2 Arsenic in vegetables

An evaluation of risk from the consumption of produce from residential and mine gardens in Yellowknife, Northwest Territories, Canada

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Summary

The soil arsenic concentrations in Yellowknife, Northwest Territories, Canada, are above national averages as a result of both the natural geology of the region and the release of arsenic-containing waste during local gold mining processes. The presence of elevated soil arsenic concentrations raised concerns about the safety of arsenic levels in residentially grown vegetables. Accordingly, the arsenic levels in voluntarily donated residential vegetables and fruits were studied. The possibility that residential soil had been historically augmented with arsenic contaminated waste from the mines prompted the study of worst-case scenario gardens. For the latter study, two gardens were constructed: one on mine property, and one using soil from a nearby lakeshore that was contaminated with arsenic.

Following washing procedures similar to those used in typical food preparation, vegetables and fruits were dried, ground, and acid-digested. Total arsenic concentrations were determined in the acid digests by hydride generation–atomic absorption spectrometry (HG-AAS) and arsenic levels in dried and ground soils from each garden were determined by neutron activation analysis (NAA).

The concentration of arsenic in soils from the residential gardens was 33 ± 14 mg/kg, which is within the range of the natural or background concentration in the soil of the Yellowknife area. A higher average arsenic concentration of 200 ± 140 mg/kg was determined in garden soils collected from a mine townsite property, which is no longer used residentially. The soils from the lake garden and mine garden contained elevated arsenic levels of 720 ± 220 mg/kg and 1560 ± 660 mg/kg respectively, which are concentrations typical of the sampled areas.

A significant finding is that arsenic concentrations in produce from Yellowknife residential gardens are almost always an order of magnitude greater than those

found in like foods in a Canadian diet survey (Dabeka *et al.*, 1993). The highest arsenic concentrations were found in leafy vegetables such as lettuce (maximum 0.27 mg/kg fresh weight) and berries (maximum 0.44 mg/kg fresh weight). Arsenic levels in vegetables grown in the lake and mine gardens were two orders of magnitude higher than in Yellowknife residential produce, with maxima of 46 mg/kg fresh weight in beets from the lake garden and 330 mg/kg fresh weight in onions from the mine garden.

The study of bioaccumulation and translocation factors (BAFs and TFs) revealed a general trend towards greater BAFs for below-ground plant parts with increasing soil arsenic concentrations. The TF data supported this by exhibiting lower values with increasing soil concentrations. These trends suggest that for these vegetables root sequestration of arsenic may be a tolerance mechanism for exposure to high arsenic levels.

The potential risk of adverse effects from the consumption of this arsenic-containing produce was evaluated by using a risk assessment approach recommended by Health Canada (1995). The goal was to determine if the estimated daily intake of arsenic exceeds the provisional maximum daily intake (PMDI) of 2.1 μg/kg per day recommended by the Food and Agriculture Organization/World Health Organization (FAO/WHO).

The risk calculation, which incorporated the consumption of other arsenic-containing foods as well as the garden produce, revealed that the PMDI is not exceeded when Yellowknife residential produce is consumed. On the other hand, the PMDI would be exceeded in most cases should the lake or mine produce be ingested, assuming that all of the arsenic in the produce is absorbed into the body. The risk was lowered by the incorporation of a bioaccessibility factor that was obtained from an extraction process that modeled gastric dissolution of arsenic. The reduction in risk (i.e. the lowering of EDIs to levels below the PMDI) was significant only for produce from the lake garden.

Therefore no increase in risk is posed to the residents consuming garden vegetables from their gardens in Yellowknife. However, produce grown in soils similar to those used in the lake and mine gardens would not be safe to eat.

Introduction

Arsenic in Yellowknife

Arsenic is a ubiquitous, naturally occurring element in the environment, ranking in abundance twentieth in the earth's crust, fourteenth in seawater, and twelfth in the human body. In spite of its ubiquity, arsenic is still nearly synonymous with poison, as some arsenic compounds were used for that purpose for centuries. While arsenic is often associated with adverse effects, its toxicity is actually dependent on its chemical form, or species (i.e. the specific combination of arsenic with other elements) (Shiomi, 1994). For example, arsenobetaine, an organoarsenic compound that is found in marine animals (Francesconi and Edmonds, 1997) and mushrooms (Koch *et al.*, 2000b; Kuehnelt *et al.*, 1997;

Table 2.1 Names, abbreviations, and chemical structures of some common arsenicals

Name	*Abbreviation*	*Chemical formula*
Arsenate, arsenic acid	As(V)	$AsO(OH)_3$, $[AsO_2(OH)_2]^-$, $[AsO(OH)_3]^{2-}$, $[AsO_4]^{3-}$
Arsenite, arsenous acid	As(III)	$As(OH)_3$, $[AsO(OH)_2]^-$, $[AsO_2(OH)]^{2-}$, $[AsO_3]^{3-}$
Monomethylarsonic acid	MMA	$CH_3\ AsO(OH)_2$
Dimethylarsinic acid	DMA	$(CH_3)_2AsO(OH)$
Arsenobetaine	AB	$(CH_3)_3As^+CH_2COO^-$

Slejkovec *et al.*, 1997), is much less toxic than arsenic trioxide, an inorganic form of arsenic (and the main historical poison). Some common forms of arsenic are summarized in Table 2.1.

Arsenic can be introduced to the environment naturally as a result of the weathering of rocks that contain arsenic-rich minerals, and geothermal activities (Matschullat, 2000). It can also enter the environment anthropogenically as a consequence of its industrial use, through the application of arsenic-containing pesticides, and through mining and smelting activities (Matschullat, 2000). A very important example of the latter is gold mining.

Yellowknife, located in the Northwest Territories, Canada (see Figure 2.1) has been an active gold mining community since 1938. The gold in Yellowknife ore is found with arsenopyrite (FeAsS), an arsenic-containing iron sulfide. Consequently, the milling of the arsenic-rich ore generates a considerable amount of arsenic waste. This waste can enter the environment in the form of solid waste (waste rock and tailings), liquid effluent, and aerial emissions from the roaster stack.

As a result of both the anthropogenic inputs of arsenic from gold mining and the natural inputs from the weathering of arsenic-containing minerals, the arsenic levels in the Yellowknife area are elevated compared with the typical Canadian background concentration range of 5 to 14 mg/kg in soils. In previous studies, the background levels have been estimated to range from 3 to 150 mg/kg in Yellowknife (Ollson, 2000; Reimer, 2002).

