Mass balance tracer techniques for integrating *in situ* soil ingestion rates into human and ecological risk assessments

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Abstract

Quantitative soil ingestion studies employing a mass balance tracer approach have been used to determine soil ingestion rate for use in human health risk assessments (HHRAs). Past studies have focused on soil ingestion in populations living in urban/suburban environments and the results have been highly variable. Moreover, there is a paucity of reliable quantitative soil ingestion data to support human health risk assessments of other lifestyles that may be predisposed to ingesting soil, such as indigenous populations following traditional lifestyles. Thus, the primary objective of the research was to determine if populations following lifestyles typical of traditional land use practices in rural or wilderness areas ingest more soil than populations living in urban or suburban environments. Further, the research investigated the use of alternative mass balance tracers, specifically isotopes of the ^{238}U and ^{232}Th decay series, to reduce soil ingestion estimate variability. Mass balance tracer methods were developed and validated in a pilot canine study, and methods using isotope tracers were adapted to permit quantification of sediment ingestion in the benthic fish *Moxostoma macrolepidotum* (Shorthead Redhorse Sucker). A pilot human soil ingestion study of 7 subjects from an Aboriginal community in British Columbia was conducted over a 3-week period. The mean soil ingestion rate calculated using the daily means of the 4 elemental tracers with the lowest food-to-soil ratios (i.e., Al, Ce, La, Si) was observed to be approximately 74 mg d^{-1} (standard deviation 91 mg d^{-1}), The median soil ingestion rate was 60 mg d^{-1}, and the 90th percentile was 196 mg d^{-1}. These soil ingestion rate estimates are higher than those currently recommended for HHRAs of adults, and higher than those obtained in most previous studies of adults. However, the estimates are much lower than the earlier qualitative assessments for subsistence lifestyles (i.e., 330-400 mg d^{-1}). The study results also demonstrated that isotopes of the ^{238}U and ^{232}Th decay series radionuclide are not reliable mass balance tracers for estimating soil ingestion in humans; however, they may be useful for quantifying soil and sediment ingestion in wildlife.

Résumé

Cette étude quantitative utilise le bilan massique, calculé à base de traceurs élémentaires, afin de déterminer le taux d'ingestion des sols nécessaire pour l'évaluation des risques à la santé humaine (ERSH).Des études antérieures ont examinées l'ingestion de sols dans certaines populations urbaines et suburbaines, cependant les résultats furent très variables. De plus, l'information présentement disponible au sujet de l'ingestion des sols est insuffisante pour soutenir l'ERSH, surtout pour autres modes de vie comme les habitudes traditionnelles des populations autochtones. Ainsi, l'objectif principal de cette thèse était d'évaluer le taux d'ingestion des sols dans une population autochtone et de déterminer si ce taux d'ingestion est élevé en comparaison aux taux d'ingestion connus pour les milieux urbains et suburbains. En plus, cette recherche estime l'utilité de traceurs chimiques alternatifs, comme les isotopes de la série ^{238}U et du ^{232}Th, dans la réduction de variabilité chez les études de bilans massiques. Les méthodes de bilan massique par traceurs furent validées sur sujets canins, et les méthodes furent également adaptées pour le poisson benthique *Moxostoma macrolepidotum* (chevalier rouge). Une étude pilote sur l'ingestion des sols chez les humains de trois semaines fut réalisée à partir de sept individuels appartenant à la première nation Xeni Gwet'in de la vallée de Nemiah, en Colombie-Britannique. Le taux moyen d'ingestion des sols, calculé selon quatre traceurs élémentaires choisis pour leurs faibles ratios aliment-sol (Al, Ce, La et Si), était d'environ 74 mg j^{-1} (écart type : 91 mg j^{-1}). Le taux médian d'ingestion de sols était de 60 mg j^{-1}, et le 90^{e} centile s'élevait à 196 mg j^{-1}. Ces taux estimatifs d'ingestion de sols sont plus élevés que ceux des études précédentes ainsi que ceux recommandés pour l'ERSH chez les adultes. However, the estimates are much lower than the earlier qualitative assessments for subsistence lifestyles (i.e., 330-400 mg d^{-1}). Cependant, ces taux d'ingestion de sols quantitatifs sont beaucoup moins élevé que ceux précédemment déterminés par méthodes qualitatives (330-400 mg j^{-1}). Les résultats de l'étude ont également démontrés que les isotopes de la série ^{238}U et du ^{232}Th ne sont pas des traceurs fiables pour l'estimation de l'ingestion de sols par bilan massique; ils pourraient cependant être utiles pour quantifier avec précision l'ingestion de sols et de sédiments chez les espèces sauvages.

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Glossary

α	Alpha decay
β	Beta decay
γ	Gamma decay
AF	Soil to water relative absorption factor for a contaminant
AIR	Acid insoluble residue
ANOVA	Analysis of variance
BSAF	Sediment to biota bioconcentration factor
BSC	Background soil concentration of a contaminant
BTM	Best tracer method
BW	Body weight
CF	Concentration factor
CTUIR	Confederated tribes of the Umatilla Indian Reservation
CV	Coefficient of variability
DEFRA	United Kingdom Department for Environment, Food and Rural Affairs
EC	Electron capture
EDI	Estimated daily intake of a contaminant
EPA	United States Environmental Protection Agency
ERA	Ecological risk assessment
FAO	Food and Agriculture Organization of the United Nations
FDA	United States Food and Drug Administration
F/S ratio	Food to soil ratio
GI tract	Gastrointestinal tract
HHRA	Human health risk assessment
HPGe	High purity germanium
IAEA	International Atomic Energy Agency

ICP/MS	Inductively coupled plasma mass spectrometry
ICP/OES	Inductively coupled plasma optical emissions spectrometry
ISO	International Organization for Standardization
LLD	Lowest level of delectability
LTM	Limiting tracer method
NIST	United States National Institute of Standards and Technology
NCRP Measurements	United States National Council on Radiation Protection and
PSQG	Preliminary soil quality guideline
RIVM	Netherlands National Institute of Public Health and the Environment
ROI	Region of interest in a spectral analysis
SF	Soil allocation factor
SIR	Soil ingestion rate
Soil pica	Abnormal and persistent ingestion of soil
SRM	Standard reference material
TDI	Tolerable daily intake limit of a contaminant
Tukey-Kramer HSU	Tukey-Kramer Honestly Significant Difference
UNSCEAR	United Nations Scientific Committee on the Effects Of Atomic Radiation

Chapter 1
Introduction

1.1 Soil ingestion estimating for risk assessment

The soil ingestion rate is a key component of Human Health Risk Assessments (HHRA), as well as soil quality guidelines that direct the remediation of contaminated sites in Canada and internationally. However, only a relatively few quantitative soil ingestion rate studies have been completed to date, and they have largely focused on assessing soil ingestion in children living in urban/suburban areas in the United States. A weakness of these studies is that they do not account for the degree of urbanization, social/economic status, regional and ethnic variation in behaviours, land cover (e.g., grass) or seasonality (Calabrese and Stanek, 1994). Moreover, although qualitative soil exposure assessments suggest that people following traditional lifestyles typical of rural or wilderness areas ingest considerably more soil than people living in an urban/suburban environment (Harper et al., 2005), there are no published quantitative assessments of soil ingestion of people living in rural or wilderness areas. Thus, it is not clear if soil ingestion rates recommended for use in HHRA are adequately protective of populations following lifestyles typical of rural or wilderness areas.

Further, soil ingestion studies completed to date have exhibited a high degree of variability. Typically, these studies have used inorganic elements commonly found in soils as mass balance tracers, where the mass of the tracers measured in excreta, the mass of tracers measured in food that is consumed and the concentration of the tracers measured in local soils are used to calculate soil ingestion. Non-elemental mass balance tracers, such as naturally-occurring radionuclides found in soil, or new, quantitative-estimating approaches to improve the precision of soil ingestion estimates to support HHRAs, have yet to be explored.

As with HHRA, a solid understanding of the mechanisms governing the fate and transport of chemical contaminants in the environment, and within organisms is a fundamental input to defensible ecological risk assessments (ERAs). Several studies using multimedia mass

balance models have been used to predict the extent of bioaccumulation of hydrophobic organic contaminants within aquatic systems and food webs. However, a potential weakness of these models is that they do not include sediment ingestion as a direct pathway for the bioaccumulation of contaminants in benthic feeding fish. Given the potential for hydrophobic organic compounds to accumulate in aquatic sediments, understanding the extent to which sediment is ingested by fish is an important metric to quantify the bioaccumulation of these chemicals in aquatic food webs. Moreover, fish is a common staple in the diet of many Aboriginal peoples of North America who follow a traditional lifestyle (Harper et al., 2005). It follows that HHRAs need to assess the exposure of these populations to contaminants in fish and other wildlife species, and in turn the exposure of these species to contaminants in sediment or soil via the ingestion pathway.

1.2 Research objectives and hypotheses

The main purpose of the research was to determine if participating in traditional activities and consuming foods traditionally collected, preserved and prepared by traditional methods will result in higher contaminant exposure from soil ingestion than the majority of the population living in urban/suburban environments. Thus, the overall hypothesis underpinning the research is:

> *"People following traditional lifestyles in rural or wilderness areas ingest more soil than people inhabiting an urban/suburban environment".*

The research was conducted in 2 parts directed at achieving the following high-level objectives:

a) Develop, evaluate and validate methods that will improve the precision and utility of soil ingestion estimates to support HHRA and ERA of contaminated sites located in rural or wilderness areas.

b) Increase our understanding of inadvertent soil ingestion and soil exposure estimates used in HHRA by conducting a quantitative soil ingestion study of a population following a traditional lifestyle and living in a rural or wilderness area.

Improvements to the precision and utility of mass balance tracer approaches and methods to estimate soil ingestion can be considered from 2 points of view. First, improvements to the accuracy, precision and utility of analytical methods used to quantify tracers in soils, food and feces may be realized with the use of alternative tracers. In this study, naturally occurring radionuclides that are amenable to non-destructive evaluation by gamma spectrometry were evaluated as candidates for use as alternatives to elemental mass balance tracers. Thus, a second hypothesis directing this research is:

> *"Radionuclides and elemental tracers in soil can reliably be employed in mass balance models to quantify soil ingestion rates for use in human health risk assessments"*.

Second, improvements to the precision and utility of soil indigestion estimates may be realized through changes in soil ingestion study approaches and study design. Accordingly, the method development work was focussed on achieving the following specific objectives and sub-objectives:

- Select the naturally occurring radionuclide candidates for evaluation as mass balance tracers in soil ingestion studies.
- Develop sample preparation and analytical techniques that will accurately and precisely measure these tracers in the sample matrices at the levels anticipated in a soil ingestion study, including:
    - Develop methods to reduce the detection limits of the gamma spectrometric analysis by pre-concentrating target analytes in the various sample matrices anticipated in soil ingestion studies.
    - Determine the particle size of soil to be analyzed that will yield the most accurate soil ingestion estimate.
    - Develop field sampling and sample handling methods that improve the utility (i.e., timeliness and cost effectiveness and safety) of soil ingestion studies conducted in rural or wilderness areas.

    - Evaluate new approaches to estimate soil ingestion with the candidate radionuclide tracers in studies of human populations.
- Test the mass balance methods developed in a pilot study of a canine subject by:
    - Confirming that candidate tracers are not absorbed in the gastrointestinal tracts of study subjects, and
    - Comparing the accuracy and precision of candidate tracers and new estimating approaches against elemental tracers that have been traditionally used in mass balance soil ingestion studies.

A secondary objective of the development work was to determine if the methods could be adapted to quantify sediment ingestion by wildlife and, more specifically, benthic fish.

Upon completion of the development work, the soil ingestion methods were used to estimate soil ingestion in a population of people engaged in activities typical of a traditional lifestyle residing in rural or wilderness areas. The following specific objectives and sub-objectives were identified for this phase of the research:

- Determine the types and scope of traditional activities practiced and the traditional foods consumed by members of the subject population that follow a traditional lifestyle.
- Determine if the consumption of locally sourced and traditionally preserved and/or prepared food items increases soil ingestion.
- Measure soil ingestion in subjects participating in a traditional activity and compare the results with estimates developed in previous soil ingestion studies, regulatory soil exposure guidelines for use in HHRA and HHRA soil exposure scenarios that have been developed for people practicing a traditional lifestyle in rural or wilderness areas.
- Evaluate the precision and utility of soil ingestion estimates calculated using the candidate radionuclide tracers and elemental tracers.

1.3 Thesis structure and content

The thesis has been divided into 8 chapters. Chapter 1 provides an introduction, establishes the purpose of the research, outlines the overall research hypothesis being evaluated and describes the content of the thesis. Chapter 2 is a critical review of the literature pertaining to the quantification of inadvertent soil ingestion and, more specifically, as it relates to soil exposure into people following traditional lifestyles. Based on the review, recommendations for improvements to soil ingestion estimating methods and study design were made to guide future soil exposure studies of people following traditional lifestyles. Chapter 2 is largely a duplicate of a paper published in Science of the Total Environment (Doyle et al., 2010). Chapter 3 describes the methods that were developed, evaluated and validated for use in a soil ingestion study of people following a traditional lifestyle. The accuracy and precision of the sampling and analytical methods used in mass balance soil ingestion studies are defined in this chapter, as well as an assessment of an alternative to the mass balance soil ingestion estimating approach. The validation of the soil ingestion estimating methods in a pilot study with a canine subject is also included in a section of this chapter. Chapter 4 is largely a duplicate of a paper published in Aquatic Toxicology (Doyle et al., 2011). The chapter describes a small study where the soil ingestion estimating methods developed to support HHRA were adapted to assess sediment ingestion in benthivorous fish. Chapter 5 provides a detailed description of the First Nation community selected to participate in a soil ingestion estimating study. The chapter includes a description of the biophysical environment that supports a traditional lifestyle and an ethno-cultural survey of community members that are most likely following a traditional lifestyle. The chapter also includes a preliminary assessment of soil ingestion from consumption of traditional and locally sourced foods. Chapter 6 provides the results of the soil ingestion study in the First Nation community described in Chapter 5. The chapter also includes a comparison of the soil ingestion estimates derived from the study with previous soil ingestion studies and regulatory guidelines for soil ingestion rates to be used in HHRAs. Chapter 7 examines the precision of soil ingestion estimates using the methods and approach used in the study described in Chapter 6. Chapter 8 provides a summary of the research, discusses the magnitude of the contribution, and it's

relevance to the scientific underpinnings of HHRA and ERA. Appendices are also included to document additional research details that were not included in the main body of the thesis.

With the exception of the first introductory chapter, portions of Chapter 3 on method development and the ultimate concluding chapter, each chapter was written as a stand-alone document that has been submitted for publication or earmarked for publication. As such, there are several areas where redundant information is presented. In particular, much of the introductory remarks, methods and reference sections of these chapters will contain information repeated from other chapters.

1.4 References

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Chapter 2

Mass balance estimating methods and their application to inhabitants of rural and wilderness areas

2.1 Introduction

Assessing the risks of adverse health effects from contaminated land is essential for making decisions regarding site management and remediation priorities. Human health risk assessment (HHRA) methods require knowledge about both hazard and exposure, and the soil ingestion rate is a critical component of assessing exposure of populations to contaminants in soil. In the 1970's growing health concerns with lead and dioxin contamination of urban soils resulted in the completion of several studies that estimated soil ingestion in children living in urban/suburban environments in developed countries (i.e., western Europe and the United States), and these studies have provided the basis for soil ingestion estimates for use in the HHRA of contaminated sites. Children were selected as the target receptor because they were considered at high risk of exposure to contaminants in soil due to their close contact with soil, and frequent hand to mouth behaviours that could increase ingestion.

However, it is not clear if children living in urban/suburban environments in developed countries are representative of all populations vulnerable to ingesting contaminated soil. Moreover, there is no reliable quantitative data to support HHRAs for activities associated with receptors living in rural or wilderness areas, or for lifestyles and occupations such as farming, where there is the potential for high exposures in the work environment and from soil adhering to locally-grown and -ingested food. These lifestyles may be predisposed to ingesting soil because they are practiced in areas where environmental conditions enhance the likelihood of soil intake (e.g., unpaved roads, outdoor recreation). In addition, the lifestyles often involve the consumption of local foods that can be contaminated with soil

particles and typically involve more traditional land use practices that increase the likelihood of direct contact with soil (e.g., local foraging of foods, preservation and preparation of foods outdoors). Populations of peoples inhabiting rural and wilderness areas, including those who follow more traditional land use practices, are widespread globally, and include inhabitants of areas near contaminated areas such as mining or smelter operations (e.g., La Oroya, Peru, Port Radium, NWT, Canada), remote military installations (e.g., Distant Early Warning line sites in the Canadian Arctic), abandoned pesticide stockpiles (e.g., African stockpiles program sponsored by the FAO and similar sites identified by the World Bank), and nuclear sites (e.g., Maralinga Islands, Hanford complex in the United States). To date, soil exposure estimates for rural and/or wilderness populations who may follow traditional land use practices have been limited to qualitative assessments of exposures of indigenous peoples based on extrapolations of data from soil ingestion studies of children and adults, (Harper et al., 2005; Harris and Harper, 1997), and radiological exposure assessments of contaminated sites (Haywood and Smith, 1992; Simon et al., 1998). As such, there is no quantitative basis for HHRA of populations that are atypical of urban/suburban environments, and there is a need for empirical soil ingestion studies of receptors following land use practices typical of rural and wilderness areas to support HHRA.

The purpose of this review is to examine soil ingestion estimates and estimating methods conducted to date and determine their applicability to the development of soil ingestion rate estimates for receptors other than children and adults living in a North American urban/suburban environment, such as populations living in rural or wilderness areas where traditional land use practices are common. As such, this review provides a basis for future studies of potentially vulnerable populations not represented in past soil ingestion studies.

2.2 Review of Soil Ingestion Study Methodologies for HHRA

2.2.1 Qualitative/semi-quantitative soil ingestion studies

A number of early papers (Table 2.1) discussed soil ingestion as it relates to risk assessment of children exposed to elevated lead in street dust and indoor paint, as well as exposure to other toxic chemicals such as dioxins. These studies attempted to quantify soil ingestion by

using qualitative assessments of behaviours that may lead to soil ingestion (e.g., mouthing of objects or hands), and semi-quantitative methods to determine the amount of soil ingested as a result of these behaviours. The soil ingestion estimates determined with these methods are highly variable, ranging from a low of 10 mg d^{-1} to a high of several grams per day. The application of such high ingestion rates in HHRAs could result in the establishment of unrealistically onerous criteria for contaminated site rehabilitation and remediation.

Table 2.1
Summary of selected early qualitative or semi-quantitative soil ingestion estimates[1]

Study	Soil Ingestion Rate (mg/d)	Methods/Commentary
Lepow et al., 1974; 1975	100	Based on observations over 3-6 hours of play and crude measurement techniques. Measured soil on hands and observed mouthing behaviour.
Day et al., 1977	10-1000	Based on observations and crude measurement techniques. Measured dirt on sticky sweets and estimated number of sweets consumed per day.
Duggan and Williams, 1977	25	Based on observations and crude measurement techniques. Measured soil on fingers and observed mouthing behaviour.
Kimbrough et al.,1984	0-10,000	Based on illustrative and conservative estimates of mouthing behaviour and amount of soil on hands.
Hawley, 1985	24-165	No data on soil intake collected. Reviewed data from previous studies and estimated soil intake rate based on nature and duration of activities.

2.2.2 Early quantitative soil ingestion studies

The first quantitative soil ingestion estimates were developed by Binder et al. (1986) who estimated soil ingestion of children in East Helena, Montana over a 3-day period. Their methods were adapted from veterinary methods to measure soil ingested by grazing animals using Al, Si and Ti as chemical tracers commonly found in soil and are not readily absorbed

[1] Adapted from LaGoy, 1987 and EPA, 1997

in the gastrointestinal tract. Fecal samples were collected from diapers and analyzed by mass spectrometry (ICP/MS), whole soil samples from each child's back yard were analyzed by X-ray fluorescence, and soil ingestion was calculated for each child using Eq. (2.1).

$$T_{ie} = (f_{ie} \times F_i) / S_{ie} \qquad (2.1)$$

where:

T_{ie} is the estimated soil ingestion for child "i" based on element "e" (g d^{-1})

f_{ie} is the concentration of element "e" in fecal sample for child "i" (μg g^{-1})

F_i is the daily fecal dry weight for child "i" (g d^{-1})

S_{ie} is the concentration of element "e" in yard of child "i" (μg g^{-1})

The study did not account for uptake of tracers in food and therapeutic products (i.e., medicines), and assumed that all tracer found in feces was derived from soil. This is a reasonable assumption when estimating soil ingestion in grazing cattle; however, the authors noted the possibility that the dietary intake of Al, Si and Ti was not negligible in their study subjects, and that it could lead to an overestimation of soil ingestion rates (i.e., inflated f_{ie} relative to S_{ie}). To compensate for the potential ingestion of non soil-derived tracers, the authors suggested that the soil ingestion rate could be calculated from the minimum value of the 3 tracers on any given day. This approach implies that if a child consumes a concentrated source of a specific tracer (e.g., via medication), then a higher soil ingestion rate for that tracer would result and the lowest soil ingestion rate value of the 3 tracers is the most accurate. Their studies concluded that soil ingestion rates based on Al and Si in feces were 181 and 184 mg d^{-1} respectively, whereas ingestion based on Ti was an order of magnitude higher. They attributed the high ingestion rates based on Ti to differences in gastrointestinal tract absorption and/or to unrecognized sources of Ti in the diet.

Two soil ingestion estimates using Ti, Al and acid insoluble residue content of soil as mass balance tracers to estimate soil ingestion in children were also conducted in the Netherlands.

A pilot study was conducted by Clausing et al. (1987), followed by a larger study by van Wijnen et al., (1990) using the same methodology for children under 3 environmental conditions: (1) day-care centers with the possibility of direct contact with soil; (2) campgrounds with a maximum probability of having direct contact with soil; and (3) a control group of hospitalized, bedridden children who were assumed to have no contact with soil. In these studies the Limiting Tracer Method (LTM) was used to calculate maximum soil ingested according to Eq. (2.2). The LTM also assumes that the maximum amount of soil ingested corresponds to the lowest soil ingestion estimate from the 3 tracers used.

$$I_a = F \times \frac{C_{af}}{C_{as}} \qquad (2.2)$$

where:

I_a is the soil intake based on tracer "a" (g d^{-1} dry wt.)

F is the feces production (assumed to be 15 g d^{-1} dry wt.)

C_{af} is the concentration tracer "a" in feces (mg kg^{-1} dry wt.)

C_{as} is the concentration tracer "a" in soil (mg kg^{-1} dry wt.)

An interesting result of the pilot study was the calculated soil ingestion rates for the control group of hospitalized children. Values for 5 of the 8 children were well over an order of magnitude higher when ingestion was calculated using Ti, compared with values calculated using Al or acid insoluble residue.

In the larger study, the soil ingestion estimates were corrected for dietary background levels using the LTM values derived from the hospitalized children. The estimated geometric mean soil intake for daycare centre children varied from 0 to 90 mg/day and for the campground these estimates ranged from 30 to 200 mg/day (dry weight). However, the use of assumed fecal weights in the studies could have severely biased the soil ingestion values, and failure to account for tracers ingested in foods or medication (i.e., assuming that tracer quantities in feces are only derived from ingested soil) would at best provide in an upper limit of the soil ingestion rate, assuming that the use of hospitalized children as controls is appropriate (i.e.,

that the tracer concentrations in hospital food were equivalent to that consumed by other subjects) (Calabrese and Stanek, 1991).

2.2.3 Mass balance soil ingestion studies

These early quantitative studies were followed by several studies that used a mass balance approach to estimate soil ingestion: a validation study of adults followed by a larger soil study of 64 children in Amherst, Massachusetts by Calabrese et al. (1989), and two major studies of soil ingestion conducted in Washington State by Davis et al. (1990) and Davis and Mirick (2006).

Calabrese et al. (1989) improved upon estimating methods by increasing the number of tracer elements used from 3 to 8 (i.e., Al, Ba, Mn, Si, Ti, V, Y, Zr), adopting a complete mass-balance approach that accounted for the contributions from food and medication, increasing the study duration from 3 days to 8 days, and validating the methodology in a smaller study of adult volunteers. The validation study involved the administration of known amounts of soil to 6 adults (i.e., as gel capsules) for 3-day periods over 3 weeks, and daily collection of duplicate meals, medications and fecal samples. The authors noted that food ingestion dry weight varied substantially between subjects (between 97 to 913 g d^{-1}), and variability in fecal output (i.e., dry weights of daily composite samples) was also large. The amount of each tracer in fecal samples was measured and compared to what was ingested in the soil capsules, and percent tracer recovery was calculated. The observed variation in recovery of some tracers for the participants was large. For example, percentage recovery values using Ba and Mn tracer values grossly exceeded 100%. The Al, Si, and Y were considered the most valid tracers because they most closely approached 100% recovery values. Tracer quantities in excess of the tracer doses contained in capsules were attributed to ingestion of soil from other sources.

The larger study of children (Calabrese et al., 1989) used the mass balance methods from the adult validation study. Duplicate food samples and daily fecal samples were collected for each subject during each study week. Eq. (2.3) provides a simplified version of their mass-balance equation.

$$S_a = \frac{F_c \times F_a}{S_c} - \frac{I_c \times I_a}{S_c} \quad (2.3)$$

where:

S_a is the soil ingested (g)

F_c is the concentration of tracer element in excreta (μg g^{-1})

F_a is the amount of feces (g)

I_c is the food concentration for tracer element (μg g^{-1})

I_a is the amount of food ingested (g)

S_c is the concentration tracer in whole soil μg g^{-1})

Tracer concentrations in soil were measured in whole soil collected from each subject's back yard. The tracer methodology does not include inputs from air and water, as these were assumed to have a negligible impact on the ingestion estimates. Excreta samples included urine. Extremely low concentrations of Ba, Mn, Ti, V, Y, Zr were found in urine samples; however, Si was found to constitute a substantial fraction of adult urine excretion, suggesting that it is absorbed in the gastrointestinal tract in adults.

Stanek and Calabrese (1991) noted that accounting for food in the soil ingestion equation is valid only if there is a one-to-one correspondence between tracer food input and tracer output. However, the amount of tracer ingested in food varies from day to day and the transit time for food from ingestion to feces also varies, resulting in a potential lack of temporal correspondence, also called transit time misalignment. Transit time misalignment can be resolved by designing studies with longer durations or by using tracers with a high soil-to-food concentration ratio. Extending the duration of the study to minimize transit time error could result in problems with subject participation and compliance with study protocols. Other considerations were the amount of time the children played in the home and outside the home (i.e., soil ingestion versus dust ingestion), the landscape (i.e., the amount of exposed soil available to be ingested), and the season.

The Davis et al. (1990) study employed a mass-balance approach using Al, Si and Ti tracers to assess daily soil ingestion in a random sample of 104 children living in Montana. Their study collected duplicate samples of all food items consumed, all feces, and some urine excreted for 4 consecutive days. Soil and house dust samples were collected only from each child's home and soil samples were not collected from other areas where the child may have ingested soil. Soil ingestion was calculated using the generic Eq. (2.4) (Davis et al., 1990).

$$S_{ie} = \frac{\left(\left((DW_f + DW_p) \times E_f\right) + E_u\right) - (DW_{fd} \times E_{fd})}{E_{soil}} \quad (2.4)$$

where:

S_{ie} is the soil ingested for child "I" based on tracer "e" (g)

DW_f is the feces dry weight (g)

DW_p is the dry weight of feces on toilet paper (g)

DW_{fd} is the food dry weight (g)

E_f is the tracer concentration in feces (μg g^{-1})

E_u is the tracer amount in urine (μg)

E_{fd} is the tracer concentration in food (μg g^{-1})

E_{soil} is the tracer concentration in soil (μg g^{-1})

To calculate ingestion, the quantity of tracers measured in non-food items (e.g., medicines) ingested during the study period was added to the amount of tracer measured in food. The values for missing fecal samples (i.e., those not collected by study participants) were calculated by multiplying the dry weight for fecal samples obtained by the number that should have been collected. The urine analysis results suggest that Si may be absorbed to a greater degree than Al, with negligible absorption of Ti. Soil ingestion rate values of 38.9, 82.4 and 245.5 mg d^{-1} were calculated based on Al, Si and Ti tracers respectively. The authors suggested that the relatively high soil ingestion estimates based on Ti were probably due to its presence in paints and paint dust. The study assumed a close temporal correspondence between materials ingested and excretion during the 4-day period. Further,

the study assumed that all ingested soil originated from the child's yard, and the tracer elements in soil were uniformly distributed throughout the subject's yard. Detailed activity data were also obtained for all subjects, and behavioural profiles were evaluated along with soil ingestion values for all 3 tracers. The planning, field sampling and laboratory work required in the study was extensive, and the authors noted that conducting a study employing a mass-balance approach requires considerable commitment from the participants. Feces collection by subject families was relatively complete and missing samples were well documented, but food sample collection was observed to be less than complete.

A second study comprising a subset of children and parents from the first study was conducted by Davis and Mirick (2006). The study design was similar to the first study, and estimated soil ingestion in children aged 3 to 8 years and parents in 19 families for 11 consecutive days using Al, Si and Ti tracers (i.e., total of 57 subjects). The families were selected based on their level of compliance in the first soil ingestion study. Detailed information on food, dietary and hygiene habits, and occupation was collected, in addition to information about time spent indoors and outdoors, and specific activities. The levels of soil ingestion observed in children were similar to those reported in the earlier study (i.e., mean soil ingestion rates ranging from 37 to 207 mg d^{-1}), and adult estimates were higher than previous estimates (i.e., mean soil ingestion rates ranging from 23 to 625mg d^{-1}). Ti provided the highest soil ingestion estimates in both children and adults, and the highest ingestion values were more variable in adults than in children. The soil ingestion estimates in children were not correlated with soil ingestion in adults from the same family. Two behaviours were correlated with increased soil ingestion: (1) geophagy in children; and (2) occupational contact with soil in adults.

2.2.4 Best Tracer Method

These early mass balance studies improved previous quantitative studies because soil intake rates were corrected using the tracer content of foods and medications, a relatively large number of children was used, and demographic and behavioural information of study subjects was collected (EPA, 1997). Nevertheless, the soil ingestion data generated remained

highly variable and of questionable reliability (Calabrese and Stanek, 1994). Uncertainties related to mass balance methods include transit time misalignment, measurement error, and/or source error (i.e., unidentified non-dietary sources of tracer). Positive error would result from the measurement of tracers in feces that were ingested in foods before the study, and negative error would result from tracer retention in the gastrointestinal tract, sometimes leading to negative soil ingestion estimates.

Transit time error is typically greatest for trace elements with higher food to soil (F/S) ratios, defined as the mass of the tracer element ingested from food over a 1-day period divided by the mass of the tracer element in 1 gram of soil. More reliable data should result from studies that have low quantities of tracer in food, longer study duration and higher sample sizes (Calabrese and Stanek, 1993). The potential for positive or negative error can be minimized by taking the median set of soil ingestion estimates with the lowest F/S ratio for each subject week. Based on these observations, the Best Tracer Method (BTM) was developed for estimating soil ingestion by mass balance modeling using inorganic tracers. The BTM ranks tracer elements according to their F/S ratios. The soil ingestion rate for each subject over a 1-week study period is calculated using the median of the 4 tracers with the lowest F/S ratio. Calculating soil ingestion rates in this manner would result in an improved detection capacity and tighter confidence limits than as calculated using previous methods.

2.2.5 Soil ingestion studies using the BTM

Calabrese et al., (1997a) conducted a major soil ingestion study of 64 children living near a Superfund site in the Anaconda, Montana area. The study lasted for 7 consecutive days and assessed soil ingestion using the BTM and included an adult validation study. As in earlier studies, all fecal samples and duplicate meal and medicine samples were collected, in addition to dust and soil samples from subject households. Fecal samples were freeze-dried and stored frozen until daily composite samples were analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) for Al, Ti and Si, and ICP-MS for Ce, Nd, La, Y and Zr. The soil equivalent (i.e., amount of the tracer element ingested per day divided by the concentration of the element in soil) measured in food for most tracers was found to

range between 61 and 120 mg d^{-1}; the tracers with the highest variability in food were La and Nd. The study accommodated missing food samples by using values based on average daily tracer levels for the same study week. Similarly, values for missing fecal samples were imputed using average daily tracer levels for the same study week.

Although use of the BTM was considered a marked improvement over previous study methodologies, soil ingestion estimates using the BTM remained vulnerable to source error. Soil ingestion results in the Anaconda study showed a fair degree of variability, with a reported mean soil ingestion estimate rate of 6.8 mg/day with a standard deviation of 74.5 mg/day, based on the 4 tracers with the lowest F/S.

2.2.6 Soil Pica and High Ingestion Behaviour

In describing the soil ingestion pathway for risk assessment applications, Sheppard (1995) suggested that soil ingestion rates in populations are lognormally distributed because of the broad range of the data, the notion that soil ingestion is never zero, and the possibility of very high values occurring. Moreover, he suggested that the overall distribution is bimodal to accommodate behaviours that involve intentional soil ingestion (i.e., soil pica and geophagy). However, soil ingestion studies to that date were primarily directed at establishing a typical or chronic soil ingestion rate in children, and to a limited extent adults, for general use in HHRAs.

Calabrese et al. (1997b) employed the BTM to estimate soil ingestion in 12 children identified by their parents as likely high soil ingesters. The importance of the study is that it attempted to quantify the soil ingestion rate for recognized high ingestion behaviour (i.e., soil pica). Soil ingestion rates associated with these high ingestion behaviours may be as important to understand as soil exposure associated with ordinary day-to-day activities. For example, in a review of United States Environmental Protection Agency (EPA) contaminated soil screening levels and the EPA risk-based clean-up criteria, Calabrese et al. (1999) reported that some children have been observed to ingest sufficient soil to incur an unacceptable risk of adverse acute effect. Their findings suggested that soil cleanup criteria based on chronic low-level exposure to soil may not be protective during soil pica episodes.

Thus, overall soil ingestion should be viewed as a composite of low-level chronic ingestion rates and episodic high ingestion rate activities.

2.3 Improving soil ingestion estimating methods

2.3.1 Regulatory Soil Ingestion Rates

The standard equation used by Health Canada to develop risk-based soil quality guidelines for the protection of human health is shown in Eq. (2.5) (CCME, 1996):

$$PSQG_{HH} = \frac{[(TDI-EDI)\times SF\times BW]}{AF_G\times SIR} + BSC \qquad (2.5)$$

where:

$PSQG_{HH}$ is the human health soil quality guideline (mg kg^{-1})

TDI is the tolerable daily intake of the contaminant (mg kg^{-1} bw d^{-1})

EDI is the estimated daily intake of the contaminant (mg kg^{-1} bw d^{-1})

SF is the soil allocation factor (percent)

BW is the body weight (kg)

SIR is the soil ingestion rate (kg d^{-1})

BSC is the background soil concentrations (mg kg^{-1})

AF_G is the relative absorption factor for soil: water in the gut (unitless)

Clearly, soil ingestion rate is a key factor in determining cleanup criteria for contaminated sites. It is surprising that relatively few soil ingestion studies, which focused primarily on one receptor (i.e., children) living in a narrow set of environmental conditions, have been completed to date.

Comprehensive reviews of the aforementioned soil ingestion and related studies have been completed by regulatory authorities in order to provide guidance for use of exposure factor values employed in HHRAs of contaminated sites. Notably, the EPA has published a handbook containing soil ingestion exposure factors (including soil ingestion rate values) to promote consistency across the various EPA program offices (EPA, 1997). The handbook provides a detailed review of the results of the qualitative and quantitative soil ingestion studies completed to date, and discusses the uncertainty in the soil ingestion rates reported. Based on this review, the US EPA recommends soil ingestion rates for use in HHRAs of 100 mg d^{-1} for toddlers is the best estimate of a mean soil ingestion rate (with an upper percentile soil ingestion rate of 400 mg d^{-1} and a reasonable central estimate of 50 mg/d for adults (no upper percentile soil ingestion rate provided). A similar review of the scientific literature was conducted by Wilson Consulting (2006) to identify the most scientifically defensible soil ingestion rates for use in contaminated site HHRAs, and the development of soil quality guidelines in Canada. They reported a wide range of soil ingestion rates recommended by various regulatory agencies worldwide, with recommended soil ingestion rates for toddlers (7 months – 4 years) ranging from 40 mg/day to 400 mg/day. Recommended rates for adults were also highly variable with recommended soil ingestion rates ranging from 0.5 to 200 mg/day. Currently, the soil ingestion rates recommended by Health Canada for use in HHRAs are 80 mg/d for toddlers, 20 mg/d for adults and 100mg/d for construction workers. There are no recommended soil ingestion rates for camping, agricultural workers, or people following traditional land use practices (e.g., indigenous peoples).

As previously noted, the studies underpinning the aforementioned regulatory guidelines were limited to assessments of children and adults living in suburban/urban environments and attendant lifestyle under relatively benign conditions. Soil ingestion estimates of receptors atypical of these environmental conditions, or lifestyles that may be more vulnerable to soil ingestion, have typically assigned a soil ingestion rate at a high confidence interval (e.g., upper 95% quantile value), as was done in the exposure assessment of Confederated Tribes of the Umatilla Indian Reservation (CTUIR) (Harper et al., 2005). The higher soil ingestion estimate for the CTUIR was based on the premise that many high soil ingestion episodes

(i.e., gram–per-day) would be observed in individuals practicing a subsistence or traditional lifestyle. Thus, as described for the soil pica child, soil ingestion can be described as a bi-modal distribution to accommodate high soil ingestion rate episodes (e.g., traditional land-use practices, camping, agriculture).

2.3.2 Soil adhesion to food

Soil ingestion via consumption of locally-prepared foods can be high. Several studies have identified soil adhesion to food items as a major pathway for ingesting soil (Haywood and Smith, 1992; Hinton, 1992; Harper et al., 2005) with soil mass loading values for common vegetables ranging from ~1 mg soil per g dry plant material for cabbage to ~10 mg soil per g dry plant material for broccoli, to a high of 260 mg soil per g dry plant material for lettuce. Further, food preservation and preparation techniques, such as drying or smoking, roasting in earthen ovens or over open fires, and grinding of seeds and nuts between stones, as well as the consumption of food outdoors may also contribute to the amount of soil found in foods.

The soil ingestion rate is a key component in the development of soil quality guidelines and is based on the aforementioned recommended values. These recommended values are in turn are based on the mass balance soil ingestion studies that employed methods, such as the BTM. However, current mass balance estimating methods used to determine the soil ingestion rates recommended by regulatory agencies may underestimate soil ingestion for rural, wilderness or traditional lifestyles because they exclude local soil adhering to food from the calculation of soil ingestion. For example, soil ingestion (S_{ie}) for a period of time (usually a day) is generically calculated by subtracting the tracers measured in food (expressed in soil equivalents) from tracers measured in feces (also expressed in soil equivalents), as provided in Eq. (2.6).

$$S_{ie}\ (kg) = \frac{\textit{Fecal tracers (mg/kg) X feces wt. (kg)}}{\textit{Tracer in soil (mg/kg)}} - \frac{\textit{Fecal tracers (mg/kg) X food wt. (kg)}}{\textit{Tracer in soil (mg/kg)}} \quad (2.6)$$

Subtracting tracers measured in food from mass balance calculations to derive ingestion rates of soil is valid if all of the food consumed is obtained from outside sources (i.e., the supermarket). However, this method is not valid when food is locally-gathered and -processed, and can be expected to contain appreciable quantities of local, and potentially contaminated, soil. If the receptor population living near a contaminated site obtains or processes a significant proportion of its food locally (e.g., home gardens, outdoor drying), then it is important that soils adhering to consumed foods be accounted for in soil ingestion estimates. This can be achieved by determining the soil content in locally-sourced foods and calculating the ingestion rate based on an assessment of the amount of local foods consumed over the year.

2.3.3 Alternative Mass Balance Tracers

As already noted, the mass balance methods developed in recent soil ingestion studies are prone to source error and transit time misalignment. Previous studies have attempted to resolve this by using tracers with low F/S ratios. However, source error can also be reduced through the use of tracers that are not common in consumer products. Titanium dioxide (TiO_2), for example, is used in many consumer products, including paints, sunscreens, air purification systems, disinfectants, anti-stain coatings, and is a common excipient in drugs, oral suspensions and pastes (FDA, 2008). Several of the studies to date have shown abnormally high soil ingestion values relative to those determined using other tracers, and the difference may be due to inadvertent ingestion of Ti in consumer products. Thus, the utility of Ti as a tracer in future studies is questionable. Other tracers, such as Si and Al, are also commonly used as food additives (e.g., baking powders, coffee whiteners, dessert mix), and in cosmetics and in drugs (Lewis and Lewis, 1989). Alternative tracers to Al, Si and Ti, that are commonly found in soils but are not as prevalent in consumer products, food additives and medicines, may provide an opportunity to improve upon current mass balance estimating methods. Absorption of tracers by the gastrointestinal tract will increase estimate uncertainty and alternative tracers, with a lower gastrointestinal uptake, would reduce this uncertainty.

The ^{238}U and ^{232}Th decay series isotopes are good candidates for use as mass balance tracers in soil ingestion studies because they are not readily absorbed in the gastrointestinal tract, are ubiquitous in soils and are generally found in food at low concentrations. Moreover, uranium and thorium are not likely ingredients in consumer products due to their heavy metal and/or radioactive characteristics. Thus, they are less likely to contribute to source error in mass balance soil ingestion studies. Not surprisingly, neither is listed in the United States Federal Drug Administration (US FDA) list of approved food and drug excipients or active ingredients that could be ingested with medicines.

