CD 2)

SUB APPENDIX E-P

**SUMMARY OF ARSENIC DATA FROM DELORO, PORT COLBORNE,
GATCHELL AND SARA**

(CD 2)

[MG1]Chris need some help with this point as well