Arsenic in food

Epidemiological studies of populations consuming drinking water with high natural arsenic concentrations (up to 1000 μg/L or more) suggest a relationship between elevated levels of arsenic exposure and the prevalence of skin, bladder and lung cancers (Chiou *et al.*, 1995; Tsuda *et al.*, 1995). In most regions of Canada, the concentration of arsenic in drinking water (usually of the order of 1 μg/L) is much lower than the provisional maximum allowable concentration of 25 μg/L (CCME, 1999). Even in Yellowknife, where elevated levels of

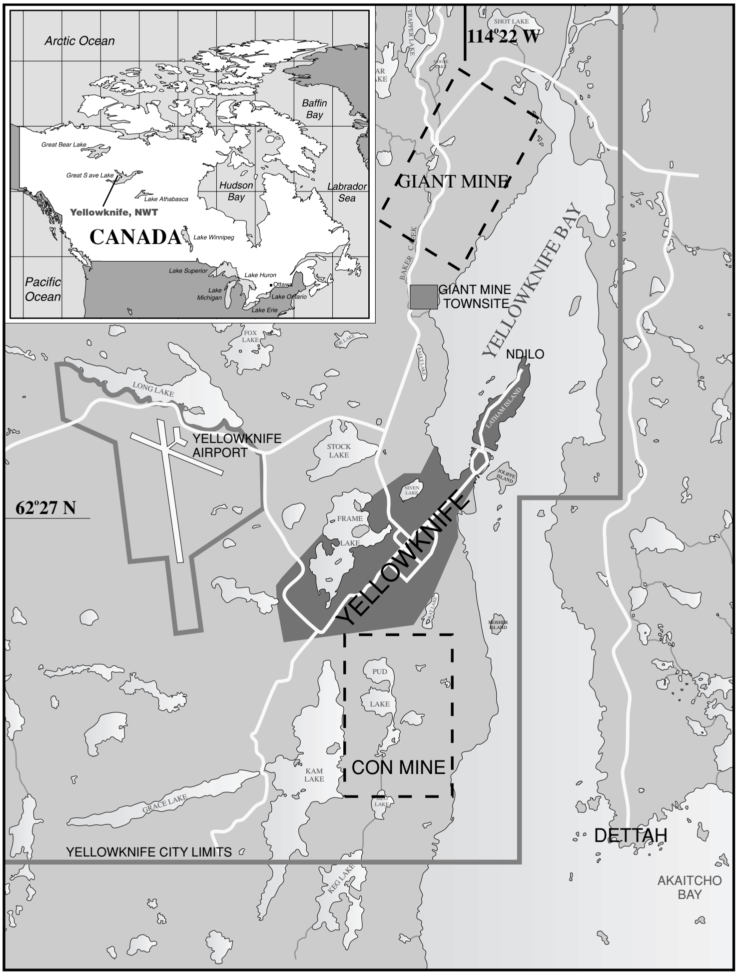

Figure 2.1 Location of Yellowknife city and mines.

arsenic occur in lakes in and surrounding the city, the arsenic concentration in the municipal supply of drinking water (obtained from a different watershed area) is less than 1 μg/L and is therefore safe to drink. Under these circumstances, the main contribution of arsenic to the human diet comes from food, and cumulative exposure is the primary concern. Indeed, total diet studies conducted by the US Food and Drug Administration (FDA) determined that food contributes 93% of the total arsenic intake in the US human diet. Of that 93%, seafood contributes 90% (Adams *et al.*, 1994, Subcommittee on Arsenic in Drinking Water, 1999) and such foods generally contain non-toxic organoarsenic compounds (e.g. arsenobetaine and arsenosugars). Other foods, such as vegetables, rice, poultry, and mushrooms, contain much lower levels of arsenic, and due to limitations in analysis methods, the arsenic in these foods has been very difficult to characterize (Subcommittee on Arsenic in Drinking Water, 1999). In cases where the growing environment contained elevated levels of arsenic, vegetables contained predominantly inorganic arsenic (Helgesen and Larsen, 1998; Pyles and Woolson, 1982).

A comprehensive survey of the arsenic content in Canadian foods was published in 1993 and is used throughout this report for comparison to our findings (Dabeka *et al.*, 1993). This survey found that the arsenic concentrations ranged from low μg/kg levels in milk and dairy products, soups, vegetables, fruit, fruit juices, and other beverages; to double digit μg/kg levels in meat and poultry, bakery goods and cereals, fats and oils, sugar and candy, and miscellaneous foods; to low mg/kg levels in fish and shellfish. In summary, all foods other than fish and shellfish contained arsenic at levels less than 50 μg/kg. From these values, the average daily intake of arsenic by a Canadian adult was calculated to be 40% of the provisional maximum daily intake (PMDI) recommended by the Food and Agriculture Organization/World Health Organization (FAO/WHO), of 2.1 (μg of arsenic)/(kg of body weight) per day, or 15 μg/kg per week (FAO/WHO, 1999; WHO, 2002).

In 1979 a survey of arsenic in Yellowknife vegetables was published, summarizing total arsenic levels in a variety of vegetables and fruits sampled from five general areas in Yellowknife (Soniassy, 1979). Arsenic levels ranged from 0.05 mg/kg fresh weight in pea pods to 2.05 mg/kg fresh weight in green onions, with an average overall concentration of 0.32 mg/kg fresh weight ($n = 42$). It was noted that the levels of the arsenic were similar to those found in previous years, but no attempt was made to predict human health risk from the consumption of the produce in this report.

Risk assessment

If a contaminant level exceeds those that constitute national criteria, such as the soil and water guidelines established by Canadian Council of Ministers of the Environment (CCME, 1999), then further investigation of the contamination is recommended, including sampling of garden vegetables. In the case of Yellowknife the majority of soil samples collected from the city exceed the recommended soil quality guideline of 12 mg/kg (CCME, 1999).

There are several ways that an assessment of risk to human health posed by a route of exposure can be conducted. In this study, the guidelines specified by Health Canada (1995) were used. The approach of this method is to determine the estimated daily intake (EDI) by all possible pathways, and then to compare this EDI with a tolerable daily intake (TDI) for non-carcinogenic substances, or with a risk-specific dose (RsD) for carcinogenic substances.

The TDI used in this study is derived from the provisional tolerable weekly intake (PTWI) of 15 μg/kg per week (corresponding to a provisional maximum daily intake, PMDI, of 2.1 μg/kg per day) of inorganic arsenic (FAO/WHO, 1999), specifically recommended for the intake of arsenic from food. This PTWI/PMDI was recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) in their last toxicological evaluation of food contaminants in 1988, in spite of the limited knowledge of adverse health effects (if any) from intake of arsenic through food, and it provides an initial basis for risk characterization.

Regulatory authorities have frequently assumed that 100% of the arsenic ingested is absorbed. However, experimental work using arsenic-contaminated soils has revealed that arsenic oral accessibility from most solid-phase compounds was substantially lower than from air or water because the arsenic was incompletely dissolved in the gastrointestinal tract (Ruby *et al.*, 1996). Therefore, it is necessary to account for incomplete absorption and accessibility of arsenic when attempting to assess accurately potential health effects associated with arsenic exposure.