2.3.4 Soil ingestion study design

The statistical power of the soil ingestion estimating model using naturally-occurring radionuclides or other tracers is an important consideration for future soil ingestion studies. A Monte Carlo model was developed to determine the number of subjects required to achieve sufficient statistical power to measure soil ingestion at an acceptable confidence interval. Levels and analytical variability for selected ^{238}U and ^{232}Th decay series isotopes in soils from the Ottawa area were determined using gamma spectrometry (Table 2.2). The data were used to determine the sampling and analytical variability of tracer concentrations in soil samples presumably attributable to spatial differences in texture. This variability would be expected in soil ingestion studies where the subjects are interacting with the environment over large areas, as would be the case for people living in rural or wilderness areas and/or following traditional land use practices.

The data presented in Table 2.2 were used to derive hypothetical mean values for the various key inputs to the mass balance algorithm (i.e., Eq. (2.3)) used to calculate soil ingestion, and these are provided in Table 2.3. Parameter distributions were used as input to a Monte Carlo model developed to derive an overall soil ingestion rate distribution. The input parameter distributions were based on the following:

a) The mean and standard deviation (SD) assigned to food and fecal samples were based on the analytical variability observed in multiple analyses of ^{214}Pb in one soil sample,

b) The mean and SD assigned to soil were based on the variability observed in soil samples collected across Ottawa (n=10),

c) The anticipated levels of ^{226}Ra (and ^{214}Pb assuming secular equilibrium) in food, and amount of food consumed were obtained from the literature,

d) The mean and SD of food and fecal weights was calculated using the coefficient of variability (CV) observed for multiple weight measurements of food and fecal samples.

The input parameter distributions for ^{214}Pb for the 3 soil ingestion scenarios are provided in Table 2.3. The resulting distribution of soil ingestion estimates based on 999 iterations of the Monte Carlo soil ingestion estimate model is shown in Figure 2.1.

The soil ingestion rate distribution developed in the Monte Carlo model can be used to calculate the minimum detectable quantity (δ) for a given sample size using Eq. (2.7) (Zar, 1999):

$$\delta^2 = {S^2}/{n} \times \left(t_{\alpha,v} + t_{\beta(1),v}\right)^2 \qquad (2.7)$$

where,

S^2 is the distribution variance (mg d^{-1})

n is the number of samples

$t_{\alpha,v}$ is the t statistic for Type 1 error

$t_{\beta(1),v}$ is the t statistic for Type 2 error

The minimum detectable soil ingestion quantities were calculated as a function of the number of subject days in a soil ingestion study and assuming the analytical variability observed in Figure 2.2.

The results showed that approximately 225 subject days, assuming one soil ingestion estimate per subject-day is obtained, would be required to detect a difference of 20 mg/d in

soil ingestion (i.e., the soil ingestion rate for adults currently recommended by Health Canada). Thus, based on sampling and analytical uncertainty alone, relatively large studies would be required to detect soil ingestion at the anticipated chronic rates for adults. Alternatively, soil ingestion studies could be designed to confirm ingestion rates during short-term high ingestion activities, where recruiting a large number of subjects is impractical. In comparison, Stanek and Calabrese (1991) developed a method to determine the detection limits of the methods used in the Calabrese et al. (1989) study of soil ingestion in children, and concluded that a sample size of approximately 90 subject-weeks is required to reliably detect a soil ingestion rate of 100 mg d^{-1}.

However, the numbers of people living in rural or wilderness regions, where environmental conditions or lifestyles may facilitate soil ingestion, who are available to participate in soil ingestion studies are likely small and the power of a soil ingestion study of these populations will be low. Further, increasing the power of the soil ingestion study by increasing the duration of the study would introduce additional uncertainty resulting from non-compliance of study subjects with sample collection protocols. Therefore, a new approach to study design must be adopted. Specifically, soil ingestion studies should be focused on quantifying specific activities with a high potential for soil ingestion (i.e., gram-per-day levels). These estimates would be prorated over a year based on a qualitative assessment of the frequency and duration of these activities, similar to the development of early qualitative estimates based on soil loading on hands and frequency of mouthing behaviour in children, then be added to an estimated chronic soil ingestion rate based on the soil ingestion studies completed to date. Quantifying soil ingestion in episodic high ingestion rate activities will also enable an assessment of the potential for acute exposures to contaminants.

Table 2.2
Gamma analysis of soil samples for ^{238}U and ^{232}Th series and other selected isotopes

Soil Sample	Bq kg^{-1}							
	^{238}U	^{210}Pb	^{214}Pb	^{234}Th	^{228}Ac	^{212}Pb	^{40}K	^{137}Cs
P-02-0711	15.7	62.0	15.2	16.7	15.9	18.3	628	7.3
P-09-0712	13.1	71.7	18.3	13.1	15.0	18.6	558	6.1
P-12-0712	15.6	68.5	13.7	15.6	14.9	15.4	571	4.8
P-15-0712	16.1	63.5	17.3	16.1	18.6	23.7	581	8.2
P-18-0712	23.4	41.2	22.7	24.0	16.5	19.8	703	1.9
P-03-0711	14.7	35.7	16.3	15.7	16.2	20.9	596	7.5
P-10-0712	30.3	50.2	21.3	32.2	21.2	25.9	635	7.0
P-13-0712	16.0	31.9	15.9	16.0	12.2	15.8	666	6.3
P-16-0712	17.5	56.3	15.9	18.8	17.7	22.8	588	10.4
P-19-0712	23.5	23.6	21.1	23.8	18.9	17.6	671	1.6
Mean	18.6	50.4	17.8	19.2	16.7	19.9	620	6.1
Standard Deviation	5.4	16.6	3.0	5.8	2.5	3.4	48	2.7
Coefficient of Variability	29%	33%	17%	30%	15%	17%	8%	45%
Variance	28.9	276.0	9.0	33.5	6.3	11.7	2370	7.5
Standard error	1.7	5.2	0.9	1.8	0.8	1.1	15	0.9

Table 2.3
Parameter values for Monte Carlo simulation of soil ingestion rate

Parameter	Value Mean (SD)	Parameter Definition/Reference
E_{fc} (Bq kg^{-1})	0.593 (0.030)	Mean activity (standard deviation) of ^{214}Pb tracer in feces. Calculated assuming 50 mg/d soil ingestion rate.
E_s (Bq kg^{-1})	17.76 (2.99)	Mean activity (standard deviation) of ^{214}Pb tracer measured in soil. Based on analyses of soils from the Ottawa area (Table 2).
W_{fd} (kg d^{-1})	1.48 (0.03)	Mean dry weight (standard deviation) of food consumed in a day. Based on data from UNSCEAR, 2000.
E_{fd} (Bq kg^{-1})	0.0110 (0.0005)	Mean activity (standard deviation) of ^{214}Pb tracer in food. Based on annual ingestion of 5.7 Bq for an adult male (UNSCEAR, 2000).
W_{fc} (kg)	0.0280 (0.001)	Mean dry weight (standard deviation) of adult feces. As reported in Davis and Mirick (2006).

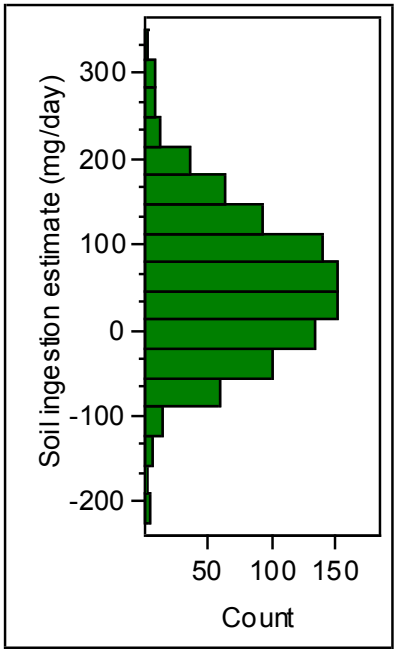

Figure 2.1
Distribution of soil ingestion estimates based on 999 iterations of a Monte Carlo model developed to show the variability in soil ingestion rate calculations due to analytical error and soil sample variability

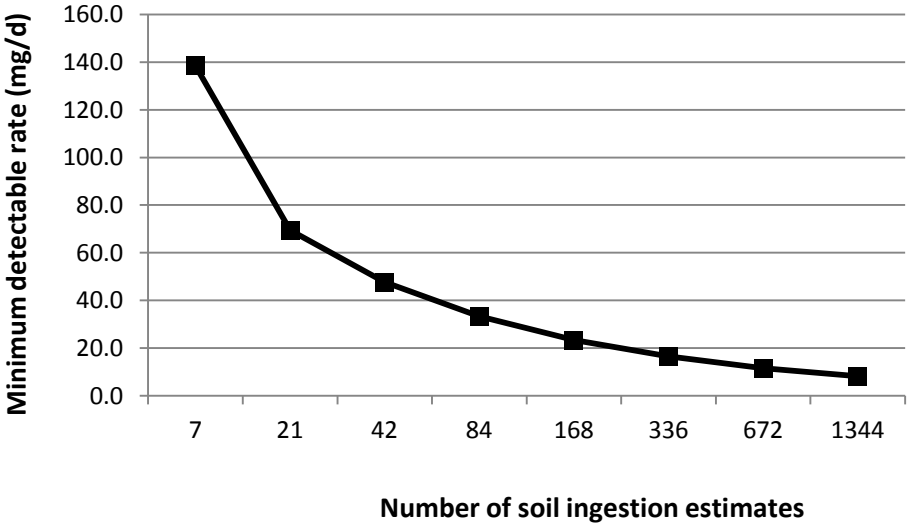

Figure 2.2
The minimum detectable soil ingestion rate for a given number of soil ingestion estimates based on the soil ingestion rate distribution shown in figure 2.1

2.3.5 Other considerations

Another important consideration in study design is that many occupations or lifestyles atypical of urban/suburban environments may involve activities conducted over large areas. Variability of soil tracer concentrations in soil ingested during a study may result from differences in soil texture in areas where specific activities are conducted. Studies conducted to date have typically assumed that soil ingestion would be confined to subjects' homes, and calculated soil ingestion rates are only based on soils collected in subjects' yards. An exception to this is the study by van Wijnen et al (1990), which assessed ingestion in children in three different environmental situations: daycare centers, campgrounds, and hospitals.

Future soil ingestion studies should therefore be designed to minimize uncertainty related to spatial variability in tracer concentrations by limiting the duration of the study to focus on specific activities that are conducted within a small area. Moreover, reducing the duration of the study to a few days will reduce uncertainties resulting from subjects not complying with sampling protocols that have been observed in longer studies.

The potential for concentration enrichment of tracers in the smaller particle size fractions of soils and the degree to which certain particle size fractions are available for ingestion by adhering to skin should also be considered in the design of soil ingestion studies using mass balance methods. Sheppard and Evenden (1992) reported that common mass balance tracers, Al and Si are enriched in smaller particle sizes and the concentration enrichment (CE) of almost all sorbed contaminants will be higher on the small clay-sized particles (<2 μm diameter) than on larger size sand particles (>50 μm diameter). Sheppard and Evenden (1994) reported that smaller particle sizes will adhere more readily to skin and showed that the 50 to 100 μm size range may be a critical size range for enrichment as larger grains and aggregates do not adhere readily to skin. Choate et al. (2006) showed that the adhered fractions of dry or moderately moist soils with wide distributions of particle sizes generally consist of particles of diameters <63 μm. Siciliano et al. (2009) showed that the average particle sizes of soil adhering to human hands were 34 μm, 105 μm, and 36 μm for agricultural soils in Saskatchewan, soils from a brownfield located in Nunavut, and for

residents of a northern urban setting respectively. Moreover, their studies suggested that metals of toxicological concern are selectively enriched in the fraction of soil that humans inadvertently ingest. Stanek et al. (1999) evaluated the impact of particle size and noted that inter-tracer agreement in soil ingestion estimates would be improved if the soil ingestion estimates were based on concentrations of tracers at finer particle sizes. Thus, the distribution of tracers across particle size fractions should be taken into consideration when assessing soil ingestion, and future studies should give consideration to tracer levels in soil particles 63 μm or smaller (i.e., the fraction that would be most associated with incidental soil ingestion and dermal loading).

2.4 Conclusions

The first attempts to quantify soil ingestion were driven by the perception that the mouthing behaviour in children increased their exposure to environmental contaminants, such as lead and dioxins, via the soil and/or dust ingestion pathway. These early soil ingestion estimates were typically high (i.e., up to grams per day), and the estimating methods used were not sufficiently robust to be used to establish defensible clean-up criteria for contaminated sites. Mass balance soil ingestion studies were thus developed to improve the defensibility of soil ingestion rates recommended by regulators for use in HHRAs. The mass balance methods employed were progressively improved such that the normal soil ingestion rates for children and adults have been substantially reduced, and the precision of the estimates has been increased.

However, these mass balance soil ingestion studies were based principally on assessments of relatively large numbers of children, augmented by smaller studies of adults, living in suburban and urban locations under controlled situations. As such, they are not necessarily representative of populations living in rural or wilderness areas with occupations or lifestyles that increase the likelihood of greater soil ingestion.

Future studies assessing soil ingestion involving populations atypical of those living in urban/suburban environments should be carefully designed to address limitations and

potential sources of bias and uncertainties associated with the conditions that will be encountered. Specifically, future studies should:

a) Modify the mass balance estimating techniques currently used in soil ingestion studies to include, where applicable, ingestion of potentially contaminated soils adhering to locally gathered, preserved, and prepared foods.

b) Be limited to assessing specific activities with a high potential for soil ingestion (i.e., grams–per-day levels) that have been highlighted in qualitative assessments. This will enable the use of smaller numbers of subjects, with the attendant loss of statistical power, to determine if these activities are associated with a significantly higher soil ingestion rate than that determined for the population at large.

c) Conduct pre-study soil surveys of areas inhabited by the subjects to ensure that the assessments are focused on activities where the potential for soil ingestion is high and limited to areas where variability in soil tracer concentrations is low.

d) Use tracer concentrations in smaller particle sizes (<63 μm) to calculate soil ingestion rates via mass balance methods.

e) Use alternative tracers, such as the ^{238}U and ^{232}Th decay series radionuclides, to calculate soil ingestion via mass balance methods. Use of these tracers may improve estimate precision by reducing source error and/or uncertainty related to gastrointestinal uptake of tracers.

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Chapter 3

Method development

3.1 Introduction

The key studies used to determine the United States Environmental Protection Agency (EPA) soil ingestion rate guidelines for use in human health risk assessments of contaminated sites employ some form of the "tracer element" methodology (EPA, 1997, 2009). These methods follow a mass balance approach where an elemental tracer commonly found in soil is measured in excreta (i.e., feces and urine) and used to calculate soil ingestion using the following the generic Eq. (3.1):

$$mass\ of\ soil = \frac{mass\ of\ tracer\ in\ \ excreta}{concentration\ of\ tracer\ in\ soil} - \frac{mass\ of\ tracer\ ingested\ in\ food}{concentration\ of\ tracer\ in\ soil} \qquad (3.1)$$

The soil ingestion estimates developed from this approach to date have been highly variable. Much of this variability is a result of positive and negative bias, and uncertainty in the mass balance methodology related to the lack of correspondence between the tracer ingested with food and the timing of its appearance in feces (i.e., transit time misalignment), non-soil derived tracers that are ingested and not accounted for (i.e., source error), sample loss, and analytical error (Stanek and Calabrese, 1995). Furthermore, soil ingestion estimate variability may also be the result of absorption of tracers in the gastrointestinal (GI) tract or the spatial variability tracer soil concentrations, when the concentration of tracers at the location where inadvertent soil ingestion occurs is different than the concentration of tracers in the soil sampled (Davis and Mirick, 2006). Moreover, soil ingestion studies require considerable planning and logistical coordination and commitment of the study subjects to the study protocols (e.g., reliable provision of food and fecal samples). Improvements to study design to minimize soil ingestion estimate uncertainty, such as increasing study duration, must be balanced against the potential negative impacts these changes may have on participant compliance and/or study implementation logistics and cost.

In preparation for a mass balance soil ingestion study of people following a traditional lifestyle typical of rural or wilderness regions of Canada, the mass balance estimating approach was re-examined to look for opportunities to improve the reliability (i.e., accuracy and precision) of soil ingestion estimates based on mass balance tracer methods. Included in this re-examination was an evaluation of naturally-occurring radionuclides measured by gamma spectrometry. The methods currently used were assessed for their utility under the conditions anticipated in a study of people following a traditional lifestyle and living in rural or wilderness areas where access to logistical support (e.g., electricity, water, shelter) may be limited.

The purpose of this chapter is to describe the selection, development and validation of the methods that would be used to conduct a soil ingestion study of a population following a traditional lifestyle and living in a rural or wilderness area. Furthermore, the precision and limits of detection were determined for sampling and analytical methods developed.

3.2 Selection of candidate isotope mass balance tracers

Naturally-occurring radionuclides are either primordial (i.e., have existed since the formation of the earth), cosmogenic (i.e., they have been formed as a result of interaction between cosmic radiation and elements on earth) or anthropogenic (they are products of man-made nuclear reactions). Primordial radionuclides are either non-series radionuclides (i.e., primordial radionuclides that decay directly to a stable isotope) or series radionuclides (i.e., primordial radionuclides that decay through a series of intermediate or daughter isotopes to a stable isotope of Pb).

The 3 naturally occurring primordial decay series radionuclides begin with the parent radionuclides ^{238}U, ^{235}U and ^{232}Th. Naturally occurring U is comprised of the following isotopes: ^{238}U, ^{235}U and ^{234}U (a daughter radioisotope of ^{238}U), with isotopic abundances of 99.274%, 0.720% and 0.006%, respectively, and ^{232}Th, has an isotopic abundance of 100% (Friedlander et al., 1955). Uranium is ubiquitous globally and found in all rocks and soils at levels ranging from 0.03 ppm (0.37 Bq/kg) in ultrabasic igneous rocks to 3 ppm (37 Bq/kg) in acid igneous rocks to 120 ppm (1500 Bq/kg) in Florida phosphate rocks (Eisenbud and

Gesell, 1997). Similarly, Th occurs globally and concurrently with U at a relatively constant U/Th mass ratio (Navas et al., 2005).

Other naturally occurring isotopes, and a selected number of anthropogenic isotopes, were rejected as potential tracers because they were not found in sufficient abundance in soils and/or their pharmacokinetics precluded their use as mass balance tracers (i.e., they are readily absorbed in the GI tract) (Table 3.1). ^{235}U series isotopes were ruled out as candidate tracers because they are found in too low a concentration for useful measurement with gamma spectrometry. Furthermore, ^{235}U is determined from its 186.5 keV peak, which is coincident with the ^{226}Ra peak at 186.1 keV. This coincidence would complicate its analysis. Gastrointestinal absorption factors (*f1*) for the isotopes being considered as mass balance tracers are shown in Table 3.2 (UNSCEAR, 2000). Note that the U, Th, Ac and Pa isotope *f1* values are low (i.e., 0.02 or less), whilst the Ra, Pb and Po isotope *f1* values were higher (i.e., 0.2 or higher). Other radionuclides commonly found in soils (e.g., K and Cs) are essentially completely taken up in the GI tract (i.e., *f1* values of 1.0).

The ^{238}U and ^{232}Th decay series isotopes were identified as candidates for further evaluation as mass balance tracers in soil ingestion studies because they are not readily absorbed in the gastrointestinal tract and are ubiquitous in soils. The ^{238}U and ^{232}Th decay series are shown in Figure 3.1a and 3.1b, respectively. Isotopes within each decay series may fractionate when passing through the GI tract resulting in secular disequilibrium of isotopes of the same decay series or alter the activity ratio between decays chains measured in the feces. However, in vitro bioavailability assays of whole sand with high levels of natural radioactivity using simulated gastric and intestinal fluids have shown that the solubility of ^{232}Th, ^{238}U and their progeny from this sand is low (i.e., less than 1% solubility) (Frelon et al., 2007). Moreover, secular equilibrium between parent and progeny isotopes was observed to be maintained during the experiment. However, these results should be taken with caution as the experiment was performed on whole sand samples where a large proportion of the ^{232}Th, ^{238}U and their progeny may be embedded in the sand matrix.

U, Ra and Th are typically found adsorbed to the surfaces of fine soil particles where they are available for mobilization whereas they are less bioavailable in coarse particles (Baeza et al., 1995). The concentrations of ^{238}U and ^{232}Th and their daughter isotopes in food items vary because of the differences in rates of uptake from soil by plants, and the degree to which the radionuclides will accumulate in animals feeding on these plants. These differences are reflected in the variability observed in reference activity concentrations of these isotopes in foods (Table 3.3). The levels of radionuclides in food items will also vary with geographical differences in soil composition, climate, and agricultural conditions that prevail in the regions where the food is cultivated. Concentrations of naturally-occurring radionuclides in water are also variable depending on the source and level of water treatment. For example Ottawa municipal water (i.e., treated surface waste) has low levels of U (~0.0005 Bq/L), whereas New Ross, Nova Scotia, well water (i.e., groundwater) U concentrations are higher (19.7 Bq/L) (Limson Zamora et al., 2002**)**.

Calabrese and Stanek (1993) and Stanek and Calabrese (1995) have shown that reliable soil ingestion tracers used in human soil ingestion studies have low food-to-soil (F/S) ratios. The F/S ratio is equal to the mg of the element consumed in food in 1 day divided by the mg of element in 1 gram of soil. The mean F/S ratios for tracers used in the Calabrese et al (1989) soil ingestion estimates ranged from 0.015 to 3.6, with the median of the top 4 tracers being 0.046. The hypothetical F/S values, based on generic activity levels of ^{238}U and ^{232}Th series isotopes in soil and ingested in food was calculated to determine if they would be suitable mass balance tracers for soil ingestion studies (Table 3.4). Based on generic ^{238}U and ^{232}Th worldwide reference activity concentrations for ^{238}U series and ^{232}Th series isotopes in soil and in the diet, F/S ratios ranging between 0.15 and 1.67 would be expected if these isotopes were used as mass balance tracers. These ratios are higher than what has been reported for elemental tracers. In particular, the hypothetical F/S for ^{226}Ra, which would be determined by measuring ^{214}Pb via gamma spectrometry, is almost 2 orders of magnitude greater than the most reliable elemental tracers that have been used in mass balance soil ingestion estimates in humans completed to date. However, the F/S for ^{228}Th, which would be determined by measuring ^{212}Pb by gamma spectrometry, was much lower, with an F/S ratio of 0.26.

Furthermore, the F/S for the radionuclide tracers could be lowered by restricting the diet to food types low in the tracer radionuclides, which would improve their reliability as a mass balance tracer. Moreover, uranium and thorium are not common ingredients in consumer products due to their heavy metal and/or radioactive characteristics and are thus less likely to contribute to source error in mass balance soil ingestion studies. For example, they are not listed in the United States Federal Drug Administration (US FDA) list of approved food and drug excipients or active ingredients (FDA, 2008) that could be inadvertently ingested with medicines or as food additives.

^{238}U and ^{232}Th decay series isotopes are readily detectable by gamma spectrometry, and the use of gamma spectrometry to measure these isotope tracers has the following potential advantages:

- Sample preparation is not labour-intensive and relatively simple (i.e., if samples are not concentrated then they are simply freeze-dried and sealed in analysis tubes).
- The analysis of many of the ^{238}U and ^{232}Th decay series isotopes is obtained in one analysis.
- Isotopic ratios and/or isotopic disequilibrium may provide an opportunity to develop a novel method of estimating soil ingestion with the use of isotopic mixing models.
- The sample remains intact after the analysis, which enables the additional analyses of samples obtained in the soil ingestion study (e.g., for contaminants).

However, the amenability of gamma spectrometric analysis of these isotopes as mass balance tracers in soil ingestion studies is not known. The following questions need to be addressed before confirming the utility of the analytical methods that would be used in such studies:

- Can gamma spectrometry detect the gamma-emitting ^{238}U and ^{232}Th decay series daughter isotopes at levels present in soils?
- Can gamma spectrometry detect the gamma-emitting ^{238}U and ^{232}Th decay series daughter isotopes at levels present in foods?

- At what activities will these isotopes be found in feces, given the range of anticipated rates of soil ingestion, and, can these isotopes be reliably detected in food samples?
- What is the analytical variability inherent in the mass balance methodology proposed, and what is the lowest detectable quantity/rate of soil ingestion based on this level of analytical uncertainty?

Table 3.1
Assessment of primordial non-series radionuclides as mass balance tracers of soil

Nuclide	Half Life[2] (years)	Radiation[2,3] (type)	Crustal Composition[2] (Bq kg^{-1})	*f1*[4]	Comments
^{40}K	1.26x10^{9}	β[5], γ[6]	630	1.00	Hi *f1*
^{50}V	6 x 10^{15}	β, EC[7], γ	2 x 10^{-5}	0.01	Low concentration
^{87}Rb	4.8 x 10^{10}	β	70	1.00	*f1* too high, pure β emitter
^{113}Cd	>1.3 x 10^{15}	β	<2 x 10^{-6}	0.05	Low concentration
^{115}In	6 x 10^{14}	β	2 x 10^{-5}	0.02	Low concentration, pure β emitter
^{123}Te	1.2 x 10^{13}	EC, X rays	2 x 10^{-7}	0.30	Low concentration, high *f1*
^{138}La	1.12 x 10^{11}	EC, β, γ	2 x 10^{-2}	5 x 10^{-4}	Low concentration
^{142}Ce	>5 x 10^{16}	α[8]	<1 x 10^{-5}	5 x 10^{-4}	Low concentration, α decay
^{144}Nd	2.4 x 10^{15}	α	3 x 10^{-4}	5 x 10^{-4}	Low concentration, α decay
^{147}Sm	1.05 x 10^{11}	α	0.7	5 x 10^{-4}	Low concentration, α decay
^{152}Gd	1.1 x 10^{14}	α	7 x 10^{-6}	5 x 10^{-4}	Low concentration, α decay
^{174}Hf	2.0 x 10^{15}	α	2 x 10^{-7}	0.002	Low concentration, α decay
^{176}Lu	2.2 x 10^{10}	β, γ	0.04	5 x 10^{-4}	Low concentration
^{187}Re	4.3 x 10^{10}	β	1 x 10^{-3}	0.80	Pure β emitter
^{190}Pt	6.9 x 10^{11}	α	7 x 10^{-8}	0.01	Low concentration, α decay

[2] Eisenbud and Gesell (1997)
[3] Friedlander et al. (1964)
[4] ICRP (1996)
[5] Beta decay
[6] Gamma decay
[7] Electron capture
[8] Alpha decay

Table 3.2
Gastrointestinal absorption factors (*f1*) for naturally-occurring radionuclides and other mass balance tracers[4]

Isotope	*f1*	Isotope	*f1*
^{238}U series:		*Other radionuclides:*	
^{238}U	0.02	^{40}K	1.0
^{234}U	0.02	^{137}Cs	1.0
^{230}Th	0.0005	*Other tracers:*	
^{226}Ra	0.2	Al	0.01
^{212}Pb	0.2	Si	0.01
^{210}Pb	0.2	Ti	0.01
^{210}Po	0.5	Ba	0.2
^{232}Th series:		La	0.0005
^{232}Th	0.0005	Ce	0.0005
^{228}Ac	0.0005	Mn	0.1
^{228}Ra	0.2	V	0.01
^{228}Th	0.0005	Zr	0.01
^{214}Pb	0.2		
^{208}Tl	1.0		

Table 3.3
Worldwide reference values for the activity concentration of natural radionuclides in food[9]

Type of Food	Radionuclide Levels (mBq kg^{-1})				
	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{228}Th
Milk Products	1	5	0.3	5	0.3
Meat Products	2	15	1	10	1
Grain Products	20	80	3	60	3
Leafy Vegetables	20	50	15	40	15
Root Vegetables and Fruits	3	30	0.5	20	0.5
Fish Products	30	100	10	-	100
Drinking water	1	0.5	0.05	.05	.05

[9] From UNSCEAR, 2000 (Appendix B Table 15)

Table 3.4
Worldwide reference values for the activity concentration of natural radionuclides in soil[10] (assumes secular equilibrium for isotopes of each decay series), annual and daily intake of the radionuclides in the diet[11], and the calculated hypothetical food-soil (F/S) ratios for ^{238}U and ^{232}Th decay series isotopes based on the reference values

Parameter	Isotope				
	^{238}U	^{226}Ra	^{232}Th	^{228}Ra	^{228}Th
Concentration in soil (Bq kg^{-1})	35	36	30	30	30
Annual dietary intake (Bq y^{-1})	5.7	22.0	1.7	15.0	3.0
Daily dietary intake (Bq d^{-1})	0.016	0.060	0.004	0.041	0.008
Calculated F/S ratio	0.45	1.67	0.15	1.36	0.26

[10] From UNSCEAR, 2000 (Appendix B Table 6)
[11] From UNSCEAR, 2000 (Appendix B Table 16)

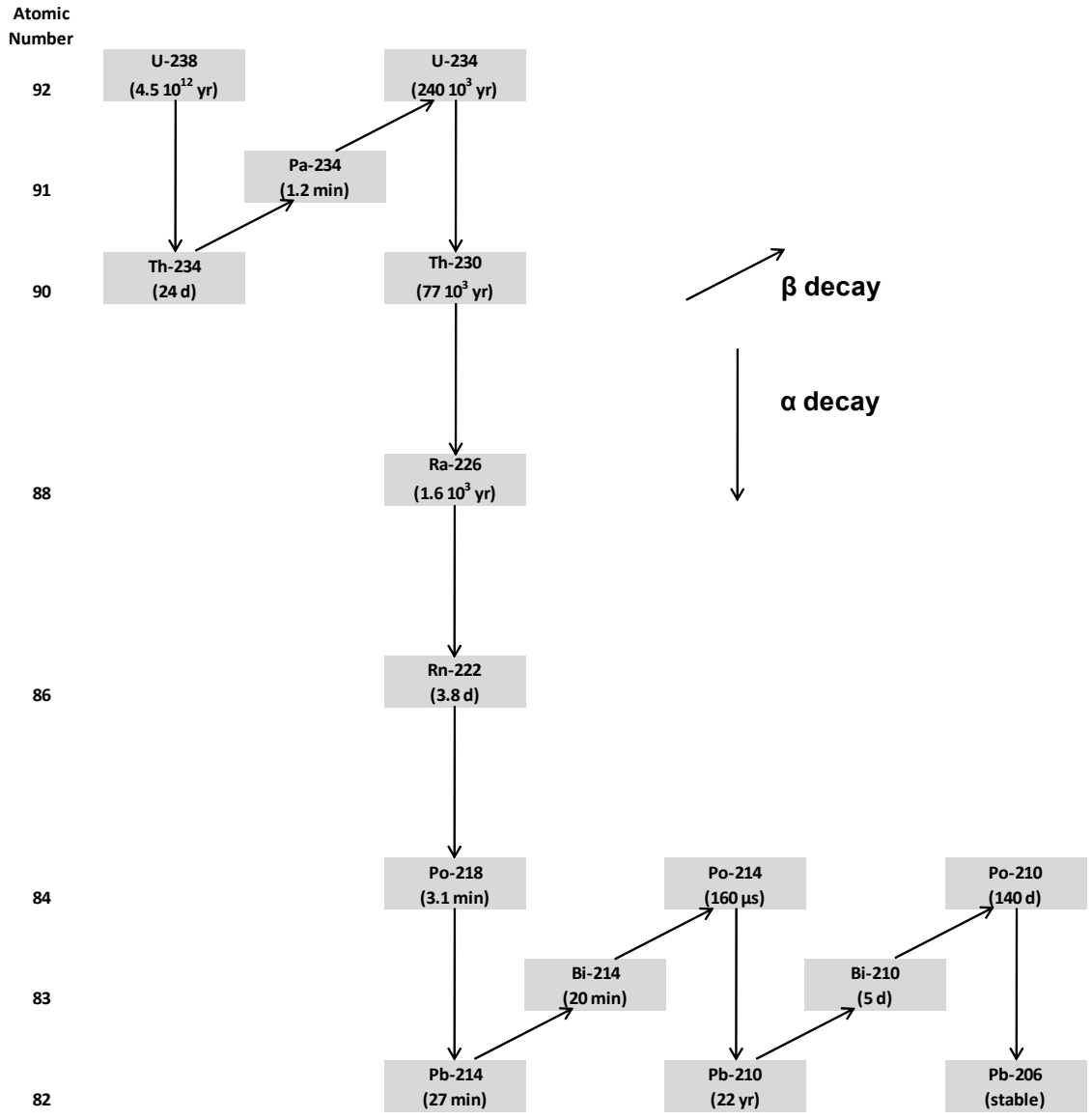

Figure 3.1a
^{238}U decay chain showing the decay series isotopes, their half-lives in years (yr), days (d), minutes (min) and seconds (s), and the decay mode for each isotope. The atomic number of each element isotope is provided on the left (adapted from Argonne, 2005).

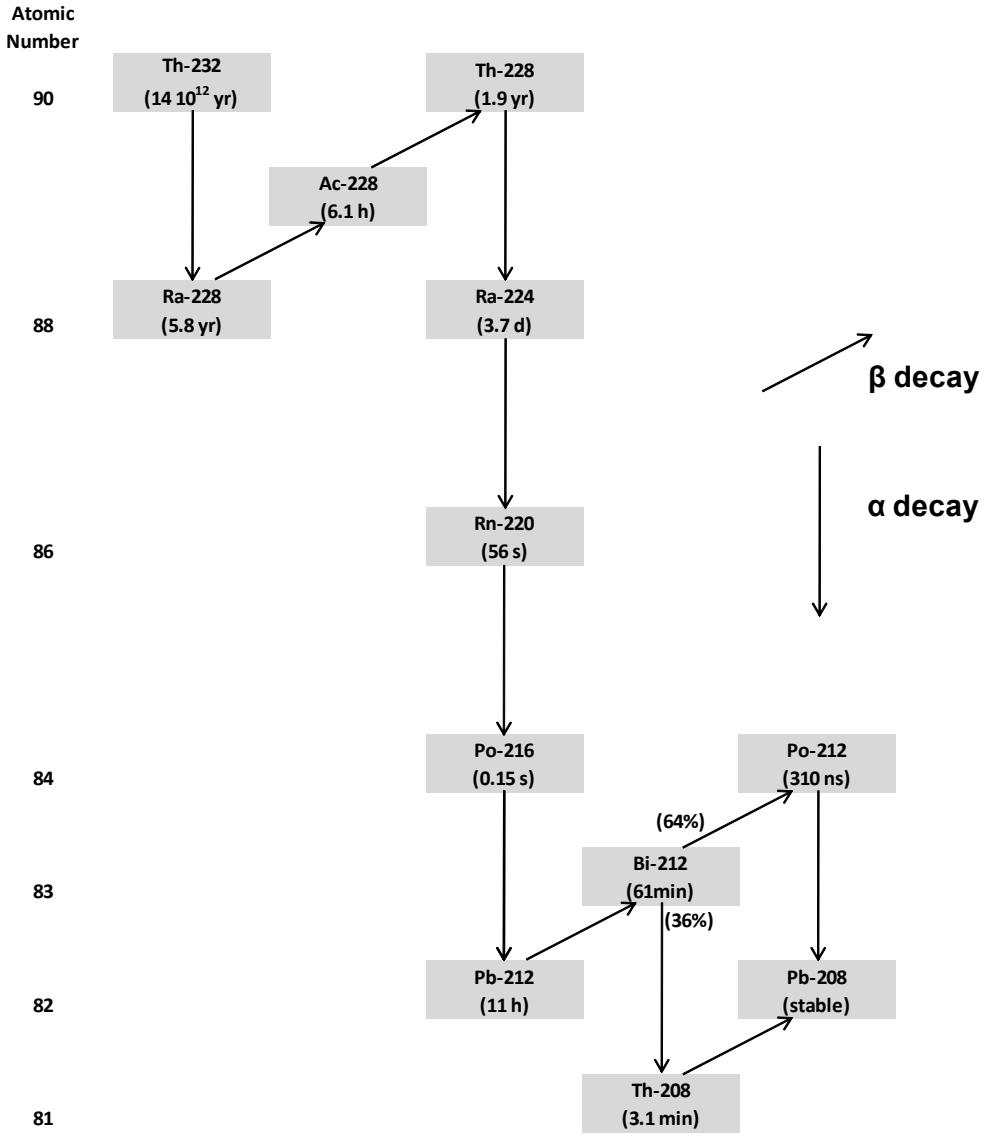

Figure 3.1b
^{232}Th decay chain showing the decay series isotopes, their half-lives in years (yr), days (d), minutes (min) and seconds (s), and the decay mode for each isotope. The atomic number of each element isotope is provided on the left. (adapted from Argonne, 2005)

3.3 Analysis of mass balance tracers

3.3.1 Gamma spectrometric analysis of isotopic tracers

3.3.1.1 ^{238}U and ^{232}Th decay series and secular equilibrium

^{238}U and ^{232}Th radionuclides are measured with gamma spectrometry via their daughter isotopes in secular equilibrium. If not subjected to chemical or physical separation, the members of a primordial radionuclide series attain a state of radioactive equilibrium (secular radioactive equilibrium) wherein the rate of decay of each radionuclide is essentially equal to that of the nuclide that heads the series. This is always the case on a global basis for each series, but local concentrations can vary widely where separation of series members has occurred. When in secular equilibrium, the activity concentration (i.e., the number of atoms disintegrating per second measured in Becquerel (Bq) per unit mass) of each radionuclide of a given series will be very nearly equal to the activity concentration of the nuclide that heads the series (NCRP, 1987a). Disequilibria in the ^{238}U decay series occurs when differences in chemical properties of the elements within the decay chain (e.g., differential precipitation, dissolution or diffusion rates, or increased dissolution of daughter isotopes through alpha recoil) result in the separation of isotopes acted upon by various environmental processes (e.g., leaching) (Ivanovich, 1994). Most isotopic disequilibria are caused by differential precipitation or dissolution of the various isotopes within a decay series (Dowdall and O'Dea 2002). Alpha recoil is the direct ejection of the recoiling nucleus from the solid phase (e.g., soil or bedrock) to the aqueous phase (i.e., water) and may account for ^{234}U enrichment in waters resulting from weathering and river transport (Chabeaux et al., 2003). As a rule of thumb, the isotopes within a decay series return to secular equilibrium after 6 half-lives of the isotope that is lost, and return to within 5% of an activity ratio of 1 after approximately 5 times the half-life of the lost daughter nuclide (Bourdon et al., 2003). Disequilibrium in the ^{238}U series in soil is primarily the result of the loss of ^{222}Rn ($t_{1/2}$=3.8d), a gas that can escape from the soil into the atmosphere. Thus, to determine ^{226}Ra levels in soils or other porous matrices, where the gaseous ^{222}Rn can escape, samples need to be stored in a sealed container for at least 21 days (~5.5 ^{222}Rn plus ^{218}Po half-lives) before analysis to permit the ^{214}Pb to achieve secular equilibrium with ^{222}Rn and ^{226}Ra). Similarly, the 21-day storage of samples

will allow ^{212}Pb to achieve secular equilibrium with ^{216}Po ($t_{1/2}$=15s), ^{220}Rn ($t_{1/2}$=56s), ^{224}Ra ($t_{1/2}$=3.7d), and ^{228}Th of the ^{232}Th decays series.

3.3.1.2 Gamma spectrometric methods

Soil ingestion study samples were analyzed using an Ortec™ high purity germanium (HPGe) detector and gamma spectrometer (model# GWL-120230, configuration # XLB-GWL-SV). The HPGe crystal is enclosed in a ~70 mm diameter aluminum capsule with a ~16 mm (diameter) by ~50 mm internal well (Figure 3.2). The coaxial HPGe crystal has a ~55 mm outside diameter, ~66 mm length, ~15 mm inside well diameter and a ~40 mm active well depth. Samples, which were normally analyzed after freeze drying, were sealed in an 8 mL gamma centrifuge tube (gamma tube) and inserted into the well of the detector, where gamma radiations, emitted at energies specific to the individual isotopes being analyzed, were detected by the HPGe crystal. In this configuration, the geometry was optimized, in that most of the gamma emissions interact with the HPGe crystal that surrounds the sample. Some samples, such as ashed food samples, were analyzed in Marinelli Beakers (Figure 3.3) fitted over the detector capsule. In this configuration, the geometry was less favourable, and only the gamma radiations emitted inwards (i.e., towards the detector) interact with the HPGe crystal. Consequently the detector efficiency was reduced when samples contained in Marinelli Beakers were analyzed. However, this loss of detector efficiency was overcome by the ability to analyze larger volume of sample in the Marinelli Beaker than the gamma tube (i.e., ~400 cc sample volume versus approximately ~4 cc sample volume, respectively).