An extraction process that mimics human gastrointestinal digestion has been developed to estimate the amount of a contaminant that is accessible to an individual as a result of digestive dissolution (Hamal *et al.*, 1998; Rodriguez *et al.*, 1999; Ruby *et al.*, 1996). For simplicity, this process will be referred to as gastric fluid extraction (GFE). We propose that the amount of arsenic available by using GFE can be utilized to calculate more accurately human health risk.

Although arsenic is a carcinogen, we will not consider the cancer risks associated with the consumption of vegetables grown in Yellowknife gardens. Such an evaluation should include estimated doses of arsenic from air, drinking water, soil ingestion, food, and skin absorption (water and soil) (Health Canada, 1995) and is a topic for future study.

Study objectives

Following the reporting of elevated levels of arsenic in soils in the Yellowknife area, concerns arose regarding the safety of garden produce grown in that area. In response, a study of the arsenic content of residential garden produce was initiated. Moreover, the possibility existed that some residents unknowingly augmented their gardens with soil that had been contaminated with mine waste. In order to model a worst-case exposure scenario (e.g. residential use of mine soil that has not been remediated), a vegetable garden was planted in Yellowknife in arsenic-contaminated soil from the Con Mine and adjoining Rat Lake areas.

The main objective of this study was to assess the potential human health risk associated with the consumption of vegetables grown in Yellowknife residential soils, and on arsenic contaminated mine soil. To do this, the following specific objectives were met:

1 levels of total arsenic in soil and produce from residential Yellowknife gardens and mine soils were quantified;
2 uptake of arsenic from soil by plants was determined, to study any biological responses to high soil arsenic concentrations;
3 estimated daily intakes were calculated and compared to the international standard described above.

Methods

Locations of gardens in the Yellowknife area

Vegetables and soil samples were collected from 10 gardens in the Yellowknife area. In order to protect the privacy of the garden owners who donated their vegetables, each location was assigned a number between 1 and 10. Locations 2 through 10 were taken from residential gardens from different areas in Yellowknife. Location 1 is a group of samples taken from two locations from residences no longer in use on a mine townsite (Giant Mine Townsite, Figure 2.1). Even though sample locations were based largely on the voluntary participation of residents, most areas from around the city were successfully represented.

The location of the mine garden was on mine property (Con Mine, Figure 2.1) in a sheltered low-lying area known to contain elevated levels of arsenic in the soil. Soil from the shore of a small lake adjacent to the mine property was used as well (referred to as the lake garden), as the soil from this area was believed to have been used to augment gardens in the area.

The soil composition of the gardens was noted at each location, and consisted of black organic soils. Residential soils had been amended with mulching agents.

Mine and lake garden preparation

The mine and lake vegetable gardens were prepared at the end of June 2001 without any amendments with mulching agents or lime. The mine plot, which consisted of two adjoining rectangles (5×6 m and 2×3 m), was tilled with shovels from 0 to 40 cm to homogenize and aerate the soil.

The lake garden, consisting of soil in planter boxes, was constructed by first homogenizing a 4 m^2 patch of soil from 0 to 60 cm. Equal amounts of gravel were placed in the bottom of five $1 \times 0.3 \times 0.3$ m planter boxes to enhance drainage, and the boxes were filled with approximately equal amounts of the homogenized lake soil. The planters were kept adjacent to the mine garden plot for the entire growth period.

The most common vegetables found in Yellowknife residential gardens were selected as the varieties to be grown in the mine and lake gardens, and the vegetable seeds and bulbs were obtained from a garden store in June 2001. Fourteen rows of vegetables were planted in the mine plot (mustard, Swiss chard, beets, radish, peas × 2, Grand Rapids lettuce, Prize Head lettuce, carrots, beans, white onions × 2, white potatoes × 2), while each lake soil planter contained a single vegetable type (beets, radish, Grand Rapids lettuce, carrots, beans). In total, 11 types of vegetables were planted. The seeds and bulbs were planted according to the spacing and depth instructions on each package. The plants were fertilized twice in June (following planting) using 10–20–10 (NPK) outdoor garden formula (Miracle Grow®). Constant rainfall during the summer precluded further application of fertilizer or watering.

Sampling and analysis of soil samples

The soil sampling program was designed to obtain samples that, when composited, would be representative of each garden as a whole. Each sample was collected with a plastic scoop, stored in a plastic bag and kept frozen during transport and until analysis. Residential garden soils were sampled when vegetable samples were collected, and mine and lake gardens were sampled prior to planting in June.

For each residential garden three to five samples were collected, one from each corner (or end, depending on the size and shape of the garden) and one from the center of the garden. In areas where only one plant was collected, only one soil sample was collected. Samples were obtained at the depths between 0 and 20 cm or between 0 cm and bedrock, if bedrock occurred at a shallower depth. The mine garden plot was divided into a 1×1 m grid system and samples were collected from 0 to 20 cm at each intersection of grid lines. A soil sample was collected from the center of each lake soil planter box from 0 to 20 cm.

A random number generator (Urbaniak and Lestick, 1997) was used to select 30% of the soil samples collected from the mine plot, which were then analyzed. All lake and composite (residential, mine and lake garden) soil samples were analyzed.

Soils were air-dried at room temperature for two to three days and then ground into a homogeneous powder using a coffee grinder or a mortar and pestle. The grinding tool was rinsed three times with 2–3 g of each new sample, which was then discarded, before homogenizing the bulk of the sample.

Composite samples were prepared from soil samples that were collected from the same garden, by adding an equal portion of each dried and ground soil sample to total 20 g (e.g. 4 g soil $\times$ five samples = 20 g). Field duplicates were included by using half the normal amount for each duplicate (e.g. as for the example above, for 4 g soil samples, 2 g of each duplicate). The composite sample was then homogenized as described above.

Neutron activation analysis (NAA) in the SLOWPOKE-2 reactor located at RMC was used to determine the total concentration of arsenic in all soil samples. Each dried and ground sample was weighed (1–2 g) into a 1.5 mL polyethylene vial and heat-sealed. The samples were irradiated at a flux of $5 \times 10^{11}/cm^2$ per s for two hours, cooled for 80–120 h, and then counted for 2 h using a GMC HpGe detector coupled with a Nuclear Data μ-multichannel analyzer (MCA).

Sampling and analysis of plant samples

Residential gardens were sampled in September 2000. Mine and lake gardens were sampled in August 2001, by uprooting the entire plant. After they were collected, residential garden samples were washed with tap water as if they were being prepared for consumption. Root vegetables were gently scrubbed with a brush to remove all dirt and each sample was carefully inspected visually to ensure that cleaning was thorough. Mine and lake garden plants, because of their small size, were subjected to a more rigorous cleaning regime that included careful separation of all plants, washings in at least three changes each of tap water and deionized distilled water (DDW) and meticulous visual inspection. Samples were then dried with Kim™ towels and stored frozen in plastic bags until further processing.

Samples were chopped while frozen, then frozen completely with liquid nitrogen, and then ground and homogenized in a blender. A portion of the frozen ground sample was weighed and then dried in a 70°C oven overnight. When dry, the sample was reweighed, and homogenized briefly in the blender or by using a mortar and pestle.

A quantity of 0.5 g of each dried sample was accurately measured (±0.0001 g) into a glass 50 mL test tube. A Teflon™ boiling stone and 10 mL of ultrapure nitric acid (Seastar Baseline) were added, and the samples were heated in a heating block from room temperature to 100°C for 1 h and then heated at 140°C for 6 h. The samples were then cooled, and 2 mL of hydrogen peroxide was added. The samples were heated at 140°C for another 1.5 h, then cooled and diluted to approximately 25 g (±0.01 g).

Analysis was carried out by diluting the samples 10-fold with 1 mol/L HCl (Fluka, puriss p.a.) and introducing them to a SOLAAR 969 atomic absorption spectrometer (AAS), outfitted with an EC90 furnace via a VP90 hydride generation (HG) system (all from Thermo Instruments Canada), in which AsH_3 was generated with a reducing solution of 1% w/v $NaBH_4$ (Aldrich) and 0.1% NaOH (Aldrich). The arsenic in the samples was quantified by using calibration curves constructed from matrix matched standards (Aldrich ICP/DCP arsenic standard).

Gastric fluid extraction (GFE) of mine and lake garden plants

The dried, homogenized mine and lake garden plant samples were extracted with 20 g of a synthetic gastric fluid containing 1.25 g/L pepsin (Sigma) and 8.77 g/L NaCl (Fluka, puriss p.a.) that had been titrated to pH 1.8 with HCl (Fluka, puriss p.a.) by shaking for one hour at 272 rpm and 37°C. Samples were then centrifuged for 30 min at 3000 rpm, and the supernatant was filtered (no. 4 filters, Whatman). A 2 g aliquot of the resulting extract was digested on a hot plate with 1 mL of ultrapure nitric acid (Seastar Baseline) and then diluted to 5 g with DDW. The digested extracts were analyzed by using hydride generation–atomic absorption spectroscopy (HG-AAS) in the same manner as the plant digests.

Statistical analysis

For statistical analyses Systat® 10 and Microsoft Excel® were used. Prior to conducting analysis of variance (ANOVA) tests, data were normalized by log transformation.

Quality assurance/quality control (QA/QC)

Quality assurance/quality control (QA/QC) measures were undertaken to ensure that the data were of high quality. Field duplicate soil samples were collected every 10 samples and these duplicates were treated as separate samples. During analysis, every batch of soil and plant samples (18–19 in a batch) included two duplicate analyses, one or two standard reference materials (SRMs) (GSS5, GSR6, NIST Montana 2710 or NRC MESS-3 for soils; Pine Needles NIST 1575 and Bush Branches GBW07603), and one blank. The blank consisted of an empty vial for soils, and 10 mL nitric acid + 2 mL H_2O_2 for plants, and they were treated in the same manner as the rest of the samples. Grinding blanks were also prepared from Ottawa sand (soils) and DDW (plants). During HG-AAS analysis, calibration was conducted after every tenth sample, and an external QC check prepared from a separate arsenic (V) source ($K_2HAsO_4 \cdot 7H_2O$, Aldrich) was included after every fifth sample. The external QC checks were within ±10% of the correct value.

For soils, the measured and certified values of SRMs agreed within 5%, except for one trial that was within 20%; all of these results were considered to be excellent or acceptable. For plants, agreement was within 15% or better, which was considered to be acceptable.

Relative standard deviations (RSDs) for field duplicates of soils ranged from 1.9% to 9%, which indicates good homogeneity during the sampling procedure. Analytical precision (obtained from the analytical duplicates) for soils ranged from 5% to 6% RSD, which is considered to be excellent.

Analytical precision for plants ranged from 2% to 49% RSD, with a mean RSD of 16%. This mean RSD is within the acceptable limit for analytical precision (20%), indicating that the analysis was conducted with good precision. For samples containing arsenic levels greater than approximately 0.5 mg/kg, the RSD ranged from 2% to 22%, indicating that the lower precision (i.e. higher RSD) was exhibited only at lower arsenic concentrations.

The precision of the GFE procedure ranged from 0.6% to 55% RSD, with a mean of 21%. Again, higher RSDs were observed for samples containing lower amounts of arsenic.

Soil blanks (empty vials) and a grinding blank of Ottawa sand contained no detectable arsenic (<3 mg/kg). Plant digestion and grinding blanks contained no detectable arsenic (<0.11 mg/kg dry weight).

Based on the accuracy and precision results reported above, a 20% error was estimated. All values were thus reported with significant figures such that this uncertainty is in the last significant figure; calculated values (e.g. means) were reported with an extra significant figure.

Results and discussion

Arsenic concentrations in soils

Arsenic concentrations in residential, mine and lake garden soils are summarized in Table 2.2. The average arsenic concentration in the residential gardens

Table 2.2 Arsenic concentrations ([As]) in soils from Yellowknife gardens

Garden location	*[As] (mg/kg dry weight)*
Residential 1	200
Residential 2	28
Residential 3	24
Residential 4	55
Residential 5	30
Residential 6	35
Residential 7	29
Residential 8	27
Residential 9	12
Residential 10	56
Mine	1600
Lake planters	700

Table 2.3 Results from analysis of single samples within gardens compared with composite samples, to show spatial homogeneity of garden soils (concentrations are dry weight)

Garden	n	*Mean (mg/kg)*	*Standard deviation (mg/kg)*	*% RSD*	*Composite (mg/kg)*
Residential 2	3	28	14	52	nd
Mine	8	1560	660	42	1600
Lake	5	720	220	31	700

nd = not determined; RSD = relative standard deviation.

was 33 ± 14 mg/kg, ranging from 12 to 56 mg/kg. Samples that were not included in this average were collected from garden location 1, which was an abandoned garden on the Giant Mine Townsite. The average arsenic concentrations were much higher in this area with an average of 200 ± 140 mg/kg, ranging from 81 to 350 mg/kg. These samples are considered separately because they are from a currently non-residential area.

Soil from the mine garden contained more arsenic (1600 mg/kg) than that from the lake garden (700 mg/kg), which is statistically confirmed by a *t*-test even when the spatial variability in the gardens is taken into account (Table 2.3) ($n = 13$, $t = 4.36$, $p < 0.05$).