The gamma spectra were analyzed using a DOS-based software program developed for the University of Ottawa (uOttawa) by Dr. Peter Appleby (University of Liverpool, U.K.). The activity A of a specific radionuclide was calculated using Eq. (3.2) (Appleby, 2001):

$$A = \frac{N}{\epsilon Y C T} \tag{3.2}$$

where,

N is the number of counts in the peak (disintegrations)

$\in$ is the detector efficiency (dimensionless)

Y is the yield of photons of an energy E (dimensionless)

CT is the count time (seconds)

The Appleby software determines activity of the isotopes of interest within the ^{238}U and ^{232}Th decay chains assuming that they are in secular equilibrium. ^{238}U activity was determined by averaging the values calculated using counts measured for the ^{234}Th peak at 63.3 keV and the values calculated from the ^{235}U peaks at 144 and 163 keV and imputing a ^{238}U activity based on the global ratio of $^{235}U/^{238}U$. ^{210}Pb was determined from the 46.5 keV peak. ^{226}Ra was determined by averaging the ^{214}Pb peaks at 352 keV and 295 keV and assuming secular equilibrium between the two isotopes. The daughter isotopes of ^{232}Th (^{228}Ac, ^{212}Pb and ^{208}Tl) were determined by their 338 keV, 238 keV and 583 keV gamma peaks respectively. The number of counts for each region of interest (ROI) was adjusted for background signal by the Appleby software. The background values around each peak were calculated from the 12 channels above and below the ROI set by the program (predetermined automatically by the software for each isotope measured) around each peak. A plot of the detector efficiency against peak energy for the gamma spectrometer at the University of Ottawa Centre for Advanced Research in Environmental Genomics (CAREG) is provided in Figure 3.4. The detector efficiency was determined by measuring the activity of standards with known activities at various energies and calculating the detector efficiency at these energies with the spectrometer configured as a well detector with samples sealed in an 8 mL gamma tube analyzed with optimum geometry and calculated by the Appleby software. The standard provided by Dr. Appleby used to calibrate the University of Ottawa spectrometer includes known activities for ^{210}Pb (46.5 keV), ^{241}Am (59.5 keV) ^{137}Cs (661.7 keV); and traces of UO_3 to determine efficiencies of the $^{238}U/^{235}U$ series peaks, and pure KCl to determine the efficiency of the ^{40}K (1460 keV) peak. The Appleby software also includes adjustment factors to accommodate differences in sample height (with attendant differences in sample

geometry) and density (resulting in attenuation of those gamma radiations that pass through the sample before reaching the detector).

As previously mentioned, the Marinelli Beaker configuration for samples was not at an optimum geometry. To compensate for this, an adjustment factor of 10.3 was applied to the detector efficiency calculation. This adjustment factor was derived from comparative analysis of a reference standard (IAEA Reference soil #375) in the well configuration and in the Marinelli Beaker configuration. Details on how the adjustment factor was derived are discussed in Section 3.3.1.3

The Lowest Level Detectable (LLD) activity (i.e., the smallest amount of activity measured in Bq that will yield a net count at 95% confidence levels) was calculated for ^{214}Pb measured in GI tract samples using Eq. (3.3) (USDOE, 1997):

$$LLD_{95\%} = \frac{\left[S_{gross}+S_b^2+S_{rb}^2\right]^{1/2}\times 3.29}{\in YCT} \qquad (3.3)$$

where,

S_{gross} is the mean number of background counts within the ROI (disintegrations)

S_b is the standard error of background counts within the ROI (disintegrations)

S_{rb} is the standard error of reagent blank counts within the ROI (disintegrations)

$\in$ is the detector efficiency at the ROI (dimensionless)

Y is the yield of photons of an isotope at energy E (dimensionless)

CT is the count time (seconds).

A blank control sample was prepared by inserting a Teflon™ septum and a quantity of epoxy resin normally used to seal samples into an empty 8 mL centrifuge tube. The blank control sample was analyzed 7 times for 82800s to obtain a mean background count and standard error. However, since chemical extraction is not required in gamma spectrometry, there is no reagent blank. For each analysis the background counts over 7 channels spanning each region

of interest (i.e., the energies corresponding to the isotopes being measured) were recorded and the mean and standard deviations calculated. The $LLD_{95\%}$ values for each isotope were then calculated using Eq. (3.3) and are summarized in Table 3.5.

The accuracy of the gamma spectrometer was determined through the comparison of the gamma spectrometric analysis of a reference standard. A 6.2 g sample of dried soil (IAEA reference soil #375) was emplaced in a 8 mL gamma tube, a Teflon™ septum was then emplaced into each tube, the tube sealed with epoxy resin and stored for at least 21 days to allow for the ^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Pb of the ^{238}U decay series, and ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Pb of the ^{232}Th decay series to reach secular equilibrium. The reference sample was analyzed for 7 trial runs to compare the mean analytical values against the reference values for analytes of interest. The results of the analysis and the reference values for key isotopes of the ^{238}U and ^{232}Th decays series are provided in Table 3.6. It was observed that there was good agreement between the mean ^{214}Pb and ^{212}Pb values measured by the University of Ottawa gamma spectrometer of 21.1 and 19.0 Bq kg^{-1}, respectively, and the decay corrected IAEA reference values of 20.0 and 21.0 Bq kg^{-1}, respectively. The precision of the analyses was also observed to be good with the standard error of the means for ^{214}Pb and ^{212}Pb values of 0.6 and 0.4 Bq kg^{-1}, respectively. These values are less than 3% of the mean value, and well within the reference 95% confidence intervals for both isotopes.

Table 3.5
Lowest limit of detection (LLD) that yields a net count at 95% confidence levels for the University of Ottawa gamma spectrometer as determined by Eq. (3.2). $\in$ is the detector efficiency and Y is the gamma yield of the isotope.

Isotope	Energy (keV)	$\in$	Y	S_{gross} Counts (82800)	S_b^2	S_{rb}^2	$LLD_{95\%}$ (Bq kg^{-1})
^{210}Pb	46.5	0.46	0.04	85.6	1.7	0.9	11.8
^{214}Pb	295.0	0.39	0.19	21.6	0.8	1.0	1.5
^{214}Pb	351.8	0.37	0.37	18.6	0.8	0.6	0.8
^{226}Ra	186.1	0.53	0.03	33.5	0.8	0.7	8.0
^{234}Th	63.3	0.59	0.04	28.8	0.8	0.5	5.7
^{228}Ac	338.5	0.37	0.12	18.6	0.7	0.7	2.3
^{212}Pb	238.0	0.41	0.44	25.9	0.9	0.8	0.7
^{40}K	1460.8	0.05	0.11	7.8	0.7	0.3	12.6
^{137}Cs	661.6	0.12	0.85	8.3	0.6	0.6	0.7

Table 3.6
Comparison of replicate trial runs of IAEA reference soil standard #375 and the decay-corrected reference values for key ^{238}U and ^{232}Th decay series isotopes and assuming secular equilibrium

Sample Description	^{214}Pb (Bq kg^{-1})	^{212}Pb (Bq kg^{-1})
IAEA standard soil #375 – trial 1	19.4	18.5
IAEA standard soil #375 – trial 2	21.0	21.3
IAEA standard soil #375 – trial 3	20.3	18.8
IAEA standard soil #375 – trial 4	21.7	19.0
IAEA standard soil #375 – trial 5	21.5	17.8
IAEA standard soil #375 – trial 6	20.2	19.5
IAEA standard soil #375 – trial 7	16.7	18.1
Mean	**20.1**	**19.0**
Standard deviation	**1.7**	**1.1**
Coefficient of variability	**8%**	**6%**
Standard error of mean	**0.6**	**0.4**
IAEA standard soil #375 – reference values	**20.0**	**21.0**
Upper 95% confidence interval	**22.0**	**25.0**
Lower 95% confidence interval	**18.0**	**17.0**

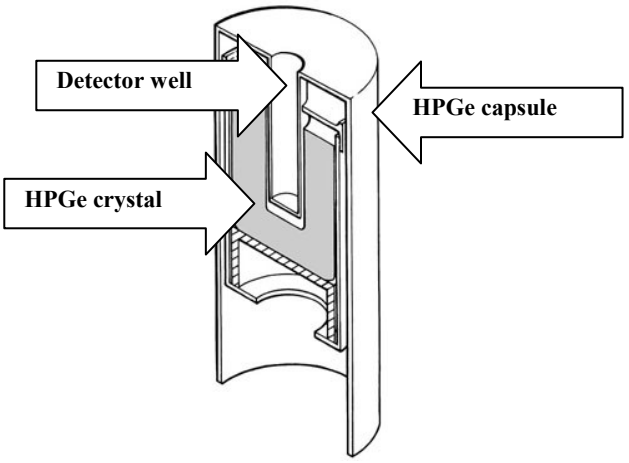

Figure 3.2
Diagram of the cross section of an Ortec detector showing the high purity germanium (HPGe) detector capsule, crystal and sample well

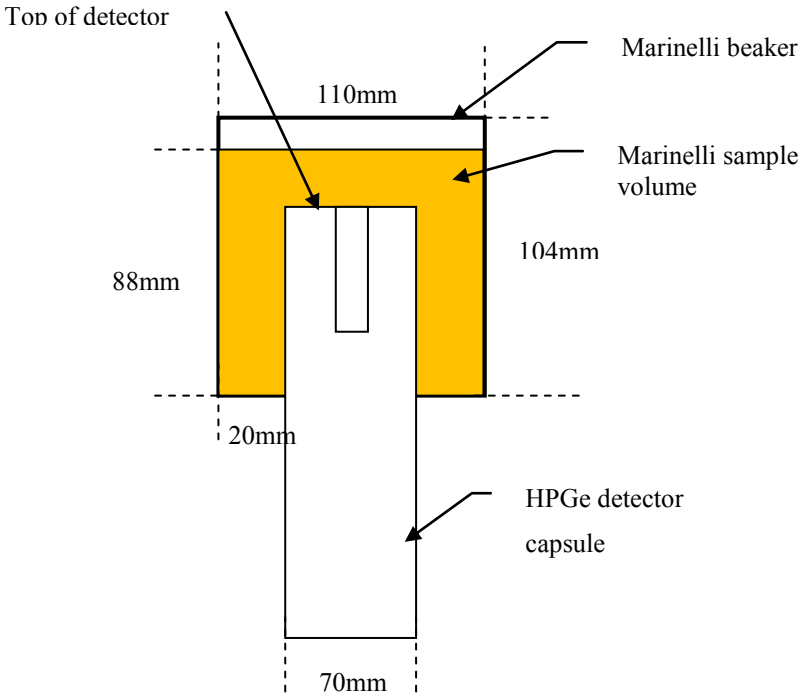

Figure 3.3
Diagram of the cross section of a Marinelli Beaker, with dimensions

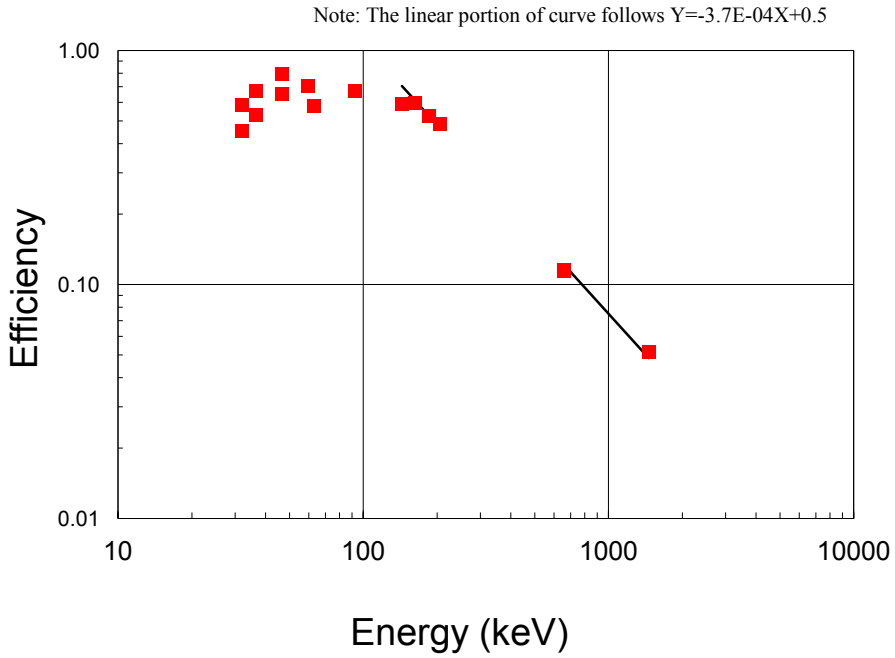

Figure 3.4
Efficiency curve developed for the University of Ottawa Ortec™ HPGe well detector (from Appleby, 2004)

3.3.1.3 Sample preparation for gamma spectrometry

The resolution or sensitivity of gamma spectrometry can be improved through the following means:

- Reducing the background sources of radiation.
- Increasing the counting time.
- Increasing the amount of sample analyzed (i.e., volume reduction and/or concentration of the analyte).

Background is caused by sources external to the detector, and sources derived from the construction of the detector. External sources are typically minimized by shielding design, and internal sources are typically minimized by using materials that are low in naturally occurring radionuclides. Excess vibration and presence of external electromagnetic fields may also contribute to background. Measures to reduce vibration and electromagnetic noise

were implemented previously, and revisiting the design and construction of the spectrometer was considered impractical. Therefore, opportunities to improve the sensitivity of the spectrometer were restricted to increasing the sample counting time and/or increasing the amount of sample analyzed. The counting time for samples was increased for two samples with low radionuclide activity levels from 82,800s to 165,600s (23 hours to 46 hours) and to 248,400s (69 hours). No improvement in the detection limit or the precision of ^{214}Pb or ^{212}Pb was observed. Thus, it was necessary to pre-concentrate samples and/or to reconfigure the sample container to increase the volume of sample analyzed to lower the detection limits of the gamma analysis of samples with low levels of radionuclides. The methods evaluated to achieve this objective were:

- Evaporation of liquid samples.
- Ashing of solid samples.
- Compaction of solid samples.
- Use of Marinelli beakers to increase sample size.
- Extraction and concentration of target radionuclides.

The gamma spectrometer well design limits the amount of sample to be analyzed to no more than 4 mL in an 8 mL centrifuge tube. Volume reduction of a large sample had to be done in a manner that minimized the loss of radionuclides of interest. The volume reduction methods developed are described in the sections below.

Water samples collected in the field and retained for gamma spectrometry were acidified with concentrated HCl to a pH <2.0, then pre-concentrated by evaporation in a rotary evaporator (Figure 3.7). A 4 L round sample flask was attached to the rotator and set into the water bath below the evaporator; the condenser column was encased on an ice pack to facilitate cooling in the condenser column and the condensate collection flask was supported by a cork ring and an adjustable jack. The evaporator was connected to a system to permit vacuum control. The evaporator system was configured such that the opening of the stopcock would draw sample directly into the sample flask through a small plastic tube (Figure 3.8). Each 2 L water sample was evaporated for 3 to 5 hours to approximately 20 mL in a water

bath maintained at 90 °C under vacuum. It was observed that dissolved solids in samples would start to precipitate when the samples were evaporated much beyond this point. Therefore, samples were further evaporated to a solid (i.e., the dissolved solids in the water sample) less than 4 cc in volume through successive additions of sample to an 8 mL gamma tube housed in an aluminum heating block maintained at 90 °C under a gentle stream of nitrogen gas to accelerate the evaporation process. Thus, the 2-step evaporation process provided a 500-fold concentration of the sample. After the sample was fully dried, a Teflon™ septum was inserted into the gamma tube; the tube was sealed with epoxy resin and then stored for a minimum of 21 days before being analysed by gamma spectrometry. The aforementioned evaporation methods were validated against a series of eight - 2 L de-ionized water samples spiked with ^{226}Ra (National Institute of Standards & Technology (NIST) Standard Reference Material (SRM) (#4969 - ^{226}Ra Radioactivity Standard) to an activity concentration of 0.1 Bq L^{-1} (Table 3.7). It was observed that the difference between the measured and actual ^{214}Pb activity concentration of the 8 samples analyzed was small, with a mean difference of 0.006 Bq L^{-1} relative to a mean analytical result of 0.106 Bq L^{-1}.

Regardless of the pre-concentration method applied, all solid samples prepared for gamma spectrometry were sealed in pre-weighed 8 mL centrifuge tubes or in pre-weighed ~500 mL Marinelli beakers and stored for at least 21 days to allow the isotopes of interest to achieve secular equilibrium. The mass of the sample analysed was obtained from subtracting the container (i.e., 8 mL gamma tube or Marinelli beaker) tare weight from the total sample and container weight. Samples earmarked for ashing were weighed, transferred to pre-weighed ceramic crucibles, re-weighed to obtain the pre-ash sample weight, then ashed at 500 °C for 9 hours and re-weighed to obtain post-ash sample weight. Ashed samples were then transferred directly to 8 mL gamma tubes (Figure 3.9) or compressed into the gamma tubes using a specially constructed die to support the tube walls (Figure 3.10a), then re-weighed to obtain gamma sample weight. Samples were compacted with a machine press by applying pressure on a piston inserted into the tube (Figure 3.10b). After compression, a Teflon™ septum was inserted into each gamma tube, sealed with epoxy resin and stored until analysed by gamma spectrometry. The volume reduction achieved (i.e., concentration factor (CF)) through

ashing or compaction varied according to the type and nature of the sample matrix being pre-concentrated. For example, the CF values for fecal samples, obtained from a mass balance soil ingestion pilot study of a canine subject (see Section 3.4), were 2.3 and 3.6 for compaction and ashing (or a combined CF of ~8), respectively, whereas the CF values for fish (sockeye) were observed to be 2.1 and 9.5 (or a combined CF of ~20), respectively.

Sub-samples of fecal samples collected in a canine pilot study were prepared by freeze-drying and emplacement directly into gamma tubes (i.e., no pre-treatment), by ashing and/or by compaction before emplacement into tubes. The results for ^{214}Pb and ^{212}Pb measured by gamma spectrometry for the 3 pre-treatment methods is shown in Figures 3.11a and b. No statistical differences were observed between the 3 pre-treatment methods for either ^{214}Pb (ANOVA F=0.77, p=0.48) or ^{212}Pb (ANOVA F=0.46, p=0.64). One ashed canine fecal sample was analyzed repeatedly for 7 trial runs to determine if the precision of the analysis was affected by the sample treatment (Table 3.8). It was observed that the coefficient of variability (CV) for the 7 trial runs was low, with values of 3% and 6% for ^{214}Pb and ^{212}Pb, respectively. These results compared reasonably well with the values obtained for the multiple analyses of the untreated IAEA reference soil standard (Table 3.8), where CV values for ^{214}Pb and ^{212}Pb were 8% and 6%, respectively.

The use of Marinelli beakers was evaluated as a potential method to increase the sample volume analysed with an attendant improvement in the detection of low levels of radioisotopes in food samples. Marinelli Beaker samples were prepared by emplacing up to 400 mL of sample into the beaker. A purpose-built plastic disc was then inserted into the beaker to separate the sample from a layer of epoxy resin sealant that is subsequently injected over the sample (Figure 3.12). As previously mentioned, the geometric configuration of the Marinelli Beaker reduces the efficiency of gamma spectrometer counting relative to the well configuration. Thus, a conversion factor was required to adjust counting values for the isotopes of concern to accommodate the loss of efficiency. Marinelli beakers were prepared with the IAEA soil reference standard #375, sealed and stored for over 21 days, then analysed by gamma spectrometry. The correction factor was determined by dividing the

decay-corrected reference values for ^{214}Pb and ^{212}Pb by the gamma spectrometric results for ^{214}Pb and ^{212}Pb (Table 3.9).

A radium extraction method was also developed in an attempt to volume reduce the samples by precipitation of Ra and Th isotopes in food samples (Appendix A). However, an initial evaluation showed that tracer recoveries from fish samples spiked with known amounts of dissolved ^{226}Ra standard (NISST ^{226}Ra Standard Reference Material #4969) achieved with the method were low (<60%), and further evaluation of the process was abandoned.

Table 3.7
^{214}Pb activity concentrations measured by gamma spectrometry of water samples inoculated with the National Institute of Standards & Technology Standard SRM ^{226}Ra Radioactivity Standard (0.1 Bq L^{-1}) and pre-concentrated by evaporation. The Δ value is the difference between the actual and measured concentrations.

Sample Description	^{214}Pb (Bq L^{-1})	Δ ^{214}Pb (Bq L^{-1})
Canine study spiked water sample #1	0.087	-0.013
Canine study spiked water sample #2	0.086	-0.014
Canine study spiked water sample #3	0.115	0.015
Canine study spiked water sample #4	0.115	0.015
Canine study spiked water sample #5	0.123	0.023
Canine study spiked water sample #6	0.117	0.017
Canine study spiked water sample #7	0.108	0.008
Canine study spiked water sample #8	0.098	-0.002
Mean	**0.106**	**0.006**
Standard deviation	**0.014**	**0.014**
Standard error	**0.005**	**0.005**

Table 3.8
Gamma spectrometric analysis of ^{214}Pb and ^{212}Pb in replicate ashed fecal samples

Sample Description	Canine fecal sample Bq kg^{-1}		IAEA Reference sample Bq kg^{-1}	
	^{214}Pb	^{212}Pb	^{214}Pb	^{212}Pb
Trial-1	6.0	3.4	17.4	18.6
Trial-2	6.3	3.0	19.4	18.5
Trial-3	5.9	3.0	21.0	21.3
Trial-4	6.1	3.5	20.3	18.8
Trial-5	5.8	2.7	21.7	19.0
Trial-6	5.8	3.2	21.5	17.8
Trial-7	5.6	3.1	20.2	19.5
Trial-8	-	-	16.7	18.1
Mean	**5.9**	**3.1**	**20.1**	**19.0**
Standard deviation	**0.2**	**0.2**	**1.7**	**1.1**
Coefficient of variability	**3%**	**6%**	**8%**	**6%**

Table 3.9
Marinelli beaker conversion factors for ^{214}Pb and ^{212}Pb analysed in Marinelli beakers developed from gamma spectrometric analysis of IAEA reference soils

Isotope activity	Measured activity		IAEA Ref375 value Bq kg^{-1}	Conversion factor
	Bq kg^{-1}	+/-		
^{214}Pb	1.97	0.11	19.8	10.1
^{212}Pb	1.77	0.08	21.0	11.9
Consolidated value				10.3

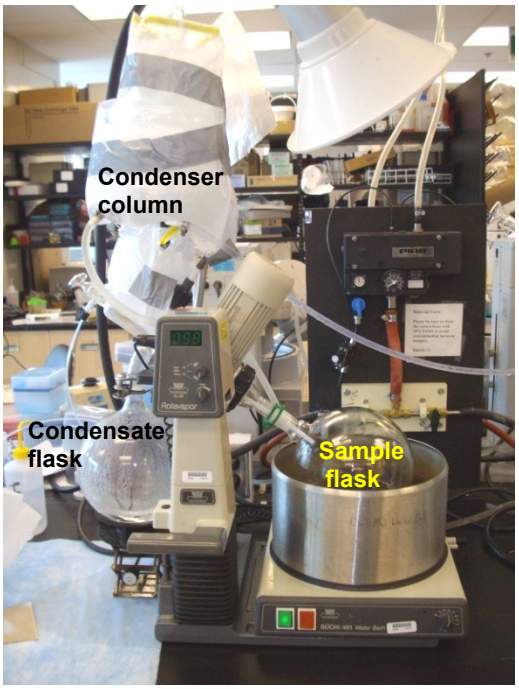

Figure 3.7
Rotary evaporator setup showing sample flask, ice packs on condenser and supported condensate flask

Figure 3.8
Close-up of rotary evaporator stopcock arrangement

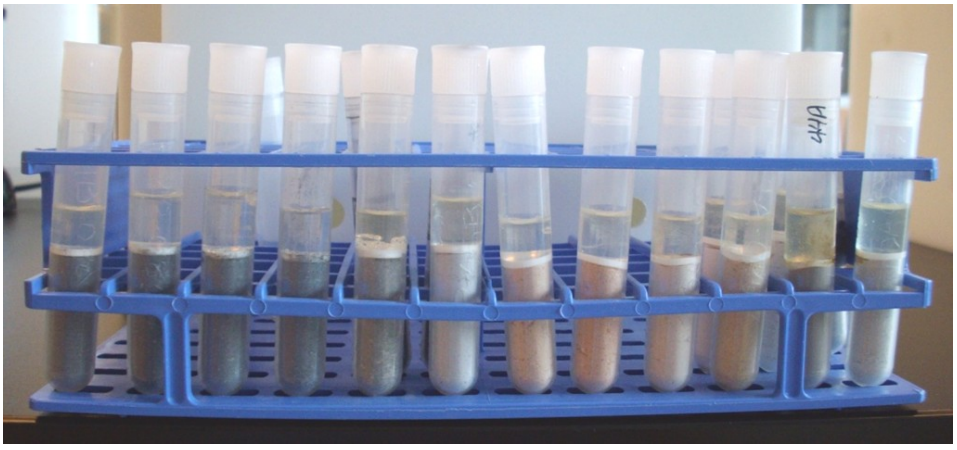

Figure 3.9
Samples packed into 8mL gamma tubes showing Teflon septa separating the sample (bottom of the tube) and the epoxy sealant

Figure 3.10a
Steel die, plunger and gamma tube

Figure 3.10b
High pressure press arrangement where plunger compresses sample in a gamma tube housed in the steel die

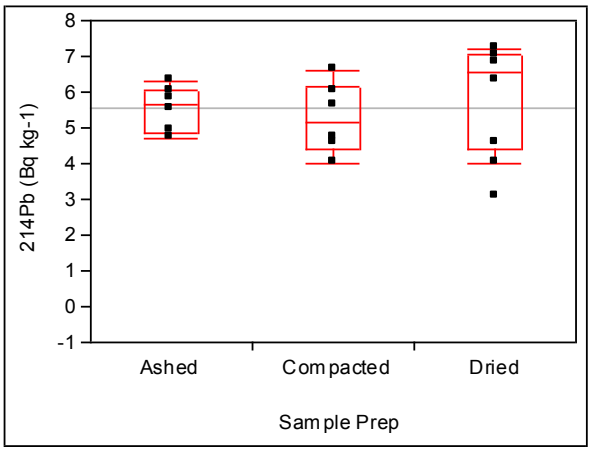

Figure 3.11a
Comparison of ^{214}Pb values for the fecal sample pre-concentration methods evaluated (ANOVA F=0.77, p=0.48)

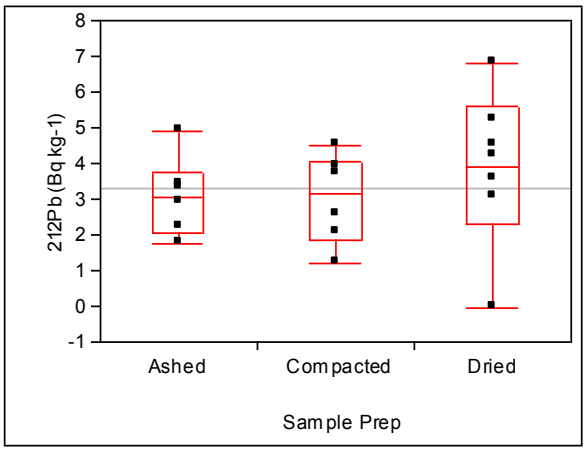

Figure 3.11b
Comparison of ^{212}Pb values for the fecal sample pre-concentration methods evaluated (ANOVA F=0.46, p=0.64)

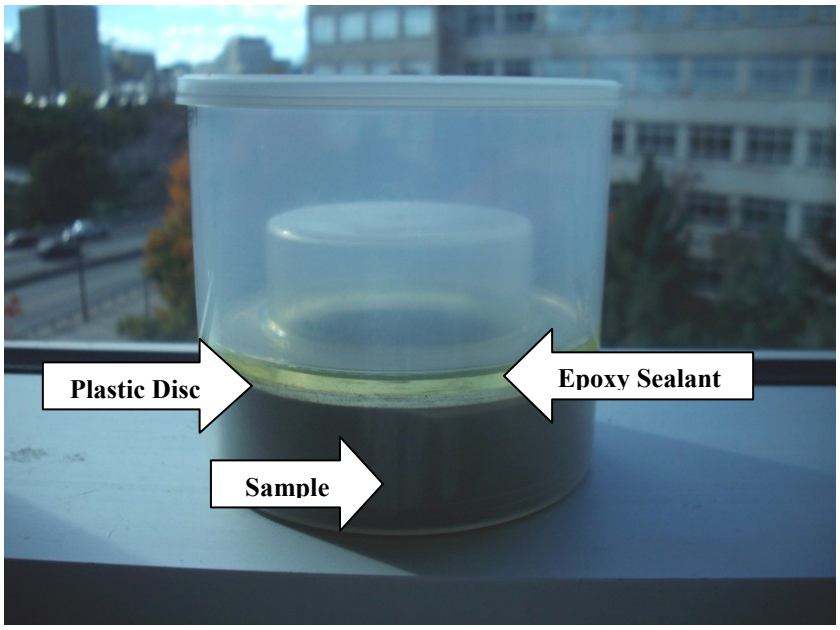

Figure 3.12
Ashed food sample in Marinelli Beaker showing sample, plastic disc and epoxy resin

3.3.2 Particle size of soil samples

Naturally-occurring radionuclides, such as the isotopes of the ^{238}U decay series, enrich in soil fractions of decreasing particle size (Megumi and Mamuro 1977; Sheppard and Evenden, 1992; Sheppard and Evenden, 1994). Further, the particle sizes of soil particulates that preferentially adhere to hands, and are thus available for ingestion, are typically less than 63 μm in size (Choate et al., 2006; Siciliano et al. 2009). If radionuclide tracers used in mass balance soil ingestion studies enrich in the smaller particle size fractions of soil that is ingested, but whole soils are analyzed to determine tracer levels, then soil ingestion estimated by mass balance tracer methods will be positively biased. Thus, soil ingestion estimates would be improved if the mass balance calculations were based on the concentration of tracers measured in finer particle size fractions (Stanek et al., 1999).

Soil samples collected during the aforementioned pilot study of a canine subject (Section 3.4) were separated into decreasing particle size fractions and analysed by gamma spectrometry to determine the extent that naturally-occurring radionuclides enrich in the smaller particle size

fractions of soil. Samples were also analysed by ICP/MS and ICP/OES for elemental tracers to determine if these tracers also enrich in smaller soil fractions. The soil fractions analysed were:

- ≥100 μm <250 μm,
- >63 μm ≥100 μm,
- <63 μm.

The mean concentrations of tracers analyzed in the particle size fractions analyzed are shown in Table 3.10. The mean activity concentrations for the particle size fractions measured were observed to be significantly different for ^{214}Pb (ANOVA F=72.8, p<0.0001; Tukey-Kramer HSU, p=0.05) and ^{212}Pb (ANOVA F=71.2, p<0.0001; Tukey-Kramer HSU, p=0.05) (Figures 3.13a and b). Other isotopes were observed to be enriched in the <63 μm by 50% relative to unfractionated soil samples. Similarly, concentration enrichments of the same scale were observed for the Al, Ba, Ce, La, Mn, Th, Ti, U, Y and Zr. The Al tracer was enriched by over 50% in the <63 μm particle size fraction relative to the ≥100 μm <250 μm resulting in mean activity concentrations that were significantly different for the particle size fractions measured (ANOVA F=243.2, p<0.0001; Tukey-Kramer HSU, p=0.05) (Figure 3.14). Interestingly, Si was observed to become depleted in the smaller particle sizes with the concentration being approximately 25% less in the <63 μm fraction relative to the ≥100 μm <250 μm fraction. The Si concentrations of the 3 fractions were significantly different (ANOVA F=52.1, p<0.0001; Tukey-Kramer HSU, p=0.05) (Figure 3.15).

Table 3.10
Mean (standard error) ^{214}Pb and ^{212}Pb activity concentrations and elemental tracer concentrations in particle size fractions of soil samples collected in a pilot mass balance soil ingestion study of a canine subject

Tracer	n	Particle size fractions – mean (standard error) concentration			
		Whole soil	≥100 <250 µm	≥63 <100 µm	<63 µm
^{214}Pb (Bq kg^{-1})	12	19.7 (1.1)	13.2 (0.7)	19.3 (0.8)	31.4 (0.8)
^{212}Pb (Bq kg^{-1})	12	20.0 (1.0)	13.2 (0.7)	20.3 (0.9)	31.0 (0.7)
Al (mg kg^{-1})	5	-	36200 (583)	49000 (547)	55600 (748)
Si (mg kg^{-1})	5	-	321600 (7393)	288000 (4950)	238800 (4554)
Ba (mg kg^{-1})	5	-	448 (11.1)	602 (24.0)	624 (33.6)
Ce (mg kg^{-1})	5	-	33.8 (2.9)	46.4 (2.6)	75.6 (2.0)
La (mg kg^{-1})	5	-	16.6 (2.9)	22.2 (1.6)	36.2 (1.1)
Mn (mg kg^{-1})	5	-	486 (23.4)	658 (35.0)	958 (49.8)
Th (mg kg^{-1})	5	-	4.1 (0.3)	5.6 (0.3)	9.4 (0.4)
Ti (mg kg^{-1})	5	-	1860 (121)	2540 (121)	2920 (168)
U (mg kg^{-1})	5	-	0.9 (0.06)	1.3 (0.02)	2.0 (0.10)
V (mg kg^{-1})	5	-	41.4 (1.9)	55.2 (1.5)	69.8 (3.6)
Y (mg kg^{-1})	5	-	14.8 (0.5)	20.8 (0.9)	26.8 (0.7)
Zr (mg kg^{-1})	5	-	58.4 (5.0)	95.8 (8.2)	169.4 10.5)

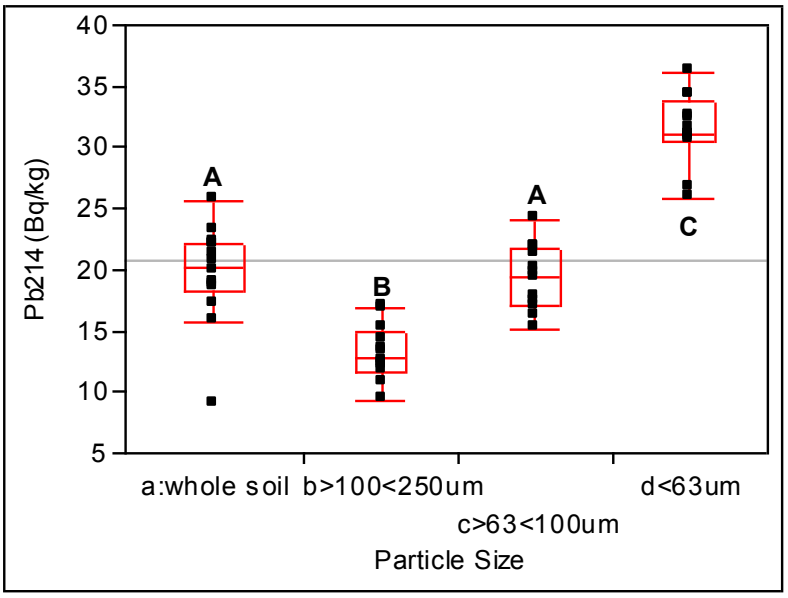

Figure 3.13a
Box plots showing median, 25% and 75% quantiles and outlier whiskers of ^{214}PB (Pb214) activity concentrations for soil particle size fractions. Letters denote significant differences in distributions (ANOVA F=72.8, p<0.0001; Tukey-Kramer HSU, p=0.05).

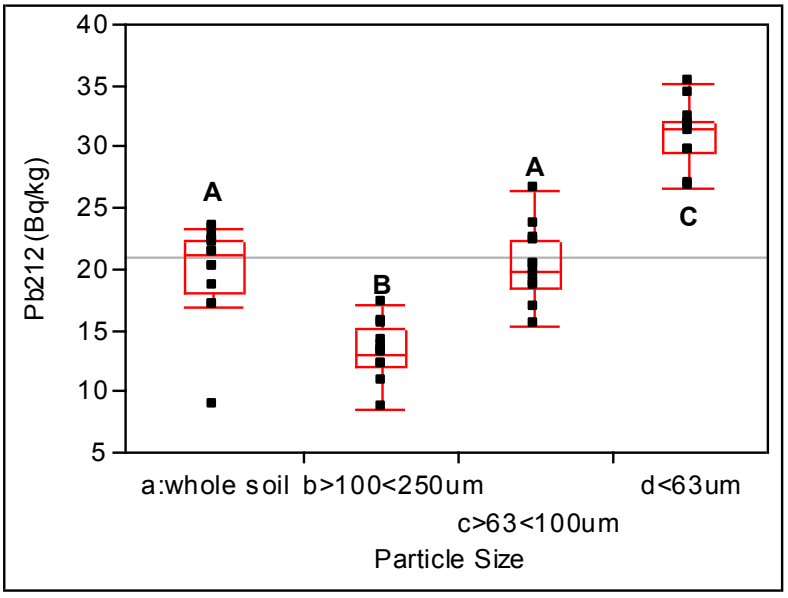

Figure 3.13b
Box plots showing median, 25% and 75% quantiles and outlier whiskers of ^{212}PB (Pb212) activity concentrations for soil particle size fractions. Letters denote significant differences in distributions (ANOVA F=71.2, p<0.0001; Tukey-Kramer HSU, p=0.05)

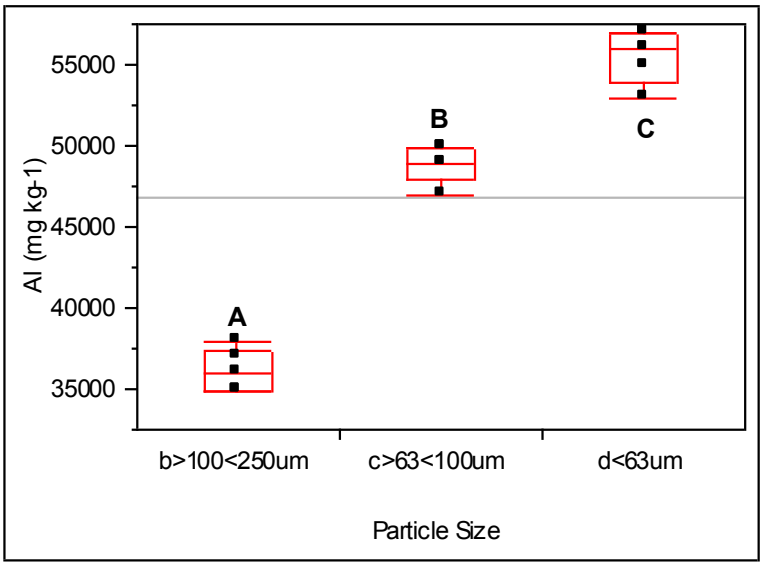

Figure 3.14
Box plots showing median, 25% and 75% quantiles and outlier whiskers of Al concentration for soil particle size fractions. The 3 distributions are significantly different (ANOVA $F=243.2$, $p<0.0001$; Tukey-Kramer HSU, $p=0.05$)

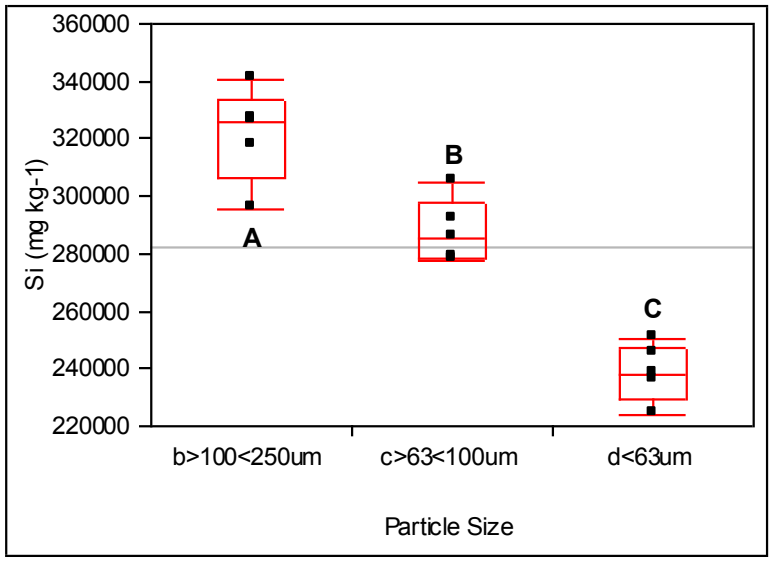

Figure 3.15
Box plots showing median, 25% and 75% quantiles and outlier whiskers of Si concentration for soil particle size fractions. The 3 distributions are significantly different (ANOVA $F=52.1$, $p<0.0001$; Tukey-Kramer HSU, $p=0.05$)

3.4 ICP/MS analysis of inorganic tracers

Analysis of the tracer elements (Al, Ba, Ce, La, Mn, Si, Th, Ti, U, V, Y and Zr) was performed by a commercial laboratory accredited by the Canadian Association for Laboratory Accreditation Inc. to ISO/IEC 17025:2005. For the analysis of Al, Ba, Ce, La, Mn, Th, Ti, U, V, Y and Zr, samples were digested using EPA Method 3052. Digested samples were then analysed by ICP/MS. Total Si was determined by sodium peroxide fusion followed by inductively coupled plasma optical emission spectrometry (ICP/OES) analysis.

Seven replicates of a soil sample obtained from the pilot study of a canine subject were sent for ICP/MS analysis of Al, Ba, Ce, La, Mn, Th, Ti, U, V, Y and Zr and ICP/OES analysis of Si to determine the precision of the analytical results (Table 3.11). The minimum detection limits (MDL) for each tracer element were provided by the contracted laboratory and are also included in Table 3.11. It was observed that the precision of the analysis of element tracers was good, with CV values for all elements less than 5%.

Table 3.11
Analysis of elemental tracers in replicate ashed fecal samples

Description		Tracer concentration (mg kg^{-1})									
	Al	Ba	Ce	La	Mn	Th	Ti	Si	U	V	Zr
CS-4Z Trial 1	52000	630	88	36	900	8.6	2700	274000	1.8	65	140
CS-4Z Trial 2	52000	630	86	34	900	8.3	2700	274000	1.8	65	150
CS-4Z Trial 3	53000	650	91	37	920	8.7	2700	274000	1.9	68	160
CS-4Z Trial 4	53000	660	91	37	920	8.7	2700	272000	1.8	67	160
CS-4Z Trial 5	51000	630	84	34	890	7.8	2600	273000	1.7	65	150
CS-4Z Trial 6	51000	630	84	33	910	8	2800	270000	1.8	66	160
CS-4Z Trial 7	53000	670	92	36	940	9	2900	271000	1.8	68	160
Mean	**52100**	**640**	**88**	**35**	**910**	**8.4**	**2700**	**272000**	**1.8**	**66**	**154**
SD	**900**	**20**	**3**	**2**	**20**	**0.4**	**95**	**0.2**	**0.1**	**1.**	**8**
CV	**2%**	**3%**	**4%**	**5%**	**2%**	**5%**	**3%**	**1%**	**3%**	**2%**	**5%**
Minimum detection limit[12]	**1**	**.01**	**0.006**	**0.001**	**0.1**	**0.01**	**0.1**	**300**	**0.002**	**1**	**0.03**

[12] MDLs provided by SGS Canada Inc., Lakefield, Ontario and based on EPA method 3052 digestion followed by ICP/MS analysis of Al, Ba, Ce, La, Mn, Th, Ti, V and Zr, and sodium peroxide fusion followed by ICP/OES analysis of Si.