Analysis of individual samples from residential garden 2, the mine garden and the lake garden was carried out to ascertain the degree of variability that might be expected in a garden as a result of the sampling method used. The results are summarized in Table 2.3 and indicated that the spatial precision (i.e. percent relative standard deviation, RSD) ranged up to 50%. The composite samples for the mine and lake gardens are within 2.5 percentage points of the mean values. These results indicate that the sampling method was adequately spatially representative, and that the composite analyses of the soils collected from the remaining gardens are a good estimate of the arsenic concentrations in each garden.

All soils contained arsenic at levels that are above the CCME soil guideline of 12 mg/kg (CCME, 1999). Arsenic concentrations found in residential garden soil samples from the city were consistent with previously reported background concentrations (3 to 150 mg/kg) in the Yellowknife area (Ollson, 2000; Reimer *et al.*, 2002); those from residential garden 1 were slightly higher. The levels in the mine and lake gardens are elevated above the local background, and are consistent with those previously reported in humic soils collected on the mine property (1140 ± 1190 mg/kg) (Hough, 2001) and from the shores of the lake (580 to 1000 mg/kg) (Ollson, 2000).

Arsenic concentrations in vegetables

Concentrations of total arsenic were determined in 23 different edible vegetable and fruit types and the results are summarized in Table 2.4. All arsenic concentrations in vegetables in this study are reported as fresh weight, since produce is most commonly consumed in the fresh (not dried) form.

In the residential gardens, leafy vegetables and greens, in general, contained the highest concentrations of arsenic, although the highest arsenic concentration in all the residential produce was found in Saskatoon berries (0.44 mg/kg fresh weight). The lowest concentrations of arsenic were below the analytical limit of detection in several residential samples, including potatoes, cabbage, peas, rhubarb, garlic, broccoli and zucchini. While below-ground vegetables, above-ground vegetables and fruits did not differ statistically in arsenic content for residential produce, in the lake and mine gardens, root (below-ground) vegetables contained the highest amounts of arsenic. Onions from the mine garden contained the highest concentration of arsenic of all the samples analyzed (330 mg/kg fresh weight), and beets, another root vegetable, contained the most arsenic in the lake garden (90 mg/kg). These findings are consistent with the general arsenic distribution in plants of the highest concentrations in roots, intermediate values in the above-ground shoots and leaves, and lowest levels in the edible seeds and fruits (Yan-Chu, 1994).

The arsenic concentrations in Yellowknife residential garden vegetables were almost always an order of magnitude greater than those found in a survey of foods from supermarkets across Canada (Dabeka *et al.*, 1993). Conversely, arsenic levels in residential vegetables collected for this study were approximately four to five times lower than those determined previously in Yellowknife (Soniassy, 1979). Lettuce and berries are the exceptions, as they appear to contain comparable concentrations of arsenic in both studies.

The arsenic concentrations in edible parts of the vegetables grown in the mine and lake gardens are much higher than those found in the residential gardens, and those reported in other studies conducted with elevated soil arsenic. Vegetables grown in loam soil treated with 100 mg/kg arsenic acid contained only trace quantities of arsenic (<0.01 mg/kg dw) (Pyles and Woolson, 1982). Carrots

Table 2.4 Arsenic concentrations ([As], mg/kg fresh weight) in edible vegetables; $n = 1$ for lake and mine gardens, except where indicated

Plant	n	*Residential gardens* *Minimum*	*Maximum*	*Average*	*Lake garden*	*Mine garden*
Carrot	6	0.020	0.07	0.045	1.3	
White and red potatoes	8	<0.02	0.07	0.031		15
Radish	1			0.17	1.8	31
Garlic	1			<0.03		
Garlic greens	1			0.11		
Onion	2	0.017	0.041	0.029		330
Onion greens	2	0.15	0.18	0.17		19
Beets	3	0.02	0.19	0.081	46	90
Beet greens	4	0.1	0.29	0.18	1.3	10
Lettuce	5	0.06	0.27	0.13	8	7.2*
Swiss chard	2	0.06	0.09	0.075		8
Kale	1			0.16		
Dill	1			0.07		
Italian parsley	1			0.10		
Oregano	1			0.23		
Cabbage	3	<0.01	0.09	0.043		
Kohlrabi	1			0.044		
Broccoli	1			<0.02		
Rhubarb	5	<0.01	0.05	0.020		
Celery	1			0.05		
Celery leaves	1			0.29		
Beans	3	0.016	0.026	0.02		
Peas	3	<0.02	0.036	0.019		1.5
Tomatoes	1			0.009		
Zucchini	1			<0.005		
Saskatoon berries	2	0.15	0.44	0.30		
Pin cherries	1			0.09		
Below ground	21	<0.02	0.19	0.048	17	120
Above-ground shoots	30	<0.01	0.29	0.104	4.7	12
Above-ground fruits	11	<0.02	0.44	0.073		1.5
Average of all (SD)				0.080 (0.086)	12 (20)	57 (105)

SD = standard deviation.
*Mean of two lettuce varieties (9.0 and 5.4 ppm).

grown in soil amended with different quantities of arsenic exhibited stunted growth with increasing soil arsenic content, with a maximum accumulation of arsenic in the carrots of 1.85 mg/kg dry weight (soil concentration of 338 mg/kg), while no carrots grew in soils containing more than 400 mg/kg arsenic (Helgesen and Larsen, 1998). Not surprisingly, carrots did not grow in the mine garden, where the soil concentration was 1600 mg/kg, but they did grow in the lake soil in the carrot planter, which contained 540 mg/kg of arsenic.

The results summarized in Table 2.4 suggest that the concentration of arsenic in garden produce increases with increasing concentration in the associated soil. Examination of this relationship[1] reveals that a linear correlation appears