3.5 Canine pilot study

3.5.1 Introduction

The use of naturally-occurring radionuclides from the ^{238}U and ^{232}Th decay series as mass balance tracers in soil ingestion studies was proposed by Doyle et al. (2010). Although several mass balance soil ingestion studies have been completed to date, there have been few validation studies of the mass balance tracer approach to estimate soil ingestion. Two pilot studies of adults were conducted by Ed Calabrese and his colleagues at the University of Massachusetts, Amherst, to validate the soil ingestion mass balance estimating methodology used in their larger studies assessing soil ingestion in children (Calabrese et al., 1989, 1997; Stanek and Calabrese, 1991, 1997). The two pilot studies assessed soil ingestion in 6 and 10 subjects respectively for 3 1-week periods. To validate their methodology, each day the study subjects were given a known quantity of soil with a known concentration of elemental tracers (e.g., Al, Ba, Ce, La, Mn, Si, Ti, V, Y and Zr) and the percent recovery of tracers as measured in subject feces, determined. Calabrese and Stanek (1995) also used mass balance estimating methods to estimate soil ingestion in an Irish Setter tracked over a 3-day period. Calabrese observed soil ingestion rates in the canine subject between 10-20 g d^{-1}, or several hundred-fold higher than soil ingestion rates observed in children.

The purpose of this pilot study was to confirm the feasibility of using naturally- occurring radionuclides from the ^{238}U and ^{232}Th decay series as mass balance tracers in a soil ingestion pilot study on a canine subject. Specifically, the study objectives were to determine if tracers could be reliably detected in feces by gamma spectrometry, develop sample collection and handling procedures, and compare the soil ingestion estimates calculated using radionuclide tracers with estimates calculated using elemental tracers. The study design included the feeding of a known amount of soil to the canine subject to confirm that the radionuclide mass balance tracers would be reliably recovered in a soil ingestion study.

3.5.2 Methods

A 1-year old Golden Retriever was identified as the subject for the pilot study. Approval to proceed with the study was obtained from the University of Ottawa Animal Care Committee (approval #BL-230) on April 16, 2009.

The study was conducted over an 8-day period at a small cottage on Big Rideau Lake, Portland, Ontario, approximately 100 km south of Ottawa. The cottage property was fully landscaped (i.e., lawn) up to the shoreline. With the exception of intermittent walks on a paved road, swims in Big Rideau Lake or boat rides, the subject spent the entire study period within the property boundaries.

The canine subject was given a daily dose of 2 g of soil (<100 μm) (i.e., the inoculant) with a known activity concentration of ^{214}Pb and ^{212}Pb and elemental tracers (i.e., Al, Ba, Ce, La, Mn, Si, Th, Ti, U, Y, and Zr) from Day 1 to Day 8 of the study. Approximately 250 g was metered out with a beaker and fed to the canine subject 2 times per day with 1 g of soil inoculant mixed into a small amount of wet dog food. The inoculant was obtained from a sample of soil collected from Rockland, Ontario that was ashed at 500 C for over 4 h in a muffle furnace. Two 500 mg glucosamine capsules were also given to the canine subject at each feeding. A measured volume of water was provided each day. The average amount of water consumed by the canine subject was determined by recording the amount of water supplied to the water dish less the amount remaining in the bowl each day. The average water consumption was observed to be approximately 1 L d^{-1}. Samples of food, water and medicines were retained for analysis. Soil samples were collected from 3 locations on the property (1 between the front of the cottage and a road and 2 between the back of the cottage and the lake), with 4 replicate samples being collected from each location (Figure 3.16). Daily fecal output was collected daily from Day 2 to Day 8 of the study and stored in pre-weighed plastic containers in a cold box until they were transported to the laboratory, where they were freeze-dried, weighed and stored until prepared for analysis. The canine subject normally provided a fecal sample within 30 minutes of eating and great care was taken not to miss any fecal output. Catching the fecal sample before it hit the ground proved difficult and

fecal samples were taken after they were provided on a grass-covered lawn area. Although contamination of the sample cannot be ruled out, dirt was not normally observed to be adhering to the fecal samples collected. Any debris adhering to fecal samples after collection was removed.

Food and fecal samples were ashed before analysis. Approximately 1 g sub-samples of ashed food, soil inoculant and fecal samples, the soil samples collected from the study site and 1 g of glucosamine were sent to a commercial laboratory accredited by the Canadian Association for Laboratory Accreditation Inc. to ISO/IEC 17025:2005 for analysis of Al, Ba, Ce, La, Mn, Si, Th, Ti, U, V, Y and Zr. The remainder of the ashed food and fecal samples, and a sample of glucosamine were compacted into 8 mL centrifuge tubes and sealed with epoxy resin. Water samples were pre-concentrated to a solid by evaporation then were compacted in 8 mL centrifuge tubes and sealed with epoxy resin. All samples to be analysed by gamma spectrometry were stored for at least 21 days before analysis to permit the naturally-occurring isotopes of the ^{238}U and ^{232}Th decay series (i.e., ^{214}Pb and ^{212}Pb, respectively) to achieve secular equilibrium with their parent radionuclides (i.e., ^{226}Ra and ^{228}Th, respectively). Samples were analyzed using an Ortec™ high purity germanium (HPGe) detector and gamma spectrometer.

The daily soil ingestion for each subject was calculated from Eq. (3.3).

$$S_a = \frac{(F_c \times F_a) - (I_c \times I_a) - (D_c \times D_a)}{S_c} \qquad (3.3)$$

where:

S_a is the soil ingested (g)
F_c is the concentration of tracer element in feces (μg g^{-1})
F_a is the mass of feces (g)
I_c is the food/water/medicine concentration for tracer (μg g^{-1})
I_a is the mass of food/water/medicine ingested (g)
D_c is the inoculant soil concentration for tracer (μg g^{-1})

D_a is the mass of soil inoculant ingested (g)

S_c is the concentration tracer in soil (μg g^{-1})

Food/soil (F/S) ratios were calculated by dividing the mass of the tracer element in 1 gram of soil into the mass of the tracer element ingested from food over a 1-day period.

3.5.3 Results and Discussion

The results from the analysis of daily fecal output collected from the canine subject during the study period are provided in Table 3.12. Analytical results for the soil samples collected from the study site, and food, soil inoculant, water and medicine (i.e., glucosamine) ingested by the canine subject are provided in Table 3.13. It was noted that some of elemental tracer levels were substantially higher in the soil inoculants than the soil sampled at the study site. Daily fecal output and food, soil inoculant, water and medicine consumption rates by the canine subject are provided in Table 3.14. The fecal output was observed to be relatively constant on Days 1, 2, 3, 4, 5, 7, and 8, ranging from 35 g to 55 g. However, a low fecal output was observed on Day 6 of the study. Substantial variability was observed in tracer concentrations in daily fecal samples, with coefficients of variability (CV) ranging from 7% to over 60%. Conversely, the tracer intake was maintained at a relatively constant level with the canine subject consuming the same amount of food and medicine before the study and every day of the study.

Daily soil ingestion rates and F/S ratios were calculated for all tracers (Table 3.15). It was observed that there was a high degree of variability in the soil ingestion rates between days and tracer types. Positive mean and median soil ingestion rates were observed for ^{214}Pb, ^{212}Pb, Ba, Ce, La, Ti, U, Y and Zr tracers. Daily soil ingestion rates, adjusted to account for tracers ingested in the daily soil inoculants, ranged from less than -14 g d^{-1} to over 17 g d^{-1} and the mean soil ingestion rate calculated with all tracers was observed to be 1.85 g d^{-1} (standard deviation 8.9 g d^{-1}) and the median was 0.9 g d^{-1}. These rates are lower than the rates observed in the Calabrese and Stanek (1995) study, which estimated daily soil ingestion rates of 10 to 20 g d^{-1}. The positive soil ingestion values suggest that either all tracers in the

soil inoculant were recovered and/or the soil ingested by the subject was greater than the extent that tracers were absorbed in the gastrointestinal tract.

Soil ingestion estimates based on mass balance tracers with high F/S are less reliable than those with lower F/S ratios because, by virtue of their low levels in foods, they will reduce uncertainty resulting from a lack of correspondence between the tracer ingested with food and the timing of there appearance in feces (i.e., transit time misalignment) (Calabrese and Stanek, 1993). Based on the F/S ratio, the most reliable radioisotope tracer was observed to be ^{212}Pb with an F/S ratio of 0.74, and the most reliable elemental tracers were observed to be Ce, La, Si and Y with F/S ratios of 0.34, 0.001, 0.14 and 0.77, respectively. The soil ingestion rates calculated with these tracers are shown in Figure 3.16. The mean soil ingestion rate calculated with these tracers for all days was observed to be 1.2 g per day with a median of 0.3 g d^{-1}. It is important to note that F/S ratios calculated may not be representative because the calculations did not include the tracers contained in the soil inoculant. When tracers in the inoculant are included in the calculation, the F/S ratios increase substantially. However, the increase in the potential for transit time misalignment resulting from the higher F/S ratio that occurs with the ingestion of additional tracer in the inoculant would be somewhat mitigated by maintaining the daily tracer input to the subject at a constant level.

The soil ingestion rates calculated with the isotope tracers were observed to be greater than when compared with all elemental tracers. The mean soil ingestion rate for the isotope tracers was observed to be 3.9 g d^{-1} (standard deviation 3.5 g d^{-1}) and the mean soil ingestion rate using the 4 element tracers with the lowest F/S ratios was observed to be 1.5 g d^{-1} (standard deviation 9.6 g d^{-1}). However, this difference is not statistically significant (ANOVA F=0.85, p=0.36; Welch ANOVA F=54.3, p=0.10). There were no statistically significant differences observed between soil ingestion rates calculated with ^{212}Pb (F/S) compared to those calculated with ^{214}Pb (ANOVA F=0.04, p=0.95) (Figure 3.19). The similarity of soil ingestion estimates using ^{214}Pb and ^{212}Pb tracers suggests that the actual absorption rates of the parent isotopes they are measuring (i.e., ^{226}Ra (f_1=0.2) and ^{228}Th (f_1=0.0005), respectively) in the gastrointestinal tract of the subject are not substantially different.

Table 3.12
Dry weight tracer concentrations for daily fecal samples collected during the soil ingestion pilot study using a canine subject

Fecal sample	Bq kg^{-1}			mg kg^{-1}										
	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	U	V	Y	Zr
Day 2	4.92	1.82	3300	67	3.4	1.6	410	5000	0.8	580	0.45	5	1.3	10
Day 3	5.82	4.85	7300	120	9.0	4.1	370	38700	0.6	580	0.61	9	3.1	16
Day 4	4.67	2.22	3800	74	4.7	2.4	390	6800	0.2	950	0.72	6	1.6	13
Day 5	6.03	3.40	4200	70	6.7	3.3	410	15500	0.6	1300	0.71	6	1.9	10
Day 6	3.09	4.51	4400	83	5.5	2.4	390	23000	0.2	720	0.45	6	1.7	23
Day 7	5.55	2.88	7200	120	8.2	3.7	460	18800	0.5	760	0.81	8	2.7	14
Day 8	6.30	3.34	6400	110	8.1	3.5	420	20500	0.4	700	0.70	8	2.6	13
Mean	**5.20**	**3.29**	**5229**	**92**	**6.5**	**3.0**	**407**	**18329**	**0.5**	**799**	**0.64**	**7**	**2.1**	**14**
Standard deviation	**1.10**	**1.11**	**1686**	**24**	**2.1**	**0.9**	**29**	**11257**	**0.2**	**254**	**0.14**	**1**	**0.7**	**4**
Coefficient of Variability	**21%**	**34%**	**26%**	**26%**	**32%**	**30%**	**7%**	**61%**	**40%**	**32%**	**22%**	**14%**	**33%**	**29%**

Table 3.13

Mean tracer concentration of soils collected from the study site, and concentrations in soil inoculant (dry weight), water, and medicine (dry weight) consumed by the canine subject

Sample	Bq kg^{-1}			mg kg^{-1}										
	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	U	V	Y	Zr
Soil (n=13)	20.5	20.8	41700	555	55	22	572	322700	4.0	2046	1.0	46	16	91
Soil inoculant	16.7	17.6	160000	680	41	19	510	626000	8.1	2800	2.4	64	26	160
Water	0.007	0.0006	0.001	0.23	<.006	<.001	0.14	6	10E-6	3E-4	3E-3	2E-05	9E-6	3E-5
Glucosamine	0.00	0.00	1700	7	0.76	0.38	13	0.1	0.1	5	0.027	0.7	<.08	0.15
Dog food	0.65	0.05	130	4.3	0.05	7E-04	78	1400	7E-02	14	<.002	0.7	<.08	0.3

Table 3.14

Daily soil inoculant, water, and medicine consumption, and the daily fecal output by the canine subject

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Mean
Food dry weight (kg)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	NS	-
Water (L)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	NS	-
Glucosamine dry weight (kg)	0.002	0.002	0.002	0.002	0.002	0.002	0.002	NS	-
Soil inoculant dry weight (kg)	0.001	0.002	0.002	0.002	0.002	0.002	0.002	NS	-
Feces dry weight (kg)	NS[13]	0.043	0.051	0.035	0.043	0.013	0.055	0.049	0.041

[13] NS – not sampled

Table 3.15
Daily soil ingestion rates calculated for each day of the pilot study for all tracers and their food/soil (F/S) ratio. The F/S ratio calculated with tracers in the soil inoculant is also shown as F/S-2

Summary	F/S	F/S - 2	Soil ingestion (g)									
			Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Mean	SD	Median
^{214}Pb ashed	6.19	7.85	3.49	6.78	0.30	5.08	-3.58	7.20	7.45	3.82	4.13	5.08
^{212}Pb ashed	0.74	2.42	2.16	9.30	1.30	4.59	-0.24	5.09	5.36	3.94	3.17	4.59
Al	1.04	8.72	-1.48	0.15	-5.51	-4.36	-7.38	0.71	-1.22	-2.73	3.06	-1.48
Ba	2.83	5.28	1.14	5.66	-0.59	0.17	-3.38	6.52	4.40	1.99	3.64	1.14
Ce	0.34	1.83	1.58	6.48	1.18	3.45	-0.56	6.33	5.39	3.41	2.77	3.45
La	0.001	0.07	0.09	0.29	0.08	0.18	-0.01	0.29	0.23	0.16	0.12	0.16
Mn	42.40	44.19	-12.46	-11.45	-20.21	-13.21	-35.53	-0.27	-8.31	-14.49	11.04	-12.46
Si	0.14	4.02	-2.01	-3.41	-3.94	-3.81	-3.93	-3.70	-4.02	-3.54	0.71	-3.81
Th	5.18	8.98	1.31	-2.32	-7.08	-2.59	-8.26	-2.31	-4.85	-3.73	3.26	-2.59
Ti	2.12	4.07	9.11	10.28	12.26	23.40	0.40	16.22	12.65	12.04	7.00	12.26
U	2.89	7.27	12.58	20.89	15.83	20.72	-2.06	33.07	23.93	17.85	10.91	20.72
V	4.81	7.61	-1.50	2.36	-2.99	-1.94	-5.95	1.95	0.95	-1.02	2.98	-1.50
Y	0.77	3.98	1.09	5.73	-0.50	1.10	-2.65	5.15	3.88	1.97	3.08	1.10
Zr	1.12	4.63	1.94	4.24	0.38	0.06	-1.43	3.74	2.33	1.61	2.05	1.94

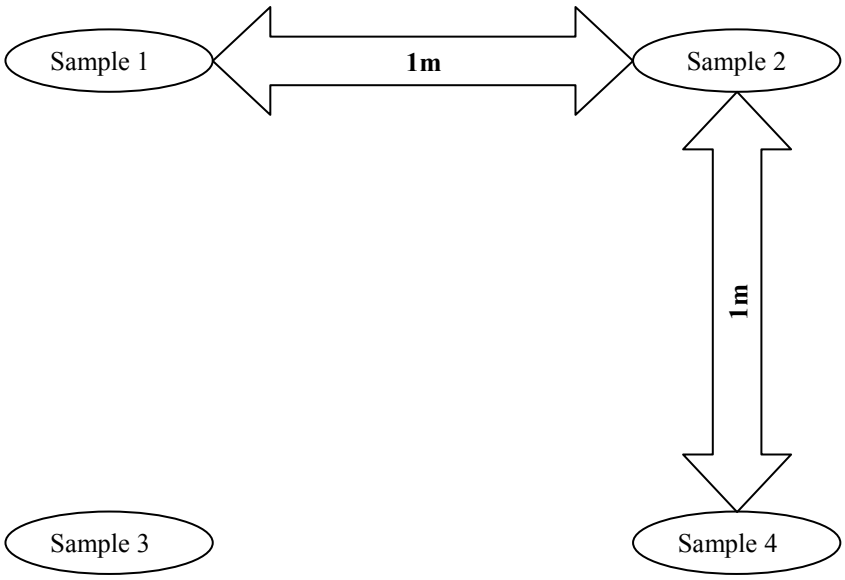

Figure 3.16
Soil sampling collection layout for each of the 3 locations on the Pilot Study site property

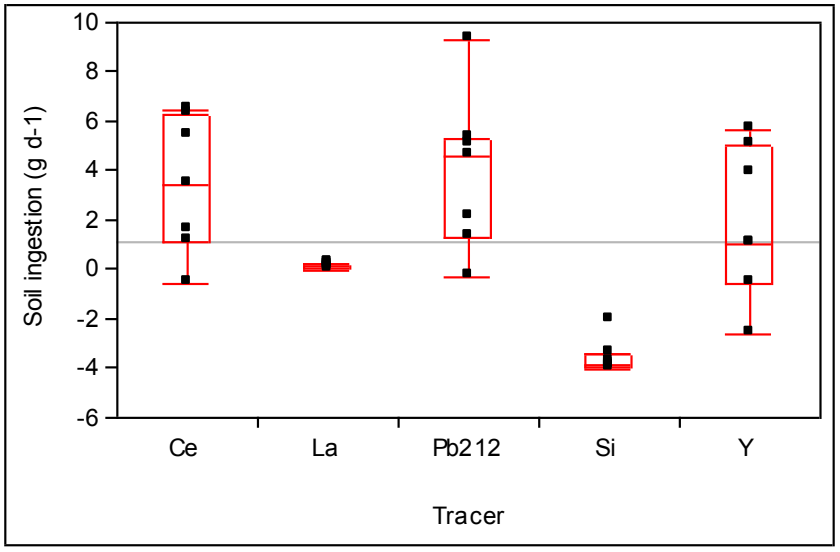

Figure 3.17
Box plots Box plots showing median, 25% and 75% quantiles and outlier whiskers of distributions of soil ingestion rates calculated for the 5 tracers with the lowest F/S ratios

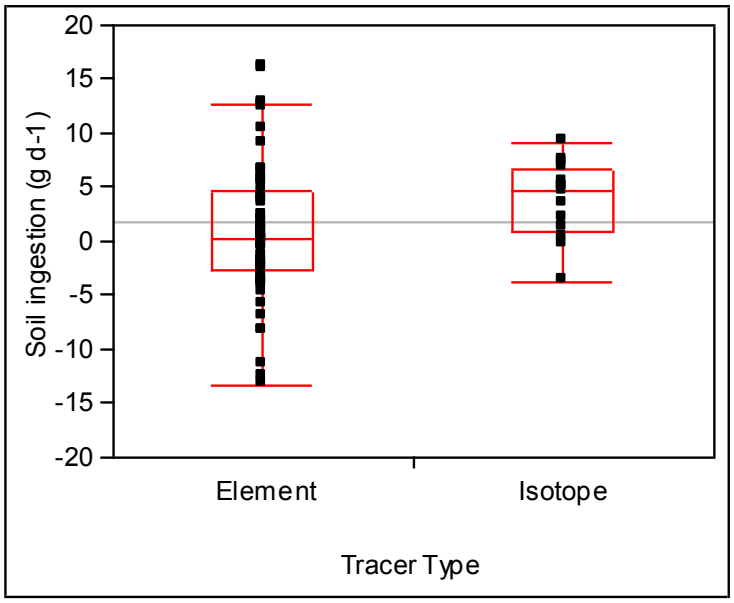

Figure 3.18
Box plots Box plots showing median, 25% and 75% quantiles and outlier whiskers of soil ingestion rates calculated using isotope tracers and elemental tracers. The distributions are not significantly different (ANOVA F=0.85, p=0.36; Welch ANOVA F=54.3, p=0.10).

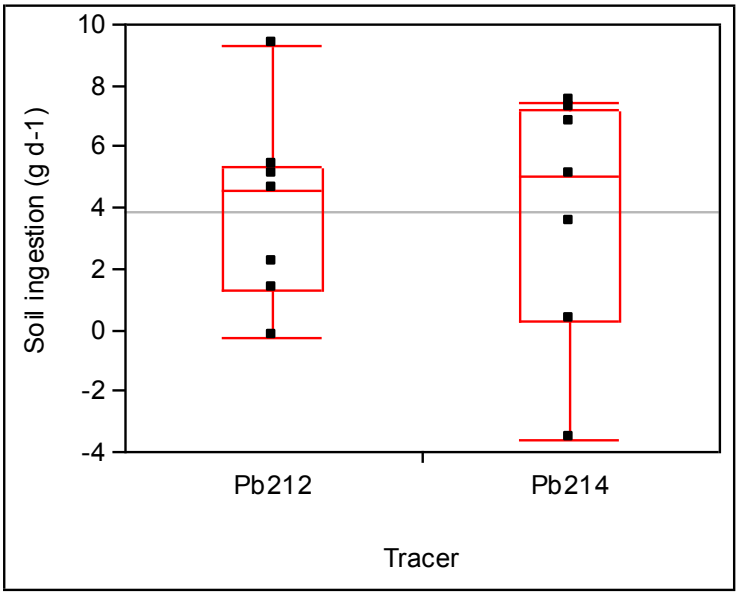

Figure 3.19
Box plots Box plots showing median, 25% and 75% quantiles and outlier whiskers of [d]istributions of soil ingestion rates calculated for ^{212}Pb (Pb212) and ^{214}Pb (Pb214) tracers. The distributions are not significantly different (ANOVA F=0.04, p=0.95).

3.5.4 Conclusions

The mean soil ingestion rate for a canine subject estimated using radionuclide and elemental tracers, adjusted to account for tracers ingested in the daily soil inoculants, was approximately 2 g d^{-1}, which is less than a previous study of a canine subject where soil ingestion was estimated in the order of tens of grams per day. No statistically significant differences were observed between soil ingestion rates estimated with the ^{214}Pb and ^{212}Pb isotope tracers and the element tracers that have typically been used in mass balance soil ingestion studies. The soil ingestion estimates calculated using the isotope tracers, after accounting for tracers in the soil inoculant, were higher than those calculated with elemental tracers, suggesting that the tracers were not being substantially absorbed in the GI tract of the subject. Thus, the use of isotope tracers in a future mass balance soil ingestion pilot study of a human population is feasible.

3.6 A method to estimate soil ingestion using isotopic tracer ratios

3.6.1 Introduction

If not subjected to chemical or physical separation, the members of ^{238}U and ^{232}Th radionuclide series will attain a state of radioactive equilibrium (i.e., secular radioactive equilibrium). When in secular equilibrium, the activity concentration (i.e., the number of atoms disintegrating per second, measured in Becquerel (Bq) per unit mass) of each radionuclide of a given series will be very nearly equal to the activity concentration of the nuclide that heads the series (NCRP, 1987a). Globally, this is the case for each series, but local concentrations can vary widely where differences in chemical properties of the elements within the decay chain result in disproportional precipitation, dissolution or diffusion, or increased dissolution of the daughter isotopes, or increased dissolution of some daughter isotopes through alpha recoil (Ivanovich, 1992). When activity concentrations of isotopes of the same decay series are measured by radiometric techniques and found to be in a 1:1 ratio, they are considered in secular equilibrium, and when imbalanced ratios are measured they are in disequilibrium. Furthermore, the ^{238}U and ^{232}Th series are commonly

found together in environmental samples at a proportion of approximately 1:1. Deviations from this proportion may be indicative of differences in soil composition and soil properties (Navas et al., 2005). Moreover, the bioavailability, uptake and re-distribution by plants of isotopes of the ^{238}U and ^{232}Th decay series can differ considerably, (Morton et al., 2001; 2002), and would result in a deviation in the ^{238}U/^{232}Th ratio from unity.

Differences in solubility or other characteristics of isotopes of the ^{238}U and ^{232}Th series that result in deviations in radionuclide ratios measured in food from what is normally found in soil may provide an opportunity to quantify the proportion of soil measured in feces using isotopic mixing models. A similar approach was proposed by Calabrese and Stanek (1992) to estimate the relative amounts of soil and dust consumed by individuals by comparing differential tracer element ratios. The purpose of this study was to investigate the potential for using secular disequilibrium and/or fractionation in the ^{238}U and ^{232}Th series measured with gamma spectrometry as an alternative method of estimating soil ingestion. To this end, the gamma spectrometric results of soil, food, water and fecal samples produced by the aforementioned canine pilot study were re-analyzed and soil ingestion estimates developed using an isotopic mixing model were compared to estimates calculated by the traditional mass balance approach.

3.6.2 Methods

The mathematical model employed to calculate soil ingestion in this study (the Isotope Ratio Method) is provided in Eq. (3.4) and Eq. (3.5). These equations were adapted from the isotopic mixing model developed by Blais (1996) to determine the relative proportion of Pb isotopes measured in lake sediments that would be expected given the differences in the ^{206}Pb and ^{207}Pb ratios of two Pb emission sources. Employing the same concept, the relative proportion of soil-derived tracers in feces, which is expected to be a function of the tracer ratios in food, soil and feces, can be calculated according to Eq. (3.4).

$$S_p = \frac{(R_f - F_r) \times 100}{S_r - F_r} \tag{3.4}$$

where:

S_p is the proportion tracers measured in feces derived from soil

S_r is the ^{212}Pb / ^{214}Pb ratio measured in soil

F_r is the ^{212}Pb / ^{214}Pb ratio measured in food

R_f is the ^{212}Pb / ^{214}Pb ratio measured in feces

Soil ingestion was then calculated using Eq. (3.5).

$$S_a = \frac{((F_c \times F_a) \times S_p)}{S_c} \quad (3.5)$$

where:

S_a is the soil ingested (g)

S_p is the proportion of tracer measured in feces derived from soil

F_c is the concentration of tracer in feces (μg g^{-1})

F_a is the mass of feces (g)

S_c is the concentration of tracer in soil (μg g^{-1})

3.6.3 Results and discussion

The soil, food and water gamma spectrometric analysis data from the canine soil ingestion pilot study that were used to derive the isotopic ratios in Eq. (3.4) are provided in Table 3.16. The mean ^{212}Pb / ^{214}Pb ratio measured in the 12 soil samples from the canine study was observed to be approximately 1, whereas the ^{212}Pb / ^{214}Pb ratio measured in the canine subject's food was observed to be approximately 0.1. A ratio for water was not obtained because the ^{212}Pb activity concentration was below the gamma spectrometer detection limit of 0.0014 Bq kg^{-1}. However, given that a ^{212}Pb activity concentration below the detection limit will yield a ^{212}Pb / ^{214}Pb ratio of 0.1 or less, using the ratio derived for food in the soil ingestion calculation was considered conservative (i.e., would not result in a positive bias of the soil ingestion estimate). The levels of ^{212}Pb and ^{214}Pb tracers from medicines were assumed to be negligible. The observed ^{212}Pb / ^{214}Pb ratio 0f 0.10 in canine food was consistent with a ratio of 0.14 calculated from dietary uptake reference values (Table 3.3) for ^{228}Th (i.e., ^{212}Pb) and ^{226}Ra (i.e., ^{214}Pb). ^{212}Pb / ^{214}Pb ratio values based on reference values

for most major food groups (Table 3.2) were observed to be less than 0.1, ranging from 0.02 for root vegetables and fruits to 0.1 for drinking water. One exception to this was the reference values for fish which yielded a theoretical ^{212}Pb / ^{214}Pb ratio of 1.0 for fish products. This order of magnitude difference in ^{212}Pb and ^{214}Pb ratio values between soil and food could be a result of the differential solubility and subsequent uptake of ^{228}Th and ^{226}Ra by plants and animals. For example, the gastrointestinal uptake factor (f_1) for ^{228}Th is 0.005, whereas the f_1 for ^{226}Ra is 0.20 (Table 3.2).

The activity concentrations of ^{212}Pb and ^{214}Pb in ashed samples of daily fecal output from the canine subject and the daily soil ingestion rates calculated using Eq. (3.5) are provided in Table 3.17. The analytical results from ashed fecal samples were used in the soil ingestion calculation. However, no ashed fecal sample was available for Day 6 of the study and the gamma spectrometric analysis of the freeze-dried sample was used in the soil ingestion calculation for that day. The mean soil ingestion rate calculated using the Isotope Ratio Method was observed to be 2.51 g d^{-1} (standard deviation 2.12 g d^{-1}). The soil ingestion estimates using the Isotope Ratio Method were greater than those calculated by the mass balance approach using ^{212}Pb as a tracer (Figure 3.20) but this difference was not statistically significant (ANOVA F=0.88, p=0.37; paired Student's t=2.2, p=0.05). However, when plotted against the mass balance tracer estimates, it was observed that the Isotope Ratio Method consistently under-estimated soil ingestion by a factor of approximately 1.5 (Figure 3.21). This under-estimation could be the result of the preferential uptake of ^{226}Ra (measured by ^{214}Pb) relative to the uptake of ^{228}Th (measured by ^{212}Pb) in the subject's gastrointestinal tract.

The advantage of the Isotope Ratio Method is that it eliminates the need for analyzing every food item consumed if a generic isotope ratio can be determined for food or food types. The disadvantage of the method is that food items with unusually high ^{212}Pb / ^{214}Pb ratios and/or store-bought (i.e., not locally-sourced foods) foods contaminated with soil, will yield erroneously high soil ingestion rates. Given these limitations, the Isotope Ratio Method may be more useful as a means to confirm that mass balance soil ingestion estimates are not

positively biased from source error or consumption of unreported foods rather than a stand-alone method to estimate soil ingestion.

Table 3.16
Activity concentrations of ^{212}Pb and ^{214}Pb in soil and food/water samples obtained from the canine soil ingestion pilot study and used to calculate soil ingestion using the isotope ratio method

Sample	^{214}Pb (Bq kg^{-1})	^{212}Pb (Bq kg^{-1})	^{212}Pb / ^{214}Pb ratio
Mean soil values (n=12)	31.4	31.0	0.99
Dry dog food - ashed	0.654	0.066	0.10
Canine study water sample	0.0130	<0.0014	<0.11

Table 3.17
Daily soil ingestion rates calculated for each day of the canine pilot study for all tracers and their food/soil (F/S) ratio. The F/S ratio calculated with tracers in the soil inoculant is also shown as F/S-2.

Sample	Fecal output (kg)	^{214}Pb (Bq kg^{-1})	^{212}Pb (Bq kg^{-1})	^{212}Pb / ^{214}Pb ratio	Soil tracer faction	Soil ingestion (g d^{-1})
Fecal output Day 2 ashed	0.043	4.9	1.8	0.37	0.30	0.75
Fecal output Day 3 ashed	0.051	5.8	4.9	0.83	0.82	6.43
Fecal output Day 4 ashed	0.035	4.7	2.2	0.47	0.42	1.01
Fecal output Day 5 ashed	0.043	6.0	3.4	0.56	0.52	2.43
Fecal output Day 6	0.013	3.1	4.5	1.46	1.53	0.33
Fecal output Day 7 ashed	0.055	5.5	2.9	0.52	0.47	2.35
Fecal output Day 8 ashed	0.049	6.3	3.3	0.53	0.48	2.51
Mean						***2.51***
Standard deviation						***2.12***
Coefficient of variability						***84%***

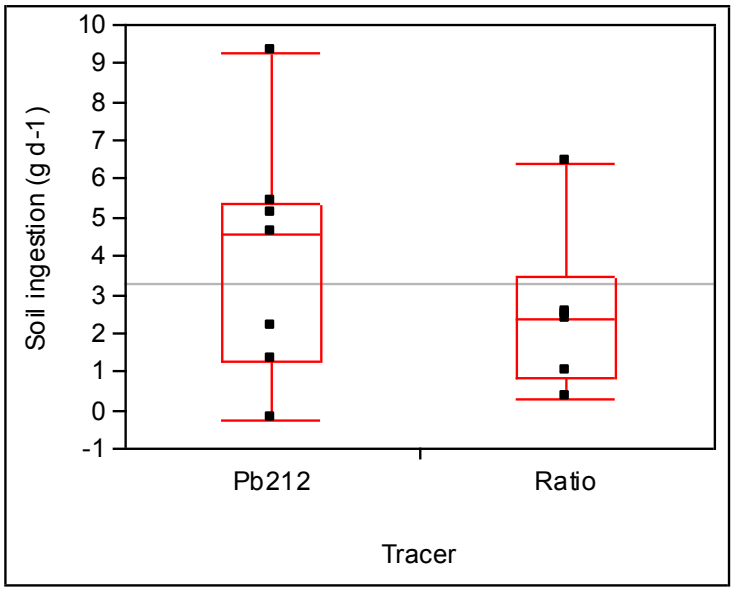

Figure 3.20
Box plots Box plots showing median, 25% and 75% quantiles and outlier whiskers of soil ingestion rates calculated using a ^{212}Pb tracer (Pb212) and the Isotope Ratio Method (Ratio). The distributions are not significantly different (ANOVA F=0.88, p=0.37).

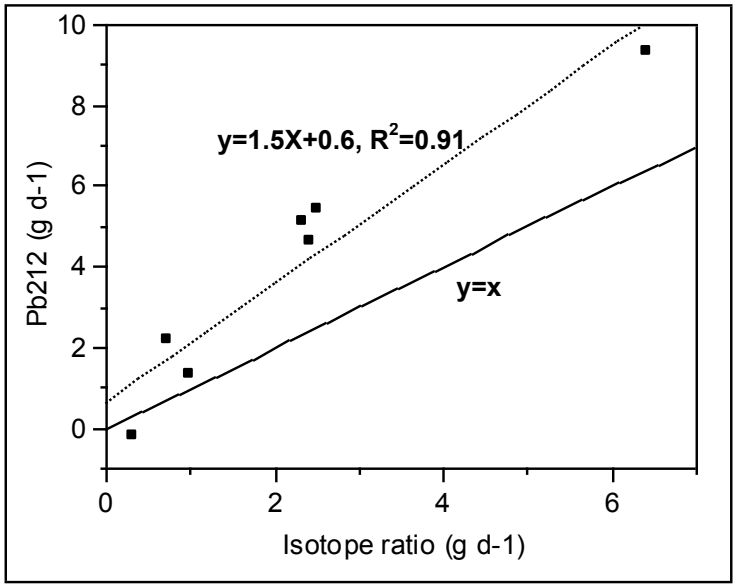

Figure 3.20
Box plots Box plots showing median, 25% and 75% quantiles and outlier whiskers of soil ingestion rates calculated with the mass balance approach using the ^{212}Pb tracer (Pb212) and the Isotope Ratio Method (Isotope ratio). The hatched line shows the best linear fit (R^2=0.91) and the solid line shows a 1:1 relationship.

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Chapter 4

A method to estimate sediment ingestion by fish

4.1 Introduction

A solid understanding of the mechanisms governing the fate and transport of chemical contaminants in the environment and within organisms is a fundamental input to defensible ecological risk assessments underpinning informed regulation of these contaminants. Contaminants normally found in low levels in wastewater discharges to the environment, such as the synthetic estrogen 17α-ethinylestradiol (EE2), have been observed to bioaccumulate in wild benthic fish (Al-Ansari, 2010). Several studies using multimedia mass balance models have been used to predict the extent of bioaccumulation of contaminants within aquatic systems and food webs (Mackay and Fraser, 2000). However, a potential weakness of these models is that they do not include sediment ingestion as a direct pathway for the bioaccumulation of hydrophobic organic contaminants in benthic fish. To address this weakness, recent studies have included sediment ingestion by fish as an exposure pathway for contaminant uptake and bioaccumulation models of aquatic systems (Moermond et al., 2004; van Beusekom et al., 2006). Given the potential for hydrophobic organic compounds to accumulate in aquatic sediments, understanding the extent to which sediment is ingested by fish is an important input to quantify the bioaccumulation of these chemicals in aquatic food webs.

Soil ingestion in cattle has been estimated by measuring inorganic tracers found in soil such as titanium (Fries et al., 1982). Beyer et al. (1994) developed a method that has been used to estimate soil ingestion in wildlife by measuring the acid insoluble residue (AIR) content of their scat and assuming a level of digestibility for their food. Levels of soil ingestion in several species of reptiles, shorebirds and mammals have been reported to range from less than 1% up to 60% of total diet and thus represent the principal route of exposure pathway for soil-borne contaminants for many wildlife species (Beyer and Fries, 2003). Calabrese and Stanek (1995) used inorganic elements (Al, Si, Ti, Y, Zr, La, Ce, Nd) found in soil as mass

balance tracers to estimate the soil ingestion rates in a canine subject and concluded that the exceedingly high soil ingestion observed demonstrated the need to evaluate soil ingestion in domestic animals and wildlife.

Although it is well known that benthic fish ingest significant quantities of sediment (Scott and Crossman, 1973), there remains a paucity of empirical sediment ingestion data for fish. A few studies have used gravimetric analysis of fish gut contents to measure sediments and detritus in benthic fish. Sule and Skelly (1985) found that the gut contents contained an average of approximately 36% potential food items, 22% unidentified organic and other matter, and approximately 42% unidentified inorganic matter and sand (i.e., sediment) in Shorthead Redhorse Suckers (*Moxostoma macrolepidotum*) sampled in Illinois between March and November, 1978. Detritus (i.e., inorganic and unidentified organic non-food items) in excess of 50% of gut contents has also been reported in the benthic fish Roach *(Rutilus rutilus)* and Bream *(Abramis brama)* (Michelsen, 1994; Tolonen et al., 2000).

Doyle et al. (2010) have proposed the use of naturally-occurring radionuclides, such as the isotopes of the ^{238}U decay series, as mass balance tracers to determine soil ingestion rates for human health risk assessments. Their proposed method measures isotope tracers, specifically ^{226}Ra in feces, local soils and food ingested by a subject to calculate a soil ingestion rate following the soil tracer approach described in Stanek and Calabrese (1991). Naturally occurring U is ubiquitous globally, and found in all rocks and soils at levels ranging from 0.03 mg kg^{-1} in ultrabasic igneous rocks to 3 mg kg^{-1} in acid igneous rocks to 120 mg kg^{-1} in Florida phosphate rocks (Eisenbud and Gesell, 1997). Unless fractioned by a chemical or physical process, ^{238}U is found in secular equilibrium with its major decay products (Bourdon et al., 2003). U, Th and Ra nuclides are readily adsorbed to mineral surfaces, and will also have a strong affinity to organic matter in riverine sediments (Chabeaux, 2003). ^{226}Ra can be determined by measuring ^{214}Pb in samples by gamma spectrometry and assuming secular equilibrium between the decay products. In this study, the mass balance tracer method has been adapted to estimate sediment ingestion by a benthic fish, such as the Shorthead Redhorse Sucker. The objective of the work is to provide quantitative data to support the development of models that include sediment ingestion to determine bioaccumulation of

contaminants found in appreciable concentrations in sediments, such as hydrophobic organic compounds, in aquatic food webs.

4.2 Methods

4.2.1 Sampling

The gastrointestinal (GI) tract was dissected from 17 Shorthead Redhorse Suckers collected by trawl net near where the City of Montreal wastewater treatment outfall discharges into the St. Lawrence River. The fish were collected over 2 sampling sessions; one in June, 2009 and a second in August, 2009. The fish were a sub-sample from a larger sample collected to assess contaminants that may be accumulating in suckers in the area. Sediment samples from 4 locations in the vicinity of where the fish were caught were collected using an Ekman dredge. Benthic invertebrate samples were not collected from the site. The GI tract was squeezed between the thumb and index finger, thereby transferring the gut contents into individual sample containers. This method removes most of the contents such that after removal, the gut is completely flat and translucent. The GI tract samples were then freeze-dried, re-weighed and compacted into 8 mL high density polyethylene centrifuge tubes. Sediment samples were also freeze-dried, weighed and compacted into the polyethylene tubes. A silicon/Teflon™ septum was inserted on top of each sample using tweezers. Epoxy was then added on top of the septum using a syringe, and the tubes were capped and stored for at least 21 days to allow ^{222}Rn. ^{218}Po and ^{214}Pb in the sample to reach secular equilibrium with ^{226}Ra.

4.2.2 Gamma spectrometry

Gamma emissions from the samples were counted using a digital, high purity germanium spectrometer (Ortec DSpec™) over a period of 23 h (82800s). ^{214}Pb activity was determined by using its gamma peaks at 352keV and 295keV. The activity A of a radionuclide, measured in disintegrations per second or Becquerel (Bq), corresponding to its energy peak(s), was calculated using the generic Eq. (4.1) (Appleby, 2001):

$$A = \frac{N}{\in YCT} \tag{4.1}$$

where,

N is the number of counts in the peak (number of disintegrations measured)

$\in$ is the detector efficiency (dimensionless)

Y is the yield of photons of an energy E (dimensionless)

CT is the count time (s)

The lowest level detectable (LLD) activity (i.e., the smallest amount of activity measured in Bq (i.e., disintegrations per second) that will yield a net count at 95% confidence levels) was calculated for ^{214}Pb measured in GI tract samples using Eq. (4.2) (USDOE, 1997):

$$LLD_{95\%} = \frac{\left[S_{gross} + S_b^2 + S_{rb}^2\right]^{1/2} \times 3.29}{\in YCT} \tag{4.2}$$

where,

S_{gross} is the mean number of background counts within the ROI (disintegrations)

S_b is the standard error of background counts within the ROI (disintegrations)

S_{rb} is the standard error of reagent blank counts within the ROI (disintegrations)

$\in$ is the detector efficiency at the ROI (dimensionless)

Y is the yield of photons of an isotope at energy E (dimensionless)

CT is the count time (seconds)

A blank sample, comprised of the Teflon™ septum and a quantity of epoxy resin normally used to seal samples inserted into an empty 8ml centrifuge tube, was analyzed 7 times for 82800s to obtain a mean reagent blank count and standard error. The accuracy and precision of the gamma analysis was determined through the multiple analyses of an International

Atomic Energy Agency (IAEA) standard reference soil (IAEA – 375 with a ^{226}Ra activity of 20 Bq kg^{-1}) for ^{214}Pb and assuming secular equilibrium with ^{226}Ra.

4.2.3 Calculation of sediment in GI tract using the "mass balance tracer" method

The mass of sediment in the gut contents of each sucker can be calculated using Eq. (4.3) (the simple mass balance tracer method).

$$W_S = \frac{E_G \times W_G}{E_S} \tag{4.3}$$

where:

W_S is the mass of sediment in GI tract (kg)

E_G is the dry weight concentration of tracer "e" in gut sample (Bq kg^{-1})

E_S is the dry weight concentration of tracer "e" in sediment sample (Bq kg^{-1})

W_G is the dry weight of gut contents (kg)

The proportion of sediment in the GI tract is calculated by dividing W_S by W_G.

The method assumes that the tracer is found in low concentrations in the food of the fish since the bioavailability of uranium, a sparingly soluble metal, is low. For example, the human gastrointestinal absorption factors (f_1) for ^{238}U and its decay isotopes are low, ranging from 0.0005 for ^{234}Th, ^{230}Pa, and ^{230}Th, to 0.02 for ^{238}U and ^{234}U, and 0.2 for ^{226}Ra (ICRP, 1996). Measured biota/sediment concentration ratios for ^{238}U decay series isotopes are low, typically much less than 1; however, uptake of uranium is much lower than radium in fish (Swanson, 1985). Moreover, a large fraction of isotopes measured in invertebrates is likely from sediment in the gut or adsorbed to the external surfaces of the invertebrates analyzed (Peterson et al., 2002). As such, the sediment ingestion estimates provided by this method are considered approximate and represent an upper bound estimate of sediment ingestion.

However, any bioconcentration of ^{226}Ra tracer in benthic invertebrate food items would result in an over-estimation of sediment ingestion in fish. A similar problem was identified in early soil ingestion studies of human populations, and was addressed by subtracting the estimated mass of tracer in the food from the mass of tracer measured in the gut contents (Calabrese et al., 1989), as shown in Eq. (4.4) (adjusted mass balance tracer method).

$$W_S = \frac{E_G \times W_G}{E_S} - \frac{E_I \times F_I}{E_S} \quad (4.4)$$

where:

W_S is the mass of sediment in GI tract (kg)

E_G is the dry weight concentration of tracer "e" in gut sample (Bq kg^{-1})

W_G is the dry weight of gut contents (kg)

E_S is the dry weight concentration of tracer "e" in sediment sample (Bq kg^{-1})

E_I is the dry weight concentration of tracer "e" in invertebrate food (Bq kg^{-1})

F_I is the dry weight of invertebrate food item (kg)

E_I was calculated by multiplying the measured activity of ^{226}Ra in sediment and a sediment-to-biota bioaccumulation factor (BSAF) of 0.016 for barium (Yankovitch, 2009). It is assumed that these 2 alkaline earth elements will have equivalent BSAF values because they have similar freshwater-to-biota bioaccumulation factors, 0.014 and 0.010 for Ba and Ra, respectively (Yankovitch, 2009). F_I was determined by dividing the dietary consumption rate of invertebrates by suckers (g hr^{-1}), by the gastrointestinal clearance time for suckers of 60 hr (Fänge and Grove, 1979). The dietary consumption rate is related to the weight of the fish and water temperature (Gobas, 1993; Arnot and Gobas, 2004), expressed as:

$$G_D = 0.022\ d^{-1} \times W_B^{0.85} \times \exp\left(0.06\ C^{-1} \times T\right) \quad (4.5)$$

where:

G_D is the dietary consumption rate (kg d^{-1})

W_B is the weight of fish (kg)

T is the mean water temperature (C)

G_D was converted from wet weight to dry weight by assuming a dry-to-wet-weight ratio of 0.25. W_B was determined from the weight of each fish sampled and T was determined as the average water temperature of 20 °C measured in the St. Lawrence River at Montreal in June and August between 1987 and 2001 (Hudon, 2010).

4.2.4 Validation of sediment ingestion estimating method

The method to estimate soil ingestion in wildlife by measuring AIR in scat (Beyer et al., 1994) was adapted to estimate sediment ingestion, and provide a first order validation of the aforementioned mass balance tracer methods for calculating sediment ingestion. In the adapted method, the AIR concentration of the contents of the sucker GI tracts was assumed to be representative of AIR in fish excrement (the AIR method).

The percentage of sediment in the gut contents of each sucker was calculated using Eq. 4.6.

$$X = {(b - y + ay)}\Big/{(ay - c + b)} \tag{4.6}$$

where:

X is the % sediment in gut (dimensionless)

y is the % dry mass AIR in GI tract contents (dimensionless)

a is the digestibility of food (dimensionless)

b is the concentration of AIR in food (mg kg^{-1})

c is the concentration of AIR in sediment (mg kg^{-1})

Given the non-destructive nature of analyzing ^{238}U decay series isotopes by gamma spectrometry, it was possible to measure the dry mass AIR content in the fish gut and in sediments by analyzing the same freeze-dried GI tract samples used for the mass balance tracer method. The samples were removed from their 8 mL tubes, oven dried at 100°C for 12

hours and their dry weights recorded. The samples were then ashed at 450 ºC for 8 hours, cooled and re-weighed. For each gram of sample, 5mL of 6N HCl was added and heated to 100 ºC on a hot plate until the sample was evaporated to dryness (approximately 1 h). The dried samples were re-extracted with hot 5% HCl (5 mL per gram of sample) and slowly filtered through ashless filter paper (Whatman 42) at low pressure. The filters were then transferred to a pre-weighed crucible, heated to 600 ºC for 2 hours, cooled and re-weighed.

The digestibility of the sucker food items used in the calculations was assumed to be 50% based on the estimated digestibility of invertebrates assumed for sediment ingestion estimates for Goldeneyes and other benthic invertebrate feeding waterfowl (Beyer et al., 2008). Concentration of AIR in food was determined by analyzing commercially available freeze-dried chironomids using the procedure described above.

Since the mass balance tracer method estimates and the AIR method estimates were derived from the analysis of the same samples, the paired t-test was used to compare the results statistically. The paired sample t-test can be considered as a one-sample t-test of the differences between the two methods and the null hypothesis is tested by determining if the differences in estimates derived from the two methods are normally distributed. Moreover, the probability of rejecting the null hypothesis (i.e., the power) for a given sample size with the paired t-test can be determined using Eq. (4.7) (Zar, 1999).

$$t_{\beta(1),v} = \frac{\delta}{S_d^2/_n} - t_{\alpha,v} \tag{4.7}$$

where:

S_d^2 is the variance of the distribution of differences between the two methods to calculate sediment in the gut (kg kg^{-1})

n is the number of samples (dimensionless)

$t_{\alpha,v}$ is the t statistic for Type 1 error assumed (dimensionless)

$t_{\beta(1),\nu}$ is the t statistic for Type 2 error for the distribution of differences between the 2 methods to calculate sediment in the gut (dimensionless)

Statistical analyses of the data (i.e., means, standard deviations, paired t-test and power analysis) were calculated using JMP® software.

4.3 Results

We noted during sample preparation that the gut contents from some GI tracts contained a large proportion of grit, presumably sediment.

The $LLD_{95\%}$ for ^{214}Pb by gamma spectrometer was determined to be 2.5 x 10^{-3} Bq per sample, or approximately 0.5 Bq kg^{-1} for a 5 g sample. All 17 samples analyzed had activity levels measured over the $LLD_{95\%}$. The 1 result near the $LLD_{95\%}$ (0.003 Bq per sample) was obtained from the analysis of a relatively small sample of 0.6 g. Assuming secular equilibrium of ^{214}Pb with ^{226}Ra, the accuracy of the gamma spectrometry was acceptable with the mean ^{214}Pb activity of 20.1 Bq kg^{-1} (standard deviation 1.7 Bq kg^{-1}; n=8) compared to the 20 Bq kg^{-1} (95% confidence interval of 18-22 Bq kg^{-1}) of ^{226}Ra in the IAEA reference standard soil.

The gamma analysis results for the sediment samples and 17 Shorthead Redhorse Sucker GI tract samples are provided in Table 4.1 and Table 4.2, respectively. The mean ^{214}Pb activity in sediment was observed to be 24.2 Bq kg^{-1} (standard deviation 7.7 Bq kg^{-1}), and the mean ^{214}Pb activity in the GI tract contents was observed to be 11.0 Bq kg^{-1} (standard deviation 3.8 Bq kg^{-1}). The mean mass of sediment in each sample GI tract contents, when calculated using the simple mass balance tracer method (Eq. (4.3)), was observed to be 1.14 g (standard deviation 0.99 g) or approximately 46% (standard deviation 16%) of the dry weight of total GI tract contents, and ranged from approximately 0.3 g to over 3 g. The mean mass of sediment in each sample GI tract contents calculated using the adjusted mass balance tracer method (Eq. (4.4)), was observed to be 0.97 g (standard deviation 0.85 g) or approximately 38% (standard deviation 13%) of the dry weight of total GI tract contents, and ranged from approximately 0.1 g to over 3 g. The sediment ingestion results calculated using the AIR

method (Eq. (4.6)) are provided in Table 4.3. It was observed that the mean proportion of sediment in the GI tracts of the suckers sampled was 0.30 with a standard deviation of 0.16. The means of the estimated proportion of sediment in the fish GI tracts calculated using the 3 methods were compared (Figure 4.1). The pairs of sediment ingestion estimates calculated using each mass balance tracer method (i.e., Eq. (4.3)) and the AIR method were found to be significantly different as determined by the paired Student's t-test ($p=0.05$) and all 3 distributions by ANOVA ($F=4.57$, $p=0.015$; Tukey Kramer HSU, $p=0.05$). However, the pairs of sediment ingestion estimates calculated when using the adjusted mass balance tracer method (i.e., Eq. (4.4)) and the AIR method were not found to be significantly different using the paired Student's t-test ($p=0.05$). The power of the paired t-test to detect a 0.08 difference in fraction of sediment in the gut as measured by the 3 methods (i.e., average difference in means) was calculated to be 0.93.

Table 4.1
Gamma spectrometer analysis of ^{214}Pb in sediments near the City of Montreal wastewater treatment facility outfall to the St. Lawrence River. Samples A and B were obtained upstream of the outfall and samples C and D were obtained downstream of the outfall.

Sample Number	Sample Dry Wt. (g)	^{214}Pb (Bq kg^{-1})
A	5.30	20.1
B	4.60	34.8
C	5.50	24.5
D	5.00	17.3
mean	**5.1**	**24.2**
SD	**0.4**	**7.7**
n	**4**	**4**

Table 4.2

Gamma spectrometer analysis of ^{214}Pb in the GI tract contents of Shorthead Redhorse Suckers sampled near the City of Montreal wastewater treatment facility outfall to the St. Lawrence River. The sampling date, fish weight (wt.), and the mean weight and standard deviation (SD) of the sediment in each GI tract calculated using equations 3 and 4 are provided for each fish sampled. The dry weight of sediment (sed.) calculated as a proportion of GI tract contents are also provided for each sample.

#	Sample date	Fish wt. (g)	Gut Dry Wt. (g)	^{214}Pb (Bq kg^{-1})	Calculated using equation 5.3		Calculated using equation 5.4	
					Wt. sed. (g)	Sed. in gut (g g^{-1})	Wt. sed. (g)	Sed. in gut (g g^{-1})
1	June	1373	0.60	5.5	0.14	0.23	0.12	0.19
2	June	815	5.10	16.4	3.47	0.68	3.14	0.62
3	August	1700	0.90	8.5	0.32	0.35	0.25	0.28
4	June	1520	2.70	10.1	1.13	0.42	0.93	0.34
5	June	880	2.50	7.7	0.80	0.32	0.71	0.29
6	June	2050	1.20	13.9	0.69	0.57	0.52	0.44
7	June	440	1.10	9.1	0.41	0.37	0.39	0.36
8	June	2700	1.30	9.0	0.49	0.37	0.33	0.26
9	June	1750	1.70	17.1	1.20	0.71	0.96	0.56
10	August	1620	5.40	14.2	3.17	0.59	2.57	0.48
11	August	1200	2.30	9.4	0.89	0.39	0.77	0.33
12	August	975	2.60	11.0	1.19	0.46	1.05	0.40
13	August	1373	1.80	8.8	0.66	0.37	0.55	0.31
14	June	620	3.00	10.3	1.28	0.43	1.19	0.40
15	June	1373	1.70	5.5	0.39	0.23	0.32	0.19
16	August	1373	1.30	13.1	0.70	0.54	0.59	0.45
17	June	1580	3.50	17.6	2.55	0.73	2.08	0.59
Mean		**1373**	**2.3**	**11.0**	**1.14**	**0.46**	**0.97**	**0.38**
SD		**546**	**1.4**	**3.8**	**0.99**	**0.16**	**0.85**	**0.13**
n		**17**	**17**	**17**	**17**	**17**	**17**	**17**

Table 4.3
Acid insoluble residue (AIR) analysis and proportion of sediment in GI tract calculations for GI tract contents of Shorthead Redhorse Suckers sampled near the City of Montreal wastewater treatment facility outfall to the St. Lawrence River. The mean sediment weight was also calculated as a proportion of GI tract contents.

#	Sample date	AIR in GI tract (g g^{-1})	Digestibility of food (g g^{-1})	AIR in food (g g^{-1})	AIR in sediment (g g^{-1})	Sediment in gut (g g^{-1})
1	June	0.66	0.5	0.02	0.8	0.11
2	June	0.54	0.5	0.02	0.8	0.29
3	August	0.38	0.5	0.02	0.8	0.28
4	June	0.56	0.5	0.02	0.8	0.29
5	June	0.38	0.5	0.02	0.8	0.30
6	June	0.33	0.5	0.02	0.8	0.19
7	June	0.47	0.5	0.02	0.8	0.26
8	June	0.35	0.5	0.02	0.8	0.11
9	June	0.34	0.5	0.02	0.8	0.20
10	August	0.16	0.5	0.02	0.8	0.68
11	August	0.51	0.5	0.02	0.8	0.40
12	August	0.19	0.5	0.02	0.8	0.52
13	August	0.37	0.5	0.02	0.8	0.24
14	June	0.39	0.5	0.02	0.8	0.25
15	June	0.30	0.5	0.02	0.8	0.09
16	August	0.28	0.5	0.02	0.8	0.45
17	June	0.19	0.5	0.02	0.8	0.48
Mean						**0.30**
SD						**0.16**
n						**17**

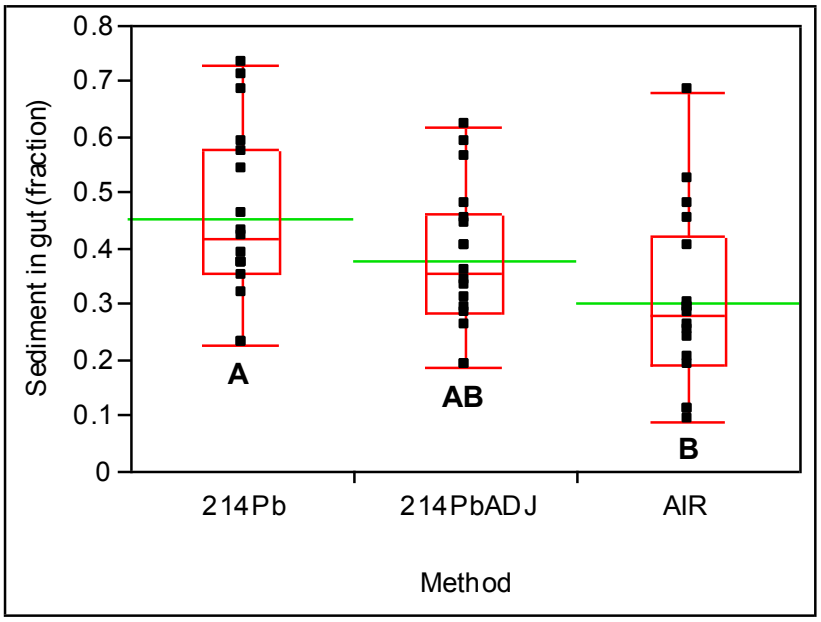


Figure 4.1
A box plot (showing medians, quartiles, outlier whiskers and mean lines) comparing the proportion of sediments in the GI tracts of the 17 Shorthead Redhorse Suckers sampled using 3 estimating methods: the simple mass balance tracer method using ^{214}Pb as the tracer in Eq. (4.3) (labelled 214Pb); the adjusted mass balance tracer method using ^{214}Pb as the tracer in Eq. (4.4) (labelled 214Pb ADJ); and using the AIR method developed by Beyer et al. (1994) (labelled AIR). Significant differences in distribution paired results for each isotopic method against AIR (paired Student's t-test, p = 0.05) and all methods (ANOVA F=4.57, p=0.015; Tukey Kramer HSU, p=0.05) are denoted by differing labels.

4.4 Discussion

The high proportion of sediment observed in the GI tracts of the Shorthead Redhorse Suckers sampled, expressed as a percentage of gut contents (46% and 38% using Eq. (4.3) and (4.4), respectively) is consistent with previous estimates of sediment and detritus ingestion by benthic fish (Table 4.4). The methods used to derive the previous estimates provided in Table 4.4 involved the qualitative segregation and identification of GI tract contents into types of materials (e.g., food or prey items, sediment). In 2 of the studies, ashing and gravimetric analysis of the material types were used to estimate the proportion of sediment in the gut. However, qualitative segregation of sediment-derived organic material from food in the gut could increase the uncertainty and variability of the results. The advantage of the mass

balance tracer method using radionuclide tracers to estimate sediment ingestion is that it calculates the mass of the entire sediment (i.e., organic and inorganic components) empirically and does not rely on a subjective segregation of gut contents. Further, the method is simple, requires little preparation time and is non-destructive, thereby allowing for the gut and sediment samples to be re-used for other purposes, such as chemical analysis of the gut contents. Moreover, the method provides flexibility in the development of bioaccumulation models in that sediment ingestion can be calculated using this method as a mass or as a proportion of gut contents. Thus, the mass transfer rate of contaminant uptake from sediment can be calculated by (a) multiplying the mass of sediment in the gut by the concentration of contaminant in the sediment divided by the residence time in the gut or (b) by multiplying the percentage of sediment in the gut by the concentration of contaminant in the sediment and the feeding rate.

The sediment ingestion estimating method assumes that the fish sampled are feeding in the area where sediments are sampled. Uncertainty in sediment ingestion estimates will increase if the fish have fed from areas with significantly different levels of naturally-occurring radionuclides than from where they were collected. The feeding behaviour of fish will be species-specific and seasonal. Uncertainty in sediment ingestion estimates may also be the result of the variability in sediment composition (i.e., levels of ^{214}Pb) in a watershed. Similarly, the spawning and post-spawning movements of benthic fish such as Catostomids are species-specific and seasonal. For example, no evidence of movement to spawning areas by the Shorthead Redhorse or Silver Redhorse (Moxostoma. anisurum) has been reported, whereas the Black Redhorse (Moxostoma duquesnei) and Golden Redhorse (*Moxostoma erythrurum*) have been reported to move short distances for spawning (Curry, 1984). Male Greater Redhorse, *Moxostoma valenciennesi,* from the Missouri and Ohio River watershed, have been reported to migrate from approximately 5 to 7 km, for males and females, respectively, during spawning (Bunt and Cook, 2001). Post-spawning movement of White suckers *Catostomus commersonii* in the Saint John River reflect small home ranges in the non-spawning months, averaging 2.6 km or less, compared to distances averaging 9.2 km during spawning (Doherty et al., 2010).

To understand how variability in tracer levels in sediment could contribute to the uncertainty of sediment ingestion estimates, sediment ingestion was calculated using ^{214}Pb levels measured in surface sediment from 12 sampling sites over an approximately 5 km section of the St. Lawrence River near Cornwall Ontario. The ^{214}Pb activity data were obtained from the ^{210}Pb sediment core dating work of the St. Lawrence River as described in Delongchamp et al. (2010). The mean ^{214}Pb activity of the 12 sites was observed to be 18.6 Bq kg^{-1} (standard deviation 7.1 Bq kg^{-1}). Using the variability of these data (i.e., the mean sediment ^{214}Pb activity ± the standard deviation) to calculate sediment ingestion by fish using Eq. (4.3) and assuming a dry sample weight of 2.3 g and a ^{214}Pb activity for gut contents of 11 Bq kg^{-1}, the calculated mass of sediment in the GI tract would vary from approximately 1.1 to 2.2 g. Estimating sediment ingestion uncertainty by this approach will require a good knowledge of both the spatial variability of tracers in sediments, and the geographic ranges of the fish species under investigation.

The validity of the estimates calculated using the adjusted mass balance tracer method (Eq. (4.4)) to estimate sediment in the GI tract of fish is supported by the relatively good comparison with estimates calculated using the AIR method. However, estimates calculated using the simple mass balance tracer method (Eq. (4.3)) were higher than those calculated using the AIR method. This validation is qualified, given that the latter method was validated by correlating AIR measured in the scat of mice fed known amounts of soil in their diets and not with the GI tract contents of fish.

The mean estimate calculated with the ^{214}Pb mass balance tracer method using Eq. (4.3) and Eq. (4.4) was approximately 50% and 25% higher, respectively, than when calculated using the AIR method. Accounting for the accumulation of the ^{214}Pb tracer in the benthic invertebrate food appears to explain some of the difference in the results from the 2 methods.

Differences may also be a result of variability in the digestibility of food items commensurate with changes in dietary intake over the seasons. The gut contents of Shorthead Redhorse Suckers can vary considerably over the course of a year with changes in habitat, behaviour and availability of specific food items (Sule and Skelley, 1985). To examine this, the mass

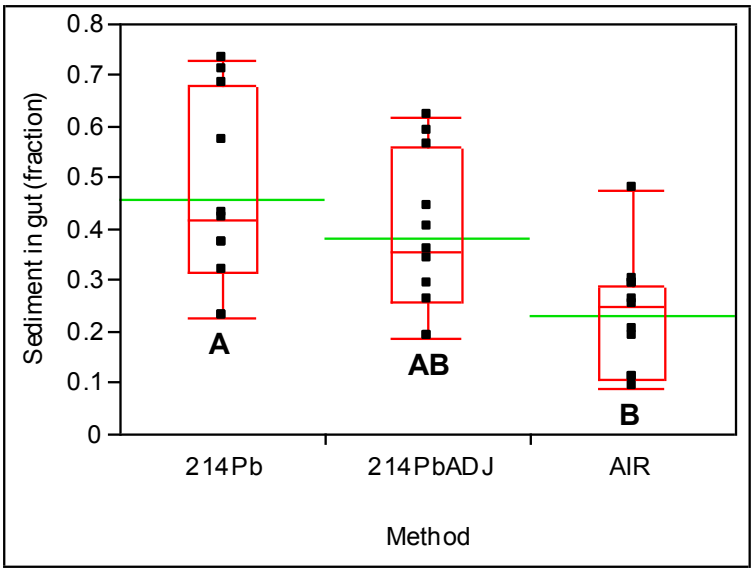
balance tracer methods were compared to the AIR method for the June and August sampling sessions in Figures 4.2a and 4.2b, respectively, and the differences in the sediment values between methods were plotted for fish sampled in June and fish sampled in August (Figures 4.3a and 4.3b). If the null hypothesis is true (i.e., there is no difference between the sediment mass balance tracer method results and the AIR method results), then the distribution of differences should be normally distributed around a mean of zero. The sediment ingestion results using the AIR method in June were observed to be substantially lower than for August; with the mean of sediment fraction in the gut values of 0.23 and 0.43, respectively. In comparison, the result of the mass balance tracer method using Eq. (4.3) was 0.46 in June and 0.45 in August; and the result using Eq. (4.4) was 0.37 in June and 0.38 in August. Interestingly, the simple mass balance tracer method-produced results for August that were closer to the AIR method than those calculated with the adjusted mass balance method. The change in sediment ingestion estimated using the AIR method suggests that the overall difference between methods may be attributable to variability in the AIR method from changes in diet and digestibility of food items rather than accounting for tracer bioconcentration in invertebrate food items. However, it is important to note that the sample size of fish sampled in August was small (n=6), and the calculated power of the test to detect a difference in means of 5% sediment in the gut was low (i.e., 0.22).

Higher estimates provided by the mass balance tracer method may also result from analyzing the entire contents of the GI tract because a portion of the non-sediment material (i.e., food) analyzed will have been absorbed in the lower portions of the gut and would therefore not be representative of the amounts ingested. Conversely, estimates calculated using the AIR method may be lower because the contents in the upper portion are not fully digested and the AIR method assumes a level of digestion that would have occurred with the discharge of excrement from the fish. The mass balance tracer method would thus be improved if only the contents of the upper portions of the GI tract were used to calculate sediment ingestion.

Table 4.4: Comparison of measured sediment content in fish gut in this study with values reported in the literature

Study	Species	Methods used to calculate sediment in gut	% sediment or detritus in gut
This study	*Moxostoma macrolepidotum*	Mass balance tracer method using Eq. (4.4)	19-59
This study	*Moxostoma macrolepidotum*	Mass balance tracer method using Eq. (4.3)	23-73
This study	*Moxostoma macrolepidotum*	AIR method	11-68
Sule and Skelley (1985)	*Moxostoma macrolepidotum*	Segregation of gut contents followed by gravimetric analysis of invertebrate food, macrophytes and detritus	17-68
Michelson, (1994)	*Rutilus rutilus*	Gut contents segregated, ashed and analyzed gravimetrically	4-40
Michelson, (1994)	*Abramis brama*	Gut contents segregated, ashed and analyzed gravimetrically	17-100
Tolonen et al., (2000)	*Rutilus rutilus*	Invertebrate food segregated, ashed and analyzed gravimetrically; relative proportions of macrophytes and detritus were estimated visually	53-72
Tolonen et al., (2000)	*Abramis brama*	Invertebrate food segregated and analyzed gravimetrically and relative proportions of macrophytes and detritus estimated visually	73

a



b

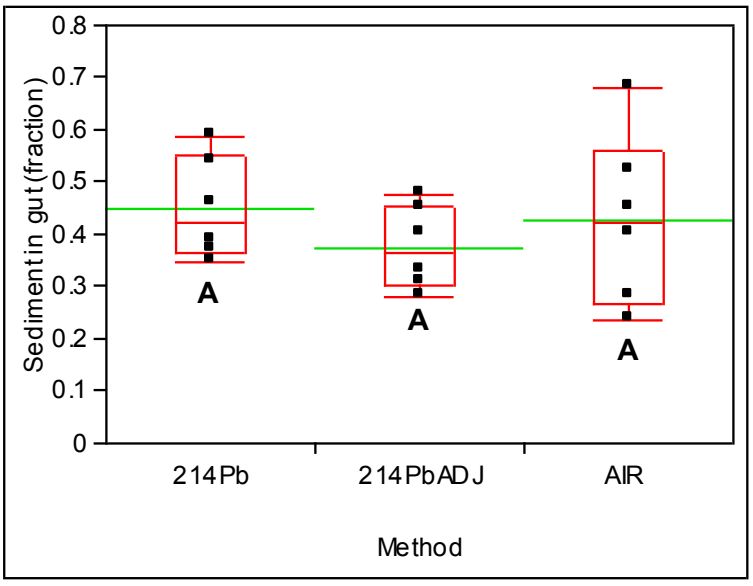
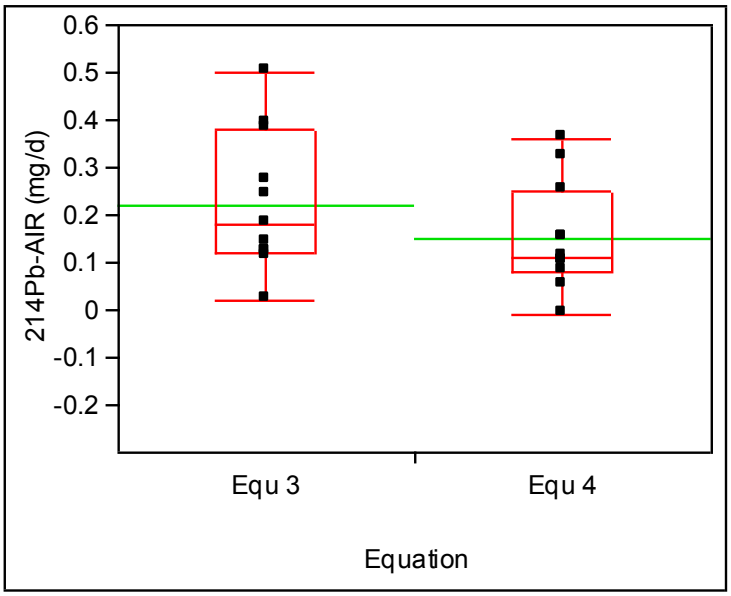


Figure 4.2
A box plot (showing medians, quartiles, outlier whiskers and mean lines) comparing the proportion of sediments in the GI tracts of the 17 Shorthead Redhorse Suckers. Significant differences in distribution means are denoted by differing labels for samples in (a) June (ANOVA F=6.25, p=0.005; Tukey Kramer HSU, p=0.05) and (b) August (ANOVA F=0.64, p=0,54).

a



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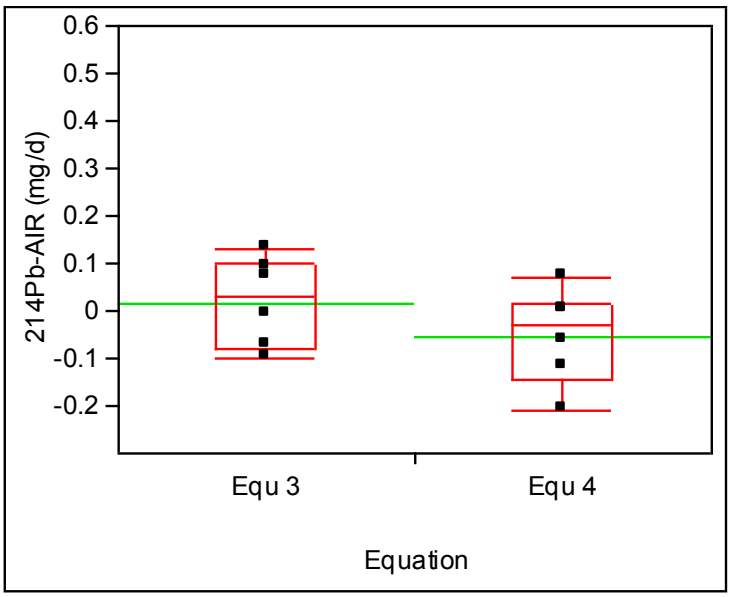

Figure 4.3: A box plot (showing medians, quartiles, outlier whiskers and mean lines) comparing the difference in sediment ingestion values calculated by the AIR method and the 2 mass balance tracer methods using Eqs. (3) and (4), sampled in (a) June and (b) August.

4.5 Conclusions

The proposed use of naturally-occurring radionuclides as mass balance tracers is a simple means to provide empirical estimates of sediment ingestion in fish. As such, it can be used as a tool to support the development of bioaccumulation models for contaminants in aquatic food chains. However, additional work is required to more fully validate the method via experiments that compare measurements of sediment content in fish against known consumption rates of sediment and food. Future studies should assess the contribution of tracers from invertebrate foods by obtaining a sample of benthic invertebrates and qualitatively determining if these items were being fed upon through visual observation of the gut contents prior to analysis. This will help determine which mass balance tracer method to use to calculate sediment ingestion. Furthermore, future studies using this method should limit the analysis of gut contents to the upper portions of the GI tract before any appreciable absorption of food has occurred.

Nevertheless, the study confirms that sediment ingestion by Shorthead Redhorse Suckers can be high (in gram quantities), representing an upper bounding average of approximately 46% of the total mass of GI tract contents. The findings in this study support the assertion that direct ingestion of sediment by benthic fish may be an important pathway for contaminant transfer in aquatic food webs.

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Chapter 5

Ethno-cultural survey of traditional food consumption and activities practiced by a First Nation community following a traditional lifestyle

5.1 Introduction

5.1.1 Background

The predominant exposure pathway to most heavy metals and non-volatile contaminants in human health risk assessment (HHRA) of contaminated sites is via the direct ingestion of soil. Accordingly, the soil ingestion rate values selected in HHRA will be a major contributor to soil quality guidelines developed for assessing the health impacts of proposed industrial sites and/or for remediating existing sites contaminated from industrial activities. Soil ingestion may occur through the inadvertent ingestion of soil or dust particles that adhere to food, objects and the hands, or the deliberate ingestion of soil (i.e., soil pica and geophagy), which is considered to be relatively uncommon (EPA, 1997, 2009). Soil ingestion can also result from the inhalation of soil particles, typically 3-10 μm particles, that become trapped in the mucous linings of the nasopharyngeal tract, bronchi, and bronchioles, and then cleared by mucociliary action and swallowed (Plumlee and Ziegler, 2005).

Recommended rates of inadvertent soil ingestion are provided by regulators to facilitate the development of exposure assessments in HHRA of contaminated sites. These rates are in the order of 20-50 mg d^{-1} for adults and 80-150 mg d^{-1} for toddlers aged 6 months to 4 years old (Table 5.1). The primary studies (i.e., studies that have generated primary soil ingestion data) that were used by the United States Environmental Protection Agency (EPA) to develop recommended values for inadvertent soil ingestion are largely based on a few quantitative assessments of relatively large numbers of children, augmented by smaller studies of adults, living in suburban and urban locations under controlled situations. As such, they are not necessarily representative of populations living in rural or wilderness areas with occupations

or lifestyles that increase the likelihood of greater soil ingestion (Doyle et al., 2010). Receptors living in environmental conditions, such as those found in the rural or wilderness regions characteristic of many regions of Canada, or that are participating in activities that may be more vulnerable to soil ingestion, are typically assigned soil ingestion rates from the high confidence intervals of soil ingestion rate distributions derived from a limited number of studies of children and adults. For example, EPA recommends a default soil ingestion rate of 330 mg d^{-1} for a construction worker, who is vulnerable to increased exposures resulting from soil-disturbing activities such as site excavation or vehicle traffic on unpaved roads, based on the upper 95% quantile soil ingestion estimate for adults reported by Stanek et al. (1997) (EPA, 2002). Similarly, Harper et al. (2002, 2005) recommend a soil ingestion rate of 400 mg d^{-1} for risk assessments of Aboriginal peoples following subsistence lifestyles in the Plateaus of the North-western United States. This exposure rate represents the upper bounding ingestion estimate for children recommended by the EPA, and is based on the assumption that traditional Aboriginal activities will have similar soil contact levels to those of construction and utility workers. In the absence of quantitative soil ingestion rate values representative of Aboriginal peoples living a traditional wilderness lifestyle, these values are reasonable.

The purpose of this study was to assess and document the traditional food consumption and harvesting activities of a Canadian Aboriginal community, and to determine if they are equivalent to those underpinning the exposure scenario for subsistence lifestyles reported in Harper et al. (2002, 2005), and accordingly, may experience elevated soil ingestion rates. The study was conducted concurrent with a mass balance soil ingestion study of subjects from the Nemiah Valley, British Columbia belonging to the Xeni Gwet'in First Nation community who were engaged in activities typical of a "traditional" or "subsistence" lifestyle common of rural or wilderness areas. The results of the mass balance soil ingestion study are reported in Chapter 6. The information will be useful in the development of soil exposure assessment to support HHRA Aboriginal communities in Canada.

This study was divided into 2 parts. First, an ethno-cultural survey was conducted whose purpose was to confirm that the traditional foods and traditional activities of the Xeni

Gwet'in First Nations community were representative of the subsistence lifestyle of Aboriginal peoples of the Plateaus of the North-western United States (Harper et al., 2002, 2005), where elevated soil exposure rates have been proposed for use in HHRA. The ethno-cultural survey was also conducted to document the environmental conditions and the traditional lifestyle of the community to support a larger quantitative mass balance soil ingestion study of subjects selected from the Xeni Gwet'in community. Second, the potential for ingesting soil from consuming traditionally-prepared food was assessed through the analysis of traditional food items, selected based on the results of the ethno-cultural survey and the availability of food items. Samples of fresh (i.e., food items not preserved traditionally) food items were obtained where available. Soils in the vicinity of food preparation and preservation were also sampled. Samples of traditionally-preserved food, fresh food and soil samples were analyzed to determine levels of inorganic soil tracers.

Table 5.1
Table summarizing recommended soil ingestion rates (mg d^{-1}) for use in HHRAs (adapted from Wilson et al., 2006)

Regulatory agency	Infant (< 6mo.)	Toddler (>6 mo. - 4 yr.)	Child/Teen (>4 yr. - 19 yr.)	Adult (>19 yr.)
United States EPA[14]		100	50	50
Health Canada	20	80	20	20
United kingdom DEFRA[15]	100	100	100	60
Netherlands RIVM[16]		150		50
World Health Organization				20

[14] United States Environmental Protection Agency
[15] United Kingdom Department for Environment, Food and Rural Affairs
[16] Netherlands National Institute of Public Health and the Environment

5.1.2 Study area

The study area is located in the Chilko River watershed in the Cariboo Forest Region of British Columbia Region and within the traditional lands of the Xeni Gwet'in First Nation (Figure 5.1). The traditional lands of the Xeni Gwet'in First Nation generally represents the land enclosed by Chilko Lake (Tsilhqox Biny) and the Chilko River (Tsilhqox) to the west, and the Taseko River (Dasiqox) to the east, with a southern boundary running through the Nemiah Valley (Xeni) (Supreme Court of British Columbia. 2007). The area encompasses plateau, glaciated mountains and transition zones of the Chilcotin and Pacific Ranges.

The study area has a moderate continental climate with cold winters, warm summers and relatively low levels of precipitation that includes the following biogeoclimatic ecosystems. The valleys and mountain slopes fall into the Sub-Boreal Pine-Spruce zone, transitioning to a Montane Spruce zone at higher elevations. It is characterized by cold, dry winters and cool, dry summers. The forest cover is dominated by upland coniferous forests comprised of mostly lodgepole pine (*Pinus contorta*) and, to a lesser extent, white spruce (*Picea glauca*) and trembling aspen (*Populus tremuloides*). The forests in this region have been significantly affected by the Mountain Pine Beetle (*Dendroctonus ponderosa*). The surrounding mountains fall into either the Engelmann Spruce - Subalpine Fir zone or the Alpine Tundra zone. These areas are characterized by cool, short growing seasons and long, cold winters in the lower altitudes, and harsh alpine conditions with low growing season temperatures and a very short frost-free period. The forest vegetation is comprised of mostly subalpine fir (*Abies lasiocarpa*), Engelmann spruce (*Picea engelmannii*), white spruce (*Picea glauca*), mountain hemlock (*Tsuga mertensiana*), and whitebark pine (*Pinus albicaulis*), many of which are stunted at the higher elevations (Meidinger and Pojar, 1991).