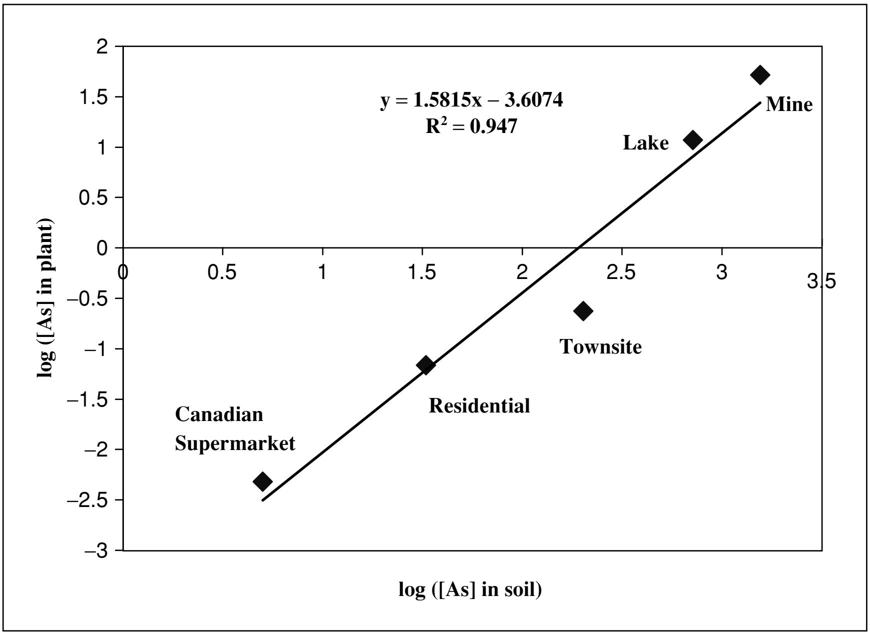

Figure 2.2 Relationship of log soil arsenic concentrations and log plant arsenic concentrations. [As] = arsenic concentration (mg/kg). Canadian supermarket values were estimated by using a typical Canadian soil concentration of 5 mg/kg and an average concentration in vegetables (Dabeka *et al.*, 1993) of 0.0048 mg/kg.

to exist between the log values of the average plant and soil concentrations (Figure 2.2). However, analysis of variance (ANOVA) of the concentrations revealed that while significant differences were present between mine, lake and residential soils, only mine plants were statistically different from residential plants in arsenic concentration ($p < 0.05$). These results are a reflection of the variability in the data, which is consistent with previous findings in Yellowknife that did not establish clear relationships between soil and plant arsenic (Hough, 2001). Considering that the soil types were all the same in the present study, the variability is likely a result of the different uptake behaviors of the plants studied.

It is important to note that during the summer of 2001, when the mine and lake gardens experiments were underway, an unusually large amount of rain fell in Yellowknife. Moreover, the mine garden was situated in a depression and did not drain well; hence some of the mine plants were partially (potatoes and carrots) or fully (onions) submerged in a pool of water. On the other hand, the lake planters appeared to drain well and consequently the plants accumulated more biomass and appeared healthier than the mine garden plants. The effect of the saturated conditions on the plant uptake of arsenic is unknown at this time.

Plant arsenic uptake

To understand how plants behave in contaminated soils in a predictive fashion, a study of how plants take up arsenic at different concentrations was conducted. Bioaccumulation factors (BAFs) were calculated as defined by equation (1).

$$\text{BAF} = \frac{([\text{As}]_{\text{plant}} \text{ in mg/kg fresh weight})}{([\text{As}]_{\text{soil}} \text{ in mg/kg dry weight})} \tag{1}$$

This calculation of BAF uses the fresh weight arsenic concentrations in plants to include the potential dilution effect of water content and to represent accurately the natural state of the plants. Dry weight soil concentrations are used because the wet and dry weights of soils were not found to differ by more than 20%, which is within the analytical error of the methods used.

When possible, translocation factors (TFs) from roots to shoots within the same plant were also calculated, as defined by equation (2) and with both concentrations in mg/kg fresh weight.

$$\text{TF} = \frac{[\text{As}]_{\text{shoot}}}{[\text{As}]_{\text{root}}} \tag{2}$$

The BAF data were examined with respect to above-ground (shoot) and below-ground (root) types of plants, as well as location (residential, lake, and mine). These data are summarized in Figure 2.3a, where an increasing trend in BAFs is observed for below-ground plants with increasing soil arsenic content. The highest mean BAF, observed in the below-ground plants from the mine garden, was significantly different from all other means, as determined by ANOVA and the below-ground mean BAFs were all different from each other. The results of ANOVA for this data set are summarized in Table 2.5; probabilities lower than 0.05 (italicized) indicate statistically significant differences between groups of data. Statistically significant differences were not observed between above- and below-ground BAFs for any other gardens, or between above-ground BAFs between neighboring gardens. However, mine BAFs were significantly different from residential BAFs. These trends imply that the ratios of plant arsenic to soil arsenic increase slightly in above-ground plants, and increase significantly with increasing soil arsenic in roots. The higher BAFs in roots, while subject to great variability, suggest that at extremely high soil arsenic concentrations, arsenic may be sequestered in the roots. Others have suggested that plants may compartmentalize arsenic in their root cells as a method to increase plant tolerance (Carbonell-Barrachina *et al.*, 1999). However, it is not known how root tissues tolerate extremely high concentrations of arsenic without exhibiting symptoms of toxicity (Creger and Peryea, 1994).

This trend is supported by the translocation (TF) data. TFs are greatest for residential vegetables, and lowest for mine vegetables (Figure 2.3b). This observation is statistically significant for the residential TFs compared with the mine but not the lake TF data set, and the other two data sets are not significantly

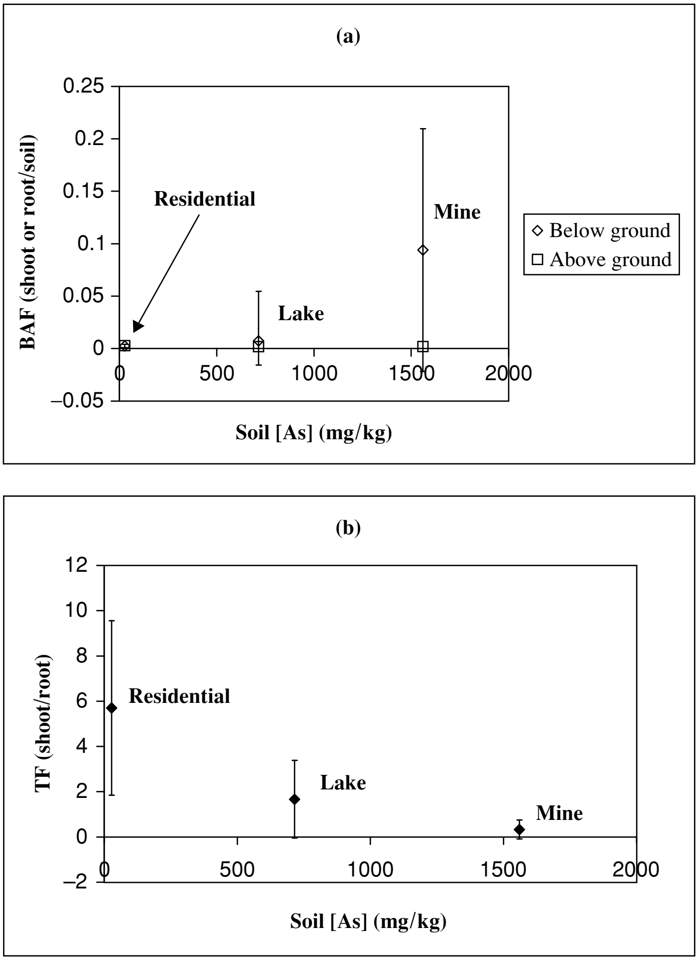

Figure 2.3 (a) Mean bioaccumulation factor (BAF) vs soil arsenic concentration (mg/kg dry weight) of below-ground and above-ground parts of plants. Error bars (± standard deviation) are for below-ground plants only; those for above-ground plants are <0.0036. (b) Mean translocation factor (TF) vs soil arsenic concentration (mg/kg dry weight) for the three gardens.

different from each other (ANOVA results, Table 2.6). The decrease in translocation from roots to shoots with increasing soil arsenic concentrations is likely a protective exclusion mechanism for these plants (Marin *et al*., 1993).