These ecosystems provide a diversity of habitats to support a wide range of large and small mammals and fowl that can be used as food sources. These include Moose (*Alces alces*), Mule Deer (*Odocoileus hemionus*), Black Bear (*Ursus americanus*), Grizzly Bear (*Ursus arctos*), Caribou (*Rangifer tarandus*), Bighorn Sheep (*Ovis canadensis)*, Mountain Goat (*Oreamnos americanus*), Lynx (*Lynx canadensis*), Cougar (*Felis concolor*), Porcupine

(*Erethizon dorsatum*), Woodchuck or Groundhog (*Marmota monax*), Beaver (*Castor canadensis*), Muskrat (*Ondatra zibethicus*), Northern Flying Squirrel (*Glaucomys sabrinu*), Snowshoe Hare (*Lepus americanus*), Ruffed Grouse (*Bonasa umbellus*), Blue Grouse (*Dendragapus obscures*) and Spruce Grouse (*Dendragapus canadensis*) (Meidinger and Pojar, 1991; BCMOE, 1998). The area also provides habitat for migrating waterfowl including Canada Goose (*Branta canadensis*), Mallard (*Anas platyrhynchos*), and Redhead (*Aythya americana*) (BCMOE, 1998). Moreover, the glacier fed Chilko Lake and Chilko River watershed provides habitat for a large number of fish species, including Bull Trout (*Salvelinus confluentus*), Chinook Salmon (*Oncorhynchus tshawytscha*), Coho Salmon (*Oncorhynchus kisutch*), Dolly Varden (*Salvelinus malma*), Mountain Whitefish (*Prosopium williamsoni*), Rainbow Trout (*Oncorhynchus mykiss*), Sockeye Salmon (*Oncorhynchus nerka*), Steelhead (*Oncorhynchus mykiss*), and Sucker (*Catostomus sp*.) (Holmes, 2001). The study area supports a wide range of shrubs, flowers, berries and non-timber forest resources that are used as traditional food or medicines. Commonly harvested food plants found in the area include Blueberries/Huckleberries (*Vaccinium spp.*), Saskatoon Berry (*Amelanchier alnifolia*), Soopolallie or Soapberry (*Sheperdia canadensis*), Raspberry (*Rubus idaeus*), Strawberry (Fragaria virginiana), Gooseberry (*Ribes lacustre*), Choke Cherry (Prunus virginiana), High Bush Cranberry (*Viburnum edule*), Cow Parsnip (*Heracleum lanatum*), Lodgepole Pine (*Pinus contorta*) Labrador Tea (*Ledum groenlandicum*) Wild Potatoes or Spring Beauty (*Clatonia lanceolata*) and Avalanche Lily or Bear Tooth, (*Erythronium grandiflorum*) (Powell, 2005).

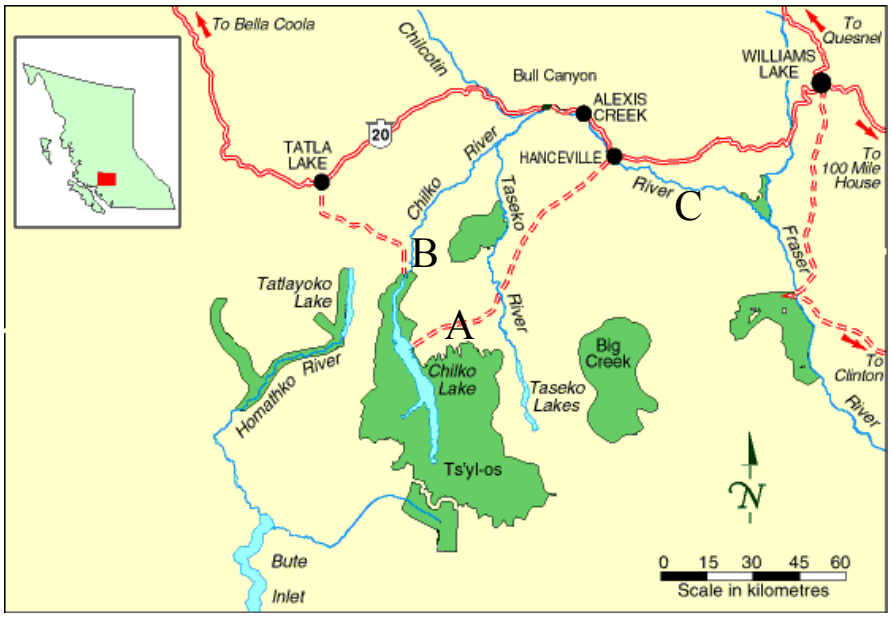

Figure 5.1
Map of the study area with an inset showing the location of the study area within British Columbia. Shaded areas denote BC Provincial Parks and protected areas.

5.1.3 Subject community

The study was conducted in cooperation with the Xeni Gwet'in First Nation community residing in the traditional lands in the Nemiah Valley approximately 230 km west of Williams Lake. Formerly known as the Nemiah Band, the Xeni Gwet'in are 1 of 6 Tsilhqot'in First Nation communities residing in the Chilcotin Plateau and Chilcotin Mountain Range in British Columbia. There were no engineered roads into the community before 1973 and supplies could only be obtained after a 3-day horse and wagon trip to Lees Corners (Hanceville) or a 1-week ride to Williams Lake. To sustain themselves before the road was constructed, the Xeni Gwet'in ran cattle and trapped through the winter, and gardened, hunted and fished in the spring and summer months. Interaction with Europeans was limited to an annual trip to drive cattle for sale and to buy seeds and dry goods in Williams Lake (Xeni Gwet'in, 2011).

An engineered road was constructed by the Canadian Army Corps of Engineers in 1973 from Konni Lake to highway 20 at Hanceville. However, the road into the Nemiah Valley is not considered up to the standard of a British Columbia Ministry of Forests roadway (Littlemore, 2000). Furthermore, there is only an undeveloped bush road from the community located between the East shore of Chilko Lake and Konni Lake to Henry's Crossing and access to Tatla Lake to the North. As such, the community remains relatively physically isolated from the surrounding communities.

The Nemiah Valley is not connected to the provincial power grid. Recently, however, the community offices, school, health centre and some households have acquired diesel generator, solar panel and battery bank centres to provide electric power. This has enabled a more widespread use of refrigerators and freezers for the longer term storage of fresh foods. There is also telephone and internet access in the Nemiah Valley that has improved communications with other communities and the outside world at large.

The Aboriginal Affairs and Northern Development Canada profile of the Xeni Gwet'in First Nations provides a summary of demographic statistics for the community (INAC, 2011). As of 2011, there were 204 registered members of the Xeni Gwet'in First Nation (106 males and 98 females) living in their traditional lands, sometimes referred to as the Brittany Triangle (Tachelach'ed), and 206 members living outside of their traditional lands. Of the resident population, over 75% have an understanding of their Aboriginal language (Tsilhqot'in) and over 70% speak it at home. Unemployment in the area is over 30% and most of the jobs in the Nemiah Valley (approximately 40%) are affiliated with the management of the First Nations Government, or Federal and Provincial government social sciences and services.

Although the community is small, the people of the Nemiah Valley have demonstrated a strong sense of their history and determination to protect their land and their traditional way of life. This determination to protect their traditional lifestyle was articulated in the August 23, 1989 Declaration to protect the Nemiah Aboriginal Wilderness Preserve (Xeni Gwet'in, 2011), that included the following statement:

"This is the spiritual and economic homeland of our people. We will continue in perpetuity: a) to have and exercise our traditional rights of hunting, fishing, trapping, gathering, and natural resources; b) to carry on our traditional ranching way of life; c) to practice our traditional native medicine, religion, sacred, and spiritual ways."

The Xeni Gwet'in's right to maintaining their traditional lifestyle and the preservation of their lands was supported by the Supreme Court of British Columbia (Supreme Court of British Columbia, 2007). Although the Court fell short of granting a declaration of Aboriginal title to their lands, it offered the opinion that Tsilhqot'in Aboriginal title exists inside the Claim Area (i.e., traditional lands in the Brittany Triangle) and British Columbia has no jurisdiction on Aboriginal title lands (Campo, 2008). Moreover, a recent Canadian Environmental Assessment Panel review of the proposed Prosperity Mine planned in the Xeni Gwet'in traditional lands concluded (CEAA, 2010):

"that the Project would result in significant adverse environmental effects on fish and fish habitat, on navigation, on the current use of lands and resources for traditional purposes by First Nations and on cultural heritage, and on certain potential or established Aboriginal rights or title."

5.1.4 Study scope and approvals

It is important to note that this study is not intended to establish the proportion and demographics of the community that practice traditional activities and consume traditional foods, but rather intentionally selected members of the population that are likely pre-disposed to soil ingestion by practicing a traditional lifestyle. Thus, the data in this study are intended to be used in risk assessments of the potentially most exposed members of the population to soil borne contamination via ingestion, rather than for the population at large.

After approximately 1 year of discussion and negotiation, a Memorandum of Understanding (MoU) was signed on July 6, 2010 with the Xeni Gwet'in First Nation Government that secured the participation of the subject community in the study. The MoU framework,

including a summary of the proposed research and plain language summary, is provided in Appendix B. Separate applications were also made to the Health Canada and University of Ottawa Research Ethics Review Boards and approval to proceed with the research study was obtained on August 11, 2010 (approval # REB 2010-0030) and July 19, 2010 (approval #H 06-10-12), respectively.

5.2 Methods

5.2.1 Ethno-cultural survey

The Elders and community members were surveyed at a traditional gathering of the Xeni Gwet'in held at a camp site at Location C (Figure 5.1) between August 14 to 21, 2010 and at Location B (Figure 5.1) between August 29 and September 4, 2010. All subjects were briefed on the objectives, the scope of their participation and their role in the study, and signed a consent form in accordance with research ethics protocols. A copy of the consent form is provided in Appendix B. A translator was made available for those interviewees who wanted to conduct the interview in their native Tsilhqot'in language. Fourteen community members and Elders (approximately 7% of the resident population of the community) were interviewed to determine the types of traditional and other locally-sourced foods consumed, the preparation and preservation methods for the traditional foods and the scope, and the location and frequency of traditional activities practiced by community members. Ten of the 14 interviewees were selected by the community as those individuals likely to consume traditional foods and participate in traditional activities. The remaining 4 interviewees were selected from the subjects participating in the soil ingestion study described in Chapter 6. The scope, location and frequency of traditional activities followed by community members were collected through a series of scripted questions in a survey form and then transferred to an electronic database that contained relevant information for each interviewee. An alpha-numeric code replaced interviewee names in the database to guarantee confidentiality of subjects participating in the study. As specified in the memorandum of understanding with the Xeni Gwet'in First Nation Government, the survey did not provide a comprehensive and

quantitative assessment of traditional foods and medicines consumed by the community in respect of their traditional knowledge property rights.

5.2.2 Analysis of traditional foods

Samples of traditional food items typically consumed by the community were obtained from community members and analyzed for elemental tracers (Al, Ba, Ce, La, Mn, Th, Si, Ti, U, V, Y and Zr). Fresh food items (i.e., same food source but not traditionally preserved) were also collected, when available, and analyzed for elemental tracers. The proportion of soil adhering to the food was calculated by dividing the difference (if any) in the tracer concentration of traditionally-preserved and/or prepared food by the tracer concentration in soils located where the food was preserved.

Analysis of the tracer elements was performed by a commercial laboratory accredited by the Canadian Association for Laboratory Accreditation Inc. to ISO/IEC 17025:2005. For the analysis of Al, Ba, Ce, La, Mn, Th, Ti, U, V, Y and Zr, samples were digested using EPA Method 3052. Digested samples were then analysed by inductively-coupled plasma mass spectrometry ICP/MS for the metal tracers. Total Si was determined by sodium peroxide fusion followed by inductively-coupled plasma optical emission spectrometry (ICP/OES) analysis.

5.3 Results

5.3.1 Ethno-cultural survey of traditional diet and activities

The ethno-cultural survey included a total of 14 interviewees, or approximately 7% of the Xeni Gwet'in community population currently living in the Nemiah Valley. Ten of the 14 interviewees were selected by the community as likely to consume traditional foods and/or participate in traditional activities. The remaining 4 interviewees were the subjects participating in the soil ingestion mass balance study. The age distribution of the interviewees was balanced, with 4 subjects less than 30 years old (28.5%), 6 subjects between 31 and 60 years old (43.0%), and 4 older than 61 years old (28.5%). Six

interviewees were female and 8 interviewees were male. A summary of the responses to the interview questions asked during the ethno-cultural survey is provided in Table 5.2.

It was observed that traditional foods are consumed throughout the year and in all seasons. Locally sourced traditional foods represented a major portion of the diet with 12 of 14 interviewees reporting that 50% or more of their diet was traditional food. Moreover, all interviewees reported eating traditional foods all of their life, whereas consumption of store bought foods varied, often including only the time since the opening of the road into the Nemiah Valley in 1973. Six of 14 interviewees reported having a garden or obtaining some of their diet from local gardens. It was also noted that the short growing season in the Nemiah Valley made the growing of vegetables difficult; however, this problem was mitigated somewhat by a program to build greenhouses in the community. It was also noted by several interviewees that consumption of traditionally sourced or grown foods was an economic necessity and/or deemed to be culturally important.

Large game and fish were the most frequently consumed traditional food items. Twelve of 14 interviewees consumed large game more than 2 times per week and 11 of 14 interviewees consumed fish more than 2 times per week. Large game animals typically consumed were moose and/or mule deer. To a lesser extent, Bighorn Sheep, Black Bear, and Mountain Goat were occasionally consumed by older community members (i.e., over 30 years old). Cougar and Lynx were also reported as food items. Caribou is also hunted in areas north of the Nemiah Valley (e.g., near Tatla Lake). The most common method for preserving large game for later consumption was drying (13 of 14 interviewees), followed by freezing (5 interviewees) and canning (4 interviewees). All parts of the animal were reported to be eaten, including the heart, liver, nose, tongue and marrow of large bones, which is considered a delicacy; however, consumption of the organ meats and offal tended to be by older community members only. Meats were eaten fresh and prepared by frying, boiling roasting over fires, or eaten in their preserved forms, as in the case of dried or canned meat. Chinook and Sockeye Salmon were the most commonly consumed fish, regularly eaten by all interviewees except 1 who would become ill after eating fish. Large quantities of these fish are caught during their spawning migration up the Chilko watershed in August and

September and stored for winter. Other fish species, such as Kokanee (non-migrating Sockeye salmon), Dolly Varden, Bull Trout, Rainbow Trout, Mountain Whitefish, Steelhead Trout, Longnose Sucker and White Sucker are also eaten. Preparation methods reported for fish included frying, roasting over open fires, baking or boiling. Suckers are sometimes impaled on a stick, then roasted over a fire and eaten. Big game and fish were typically eaten fresh in season (e.g., in autumn during the Sockeye and Chinook salmon spawning runs) or dried and stored for later consumption. Game meat is typically cut into thin strips, salted and hung on racks to dry (Figures 5.2a and 5.2b). The smoke from a small green willow fire lit under the drying racks is maintained to keep flies off the meat. Drying was the predominant method for preserving fish, as reported by 12 of 13 interviewees who ate fish. Fish are gutted and the eggs (if present) and heads removed and retained. The fillet portions of the fish are then splayed/butterflied into one continuous thin layer, salted and dried on racks (Figures 5.3a and 5.3b). Salmon are hung for 3-5 days to reach the proper level of dryness, which is determined by pressing the flesh for firmness (similar feel as when pressing a well done steak). Fish eggs and heads are also dried. Smoke from a small fire is also used to keep flies off of the drying fish. Fish were also frozen, canned or smoked. Some interviewees now freeze food items; however, this option is not available for many community members as electricity to power freezers is limited to those households with solar/diesel generator power supplies. Fish were also preserved by smoking or canning for later consumption.

A wide range of small game and waterfowl also represent an important contribution to the diet of the community members interviewed. Groundhogs and wild chicken (i.e., Blue Grouse) were the most common small game food items reported. Beaver, muskrat and rabbit are also commonly consumed. It was also noted by some of the interviewees that consuming small game was in decline commensurate with the decline in back country travel by horseback, where these animals were hunted for food during the journey. Waterfowl, such as ducks (Mallards, Redheads) and Canada Geese are eaten when available; however, several interviewees noted that they are less popular as food items than in the past because of fears that they may have fed in polluted waters during their migration. Porcupine has also been eaten in the past, but is no longer found in the area. One interviewee reported eating

Ptarmigan. Small game and waterfowl are usually eaten fresh, fried, roasted or boiled and only occasionally dried.

The traditional plants consumed by the community members interviewed were predominated by the wide variety of berries available, medicinal plants and herbs, and the roots of wild plants. Questions relating to specific medicinal plants gathered and consumed were not included in the survey to protect the Xeni Gwet'in traditional knowledge; however, the frequency of gathering these items was discussed. Wild berries were eaten by all interviewees and at least a couple of times per week by 50% of the community members surveyed. Wild berries that are regularly eaten include Soopolallie (used to make Indian Ice Cream), Huckleberry, Blueberry, Raspberry, Saskatoon Berry, Gooseberry, Choke Cherry, Strawberry, which are eaten fresh when in season, or canned or made into jams for non-seasonal use. Berries have also been traditionally dried on grass mats in the sun, and then stored. Wild Rhubarb is another plant eaten, raw, or stewed and canned. Consumption of leafy plants was not reported by the interviewees, except for Labrador Tea, which is dried then steeped into tea and drunk. Roots and tubers are also an important source of traditional food. Wild Potatoes and Bear Tooth are common food items consumed by members of the Xeni Gwet'in community (Powell, 2005). Thirteen community members interviewed included wild potatoes in their diet and 6 interviewees consume Bear Tooth. Several community members reported that the Xeni Gwet'in have traditionally made an annual trip up Potato Mountain between Lake Tatlayoko and Chilko Lake to harvest the wild potato, which is considered a delicacy to their people. However, several interviewees reported that the annual treks up Potato Mountain have diminished since the opening of the road in 1973 and the arrival of the automobile in the Nemiah Valley. The roots are typically removed from the ground, washed, and then fried or baked in the ground under a fire (i.e., pit baking). Wild Onion and Bear Tooth are also common food items for the community as reported by 8 and 6 interviewees, respectively. Wild Onion can be eaten raw or, as normally done with Bear Tooth, pan-fried or boiled. The runners of "Silver Root", presumably Cinquefoil (*Potentilla anserine*), are appreciated for their sweetness and are eaten after boiling. Only 3 of 14

interviewees reported eating wild mushrooms (either Morels (*Morchella spp.*) or Pine mushrooms (*Tricholoma magnivelare*)), although they are commonly found in the area.

Traditional activities of members of the Xeni Gwet'in First Nation and/or greater Tsilhqot'in community together make an important contribution to the cultural and spiritual well-being of the people of the Nemiah Valley. Thirteen of 14 interviewees attended 4 or more community cultural gatherings each year and all interviewees attended at least 1 of the local rodeos per year. The gatherings often commemorate important events in the past or are used to reinforce cultural practices and traditions for the younger generation. These activities are conducted, for the most part, outdoors in the summer in dry and dusty conditions and are usually 2-3 days in duration, but may last up to and up to 8 days. Rodeos, in particular, include activities commonly that generate large amounts of dust. Gathering medicinal plants and harvesting food plants was also a common activity for 12 of 14 community members interviewed. It was noted by most interviewees that trips to collect medicinal plants were conducted approximately 2 times per year over 1 or 2 days. It was also noted that the frequency of trips for seasonal food items have diminished lately because the crop of berries has been poor. Hunting and fishing are important traditional activities practiced by community members with 13 of 14 interviewees reporting some level of participation in these activities; however, a few of the elders interviewed indicated that they have not hunted or fished recently because of their advancing age. The frequency and duration of hunting and fishing trips varied considerably among interviewees, ranging from a couple of times per year for 1 or 2 days to daily. Several interviewees commented that the amount of time spent hunting and fishing is becoming limited because non-traditional work/employment obligations precluded their ability to go out on the land to hunt and fish.

Table 5.2

Summary of traditional foods and activities practiced by members of the Xeni Gwet'in community interviewed in August, 2011

Traditional Food or Activity \ Interviewee	**I-1**	**I-2**	**I-3**	**I-4**	**I-5**	**I-6**	**I-7**	**I-8**	**I-9**	**I-10**	**I-11**	**I-12**	**I-13**	**I-14**
Age (years)	72	54	45	64	60	29	29	85	44	87	47	50	24	20
Sex[17]	F	F	M	F	F	F	M	M	M	F	M	M	M	M
Seasonality- Proportion of year consuming traditional foods (mos./yr.)	12	12	12	12	12	12	>10	12	12	12	12	12	12	12
Proportion of diet from traditional foods (%)	50	50	20-40	>80	50	<25	60-80	60-80	50	30-80	50	50	50	50
Traditional food consumption (% of life)	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Store-bought food consumption (% of life)	25	75	50	50	75	100	100	<10	75	33	100	100	100	100
Do you have a garden	Y	Y	Y[18]	Y	N	N	N	N	N	Y	N	N	Y	N
Frequency of wild food consumption[19]														
Big game animals	D	D	M	D	D	D	D	D	F	O,S	D	D	D	F
Small game animals	O	R	R	R	R	N	O	M,O	O	O,S	F	M,S	O	O
Water and game birds	R	R	R	R	N	N	O	R	O,S	O,S	R,S	M,S	N	R
Fish	F	F	M	F	F	N	F	D	D	M,S	D	D	F	F

[17] M-male, F-female

[18] Obtains some of his vegetables from his mother's garden

[19] Frequency legend: D-daily >6 times/week, F-frequently (~2-4 times/week), M-moderately (~1-4/month), O-occasionally (<12 times/year), R-rarely (1 time/2to5 years), S-seasonally (when seasonally available), N-never

Traditional Food or Activity \ Interviewee	**I-1**	**I-2**	**I-3**	**I-4**	**I-5**	**I-6**	**I-7**	**I-8**	**I-9**	**I-10**	**I-11**	**I-12**	**I-13**	**I-14**
Vegetation, berries, plants	O,S	O,S	O,S	F, S	M,S	F	F	D,C,N	O,S	F	F	D	O	O
Roots/tubers	O,S	O,S	O,S	R	R	O,S	O,S	N	O,S	O,S	O,S	F,S	N	O
Mushrooms	N	N	N	N	N	N	N	N	O,S	O,S	O,S	NA	N	N
Other	N	N	N	N	N	N	N	N	N	N	N	R	N	N
Wild food preservation methods[20]														
Big game animals	D,N	D,N	D,F N	D,C,F	D,F,C	F,N	D,N	D,N	D,C,N	D,C,N	N,D,F	D,N	D,N	N,D
Small game animals	N	N	D,N	N	N	N/A	N	D,N	N,D	N	N	N,D,S	N	N
Water and game birds	N	N	N	N	N/A	N/A	N	N	N	N	N	N	N/A	N
Fish	D,N	D,N	D,N	D,N,C	F,D	N/A	D,N	N	D,N	D,N,C,F	D,N,S	D,N,C	D,N	D,N
Vegetation, berries, plants	N	N	N, D	N,D	N	C,D	N,C	D,C,N	N,C	N,C	N,C	N,C,D	N,C,D	N,C
Roots/tubers	N	N	N	N	N	N	N	N/A	N,D	N	N	N	N	N
Mushrooms	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N	N,D	N	N/A	N/A	N/A
Frequency of participating in traditional activities (times/year)														
Traditional gatherings	4	4	5-6	5	5	5	4	4	5-6	10	4	5	2	3-4
Plant/medicine gathering	0	3-4	1-2	1-2	1	7	1	0	<1	1-2	2	4	2	2
Fishing/hunting	0	0	1-2	72	>25	>25	0	2-3	>50	2-3	>100	>100	>50	>50
Rodeo	3	10	3-4	2	1-2	2	5	2-3	1-2	5-6	2	2-3	1	3

[20] Preservation techniques legend: D-dried, S-smoked, F-frozen, C-canned, N-not preserved (i.e., eaten fresh), N/A-not applicable

Fig. 5.2a
Moose meat being cut into thin strips and prepared for drying

Fig. 5.2b
Moose meat being dried on racks in open air

Fig. 5.3a
Sockeye Salmon being butterflied and prepared for drying

Fig. 5.3b
Sockeye Salmon being dried on racks in open air

5.3.2 Analysis of traditional foods

Traditional foods were collected during the soil ingestion study. Unfortunately many traditionally-prepared foods were not available because they were out of season. Consequently, only 4 samples of traditionally-preserved foods (i.e., 1 dried moose sample and 3 dried salmon samples), 1 sample of raw (i.e., unpreserved) fish, and 1 sample of wild potato were collected. The sample of raw fish was obtained from the traditional commercial fishery on the Chilko River being developed by the Xeni Gwet'in community and was temporarily stored in a vat of brine and ice before being collected. The small sample (79 g wet weight, 0.7 g ashed weight) of wild potato obtained had been thoroughly washed and

ready for eating. A sample of store- bought peeled and unpeeled potatoes were also collected as a surrogate to provide a comparison with the wild potato.

The concentrations of elemental tracers in analyzed food items are provided in Table 5.3. Analysis of Si could not be completed for these samples due to problems with the dissolution step and/or the limited mass of sample available for analysis. Elemental tracer concentrations in wild potato were over an order of magnitude higher than the peeled potato sample (i.e., Al, Ce, La, Mn, Th, Ti and Y). Element concentrations in the dried moose were typically low and on the same scale as dried fish. Interestingly, the element concentrations in the fresh fish sample were either of the same scale (Ce, La, Ti, V, U and Y) or higher (Al, Ba, Th, Zr) than the dried fish samples. Mn was the only tracer that was higher in the raw fish sample compared to the dried fish sample. It is possible that the higher tracer concentrations in the raw fish are from the brine solution required to temporarily store the fish by the commercial fishery.

Table 5.3
Concentrations of elemental tracers in traditional food samples collected from the Nemiah Valley (ND means not detected)

Food Samples		Al	Ba	Ce	La	Mn	Th	Ti	V	U	Y	Zr
		μg g^{-1}										
TF-1	Wild potatoes	2,600	610	1.3	0.71	1,500	0.10	160	5	0.04	0.83	1.8
HF-16	Peeled potatoes	37	9.6	0.1	0.06	120	0.01	9	1	0.01	0.04	0.6
HF-19	Unpeeled potatoes	280	43	0.29	0.14	210	0.05	21	3	0.32	0.09	0.4
TF-2	Dried salmon	180	6.6	0.1	0.04	18	0.01	21	<1	0.02	0.05	0.3
TF-3	Dried moose	220	5.0	0.1	0.04	14	0.01	16	<1	0.02	0.05	0.3
TF-4	Dried salmon	130	8.2	0.23	0.11	23	0.02	29	1	0.03	0.11	0.6
TF-5	Dried salmon	480	9.2	0.16	0.07	10	0.03	23	<1	0.02	0.05	0.8
TF-6	Raw salmon	1,100	22.0	0.3	0.16	7	0.10	28	<1	0.05	0.03	2.9

5.4 Discussion

5.4.1 Ethno-cultural survey

The climatic conditions typical of the study area, and the traditional food diet, residence conditions and the types of cultural practices followed by the Xeni Gwet'in are similar to those of the Spokane Tribe living in plateaus of the North-western United States, as reported in the Harper et al. (2002, 2005) exposure assessment of peoples following traditional or subsistence lifestyles. The Plateaus and the arid montane areas of the northern Columbia Basin (elevation 718m) have an annual precipitation of 478 mm y^{-1}, an average maximum temperature in August of 28.3 °C, and an average minimum temperature in August of 12.6 °C (DRI, 2011). The study area (elevation 870m) has an annual precipitation of 434 mm y^{-1}, an average maximum temperature in August of 22.5 °C and an average minimum temperature in August of 5.1 °C (Environment Canada, 2011). There is a predominance of fish and big game in the diet of both groups, supplemented by berries and roots. Outdoor cultural gatherings, hunting and food gathering trips and sporting events, with their attendant potential for enhanced soil exposure, are important to both communities, and are attended on average approximately once per month in both communities. Thus, if the assumptions underpinning an exposure scenario for subsistence lifestyles reported in Harper et al. (2002, 2005) hold true, then the Xeni Gwet'in community is potentially exposed to of 400 mg d^{-1} of soil.

The Xeni Gwet'in community have clearly articulated their resolve in maintaining a traditional lifestyle within their traditional territories. As such, the population of the Nemiah Valley will likely continue to participate in activities that increase their day-to-day contact with soil. The ethno-cultural survey results show that the consumption of traditional foods is a vital component of the Xeni Gwet'in diet. Moreover, the limited availability of alternative food preservation methods, the economic pressures on most community members and the logistical challenges of obtaining store-bought foods, suggests that soil exposure from the local sourcing of food and medicines, and the use of traditional preservation techniques will continue well into the future.

5.4.2 Traditional foods

Although the sample size was small, the concentration of tracer elements in foods (i.e., fish and big game) traditionally preserved by drying were observed to be low and equivalent to or less than concentrations observed in food items not dried. Accordingly it is unlikely that these food items have become contaminated with appreciable amounts of soil and dust from the drying process. However, it is important to note that drying will take place in many locations under a variety of environmental conditions and this limited study may not be representative of the potential for ingesting soil through the drying of foods.

The sample of wild potato was observed to have high levels of all tracers, when compared to store-bought potatoes. Assuming a mean level of Al in soils in the Nemiah Valley of 70 mg g^{-1} and a mass of 1.82 mg of Al in the food sample (2.6 mg g^{-1} x 0.7 g of ashed sample), the 79 g of wild potato contains approximately 26 mg of soil. This represents soil exposure of approximately 33 mg of soil per 100 g serving of wild potato. Given that roots were identified as a common food item eaten when in season, this could be an important pathway for soil exposure. Moreover, the ethno-cultural survey indicated that roots were often cooked by pit-baking that could further increase soil contamination of traditionally-prepared food items. Other foods may be contaminated with soil during their preservation or preparation, such as berries dried on mats or meats roasted over open fires, and quantitative data estimating soil exposures from these practices is not widely available.

5.5 Conclusions

The traditional lands of the Xeni Gwet'in in the Nemiah Valley B.C. have ecosystem characteristics and habitats that support the traditional lifestyle of the inhabitants. The Xeni Gwet'in First Nation government has clearly articulated the importance of a traditional lifestyle to the well-being of the community. A preliminary assessment of traditional foods has shown that some items, specifically roots, may have substantial amounts of soil adhering to the food items. However, these preliminary assessments did not show that soil adhesion results from the traditional drying of fish or meat outdoors. The environmental conditions and the types and frequency of traditional activities practiced by the members of the Xeni Gwet'in community interviewed are similar to the subsistence lifestyles of indigenous

communities living in rural or wilderness areas of the North-western United States, where soil exposure scenarios that are in the order of hundreds of mg d^{-1} have been proposed. These soil exposure rates are much higher than the guidelines recommended by regulatory agencies for the HHRA of contaminated sites. Given the paucity of quantitative soil ingestion data for people following a traditional lifestyle typical of many rural or wilderness areas, soil ingestion studies in remote communities engaged in traditional activities and consuming traditional foods.

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Chapter 6

Soil ingestion in people following a traditional lifestyle

6.1 Introduction

6.1.1 Background

The predominant exposure pathway for most heavy metals and non-volatile contaminants in human health risk assessment (HHRA) of contaminated sites is via the direct ingestion of soil. Accordingly, the soil ingestion rate values selected in HHRA are a major contributor to soil quality guidelines developed for assessing the health impacts of proposed industrial sites and/or for remediating existing sites contaminated from historical industrial activities. Soil ingestion may occur through the inadvertent ingestion of soil or dust particles that adhere to food, objects and hands, or the deliberate ingestion of soil (i.e., soil pica and geophagy), which is considered to be relatively uncommon (EPA, 1997). Soil ingestion can also result from the inhalation of soil particles, typically between 3-10 μm particle size, that become trapped in the mucous linings of the nasopharyngeal tract, bronchi, and bronchioles, and, then cleared by mucociliary action and swallowed (Plumlee and Ziegler, 2005). Several studies have been conducted to estimate inadvertent soil ingestion in humans. The following methodologies have been employed (EPA, 1997; 2009):

a) The "tracer element" method, where elements commonly found in soil are measured in excreta (e.g., feces and urine) and soil, and these values are used to calculate the mass of soil ingested. These studies are termed "mass balance tracer" studies when the soil ingestion calculation accounts for tracers in food and medicine.

b) The "biokinetic model comparison" method, where a biokinetic model of an element (e.g., lead) is used to calculate the mass of soil ingested given the measured concentration of the element in the blood of a subject.

c) The "survey response" method, where questions regarding the frequency of mouthing behavior and ingestion of non-food items are used together with tracer (or other) study results to estimate soil and dust ingestion rates.

d) Qualitative/semi quantitative assessments, where the types and frequency of specific behaviours are observed in subjects and quantitative data from other studies (e.g., soil/dust adherence to hands) are used to infer a soil ingestion rate.

Recommended rates of inadvertent soil ingestion are provided by regulators to facilitate the development of exposure assessments in HHRA of contaminated sites. Primary studies (i.e., studies that have generated primary soil ingestion data) that were used by the United States Environmental Protection Agency (EPA) to develop recommended values for inadvertent soil ingestion are listed in Table 6.1. Inadvertent soil ingestion does not include the intentional ingestion of soil, as in the case of soil pica or geophagy. The recommended inadvertent soil ingestion rates for use in HHRAs made by the EPA and other regulatory agencies are largely derived from the aforementioned studies and are summarized in Table 6.2. It is noted that these recommendations are based on a few quantitative assessments of relatively large numbers of children, augmented by smaller studies of adults, living in suburban and urban locations under controlled situations. As such, they are not necessarily representative of populations living in rural or wilderness areas with occupations or lifestyles that increase the likelihood of greater soil ingestion (Doyle et al., 2010). Moreover, there have been no quantitative soil ingestion studies of a Canadian population (Wilson et al., 2006). Soil ingestion rates for receptors living in environmental conditions typical of rural or wilderness regions characteristic of many regions of Canada, or that are participating in activities that may be more vulnerable to soil ingestion, are normally assigned a soil ingestion rate at a high confidence interval (e.g., upper 90% quantile) of the distribution of soil ingestion rate estimates generated from the limited number of studies of children and adults completed to date. Default soil ingestion rates for HHRA are not derived from mass balance soil ingestion studies of adults participating in activities that may be vulnerable to high soil ingestion. For example, the United States EPA recommends a default soil ingestion rate of 330 mg d^{-1} for a construction worker who is vulnerable to increased exposures resulting from soil-disturbing activities such as site excavation or vehicle traffic on unpaved roads (EPA, 2002). The 330 mg d^{-1} value represents the 95th percentile of the adult soil ingestion rates reported by Stanek

et al. (1997). This soil ingestion rate of 330 mg d^{-1} has also been assumed for United States military personnel during training or deployments (USAPHC, 2010). Moreover, Harper et al. (2002, 2005) recommended a soil ingestion rate of 400 mg d^{-1} for Aboriginal peoples following subsistence lifestyles in the Plateaus of the North-western United States. This value is upper bounding ingestion estimate recommended by the EPA for children, with the additional assumption that traditional subsistence activities will have similar soil contact levels to that of construction and utility workers or deployed military personnel. Thus, populations participating in activities vulnerable to enhanced soil ingestion may be under protected if HHRAs of contaminated sites use the soil ingestion rates provided in Table 6.2. The soil ingestion estimates derived from the aforementioned mass balance tracer studies are highly variable and prone to uncertainties, such as unquantified ingestion of tracers (source error), unexpected gastrointestinal uptake of tracers, and/or sampling and analytical error. The precision of soil ingestion estimates in subsequent studies may be improved with the use of additional mass balance tracers. For example, ^{238}U and ^{232}Th decay series isotopes have been suggested by Doyle et al. (2010) as potential tracers because they are not common ingredients in foods or consumer products, they are ubiquitous in soils and are relatively easy to measure precisely by non-destructive radio-analytical methods (e.g., gamma spectrometry). Radioisotope tracers have not strictly been considered as mass balance soil ingestion tracers in soil ingestion studies completed to date. However, one study of the physical mobilization and assimilation of Th and U series isotopes in families residing on farms near thorium mining operations in Brazil estimated the contribution of soil based on the ^{228}Th to ^{232}Th ratios in fecal samples (Linsalata et al., 1989).

This pilot study is directed at obtaining the first quantitative soil ingestion rates, using mass balance tracer methods, of a Canadian population following a traditional lifestyle typical of rural or wilderness communities. The purpose is to determine if soil exposure of rural or wilderness communities may experience exposure to soil via the ingestion pathway that is greater than the ingestion values developed for the population at large, which have been used to underpin HHRAs and regulatory decisions pertaining to contaminated sites. The study is also directed at comparing the utility of ^{238}U and ^{232}Th decay series isotopes with more traditional elemental tracers, and to identify potential improvements to mass balance tracer estimating methods.

Table 6.1

Table summarizing the key soil ingestion studies underpinning regulatory guidance for soil exposure pathway in human health risk assessments. "Key studies" are studies that were used to develop the United States Environmental Protection Agency (EPA) soil ingestion recommendations for HHRA and "relevant studies" are studies that provide useful information for evaluating the reasonableness of the data provided in the key studies (from EPA, 1997; 2009). A study of adults (Stanek et al., 1997) has also been included in the table.

Study	Description	Methodology
Key Studies		
Calabrese et al., 1989	Study of a non-random sample of 64 children between 1 and 3 years old for 8 days over a 2-week period in Amherst Massachusetts.	Mass balance tracer method using Al, Ba, Mn, Si, Ti, V, Y and Zr as tracer elements. The study accounted for tracers in excreta (i.e., feces and urine), as well as in food, beverages and medicines.
van Wijnen et al., 1990	Study of 292 children in daycare centres, 78 children in campgrounds and 15 children in hospital in cities and suburbs of Amsterdam and Utrecht, the Netherlands.	Mass balance tracer method using Al, Ti and acid insoluble residue (AIR). Termed the Limiting Tracer Method (LTM), the soil ingestion rate was calculated using daily values of the tracer yielding the lowest soil ingestion value. The study assumed that the 15 hospitalized children were not exposed to soil and used the tracer loading in excreta to account for dietary intake of tracers in the mass balance calculations
Davis et al., 1990	Study of 104 randomly selected children between 2 and 7 years old over a 7-day period in the 3-city area of northwest Washington State.	Mass balance tracer method using Al, Si and Ti. The study accounted for tracers in excreta (i.e., feces and urine), as well as in food, beverages and medicines.
Calabrese et al., 1997	Study of a random sample of 64 children between 1 and 3 years old for 8 days over a 2-week period.	Mass balance tracer method using Al, Ce, La, Nd, Si, Ti, Y and Zr tracer elements. The study accounted for tracers in excreta (i.e., feces and urine), as well as in food, beverages and medicines.

Study	Description	Methodology
Davis and Mirick, 2006	Study of children and adults from a non-random subset of 19 families (i.e., 1 child and both adults) selected from the Davis et al. (1990) Washington State study over an 11-day period.	Mass balance tracer method using Al, Si and Ti. The study accounted for tracers in excreta (i.e., feces and urine), as well as in food, beverages and medicines. Occupational and recreational behaviours of subjects were recorded and correlated with measured soil ingestion rates.
Relevant Studies		
Binder et al., 1986	Study of 59 children between 1 and 3 years old in East Helena, Montana.	Al, Si and Ti tracers were measured in excreta (i.e., feces and urine that was collected in diapers) and in soil to calculate soil ingestion. The daily fecal output dry weight was assumed to be 15 g. There was no attempt to account for tracers ingested in foods and medicines.
Clausing et al., 1987	A pilot study of 18 Dutch children between 2 and 4 years old in a nursery school over a 5-day period and 8 hospitalized children without contact with soil. This study provided the basis for the larger soil ingestion study conducted by vanWijnen et al. (1990).	Used the LTM method similar to vanWijnen et al. (1990).
Calabrese et al., (1990)	A pilot study of 6 adults in Amherst, Massachusetts for 9 days over a 3-week period to validate the methods used in the larger study of children by Calabrese et al. (1989).	Using methods similar to Calabrese et al. (1989), soil ingestion was calculated for the subjects after they ingested capsules containing 0 mg d^{-1}, 100 mg d^{-1} and 500 mg d^{-1} to determine the percent recovery of tracers using their mass balance methods. Soil ingestion calculated during the first week (i.e., where 0 mg d^{-1} was ingested in capsules) was used to determine soil ingestion in adults.
Stanek et al., (1997)	A pilot study of 10 adults in Amherst, Massachusetts for 4 7-day periods to validate the methods used in the larger study of children by Calabrese et al. (1997).	Using methods similar to Calabrese et al. (1990), soil ingestion was calculated for the subjects after they ingested capsules containing 0 mg d^{-1}, 20 mg d^{-1}, 100 mg d^{-1} and 500 mg d^{-1} to determine the percent recovery of tracers using mass balance tracer methods.

Table 6.2
Summary of the recommended soil ingestion rates (mg d^{-1}) for use in HHRAs recommended by selected regulatory agencies for various age groups (adapted from Wilson et al., 2006)

Regulatory agency	Infant (< 6mo.)	Toddler (>6 mo. - 4 yr.)	Child/Teen (>4 yr. - 19 yr.)	Adult (>19 yr.)
United States Environmental Protection Agency		100	50	50
Health Canada	20	80	20	20
United Kingdom DEFRA[21]	100	100	100	60
Netherlands RIVM[22]		150		50
World Health Organization				20

[21] United Kingdom Department for Environment, Food and Rural Affairs
[22] Netherlands National Institute of Public Health and the Environment

6.1.2 Study area

The study area is located in the Chilko River watershed in the Cariboo Forest Region of British Columbia and within the traditional lands of the Xeni Gwet'in First Nation approximately 230 km west of Williams Lake (Figure 6.1). A detailed description of the study area, the subject community and the traditional lifestyle practiced by community members is provided in Chapter 5. The traditional lands of the Xeni Gwet'in First Nation generally represent the land enclosed by Chilko Lake (Tsilhqox Biny) and the Chilko River (Tsilhqox) to the west, and the Taseko River (Dasiqox) to the east, with a southern boundary running through the Nemiah Valley (Xeni) (Supreme Court of British Columbia. 2007). The area encompasses plateau, glaciated mountains and transition zones of the Chilcotin and Pacific Ranges.

The soil ingestion study was conducted at the following locations:

- Nemiah Valley (Figure 6.1 – Location "A").
- Henry's Crossing (Figure 6.1 – Location "B").
- Farwell Canyon (Figure 6.1 – Location "C").

The surficial geology and geochemical characteristics of the study area is a complex mixture of bedrock, of both marine sedimentary and volcanic origins, overlain within the Nemiah Valley by Pleistocene gravel, glacial tills, silt and clay. The geological characteristics of the study area can be summarized as follows (GSC, 1935; Schiarizza et al 1994; Umhoefer et al., 2002):

- The area north and west of Chilko Lake is comprised of mainly Jurassic and Cretaceous sedimentary rocks.
- The area in the vicinity of Location A is comprised of a mix of Triassic intercalated shale and lithic sandstone, siltstone, shale and pebble conglomerates, and Jurassic andesitic volcanic rock and volcanoclastics.

- The area in the vicinity of Location B is comprised of mainly Upper Jurassic and Lower Cretaceous marine and non-marine sedimentary rocks, Quaternary/Neogene alluvium and volcanic lithic sandstones.
- The area in the vicinity of Location C is comprised of mainly Cretaceous sedimentary and Fraser Plateau volcanic rocks.

The sedimentary rock (i.e., sandstones) in the region is typically quartz poor, ranging from lithanarites to feldspathic litharenites to lithic arkoses. Soils originating from plagioclase andesite and arkose sandstones are predominated by feldspar lithic components and a chlorite cement ($(Mg,Fe,Al)_6$ $(Si,Al)_4O_{10}(OH)_8$). Plagioclase minerals are composed of sodium aluminum silicates ($NaAlSi_3O_8$), such as Albite, or by calcium aluminum silicates ($CaAl_2Si_2O_8$), such as Anorthite (Leet and Judson, 1971).

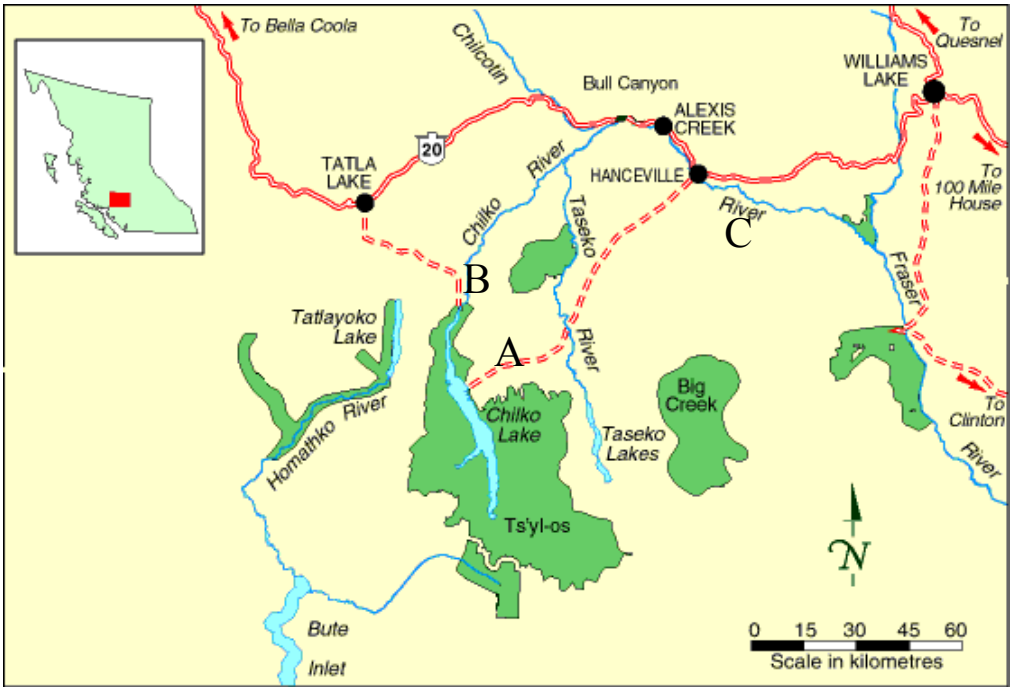

Figure 6.1
Map of the study area with an inset showing the location of the study area within British Columbia. Shaded areas denote BC Provincial Parks and protected areas. Solid lines denote paved road and hatched lines denote dirt or gravel road.

The study area has a moderate continental climate with cold winters, warm summers and relatively low levels of precipitation. As such, the conditions in the study area are conducive to the production of dust clouds resulting from vehicular traffic, winds and/or activities that stir up soils (e.g., horse and cattle movements).

The study was conducted in cooperation with the Xeni Gwet'in First Nation community residing in the traditional lands in the Nemiah Valley. Formerly known as the Nemiah Band, the Xeni Gwet'in is 1 of 6 Tsilhqot'in First Nation communities residing in the Chilcotin Plateau and Chilcotin Mountain Range in British Columbia. An engineered gravel and dirt road was constructed by the Canadian Army Corps of Engineers in 1973 from Konni Lake to highway 20 at Hanceville. However, the road into the Nemiah Valley is not considered up to the standard of a British Columbia Ministry of Forests roadway (Littlemore, 2000). To sustain themselves before the road was constructed, the Xeni Gwet'in ran cattle and trapped wildlife through the winter, and gardened, hunted and fished in the spring and summer months (Xeni Gwet'in, 2011).

The Nemiah Valley has ecosystem characteristics and habitats that support the traditional lifestyle of the inhabitants and the Xeni Gwet'in First Nation government has clearly articulated the importance of a traditional lifestyle to the well-being of their community. The environmental conditions and lifestyle practiced in the community are similar to the subsistence lifestyles of indigenous communities living in rural or wilderness areas of the North-western United States, where soil exposure scenarios that are in the order of hundreds of mg d^{-1} have been proposed (see Chapter 5). These soil exposure rates are much higher than those recommended by regulatory agencies for the HHRA of contaminated sites. Given the paucity of quantitative soil ingestion data for people following a traditional lifestyle typical of many rural or wilderness areas, soil ingestion studies of traditional activities and traditional foods are warranted.

6.1.3 Study scope

It is important to note that this study was not an epidemiological study of soil ingestion, but rather intentionally selected members of the population that would be pre-disposed to soil ingestion via the practice of a traditional lifestyle. Thus, the data in this study are intended to

be used in risk assessments of the members of the population (i.e., the receptors) who likely experience the highest exposures to soil borne contamination via ingestion.

After approximately 1 year of discussion and negotiation, a Memorandum of Understanding (MoU) was signed on July 6, 2010 with the Xeni Gwet'in First Nation Government that secured the participation of the subject community in the study. The MoU framework, including a summary of the proposed research and plain language summary, is provided in Appendix B. Separate applications were also made to the Health Canada and University of Ottawa Research Ethics Review Boards and approval to proceed with the research study was obtained on August 11, 2010 (approval # REB 2010-0030) and July 19, 2010 (approval #H 06-10-12), respectively.

6.2 Methods

6.2.1 Mass balance soil ingestion study design

The specific methods used in the study are summarized below. Detailed descriptions of the sample collection, preparation and analytical methods are provided in Chapter 3 of this thesis.

The study involved 7 adult volunteer subjects (>20 years old), 4 days per week over a 3-week period between August 16 and September 2, 2011. Four subjects were resident community members of the Xeni Gwet'in and 3 were not. All participants in the study were briefed on the objectives, the scope of their participation and their role in the study, and signed a consent form in accordance with research ethics protocols. A copy of the consent form is provided in Appendix B. The subjects were also briefed each week on the protocols for providing fecal samples.

In week 1 of the study, subject F was working clearing debris from 5 locations at salmon spawning creeks in the Nemiah Valley (Location A) during the day, and living in a cabin near the shore of Chilko Lake in the evening. Subject G camped and attended a cultural gathering of the Xeni Gwet'in First Nation at Location C. Week 1 was 5 days in duration, and food consumption was monitored on days 0, 1, 2 and 3 and fecal samples were collected on days 1, 2, 3 and 4. Weeks 2 and 3 of the study were conducted at Location B (Henry's

Crossing), and were only 4 days in duration. The shorter study duration in weeks 2 and 3 was caused by limitations in the availability of study subjects. Each week, food consumption was monitored on days 0, 1, and 2, and fecal samples were collected on days 1, 2, and 3. Four of the 6 study subjects travelled to Location B (Henry's Crossing) from the Nemiah Valley (subjects A, B, C, D, and F), and 2 of the 6 subjects travelled from the Williams Lake area (subjects E and G). The subjects set up camp in the morning after arrival at Location B, then fished and/or hunted in the afternoon. Subjects spent all day outdoors and slept in single person tents at night. On days 2 and 3 of the week, subjects participated in establishing a commercial First Nations fishery on the Chilko River. Daily activities included collecting Sockeye salmon using traditional methods, such as "dip nets", or seine nets along the shore, weighing, bleeding and cleaning each fish, and storing the catch in a mixture of brine and ice. The late afternoon and evening involved scouting of new dip net locations by hiking up the shore of the river or fishing for Sockeye and Chinook salmon with rod and reel, in addition to routine camp activities (e.g., eating and clean-up, collecting and cutting firewood, etc.). No other demands were placed upon the subjects participating in the study, and several participants took the opportunity to fish with rod and reel and/or hunt in the evenings. The activities and location for the subjects participating in the 3 week are summarized in Table 6.3. The activities included in the study (i.e., traditional fishing, attending gatherings, etc.) were selected because, based on initial discussions with community leaders and the information collected in the ethno-cultural survey, they were typical of traditional community activities (see Chapter 5).

Soil ingestion was estimated using a mass balance tracer methodology. The tracers selected for this study were ^{214}Pb (measuring ^{226}Ra), ^{212}Pb (measuring ^{228}Th), Al, Ba, Ce, La, Mn, Si, Th, Ti, U, V, Y and Zr. The gastrointestinal absorption factors for these tracers are provided in Table 6.4. The daily soil ingestion for each subject was calculated from Eq. (6.1).

$$S_a = \frac{F_c \times F_a}{S_c} - \frac{I_c \times I_a}{S_c} \qquad (6.1)$$

where:

S_a is the soil ingested (g)

F_c is the concentration of tracer element in feces ($\mu g\ g^{-1}$)

F_a is the mass of feces (g)

I_c is the food concentration for tracer element ($\mu g\ g^{-1}$)

I_a is the mass of food ingested (g)

S_c is the concentration tracer in soil ($\mu g\ g^{-1}$)

A daily soil ingestion rate was calculated for each subject using the food intake on Day 0, Day 1 and Day 2 (and Day 3 for subjects in week 1). A 24 h transit time was assumed, and the fecal output (i.e., the F_a, and F_c parameter values from the analyses of the daily fecal samples) was obtained for Day 1, Day 2 and Day 3 (and Day 4 for subjects in week 1) of each study week. Samples of urine, sweat or tears were not taken. Food intake (I_a) was calculated as the product of the number of portions of each food type ingested (recorded in daily food ingestion logs) and the pre-weighed portion size. The portion weights were converted to dry weight by dividing the wet weight by a dry weight concentration factor derived in the lab for each food item analyzed. The types and quantity of medications taken by each subject were also recorded. I_c was derived from the analysis of the food item types. S_c was obtained from the mean tracer level in <63μm particle size soil obtained from the location where the subjects were working during that particular study week. The <63μm particle size was used because this fraction best represents the fraction that adheres to hands, and is thus most likely to be ingested (Doyle et al., 2010).

Table 6.3
Summary of the mass balance soil ingestion design for 3-week period, including week number, location, subject identifier code and activities for each week. Week 1 was August 14-18, Week 2 was August 23-26 and Week 3 was August 30 to September 3, 2010.

Week	Location[23]	# of Subject(s)	Activity
1	A	1	Days spent in maintaining salmon spawning areas in Nemiah Valley (e.g., beaver dam removal, stream bed reconstruction). Overnight spent in cabins. Food was prepared and consumed outdoors and/or in the cabin.
1	C	1	Participation in a traditional gathering of community Elders and Xeni Gwet'in community members (traditional food gathering and preservation, traditional games and language training of young). Entire time spent at camp (overnight in tents) or in transit to and from camp to the Nemiah Valley. Food was prepared and consumed outdoors.
2	B	6	Activities to develop a traditional fishery on Chilko River, including walking the shoreline to locate fishing areas, dip netting and seine netting of fish, handling and bleeding and packing of fish in ice for transport. Hunting and rod/reel fishing were common activities in the evenings. Entire time spent at camp (overnight in tents). Food was prepared and consumed outdoors.
3	B	6	Activities to develop a traditional fishery on Chilko River, including walking the shoreline to locate fishing areas, dip netting and seine netting of fish, handling and bleeding and packing of fish in brine and ice for transport, and hiking up Potato Mountain to locate a water diversion. Hunting and rod/reel fishing were common activities in the evenings. Entire time spent at camp (overnight in tents). Food was prepared and consumed outdoors.

[23] Figure 4.1

Table 6.4
Gastrointestinal absorption factors (*f1*) for natural radionuclides and other mass balance tracers[4].

Isotope	*f1*	Element	*f1*
^{238}U series:		*Elemental tracers:*	
^{238}U	0.02	Al	0.01
^{234}U	0.02	Si	0.01
^{230}Th	0.0005	Ti	0.01
^{226}Ra	0.2	Ba	0.2
^{212}Pb	0.2	La	0.0005
^{210}Pb	0.2	Ce	0.0005
^{210}Po	0.5	Mn	0.1
^{232}Th series:		V	0.01
^{232}Th	0.0005	Zr	0.01
^{228}Ac	0.0005		
^{228}Ra	0.2		
^{228}Th	0.0005		
^{214}Pb	0.2		
^{208}Tl	1.0		

6.2.2 Soil sample collection and sample processing

Soil samples were collected at the 3 locations identified in Figure 6.1. Samples were collected by scraping the surface soil from a 10 cm by 10 cm area to a depth of 2 cm, yielding approximately 200 cc of sample. At location B and location C, 5 samples were collected in a cross formation 25 m apart (Figure 6.2). A soil sample was collected at each of the 3 areas in the Nemiah Valley (Location A) where work was performed. Seven soil samples were also collected along the main travel route transecting the study area. The samples were collected along the main road into the Nemiah Valley beginning at the Vedan River Crossing in the most Eastern portion of the study area, through to Konni Lake to the eastern shore of Chilko Lake, then north along the east side of the lake to Henry's Crossing, then crossing the Chilko River to Choelquot Lake located in the most western portion of the study area (Figure 6.3). All soil samples were collected in WhirlPak™ plastic sample bags, labelled and shipped to the laboratory in Ottawa.

In the laboratory, soil samples were oven-dried for approximately 24 h at 90 ºC, lightly de-consolidated in a ceramic mortar with a rubber pestle and sieved into >2 mm, <2 mm>250 µm, 250 µm >63 µm, and <63 µm particle size fractions. An approximately 4 cm^3 sub-sample of the <63 µm particle size fraction for each soil sample was packed into an 8 mL tube. A Teflon™ septum was then inserted into the gamma tube and the tube was sealed with epoxy resin and stored until analysed by gamma spectrometry. A second 1 g subsample of the <63 µm soil fraction was transferred to a 20 mL glass vial and stored until analysis by inductively coupled plasma mass spectrometry (ICP/MS) for metals and inductively coupled plasma optical emission spectrometry (ICP/OES) for Si.

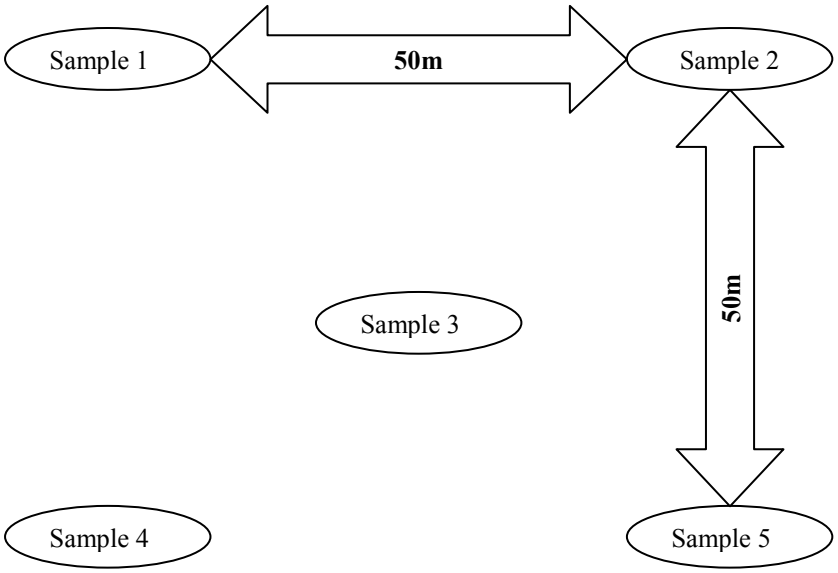

Figure 6.2
Soil sampling collection layout for Locations B and C

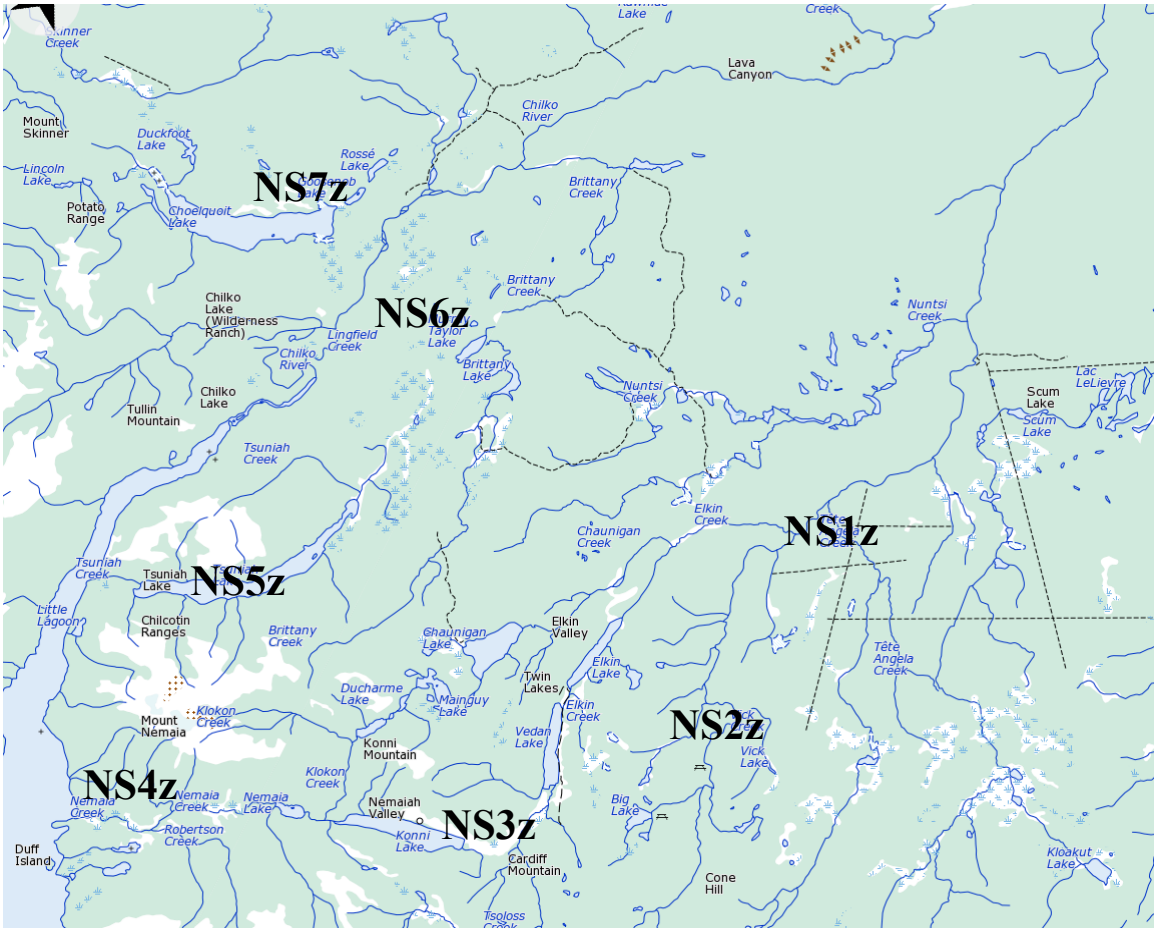

Figure 6.3
Locations where soil samples were collected along the main travel route through the Nemiah Valley

6.2.3 Food and water sample collection and sample processing

In previous mass balance studies, duplicate samples of entire meals were collected from each subject home. Given that this study was conducted in a remote location with only limited secure storage space (i.e., to protect the samples from animals), storage of duplicate meals and snacks for all subjects over the study period was considered impractical. Instead, tracer ingestion was calculated by quantifying the foods consumed for each subject for each day and analyzing matching samples of each food item for tracer concentration. All foods (breakfast, lunch, dinner and snacks) were provided to the subjects beginning on lunch Day 0 and ending with lunch Day 4 of each week (i.e., the time spent in the field camp). The types of meals planned, food items provided and preparation methods were kept the same for each

week. Duplicate samples of food types provided to the subjects were collected when provisions were purchased and, frozen where necessary, then shipped to the laboratory. The water consumed at Location A was obtained from Chilko Lake, and the water consumed at Location B was obtained from the Chilko River at Henry's Crossing. The water consumed at Location C was obtained from Location A, and transported to the field camp near Farwell Canyon. Approximately 2.5 L samples of water were collected from both locations in 1 L polyethylene bottles, shipped to the laboratory then acidified to a pH<2.0 with concentrated HCl. Average weights of the specific food portions (e.g., slices of meat, servings of potato, cups of tea) served were predetermined in the laboratory and/or in the field, and the number of servings of each food item was carefully logged for each subject for each meal, including snacks. Food consumption for each subject was tracked from lunch Day 0 until the end of Day 3 (i.e., including dinner and evening snacks). Each subject was also interviewed to determine the types of foods eaten for breakfast on Day 0 relative to the servings provided by the study. Samples of foods provided to the study subjects were procured and retained for analysis. Food samples were ashed at 500 °C for 9 hours and weighed. Ashed samples were then packed into Marinelli Beakers with a purpose-built plastic disc inserted into the Marinelli Beaker on top of the sample, then sealed with epoxy resin and stored until analysed by gamma spectrometry for ^{214}Pb and ^{212}Pb. A 1 g sub-sample was collected of all food types and water samples and transferred to 20 mL glass vials and stored until analysed by ICP/MS for metals and ICP/OES for Si.

Water samples were pre-concentrated by evaporation. For each sample, approximately 2 L of water was evaporated under vacuum to approximately 20 mL using a rotary evaporator in a 90°C water bath. The concentrated sample was further evaporated to a solid (i.e., solids dissolved in the water sample) through successive additions of sample to an 8 mL gamma tube in an aluminum heating block maintained at 90°C that was gently irrigated with a stream of nitrogen gas to accelerate the evaporation process. After the sample was fully dried, a Teflon™ septum was inserted into the gamma tube, the tube was sealed with epoxy resin and stored until analysed by gamma spectrometry.

6.2.4 Fecal sample preparation

Daily fecal samples were obtained from each subject from Day 2 until the end of Day 3. Portable commodes and pre-labelled and pre-weighed sample containers (Fisher Scientific autoclavable polypropylene biohazard sample bags, catalogue number 01-826-5) were provided to the subjects for the collection of fecal samples. Urine samples were not collected. Samples were sealed by the subject with 6-inch cable ties (zip-ties) and placed on ice in a large cooler lined with a polypropylene bag. Each day, the subjects reported the time(s) the fecal sample(s) was/were provided, and the sample bag number(s). For the 4-day sampling period, the fecal sample bags were frozen and transferred to a clean over-pack (i.e., second bag). At the end of the study, the frozen samples were sealed in large sample coolers in accordance with IATA Dangerous Goods Regulations Packing Instruction 602. Samples were then stored in a freezer until they were shipped by air cargo under refrigeration. Upon receipt, the fecal samples were transferred into dedicated freezers for storage until further processing.

Safe work protocols were developed to mitigate risks associated with the preparation and analysis of fecal samples (Appendix C). All fecal sample handling in the laboratory was conducted under a fume hood, except when samples were being transferred from freezers to the fume hood or a muffle furnace. Laboratory personnel were required to wear protective gloves, eyewear and dust masks as set out in pre-established safe work protocols. Fecal sample bag cable ties were removed the sample bags were weighed, and transferred to evaporation dishes. Samples were dried in the sample bags in an oven (enclosed in the fume hood) for approximately 48 hours at 90 °C then re-weighed. Fecal matter was then removed from the sample bags into pre-weighed crucibles, ashed at 500°C for 9 hours and weighed. The ashed fecal samples were then consolidated, as required, into composite samples representing each study day for each subject and compressed into 8 mL tubes using a specially constructed die that supports the tube walls. The sample was compacted in the tube by use a machine press to apply pressure to a piston. A Teflon™ septum was inserted into each gamma tube, the tube was sealed with epoxy resin, and stored until analysis by gamma spectrometry. After analysis, a 1 g sub-sample was removed from each 8 mL tube and transferred to 20 mL glass vials and stored until analysis by ICP/MS for metals and ICP/OES for Si.

6.2.5 Analytical methods for tracers

6.2.5.1 ICP/MS

Analysis of the tracer elements (Al, Ba, Ce, La, Mn, Si, Th, Ti, U, V, Y and Zr) was performed by a commercial laboratory accredited by the Canadian Association for Laboratory Accreditation Inc. to ISO/IEC 17025:2005. For the analysis of Al, Ba, Ce, La, Mn, Th, Ti, U, V, Y and Zr, samples were digested using EPA Method 3052 (i.e., digested in concentrated nitric acid and hydrofluoric acid using microwave heating). Digested samples were then analysed by inductively coupled plasma mass spectrometry (ICP/MS) for the metal tracers. Total Si was determined by sodium peroxide fusion followed by inductively coupled plasma optical emission spectrometry (ICP/OES) analysis.

6.2.5.2 Gamma spectrometry

All samples to be analysed by gamma spectrometry were stored for at least 21 days to permit the naturally occurring isotopes of the ^{238}U and ^{232}Th decay series (i.e., ^{214}Pb and ^{212}Pb, respectively) to achieve secular equilibrium with their parent radionuclides (i.e., ^{226}Ra and ^{228}Th, respectively). Samples were analyzed using an Ortec™ high purity germanium (HPGe) detector and gamma spectrometer. Soil and fecal samples were analyzed in 8 mL gamma tubes inserted into the well detector, where gamma radiations, emitted at energies specific to the individual isotopes being analyzed, are detected by the HPGe crystal. In this configuration, the geometry is optimized in that most of the gamma emissions will interact with the HPGe crystal that surrounds the sample. Food samples in Marinelli Beakers are fitted over the detector for analysis. In this configuration, the geometry is less favourable and only the gamma radiations emitted inwards (i.e., towards the detector) interact with the HPGe crystal. Consequently, the detector efficiency is reduced when samples contained in Marinelli Beakers are analyzed. However, this loss of detector efficiency was overcome by the ability to employ the Marinelli Beakers to analyse much larger samples relative to the gamma tube (450 cm^3 versus approximately 4 cm^3). All samples were counted for 82800 s (i.e., 23 hours).

The gamma spectra were analyzed using a DOS-based software program developed and provided by Dr. Peter Appleby (University of Liverpool, U.K.). The activity A of a specific radionuclide is calculated using Eq. (6.2) (Appleby, 2001):

$$A = \frac{N}{\in YCT} \quad (6.2)$$

where:

N is the number of counts in the peak (disintegrations)

$\in$ is the detector efficiency (dimensionless)

Y is the yield of photons of an energy E (dimensionless)

CT is the count time (seconds)

^{226}Ra was determined by averaging the ^{214}Pb peaks at 352 keV and 295 keV, and assuming secular equilibrium between the two isotopes (Appleby, pers. comm.). The daughter isotopes of ^{232}Th (^{228}Ac and ^{212}Pb) were determined by their 338 keV and 238 keV gamma peaks, respectively.

6.2.6 Statistical analysis

Statistical analyses of the data were calculated using JMP® or Microsoft Excel™ software. Analysis of variance (ANOVA) was used to compare normal or near normal distributions with similar variance. When distributions had different variances, then Welsh ANOVA was used to determine if differences in the distributions were statistically significant. Differences in variances were determined by the Levene test.

6.3 Results

6.3.1 Study conditions

The conditions during the 3-week study period between August 16 to September 4, 2010 were generally warm during the day, cool at night and dry. The weeks preceding the study were characterized by a series of major forest fires in the area that continued to burn during Week 1, and subsequently subsided in Weeks 2 and 3. However, the active fires were at approximately 100 km or more of mountainous terrain from the actual study sites. The mean daily temperature, mean daily maximum temperature and monthly precipitation measured at the Environment Canada Tatlayoko Lake weather station (approximately 21 km west of Henry's Crossing) for the month of August were 14.6 ºC, 24.5 ºC and 13.4 mm, respectively (Environment Canada, 2011). The weather conditions near the study area over the 3-week

study period are summarized in Table 6.5, showing the key mean weather parameters for the 5 days beginning Sunday through to Thursday of each week when the soil ingestion study was conducted. Winds were moderate and were reported to be less than 30 km h^{-1} at Tatlayoko Lake throughout the study period.

Table 6.5
Weather data for Tatlayoko Lake during the soil ingestion study period (Environment Canada, 2011)

Week\Parameter	Mean maximum temperature (ºC)	Mean temperature (ºC)	Precipitation (mm)
Week 1: August 15 to 21	29.2	16.4	0.0
Week 2: August 22 to 28	21.4	12.7	6.4
Week 3: August 29 to September 4	20.1	11.3	0.0
August mean	24.5	14.6	13.4

6.3.2 Soil samples

The tracer levels measured in the soil sampled at the 3 soil ingestion study locations are summarized in Table 6.6. The variability in the concentrations of the elemental tracers measured at each study location was relatively low, with coefficients of variability (CV) less than 20% for most tracers. However, the variability in the radionuclide tracers was higher than the elemental tracers, with CV values ranging from 3% to 81% and for the radionuclide tracers and ranging from <1% to a high of 43% for the elemental tracers. The 7 samples transecting the study area were observed to have slightly higher tracer concentration CV values than those taken with each study location. Variability in the Si and Ba tracers was consistently low, with CV values less than 10% at all three study locations and over the 7 samples transecting the study area. The CV of the Al tracer was also <10% for locations B, C and the samples transecting the study area. The CV for Al in samples from location A (Nemiah Valley) was high at 43%. However, the number of samples analyzed was low (n=3) and the variability is attributed to 1 sample with an Al concentration of 32,000 mg kg^{-1}, compared to concentrations in the order of 60,000 to 80,000 mg kg^{-1} for the other areas. This result may be due to an analytical error, or that one soil sample was derived from a different

parent bedrock material or diluted with organic material. For example, the Nemiah Valley is predominated by Pleistocene till overlying andesitic rocks. Andesite is an extrusive igneous rock containing mostly plagioclase minerals that can be either rich in sodium aluminum silicates ($NaAlSi_3O_8$), such as Albite or Oligoclase, or dominated by calcium aluminum silicates ($CaAl_2Si_2O_8$), such as Bytownite or Anorthite. Accordingly, soil derived from mostly sodium aluminum silicate parent material will have much less Al than soil derived from mostly calcium aluminum silicates.

The variability of isotopic tracers was relatively low within samples taken at each location, but varied considerably between locations, and across the entire study area. The mean $^{212}Pb/^{214}Pb$ activity ratio for the soil samples from Farwell Canyon (Location C), the Nemiah Valley (Location A) and Henry's Crossing (Location B) was 0.70, 0.51 and 0.52, respectively. Interestingly, these values are lower than the worldwide average for $^{232}Th/^{238}U$ activity ratio of 0.9 (Evans et al, 1997). Moreover, the $^{212}Pb/^{214}Pb$ activity ratio decreased from approximately 0.70, observed in soils collected at Farwell Canyon and Location NS1z in the eastern edge of the study area, to approximately 0.5 in the western edge of the study area (Fig. 6.4). Variability in the activity ratio could be a result of differences in the parent bedrock or geochemical processes that have resulted in disequilibrium in one or both of the $^{232}Th/^{238}U$ decay series.

Changes in ^{212}Pb levels resulting from disequilibrium in the ^{232}Th decay series will be reflected by $^{228}Ac/^{212}Pb$ activity ratios, where values greater than unity are indicative of a loss of ^{228}Ac daughters (i.e., ^{228}Th, ^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Pb) or of ^{228}Ac enrichment. Accordingly, Fig. 6.5 also shows the $^{228}Ac/^{212}Pb$ activity ratio corresponding to the $^{212}Pb/^{212}Pb$ ratios in the aforementioned soil samples analyzed from Farwell Canyon and Nemiah Valley. Directional changes in the $^{212}Pb/^{214}Pb$ ratio were observed to correspond to directional changes in the $^{228}Ac/^{212}Pb$ ratio in 6 of the 8 samples suggesting that some sort of physio-chemical process was either enriching ^{228}Ac or removing the other ^{232}Th daughters from the soils in the Nemiah Valley.

Table 6.6
Tracer levels measured in soil samples from the soil ingestion study area and across the Nemiah Valley (NV is Nemiah Valley or Figure 6.1, location A; HC is Henry's Crossing or Figure 6.1, location B; FW is Farwell Canyon or Figure 6.1, location C; NS are samples taken every 15 km bisecting the Brittany Triangle roughly from east to west as shown in Figure 6.3)

Sample Number	Bq kg^{-1}			μg g^{-1}											
	^{214}Pb	^{228}Ac	^{212}Pb	Al	Ba	Ce	La	Mn	Th	Ti	U	V	Y	Zr	Si
FW-Mean	14.7	11.1	10.2	72,400	550	28.8	13.2	1,022	3.1	5,680	0.8	122	14.2	62.4	229,800
FW-SD	1.8	1.7	0.5	5,030	35.4	2.2	1.1	80	0.2	814	0.1	18	1.6	7.0	6,600
CV	12%	16%	5%	7%	6%	8%	8%	8%	6%	14%	11%	15%	12%	11%	3%
n	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
NV-Mean	15.0	9.3	7.9	63,333	447	22.7	10.3	767	1.9	3,567	0.9	123	12.0	47.7	270,000
NV-SD	2.3	1.6	0.4	27,301	5.8	1.2	0.6	115	0.1	635	0.0	23	0.0	9.8	18,200
CV	15%	17%	7%	43%	1%	5%	6%	15%	6%	18%	2%	19%	<1%	21%	7%
n	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
HC-Mean	15.5	8.2	8.0	66,800	500	23.8	10.8	980	2.1	3,720	1.1	103	13.2	37.2	240,800
HC-SD	0.4	1.2	0.8	2,864	25.5	0.8	0.4	76	0.1	130	0.2	7	0.8	3.1	7,250
CV	3%	15%	10%	4%	5%	4%	4%	8%	4%	4%	22%	7%	6%	8%	3%
n	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
NS-1Z	52.0	34.2	36.2	71,000	390	25.0	12.0	680	2.4	4,700	0.87	110	13.0	49.0	236,000
NS-2Z	17.4	10.0	11.5	82,000	460	28.0	13.0	910	2.6	4,000	1.1	130	15.0	52.0	246,000
NS-3Z	19.8	10.7	11.9	76,000	420	21.0	9.7	700	1.8	3,600	0.92	120	14.0	49.0	247,000
NS-4Z	18.1	9.8	9.9	76,000	450	29.0	14.0	770	2.5	3,200	1.4	110	18.0	33.0	255,000
NS-5Z	11.5	9.0	7.3	70,000	460	23.0	11.0	690	2.0	3,000	0.77	97	12.0	31.0	244,000
NS-6Z	13.9	7.3	6.9	69,000	440	21.0	9.8	870	1.9	2,700	1.1	86	13.0	28.0	245,000
NS-7Z	13.8	6.5	6.8	66,000	390	21.0	9.5	830	1.8	2,900	0.75	81	11.0	23.0	247,000
NS-Mean	20.9	12.5	12.9	72,900	430	24.0	11.3	779	2.1	3,440	1.0	105	13.7	37.9	245,700
NS-SD	14.0	9.7	10.5	5,400	30.6	3.4	1.8	93	0.3	710	0.2	18	2.3	11.8	5,600
CV	67%	77%	81%	7%	7%	14%	16%	12%	16%	21%	23%	17%	17%	31%	2%

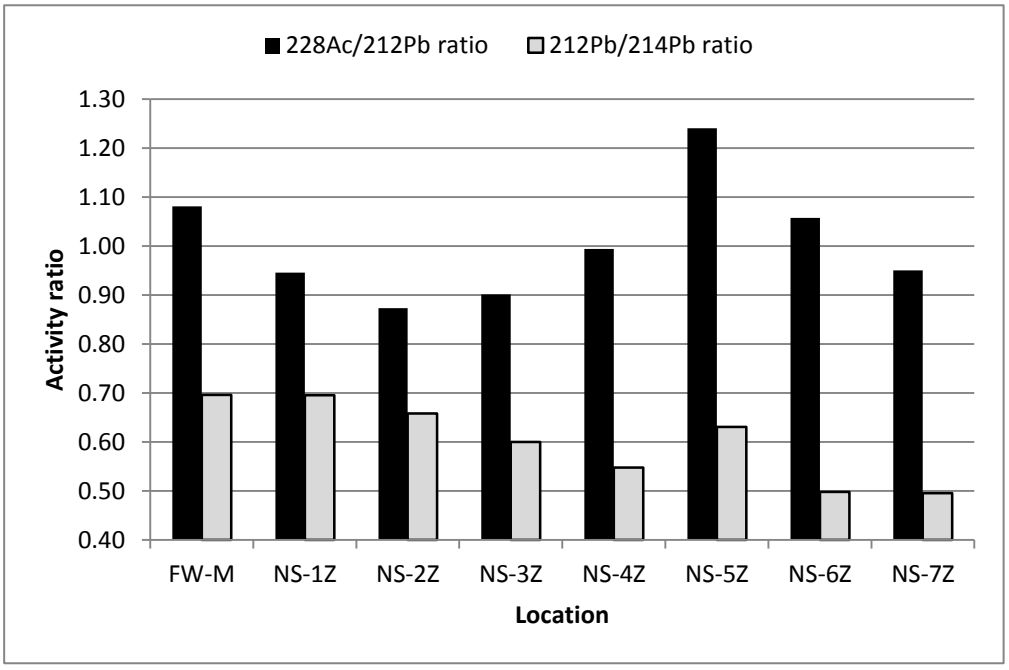

Figure 6.4
$^{212}Pb/^{214}Pb$ and $^{228}Ac/^{212}Pb$ activity ratios for soil samples collected at Farwell Canyon (Location C) and at various locations bisecting the Nemiah Valley (shown in Figure 5.2)

6.3.3 Food samples and daily tracer consumption rates

The analytical results for samples of food items consumed during the soil ingestion study are provided in Table 6.7. The number of portions and mass of food consumed by each subject for each day of the soil ingestion study is provided in Appendix D. It was observed that the total wet weight of the food consumed over the study period by all participants was approximately 55 kg or approximately 14 kg dry weight, assuming a moisture content of 75%. The daily tracer intake by each subject, calculated from the measured tracer concentrations in food types and the recorded mass of food ingested is provided in Appendix E. A summary of daily tracer consumption rates for each tracer across all subjects is provided in Table 6.8.

It has been shown that the uncertainty of soil ingestion estimates using the mass balance tracer method is greatest for tracer elements with higher food/soil (F/S) ratios, defined as the mass of the tracer element ingested from food over a one day period divided by the mass of the tracer element in 1 gram of soil (Calabrese and Stanek, 1993). Accordingly, to identify

the most reliable tracers, daily food soil ratios (F/S) were calculated for each subject based on the calculated daily tracer consumption by each subject, and the mean tracer concentrations measured in soils collected from Henry's Crossing (Table 6.9). It is noted that the number of food sample types that were below the minimum detection limit (MDL) for V and ^{212}Pb tracers was high, with 17 and 11 out of a total of 19 analyses below detection, respectively. For samples where the tracer levels were less than the minimum detection limit, a value of ½ of the MDL was used in the calculation of daily tracer intake.

The variability of the daily intake of tracers was observed to be moderate, as reflected by CV values ranging between 25% and 65% in 10 of the 13 tracers. The highest variability was observed in the ingestion of ^{212}Pb, Th and Ti tracers, with CV values of 66%, 82% and 108%, respectively. The high variability in the ^{212}Pb values is likely the result of the analytical results being below the detection limits in many of the food items. The variability in daily consumption rates for Ti were likely the result of the tracer concentrations in granola bars and doughnuts being 2 orders of magnitude higher than the Ti levels measured in the other food types. It was noted that both of these food items contained processed toppings (i.e., coloured icing), and these high levels are possibly due to TiO_2, a common colouring agent in processed foods and consumer products. Elevated levels of Al were also observed in pancake mix and doughnuts, probably due to aluminum sulphate in baking powder, which is used as a leavening agent.

Al, V, Si, La and Ce, were observed to be the most reliable tracers, with mean F/S values of 0.06, 0.07, 0.08, 0.05, 0.13 and 0.13, respectively, and CV values ranging between 47% and 67%. However, it is noted that the F/S values for V are based on only 2 analyses of food samples above the detection limit, and its value as a mass balance tracer is questionable. Thus, the 4 most reliable tracer identified in this study are Al, Si, La and Ce. Al and Si are considered 2 of the most reliable tracers that have been used in previous soil ingestion studies (Stanek et al., 2001). This observation is supported by the current study where those elements were observed to have lower F/S values than La and Ce for each study day, with the exception of 2 days, when Si had slightly higher or comparable F/S values. The remaining radioisotope tracers were observed to have relatively high F/S ratios, and therefore less would be deemed less reliable than the aforementioned elemental tracers.