Gastric fluid extraction (GFE)

Gastric fluid extraction (GFE) was conducted on the plants that contained high levels of arsenic to estimate the portion of arsenic that might be bioaccessible to

Table 2.5 ANOVA results for bioaccumulation factors (BAFs) of above-ground (shoots) and below-ground (roots) plants from soil, from the three gardens: matrix of pairwise comparison probabilities following Bonferroni adjustment. Italicized numbers ($p < 0.05$) indicate that a statistical difference exists

	n	*Lake above*	*Lake below*	*Mine above*	*Mine below*	*Residential above*	*Residential below*
Lake above	5	1					
Lake below	5	1	1				
Mine above	8	1	1	1			
Mine below	8	*0.006*	*0.03*	*0.005*	1		
Residential above	41	0.48	0.101	*0.025*	*0*	1	
Residential below	21	0.088	*0.016*	*0.003*	*0*	1	1

Table 2.6 ANOVA results for translocation factors (TFs) from residential, lake and mine gardens: matrix of pairwise comparison probabilities following Bonferroni adjustment. Italicized number ($p < 0.05$) indicates that a statistical difference exists

	n	*Lake TF*	*Mine TF*	*Residential TF*
Lake TF	5	1		
Mine TF	8	0.205	1	
Residential TF	6	0.251	*0.002*	1

Table 2.7 Arsenic concentrations ([As], mg/kg fresh weight) and extraction efficiency (EE) from gastric fluid extraction of edible parts of plants from mine and lake gardens

Plant	*Mine garden*			*Lake garden*		
	Plant [As]	*Gastric fluid extractable [As]*	*%EE*	*Plant [As]*	*Gastric fluid extractable [As]*	*%EE*
Carrots				1.3	0.17	13
Red potatoes	15	6	37			
Radishes	31	6	19	1.8	0.27	15
Onion	330	0.18	0.1			
Onion greens	19					
Beets	90			46	33	68
Beet greens	10			1.3	0.5	12
Prize Head lettuce	9	7	78			
Grand Rapids lettuce	5	1.0	19	8		
Swiss chard	8	10	120			
Peas	1.5	1.0	70			
Average (SD)		4.4 (3.6)	49 (42)		8.4 (16)	27 (27)
Average % EE of all plants from both gardens (SD)						41 (38)

SD = standard deviation.

the human gastrointestinal tract. The results for edible plants are summarized in Table 2.7.

Sample size sufficed for the extraction of only a limited number of samples ($n = 7$ for mine garden, $n = 4$ for lake garden). Most extraction efficiencies were less than 100%, although they ranged from less than 1% to 100% and averaged 41%. This finding is consistent with GFE extraction efficiencies for other plants from Yellowknife (Koch *et al.*, 2002). No statistically significant differences were found in GFE extracted arsenic amounts or extraction efficiencies between the two gardens (t test, $p > 0.05$).

Risk posed by the consumption of Yellowknife garden vegetables

Given that the levels of arsenic in Yellowknife vegetables from residential gardens are typically 10 times higher than the national average, the question is:

are they safe for human consumption? Moreover, to what extent does the risk increase for the mine and lake gardens?

The risk assessment approach was to determine whether the increase in the estimated daily intake (EDI), through the consumption of arsenic-containing vegetables grown in Yellowknife, causes the provisional maximum daily intake (PMDI) recommended by FAO/WHO (2.1 μg/kg per day) to be exceeded.

The EDI of arsenic from vegetables was calculated as described by equation (3).

$$EDI = ED_f = \frac{CF \times CR \times EF \times PH \times AF}{BW} \tag{3}$$

where:
EDI = estimated daily intake
ED_f = estimated dose from food: as μg of the contaminant eaten per kg of body weight per day (μg/kg per day)
CF = concentration of arsenic in food: the concentration of the contaminant in the food group is expressed as μg/g (mg/kg)
CR = consumption rate: the amount of each individual food consumed per day expressed as grams per person per day (g/person per day)
EF = exposure factor: indicates how often the individual has eaten the contaminated food in a year (unitless, with a maximum value of 1.0)
PH = percentage of the food that is home-grown. Health Canada suggests that for residential gardens this amount is 7% (i.e. PH = 0.07)
AF = accessibility factor: indicates the fraction that is accessible following ingestion and digestion in the human gastrointestinal tract (unitless, with a maximum value of 1.0)
BW = body weight: the average body weight in kilograms (kg) based on an individual's age group.

To put these data into the perspective of the typical Canadian diet, total EDIs were also calculated. This calculation consisted of adding the garden vegetable EDIs to the amounts of arsenic that are estimated to be ingested by Canadians from the consumption of all foods (Dabeka *et al.*, 1993).

Several assumptions were made in the risk calculation.

1. For the purposes of the worst-case scenario for human health risk assessment, 100% of the arsenic is assumed to be inorganic. Previous studies have shown that inorganic arsenic forms are predominant in terrestrial plants from Yellowknife (Koch *et al.*, 2000a).
2. The concentration of arsenic in the food is the average for each garden (Table 2.4) (expressed as fresh weight), since only a limited number of plants were successfully grown in the mine and lake gardens.
3. The consumption averages for daily intake of all vegetables were taken from the Human Health Risk Assessment for Priority Substances (Health Canada, 1994) and are based on a nutritional survey conducted from 1970 to 1972 and published in 1977 (National Health and Welfare, 1977).

4 Eleven categories based on age, sex, weight, and differing daily consumption rates are published (Health Canada, 1995); these were summarized into four categories for the EDI calculation for the garden produce, because body weights and food intakes are the same for males and females at 12–19 years of age, and for all males and females older than 20 years. However, the 11 categories were used in the calculation of total EDIs, because the Canadian EDIs differ for each category (Dabeka *et al.*, 1993). These categories are generalized, since an obvious range of weights and daily consumption rates exists that cannot be taken into consideration in this model.

5 Residential, mine and lake garden produce were considered to be home-grown food and therefore the recommended value of 7% (i.e. 0.07) was used for PH.

Two scenarios were generated by calculating EDIs with two accessibility factors for each of the three garden types. For Scenario 1, all the arsenic was assumed to be accessible (AF = 1) and for Scenario 2, the arsenic was assumed to be only as accessible as the GFE method predicts. In the latter case, the mean GFE extraction efficiencies were used for the mine garden (49%, AF = 0.49) and the lake garden (27%, AF = 0.27), and the overall mean was used for the residential gardens (41%, AF = 0.41) from Table 2.7.

The EDIs from the consumption of garden vegetables are summarized in Table 2.8, and total EDIs, which incorporate arsenic from all food sources, are found in Table 2.9. The general trends that emerge from these data are that in all cases the EDIs for children in the age groups 1–4 years and 5–11 years are higher than those of all the other age and gender groups. This is the result of a smaller body weight (20–25% of other age groups) for these groups combined with a consumption rate that is not proportionally smaller (≥50% of other age groups). In addition, the EDI of arsenic tends to be slightly higher on average for males in all categories. This can be attributed to higher consumption rates of foods. These findings are not surprising, as these trends are also true for the Canadian averages (Dabeka *et al.*, 1993).

In all cases, the consumption of vegetables from Yellowknife residential gardens does not significantly increase the EDI, and does not increase the total EDIs above the PMDI specified by FAO/WHO. At the other extreme, the consumption of mine-grown garden vegetables causes the EDIs to exceed the PMDI in all age and weight groups and for both scenarios.

When Scenario 1 is assumed for the lake garden, the PMDI is exceeded for all age groups. However, the use of the GFE extractable amounts for the accessibility factor causes the total EDIs to decrease so that the PMDI is exceeded only for toddlers and children. This is an interesting result as it highlights the mitigating effect of using a less conservative AF. However, considering that the extraction efficiency from GFE ranged up to 100%, it may be prudent to continue to use the more conservative estimates.

Thus, although residents of Yellowknife may be consuming vegetables that contain arsenic concentrations that are approximately 10 times greater than

Table 2.8 Estimated daily intakes (EDIs) of arsenic (μg/kg) from consumption of vegetables grown in Yellowknife gardens. Italicized numbers exceed the PMDI of 2.1 μg/kg per day

Consumption rates and body weights

Category	*Toddler*	*Child*	*Teen male/female*	*Adult male/female*
Age (years)	1 to 4	5 to 11	12 to 19	20+
Weight (kg)	13	27	57	70
Canadian average consumption of vegetables (g/person per day)*	125	198	250	250

Most conservative – all arsenic bioaccessible (Scenario 1)

	Average [As] in produce (mg/kg fresh weight)	*AF*	*Estimated daily intake of arsenic (μg/kg)*			
Residential	0.080	1	0.054	0.041	0.025	0.020
Lake	12	1	*7.9*	*6.0*	*3.6*	*2.9*
Mine	57	1	*38*	*29*	*18*	*14*

Less conservative – limited arsenic bioaccessibility (Scenario 2)

	Average [As] in produce (mg/kg fresh weight)	*AF*	*Estimated daily intake of arsenic (μg/kg)*			
Residential	0.080	0.41	0.022	0.017	0.010	0.008
Lake	12	0.27	*2.1*	*1.6*	*0.97*	*0.79*
Mine	57	0.49	*19*	*15*	*8.6*	*7.0*

*Health Canada (1995).

those found in vegetables from Canadian supermarkets, there is no indication that this consumption incurs an increased health risk.

On the other hand, the consumption of vegetables grown in the lake and mine gardens is considered to be unsafe.

Conclusions

Arsenic concentrations in residential garden soils from Yellowknife are within the previously reported background concentrations for the area, with Giant Mine Townsite soils being six to seven times higher than other residential soils. The mine and lake garden soils, while elevated in arsenic concentration, are typical of their locations.

The concentrations of arsenic in produce from Yellowknife residential gardens are approximately 10 times higher than those found in produce from supermarkets

Table 2.9 Total estimated daily intakes (EDIs) of arsenic (μg/kg) from consumption of vegetables grown in Yellowknife gardens, adding Canadian EDIs (Dabeka *et al*., 1993: 14). Italicized numbers are above the PMDI of 2.1 μg/kg per day; (1) = Scenario 1; (2) = Scenario 2

Category	*Child M/F*		*Male*				*Female*				*M/F*
Age	1–4	5–11	12–19	20–39	40–64	65+	12–19	20–39	40–64	65+	All ages
Weight (kg)	13	27	57	70	70	70	57	70	70	70	70
Canadian estimated daily arsenic intakes (μg/kg)*	1.15	1.11	0.72	0.83	0.61	0.51	0.56	0.49	0.75	0.37	0.54
Residential (1)	1.20	1.15	0.74	0.85	0.63	0.53	0.58	0.51	0.77	0.39	0.56
Lake (1)	*9.02*	*7.11*	*4.31*	*3.76*	*3.54*	*3.44*	*4.15*	*3.41*	*3.68*	*3.29*	*3.47*
Mine (1)	*39.5*	*30.4*	*18.2*	*15.1*	*14.9*	*14.8*	*18.1*	*14.7*	*15.0*	*14.6*	*14.8*
Residential (2)	1.17	1.12	0.73	0.84	0.62	0.52	0.57	0.50	0.76	0.38	0.55
Lake (2)	*3.27*	*2.73*	1.69	1.62	1.40	1.30	1.53	1.28	1.54	1.16	1.33
Mine (2)	*19.9*	*15.4*	*9.29*	*7.81*	*7.60*	*7.49*	*9.13*	*7.47*	*7.74*	*7.35*	*7.53*

*Dabeka *et al*., 1993.

across Canada. The produce grown in the more elevated soils contain arsenic concentrations two orders of magnitude greater than those in residential produce.

While the mine garden produce contained higher levels, on average, than the lake garden produce, the great variability in arsenic content precludes the prediction of plant arsenic content based on soil arsenic concentration. The examination of bioaccumulation and translocation factors, while revealing the propensity for arsenic to be accumulated in the roots rather than the shoots, also did not allow for any generalized predictions.

The risk assessment, consisting of a comparison of estimated daily intakes (including intakes from sources other than local produce) to a safe level recommended by FAO/WHO, reveals that locally grown Yellowknife produce from residential gardens is safe to eat. However, vegetables from the lake and mine gardens should not be consumed.

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Note

1 Canadian supermarket values were estimated by using a typical Canadian soil concentration of 5 mg/kg (CCME, 1999) and the average concentration of vegetables in Dabeka *et al.* (1993) of 0.0048 mg/kg.

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