Table 6.7
Tracer concentrations in ashed food samples. The number of samples below the detection limits is noted for each tracer

Sample	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Y	Zr
	Bq kg^{-1}		μg g^{-1}											
Ham	<MDL	<MDL	590	5	0.29	0.120	10	<700	0.04	54	< 1	0.088	0.100	1.10
Sausage	0.8	<MDL	280	6	0.15	0.068	32	1,000	0.02	26	< 1	0.025	0.043	0.72
Eggs	6.6	<MDL	200	27	0.1	0.044	34	1,100	0.01	13	< 1	0.010	0.007	0.63
Bacon	<MDL	<MDL	80	2	0.05	0.023	4	<700	<0.01	7	< 1	0.006	<0.004	0.37
Pasta	4.3	2.0	150	160	0.11	0.055	1,000	1,200	0.02	10	< 1	0.027	0.016	0.47
Spaghetti / meat sauce	<MDL	0.8	410	26	0.3	0.140	89	2,000	0.04	30	< 1	0.037	0.130	0.68
Sauerkraut	1.1	0.4	20	16	0.03	0.019	42	990	0.01	3	< 1	0.048	<0.004	0.18
Granola bars	2.6	1.4	1,700	52	0.11	0.075	360	2,700	0.03	9600	< 1	0.021	0.079	3.00
Cookies	2.1	0.8	100	52	0.10	0.049	500	2,700	0.03	11	< 1	0.022	0.021	0.28
Pancake mix	2.4	<MDL	1,200	14	0.23	0.130	77	1,300	0.06	11	1.0	0.390	0.210	1.10
Lettuce/salad	2.6	<MDL	190	14	0.15	0.073	210	1,400	0.03	14	< 1	0.045	0.037	0.36
Cheese	0.9	<MDL	20	20	0.02	0.011	6.6	2,700	<0.01	38	< 1	0.012	0.011	0.17
Dognuts	3.7	2.1	220	26	0.27	0.130	120	2,300	0.13	61000	< 1	0.06	0.140	5.90
Peaches/Plums	<MDL	<MDL	100	2	0.06	0.031	26	<700	0.02	9	< 1	< 0.002	0.025	0.25
Apples and oranges	2.8	<MDL	110	78	0.12	0.065	79	740	0.07	23	< 1	0.034	0.096	2.20
Beef	<MDL	1.0	100	35	0.06	0.029	12	1,300	0.01	14	< 1	0.015	0.022	1.00
Bread	3.0	<MDL	140	35	0.24	0.120	230	1,300	0.03	14	< 1	0.077	0.110	0.40
Smoked Meat	0.9	0.8	90	22	0.10	0.087	29	1,300	0.02	5	< 1	0.021	0.047	0.57
Unpeeled Potatoes	<MDL	<MDL	280	43	0.29	0.140	210	1,300	0.05	21	3	0.320	0.090	0.44
Samples below detection limits	6	11	0	0	0	0	0	3	2	0	17	1	2	0

Table 6.8
Mean, standard deviation (SD) and coefficient of variability (CV) for daily tracer consumption rates during the soil ingestion study for all soil ingestion study subjects

Daily tracer ingestion	Nuclides (Bq)		Metals (µg)										
	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
Mean	0.032	0.021	4,860	519	3.6	1.7	2,360	22,300	2.2	1,780	8.4	1.3	17.2
SD	0.009	0.014	1,970	190	1.2	0.4	1,170	10,800	1.8	1,730	4.4	5.4	6.2
CV	28%	66%	41%	37%	34%	27%	49%	48%	82%	98%	52%	41%	36%
n	44	44	44	44	44	44	44	44	44	44	44	44	44

Table 6.9
Mean, standard deviation (SD) and coefficient of variability (CV) of food/soil (F/S) ratios calculated across each tracer for all soil ingestion study subjects

F/S Ratio	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
Mean	1.88	2.11	0.06	0.91	0.13	0.13	2.18	0.08	0.79	3.79	0.07	1.21	0.34
SD	0.90	1.67	0.03	0.49	0.07	0.06	1.41	0.05	0.75	4.19	0.05	0.70	0.18
CV	48%	79%	54%	54%	52%	47%	65%	64%	95%	110%	67%	58%	53%
n	44	44	44	44	44	44	44	44	44	44	44	44	44

6.3.4 Fecal samples

Fecal samples were successfully collected each day from all subjects; however, one fecal sample was lost (Subject D, Week 2, Day 3). The dry weight of daily fecal output for each subject was measured and the data are summarized in Table 6.10. It was observed that the total dry weight of fecal output over the study period for all subjects was approximately 3.7 kg, or approximately 26% of the total dry weight of food consumed. Daily concentrations of tracers for all subjects over the duration of the study are provided in Appendix F and daily mass of tracers in feces are provided in Appendix G, and mean and median fecal tracer concentrations for all subjects over the duration of the study are summarized in Table 6.11. The daily fecal output for all subjects for each day is shown in Figure 6.5. The mean fecal dry weights for all subjects on Day 1, Day 2 and Day 3 of the study were observed to be 36.6 g, 45.4 g and 44.6 g, respectively. Although it was observed that the mean fecal dry weight was approximately 10 g lower on Day 1 compared to Days 2 and 3, the difference was not significant (ANOVA, $F=1.48$, $p=0.24$; Welch ANOVA, $F=1.14$, $p=0.34$). The increase in the daily fecal dry weight on Days 2 and 3 may be a result of increased total food intake or an increase of cellulose fibre in the diet provided to the subjects during the study.

Table 6.10
Mean, standard deviation (SD), coefficient of variability (CV) median, and upper and lower 95% confidence limits of the mean of the daily fecal output dry weight for each soil ingestion study subject

Subject	n	Dry weight (g)					
		Mean	Std Dev	CV	Median	Lower 95%	Upper 95%
A	6	43.2	9.0	21%	44.4	33.8	52.7
B	6	32.7	19.1	58%	30.0	12.6	52.8
C	6	40.7	13.0	32%	39.3	27.1	54.3
D	5	32.0	11.2	35%	31.9	18.1	46.0
E	3	41.4	6.3	15%	42.7	25.6	57.2
F	7	39.9	21.2	43%	51.4	20.4	59.5
G	10	49.8	15.7	31%	51.0	38.6	61.0

Table 6.11
Mean, standard deviation (SD), coefficient of variability (CV) and number (n) of the tracer concentration in ashed daily fecal output from all soil ingestion study subjects

	Nuclides (Bq kg^{-1})		Metals (ug g^{-1})										
	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
Mean	11.5	6.0	1673	179	1.29	0.74	1271	6821	0.30	3237	4.5	0.4	4.4
SD	4.0	2.6	650	35	0.97	0.52	527	4045	0.36	3602	2.6	0.2	2.0
Median	11.0	5.3	1600	180	1.00	0.56	1200	6350	0.22	2300	4.0	0.4	4.0
n	43	43	43	43	43	43	43	30	43	43	43	43	43

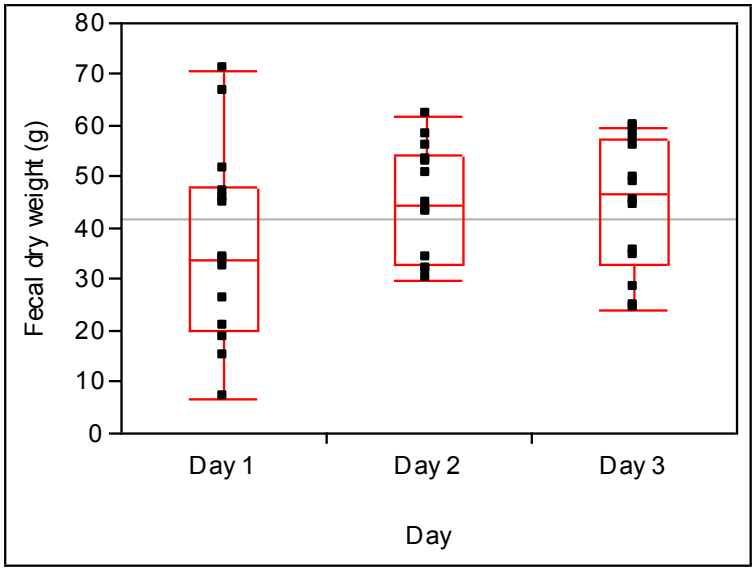

Figure 6.5
Box plots (showing medians, quartiles, outlier whiskers and mean lines) of daily fecal output dry weight for each day of the study period for all subjects (ANOVA, F=1.48, p=0.24; Welch ANOVA, F=1.14, p=0.34)

6.3.5 Mass balance soil ingestion estimates

Daily soil ingestion rates calculated for each subject for each tracer over the duration of the soil ingestion study are provided in Appendix H. A summary of soil ingestion for each week for all subjects is provided in Table 6.12, and a summary of soil ingestion for each subject over the duration of the study is provided in Table 6.13. The soil ingestion rate, calculated for the 4 most reliable tracers (i.e., Al, Si, La and Ce or the 4 tracers with the lowest F/S ratios excluding V) is provided in Table 6.14. There were difficulties with the Si analysis of 13 fecal samples due to insufficient sample. As such there were no completed estimates for Si in these cases, resulting in no Si-based soil ingestion estimates for Subject A in the study. Given that Subject A was observed to have the highest soil ingestion rate of all subjects, based on soil ingestion estimates using the Al tracer, the missing soil ingestion analyses may represent a negative bias in soil ingestion estimate based on the combined Al and Si tracers, and the 4 most reliable tracers. The soil ingestion rate distributions estimated for each tracer are shown in Figure 6.6, and their means were observed to be significantly different (ANOVA, Tukey-Kramer HSD, $p = 0.003$), with soil ingestion estimates obtained using La being significantly higher than Al and Si ($p<0.003$), but not Ce.

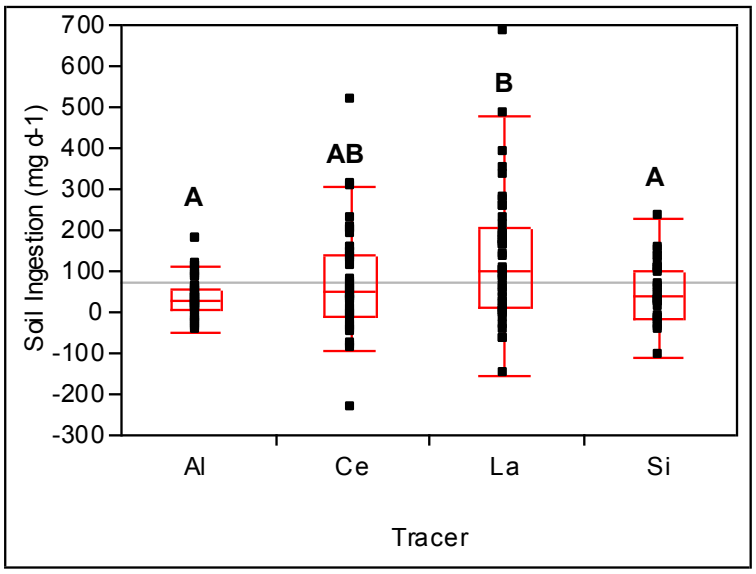

Figure 6.6
Box plots (showing medians, quartiles, outlier whiskers and mean lines) of the frequency distributions of daily soil ingestion estimates for all study subjects for the 4 most reliable tracers. Significant differences in distribution means (Welch ANOVA $F=5.13$, $p<0.003$; Tukey-Kramer HSD, $p = 0.05$) are denoted by differing labels.

Table 6.12
Mean, standard deviation (SD), and median of the daily soil ingestion rates calculated for each study week for all subjects

Subject	Soil ingestion rate (mg d^{-1})												
	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
Week 1													
Mean	950	-242	32	556	-6	46	5,610	66	-768	141	76	412	-85
SD	1,866	2,563	57	1,005	128	134	6,619	57	1,176	1,020	95	963	250
Median	-8	-59	45	374	-5	22	2,580	61	-495	515	96	542	21
n	8	8	8	8	8	8	8	8	8	8	8	8	8
Week 2													
Mean	1,215	841	30	594	96	152	2,857	62	-530	-302	171	586	223
SD	991	1,530	45	588	131	127	2417	79	669	6,168	144	1,038	499
Median	1,192	470	27	434	60	117	2238	47	-400	-586	127	480	98
n	18	18	18	18	18	18	14	18	18	18	18	18	18
Week 3													
Mean	1,353	1,543	46	586	84	153	3,288	22	118	-1902	79	405	69
SD	2,099	3,174	58	804	120	191	3,109	77	1,558	4,608	157	1,277	326
Median	963	394	33	589	53	158	2,971	4	0.3	-1222	65	97	36
n	17	17	17	17	17	17	17	8	17	17	17	17	17

Table 6.13
Mean, standard deviation (SD), and median of the soil ingestion rates calculated for each subject over the duration of the study for each tracer

Subject / Parameter	Soil ingestion rate (mg d^{-1})												
	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
A - Mean	1349	-13	59	536	27	73	1899	-	-910	-72	160	239	326
A - SD	1392	1683	72	701	79	82	2259	-	750	7445	191	355	781
A - Median	894	82	38	459	34	78	1674	-	-1116	-1218	137	369	176
A - n	6	6	6	6	6	6	6	0	6	6	6	6	6
B - Mean	881	1950	41	254	44	69	1769	2	225	-431	45	229	0
B - SD	2996	4211	65	556	95	126	1697	79	291	6646	77	1831	236
B - Median	-428	117	14	128	-2	2	1873	1	186	-2819	48	-278	-40
B - n	6	6	6	6	6	6	6	6	6	6	6	6	6
C - Mean	1081	402	5	440	14	62	2107	-14	-705	-4019	40	-176	-62
C - SD	1606	1780	49	769	82	85	2888	51	718	5084	67	422	240
C - Median	863	147	-1	361	15	64	1626	-38	-932	-4764	56	-17	-62
C - n	6	6	6	6	6	6	6	3	6	6	6	6	6
D - Mean	1427	-22	31	214	231	368	1616	59	-927	-218	114	143	-68
D - SD	954	895	28	392	195	220	1343	74	516	4667	84	424	197
D - Median	1500	-62	39	349	227	350	1903	19	-905	168	99	143	-46
D- n	5	5	5	5	5	5	5	5	5	5	5	5	5
E - Mean	1032	1585	23	1018	117	180	6385	102	-134	-4037	244	778	104
E - SD	346	593	9	366	40	47	2856	0	305	7494	164	394	139
E - Median	1228	1328	20	1109	123	187	5046	102	-273	-5835	174	614	160
E - n	3	3	3	3	3	3	3	2	3	3	3	3	3
F - Mean	1394	1283	23	608	44	78	8940	44	-78	-213	45	154	-138
F - SD	2177	1375	72	1377	125	146	8395	60	346	1398	104	1247	190
F - Median	1565	1450	27	256	36	64	7278	43	35	135	56	49	-144
F - n	7	7	7	7	7	7	7	7	7	7	7	7	7
G - Mean	1208	846	41	800	59	111	3518	105	-524	1017	184	1125	284
G - SD	1285	3028	37	743	145	139	2046	68	1145	1300	187	966	389
G - Median	1493	335	36	703	53	91	3526	100	-205	793	107	1056	256
G - n	10	10	10	10	10	10	10	10	10	10	10	10	10

Table 6.14
Mean, standard deviation (SD), coefficient of variability (CV), the upper 95% confidence limits of the mean (Upper 95%), the median, the 75th and 90th percentiles and the maximum for the distribution of daily soil ingestion estimates calculated for for the 4 most reliable tracers, and the calculated with the daily mean rate for 4 most reliable tracers (Al, Si, La and Ce), and for Al and Si.

Level	n	mg d^{-1}							
		Mean	SD	CV	Upper 95%	Median	75% Quantile	90% Quantile	Maximum
Al	43	36.9	51.9	141%	52.8	31	61	110	177
Ce	43	72.2	179.5	179%	112.1	51	142	217	516
La	43	132.6	158.6	120%	181.4	104	211	343	683
Si	30	49.4	73.7	149%	76.9	40	102	145	231
Mean of 4 tracers	43	74.4	91.1	122%	102.5	60	134	193	296
Mean of Al and Si	43	42.7	53.3	125%	59.1	38	93	106	177

6.4 Discussion

6.4.1 Soil ingestion estimates

This study has largely been directed at addressing the lack of quantitative soil ingestion data to support HHRA exposure scenarios for populations living in rural or wilderness areas of Canada. To this end, the study has assessed soil ingestion that would be incurred participating in wilderness camping and activities related to traditional fishery practices of a First Nation in the interior of British Columbia. It is important to note that the soil ingestion estimates in this study are based on the inadvertent ingestion of soil from participating in what were deemed to be "intermediate contact" activities, such as camping, hunting or fishing, and did not include ingestion related to "high contact" activities and/or ingestion of soil in traditional foods. Thus, soil ingestion rates for First Nations inhabitants of wilderness areas who engage in traditional subsistence activities could be higher. Moreover, the soil ingestion estimates in this study do not include the contribution from ingesting soil adhering to locally-sourced and/or -preserved food, and this contribution would be expected to increase soil ingestion rate in community members that consume traditional foods. Although these activities are not necessarily representative of those that would result in the highest rates of soil ingestion (i.e., grams per day), the activities, environmental conditions, and time spent outdoors engaged in traditional activities are substantially different from the activities ordinarily encountered in urban or suburban lifestyles. Thus, it was hypothesized that soil exposure rates for the study subjects would be measurably greater than for studies of urban/suburban populations. To test the hypothesis, the results of this study were compared to the results of previous studies of adults and children, as well as regulatory soil ingestion rate guidelines for use in HHRA.

Table 6.15 compares the distribution of soil ingestion estimates reported in the key and relevant studies underpinning the soil ingestion guidelines identified in Table 6.1 with the soil ingestion estimates derived from the mean values of the most 4 most reliable tracers in this study, and those calculated Al and Si values. Raw data from the soil ingestion study of children at the Anaconda superfund site by Calabrese et al. (1997) and the soil ingestion study of children in Washington by Davis et al. (1990) have also been included in the discussion of results from this soil ingestion study. Data from the aforementioned studies

were obtained courtesy of Professor Ed Stanek from the University of Massachusetts, Amherst (UMass, 2005).

The mean soil ingestion rate of approximately 74 mg d^{-1}, estimated using the 4 most reliable tracers, are much higher than the 6 mg d^{-1} rate calculated with the Best Tracer Method (BTM^{25}) employed in the Calabrese et al. (1997) study of adults. Further, the soil ingestion rate of approximately 50 mg d^{-1}, calculated using the Si tracer in this study, was greater than the 23 mg d^{-1} and 26 mg d^{-1} calculated using Si for Mothers and Fathers, respectively, in the Davis and Mirick (2006) family study. Conversely, the 37 mg d^{-1} calculated using the Al tracer in this study was less than the 92 mg d^{-1} and 68 mg d^{-1} calculated using Al for Mothers and Fathers, respectively, in the Davis and Mirick (2006) study. The median soil ingestion rate values using the 4 most reliable tracers, Al or Si were generally observed to be higher than median values reported in previous studies of adults, except the in one instance, where soil ingestion was calculated with the Al tracer in the Calabrese et al. (1990) study. When compared to soil ingestion rates recommended by regulatory agencies for use in HHRAs (Table 6.2), the rates measured in this study are typically higher. Moreover, the 90^{th} percentile for the soil ingestion rates are much higher than the regulatory guidelines for adults, with values of 193 mg d^{-1} and 124 mg d^{-1} for estimates based on the 4 most reliable tracers, and the Al and Si tracers, respectively. However, these regulatory guidelines are based on reasonable central estimates of soil ingestion and the 90^{th} percentile values from this study are lower than the aforementioned rates assigned for construction workers, military personnel or populations following subsistence lifestyles.

The mean soil ingestion rate estimates calculated in this study were generally observed to be higher, comparable to, or lower than estimates reported in studies of children. The mean soil ingestion rate of approximately 74 mg d^{-1} estimated with the 4 most reliable tracers was higher than the mean rate estimated in the Calabrese et al. (1997) of children that used Al and Si tracers, and comparable to the van Wijnen et al. (1990) study of children in a daycare centre using the Limited Tracer Method (LTM^{24}), and the Davis et al. (1990) study that also used Al and Si tracers. However, the soil ingestion values estimated in this study were observed to be substantially lower than those estimated for children in campgrounds using the LTM. Furthermore, the soil ingestion values estimated in this study were substantially

lower than the original results of the Calabrese et al. (1989) study. However, the median values in this study were observed to be comparable to or higher than median values estimated in the aforementioned studies of children. The median soil ingestion rate of 32 mg d^{-1} determined in this study using the Al and Si tracers is comparable to the Calabrese et al. (1989) and Davis et al. (1990) studies, but higher than the Calabrese et al. (1997) study. The upper 95% confidence limit of the mean soil ingestion rates calculated in this study were observed to be less than the rates recommended for HHRA of children between 6 months and 4 years old (i.e., toddlers) in Table 6.2. However, the upper 90% quantile of the distribution is higher or of the same scale as the aforementioned recommended soil ingestion rates for toddlers (i.e., 80 mg d^{-1}). Given that the highest soil ingestion rates used in HHRAs are based on toddlers rather than adults, it would be of interest to determine if the rate of soil ingestion for children living in rural or wilderness areas, and following a traditional lifestyle, is within regulatory guidelines. To this end, future studies of toddlers in these populations are warranted.

There was no statistically significant difference between soil ingestion rates estimated for each subject (ANOVA F=0.62, p=0.71). However, it was noted that the two subjects with the highest soil ingestion rates, based on the daily mean values of the 4 most reliable tracers, were senior members of the team that were most active in the collection of fish for the traditional fishery. There was no statistically significant difference (ANOVA F=0.95, p=0.39) between soil ingestion rates measured in weeks 2 and 3 of the study, when activities related to the traditional fishery were conducted, and the estimates from week 1 (Figure 6.7), where the subjects were noted to be participating in activities that required direct contact with soil or sediments. The median soil ingestion rate for the 4 most reliable tracers measured in week 1 was observed to be 37 mg d^{-1}, compared to median values of 62 and 55 mg d^{-1} in weeks 2 and 3, respectively. Although a link between the level of physical activity cannot be demonstrated statistically in this study, given that detailed activity logs for each subject were not kept, future studies should explore differences between specific subject activities and soil ingestion rate.

Overall, however, the soil ingestion rates measured in this study are only incrementally greater than those observed in previous studies, and are not in the order of the gram per day

soil exposure scenarios proposed for subsistence lifestyles. However, as previously noted, the soil ingestion rate estimates reported in this study are considered conservative (i.e., less than actual values) because the ingestion of soil adhering to locally sourced and traditionally prepared food and the contribution to the soil ingestion rate estimates from 'high-contact" activities were not included. Thus, more work is required to firmly establish recommended soil ingestion rates to adequately protect people practicing traditional lifestyles typical of rural or wilderness areas. To this end, soil ingestion studies for potentially higher soil contact activities (e.g., root digging, attending and/or participating in rodeos, ploughing, etc.) are warranted.

The validity of soil ingestion estimates determined using mass balance tracer methods is based on the following generic assumptions (Stanek and Calabrese, 1991):

a) The tracer element is not present, or present at low concentrations, in the food, water or medicines consumed during the study.

b) If the tracer is present in food, then there is a one-to-one correspondence between the intake of tracer from food, water and medicines, and tracer output in feces after a defined lag or transit time, thereby allowing the calculation of soil ingested by subtracting the amount of tracer contained in food (a lack of a one-to-one correspondence is termed transit time misalignment).

c) The tracer is not absorbed in the gastrointestinal tract.

d) All tracers ingested in food and medicine are accounted for (i.e., source error resulting from inadvertent and unmeasured ingestion of tracers in consumer products) is eliminated.

e) The tracer is uniformly present at high (measurable) concentrations in soils where the study is being conducted.

The lack of correspondence between tracer intake and output can be offset by selecting tracers with low F/S ratios, increasing the duration of the study or reducing the day-to-day variability in tracer intake. In this study, the uncertainty related to assumptions "a" and "b" was largely addressed by basing the soil ingestion estimates on those with the lowest F/S

ratios. Given that the study duration could not be increased due to constraints in the availability of the subjects, uncertainty related to transit time misalignment was further reduced through the provision of daily food rations to study subjects that resulted in a consistent daily intake of tracers by all subjects. For example, fresh meats and vegetables were observed to have uniformly low tracer levels, and the diets provided were predominated by fresh meats and vegetables and contained a minimum of processed foods that could contain high levels of tracers. Exceptions to this were the high tracer levels measured in granola bars, doughnuts and pre-made pancake mix that were attributed to tracers in food additives (i.e., coloured icing and leavening agents). Elimination of these processed foods would further decrease the variability of tracer intake in future soil ingestion studies. Moreover, the Nemiah study subjects were not taking medications containing these tracers as active ingredients or excipients. The uniformly low tracer levels in foods were reflected by the relatively low CV of food intake in subjects observed over the duration of the study. For example, the CV values for the 4 most reliable tracers (Al, Ce, La and Si) used in this study were 41%, 34%, 27% and 49%, respectively, compared to values of 168%, 74%, 99% and 68%, respectively, for these tracers in the Stanek et al. (1997) study of adults.

The 4 most reliable tracers used in this study are poorly absorbed in the gastrointestinal tract (assumption "c"). Specifically, gastrointestinal absorption factors (i.e., f_1 or the mass of tracer absorbed divided by the mass of tracer ingested) used in pharmacokinetic modelling of radionuclides in humans recommend f_1 values of 0.01, 0.005, 0.005 and 0.01, for Al, Ce, La and Si, respectively (ICRP, 1996). Moreover, Al and Si, originating from Plagioclase minerals, (i.e., $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$) in the bedrock found in the study area are insoluble or only sparingly soluble in water (CRC, 1993). The uncertainty related to source errors (i.e., assumption "d") was minimized by virtue of conducting the study in a remote location, where the potential for problems due to unmeasured tracer sources (e.g., newspaper ink, urban dust and exhausts containing metals), and unrecorded food items (e.g., candies, snacks) is low. The levels of the most reliable tracers used in the study were readily measurable in soils, and the variability in soils was generally observed to be low at each site (assumption "e"). The CV values were less than 5% for the 4 most reliable tracers at Henry's Crossing (Location C), where 2 of the 3 weeks of the study were completed, and at Farwell Canyon. The Al concentration in soil samples from the Nemiah Valley was observed to be an

exception, with a CV value of 43%. However, this variability would only be expected to affect one subject for 1 week of the study. Soil ingestion estimate uncertainty was further reduced by calculating the soil ingestion rates using the concentration or depletion of tracers in the <63μm soil fraction, thereby reducing the impact of tracer enrichment in the smaller particle size fractions that will be preferentially ingested. Because of the potential for transit time misalignment of tracer inputs and tracer outputs, the ability to detect low levels of soil ingestion via the mass balance tracer method is encumbered by factors that increase the "signal to noise" ratio (Stanek et al., 2001). For example, sampling and analytical variability of food, fecal, and soil samples alone will result in a minimum detection level of 20 mg d^{-1}, according to estimates for ^{214}Pb using 225 subject days in a hypothetical mass balance tracer study (Doyle et al., 2010). Other factors that potentially contribute to the "noise" include variability of tracer levels in consumed foods, and/or variability in actual soil ingestion over the duration of the study within or between subjects. The negative effect of these factors on the precision of mass balance tracer soil ingestion estimates can be reduced by increasing the duration of the study, thereby diluting the impact of transit time misalignment, and/or increasing the number of study subjects. However, implementing such changes would substantially increase the required cost and workload. Moreover, a substantial increase in subjects is simply not possible for very small populations. In the current study variability in the levels of tracers in foods were reduced by providing a uniform diet over the duration of the study for all subjects, and by ensuring that all subjects lived under the same environmental conditions and participated in similar activities. The soil ingestion rate distributions observed in the 3 studies (i.e., Anaconda, Davis and Nemiah) are shown in Figure 6.8, and the variance of soil ingestion estimates based on the Al tracer were observed to be unequal between the 3 studies (Levene test F=2.95, p=0.054). This difference in variance is reflected in the standard deviations on the mean soil ingestion rates reported for the Davis, Anaconda and Nemiah studies of 145 mg d^{-1}, 96 mg d^{-1} and 52 mg d^{-1}, respectively. Similarly, daily Al intake in food by subjects in the 3 studies provided in Figure 6.9, shows that the variance in the daily Al intake in food by subjects in the 3 studies were unequal (Levene test F=30.1, p=0.0001). Thus, as implied by using tracers with low F/S ratios, lower variance in tracer intake in food results in lower variance (i.e., higher precision) in the estimated soil ingestion rate distribution.

Table 6.15
Selected soil ingestion rate estimates for mass balance tracer studies reported as the "key studies" underpinning the EPA soil ingestion recommendations for HHRA summarized in Table 5.3 (from EPA, 2009; van Holderbeke et al., 2007; Wilson, 2006; UMass, 2005)

Study and tracer/method	n	Soil ingestion rate (mg d^{-1})			
		Mean	Standard Deviation	Median	90th Percentile
Key Studies of Children					
Calabrese et al., 1989					
• Al	64	153	852	29	
• Si	64	154	693	40	
van Wijnen et al., 1990					
• Daycare centres (LTM)[24]	162	69	286		
• Campgrounds (LTM)	78	120			
Davis et al., 1990					
• Al	101	39	145	25	145
• Si	101	82	122	59	218
Calabrese et al., 1997					
• BTM[25]	256	7	74	20	73
• Al	64	3	96	-3	67
• Si	64	-16	57	-18	38
Studies of Adults					
Calabrese et al. (1990)					
• Al	6	77	65	57	
• Si	6	5	55	1	
Stanek et al. (1997)					
• BTM	10	6	165	-11	201
• Al	10	12	31	5	
• Si	10	-20	37	-24	
Davis and Mirick (2006)					
• Mothers (Al)	19	92	218	0	
• Mothers (Si)	19	23	37	5	
• Fathers (Al)	19	68	130	23	
• Fathers (Si)	19	26	49	0.2	
This study					
• Al, Ce, La, Si	43	74	91	60	193
• Al	43	37	52	31	110
• Si	30	49	74	40	145

[24] LTM is the lowest soil ingestion rate of estimates generated from Al, Ti or Acid Insoluble Residue tracers and corrected for ingestion of tracers consumed in food and medicine.
[25] BTM is the best tracer method where the soil ingestion estimate is based on the median of values calculated for the 4 tracers with the lowest food/soil ratio.

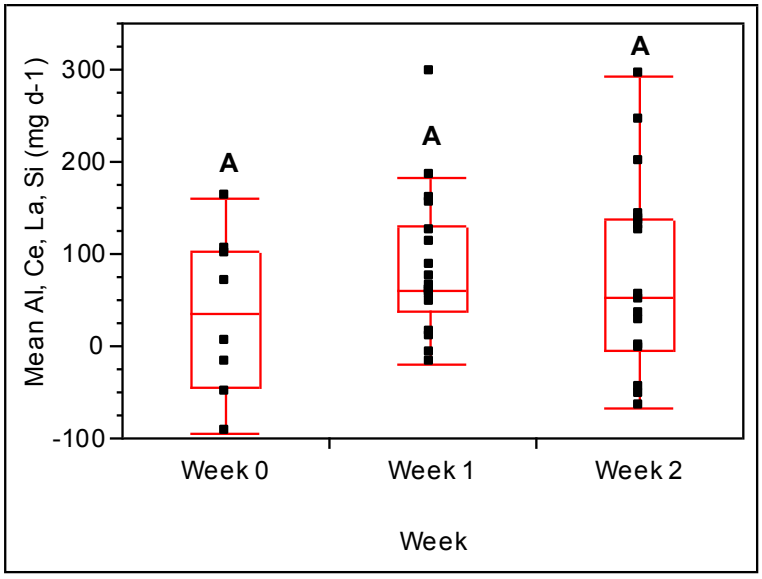

Figure 6.7
Box plots (showing medians, quartiles, outlier whiskers and mean lines) of daily soil ingestion rate distributions (based on mean values for 4 most reliable tracers) for each study week of the Nemiah study. The distributions are not significantly different (ANOVA F=0.95, p=0.39).

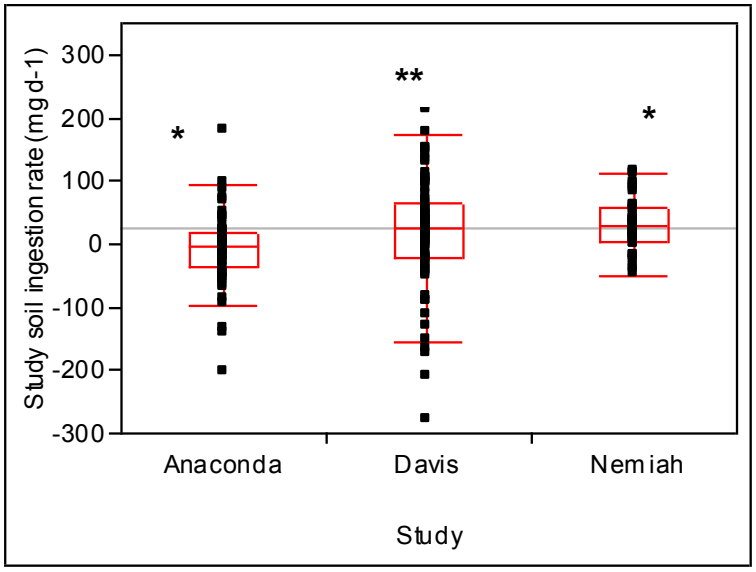

Figure 6.8
Box plots (showing medians, quartiles, outlier whiskers and mean lines) of the frequency distributions of daily soil ingestion estimates using the Al tracer in the Anaconda study (Calabrese et al., 1997), the Davis study (Davis et al., 1990) and this study (Nemiah study) showing median, 25% and 75% quantiles and outlier whiskers. The *'s correspond to variances that are unequal (Levene test F=2.95, p=0.054).

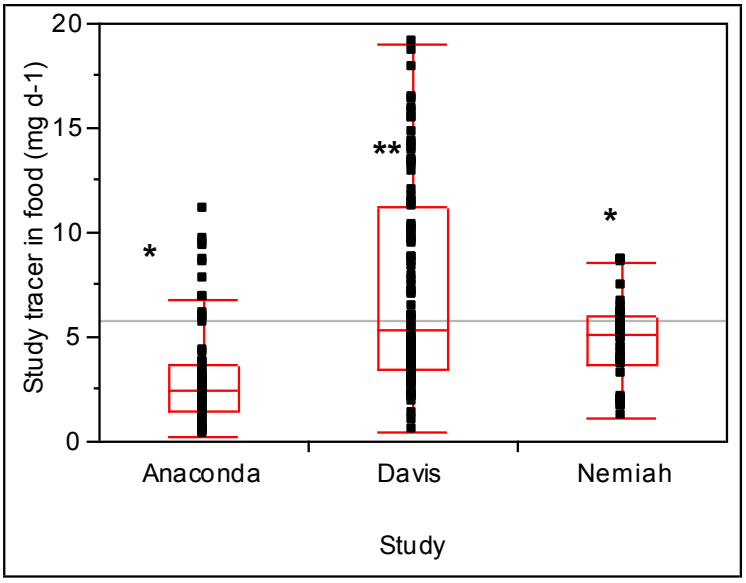

Figure 6.9
Box plots (showing medians, quartiles, outlier whiskers and mean lines) of the frequency distributions of daily Al tracer ingestion rates in food in the Anaconda study (Calabrese et al., 1997), the Davis study (Davis et al., 1990) and this study (Nemiah study) showing median, 25% and 75% quantiles and outlier whiskers. The *'s correspond to variances that are unequal (Levene test F=30.1, p=0.0001).

6.4.2 Utility of isotope tracers

The F/S ratios and soil ingestion rate estimates calculated using naturally occurring radioisotopes (^{238}U and ^{232}Th decay series) were observed to be more than an order of magnitude higher than those determined using the 4 most reliable elemental tracers. Moreover, the soil ingestion estimates were observed to be highly variable as reflected by standard deviations in the order of g d^{-1}. This high variability could be due to the relatively high variability of the radioisotope tracers detected in soils from the three study sites, and in particular samples collected throughout the Nemiah Valley. Furthermore, much of the problem in determining soil ingestion using the isotopic tracers of the ^{238}U and ^{232}Th decay series was related to the difficulty in precisely measuring them in food. Although the analytical techniques used to detect these isotopes could be improved, the new methods would likely preclude the non-destructive beneficial characteristic of gamma spectrometry, and it is considered doubtful that they would prove to be any more reliable as tracers than the elemental tracers currently used.

6.5 Conclusions

This study represents the first quantitative soil ingestion study of a Canadian population, and the first of a population following a traditional wilderness lifestyle. Furthermore, this study is one of only a few quantitative soil ingestion studies of adults. As such, it constitutes an important contribution to the available research on this poorly understood exposure pathway used for the HHRAs of contaminated sites.

The mean and median soil ingestion rates measured in this study (i.e., 74.4 mg d^{-1} and 60 mg d^{-1} for the 4 most reliable tracers, respectively) are comparable or higher than the rates currently recommended by regulatory agencies for adults, based on reasonable central estimates of soil ingestion, which range from 20 mg d^{-1} to 100 mg d^{-1}. Moreover, the 90th percentile of the distribution of measured soil ingestion rates is in the order of 100 to 200 mg d^{-1}, and thus, much higher than those recommended for HHRAs of contaminated sites. Thus, the results from this study support the hypothesis that members of a community living in a rural and wilderness areas who practice a traditional subsistence lifestyle experience higher soil ingestion rates than adults living in suburban/urban environments. This difference is substantial, but nevertheless, is less than the 400 mg d^{-1} scenario used to underpin qualitative exposure assessments for communities in the North-western United States that follow a similar lifestyle and estimates for construction workers or military personnel. However, the participants' activities during this study included mostly medium contact activities such as outdoor camping, hunting, and fishing, and further studies of adults would be required to determine if high-contact activities such as root digging and cultivating appreciably increase soil ingestion rates. Moreover, assuming that children are more susceptible to inadvertent soil ingestion, further studies of children living under rural and wilderness conditions, and involved traditional activities, are required to determine if soil ingestion rates currently recommended for HHRAs of contaminated sites are adequately protective for this receptor.

The study design, which included a group of subjects living under the same environmental conditions and consuming the same array of food items, reduced the variability of tracer intake from food and the mass of fecal output. As a result, the variance values associated with the soil ingestion rates estimated in this study were substantially lower than those of previous mass balance tracer studies (i.e., improved precision). This variability could be

further reduced by eliminating processed foods that contain commonly used mass balance tracers, such as Al, from the subject's diet during the study. Al and Si were the most reliable tracers used in this study, based on their low F/S ratios, and the low variance of calculated soil ingestion rate estimates. Isotopes of the ^{238}U and ^{232}Th decay series were deemed not to be reliable as mass balance tracers for soil ingestion studies of human populations.

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Chapter 7

Soil ingestion estimate variability and minimum detection limit

7.1 Introduction

The statistical power of the mass balance tracer estimating methods is an important consideration in soil ingestion studies. However, communities in rural or wilderness areas where people follow a traditional subsistence lifestyle are typically small and the number of available subjects in these communities is limited. Moreover, the location and short duration of many traditional activities will constrain the duration of the study, and subsequently reduce the statistical power. Thus, the question of power in soil ingestion studies of populations in rural or wilderness areas is paramount.

Doyle et al. (2010) (Chapter 2) developed a Monte Carlo model to determine the number of subjects required to achieve sufficient statistical power to measure soil ingestion in a population following a traditional lifestyle at an acceptable confidence interval. The model was structured to simulate the sampling and analytical variability that could be anticipated in a mass balance using ^{214}Pb measured by gamma spectrometry as a mass balance tracer. The purpose of the model was to determine the minimum quantity of ingested soil that could be detected in a mass balance study for various numbers of study subject-days (i.e., the product of the number of study subjects and study duration in days). The results showed that approximately 225 subject days, assuming one soil ingestion estimate per subject day is obtained, would be required to detect a difference of 20 mg d^{-1} in soil ingestion (i.e., the soil ingestion rate for adults currently recommended by Health Canada) using ^{214}Pb as a tracer. Thus, based on sampling and analytical uncertainty alone, relatively large studies would be required to detect soil ingestion at or below the regulatory guideline for adults.

A soil ingestion study was conducted in the Xeni Gwet'in First Nations community inhabiting the Nemiah Valley, British Columbia (Chapter 6). The study involved 7 volunteer subjects followed 4 days per week over a 3-week period, and produced 43 soil ingestion rate

estimates. The Al tracer was observed to be the most reliable, having the lowest food to soil (F/S) ratio of the tracers used in the study. The mean soil ingestion rate, based on the 43 soil ingestion estimates calculated with the Al tracer, was observed to be ~37 mg d^{-1} (standard deviation ~52 mg d^{-1}), and the median value was observed to be ~31 mg d^{-1}. The soil ingestion rate estimates based on the 43 mean daily soil ingestion estimates calculated with the 4 most tracers deemed to be the most reliable based on F/S ratio (i.e., Al, Ce, La, Si) was observed to be ~74 mg d^{-1} (standard deviation ~91 mg d^{-1}), and the median was observed to be ~60 mg d^{-1}.

7.2 Methods

The Monte Carlo soil ingestion model is provided in Appendix I. The model parameter values used in the mass balance algorithm calculation (Eq. (7.1)) are provided in Table 7.1.

$$S_a = \frac{F_c \times F_a}{S_c} - \frac{I_c \times I_a}{S_c} \qquad \text{(Eq. 7.1)}$$

where:

S_a is the soil ingested (g)

F_c is the concentration of tracer element in feces (μg g^{-1})

F_a is the dry mass of feces (g)

I_c is the food concentration for tracer element (μg g^{-1})

I_a is the mass of food ingested (g)

S_c is the concentration of tracer in soil μg g^{-1})

The parameters used to derive hypothetical mean soil ingestion estimates were based on the observed values in the Nemiah Valley soil ingestion study (Chapter 6). The model allows for input parameters to be randomly selected from a predetermined distribution that reflect the observed and/or estimated variability of each parameter. For example, the values for the concentration of tracer in soil were derived from the observed distribution of tracer concentrations measured from soil samples collected across the Nemiah Valley. Thus, the soil ingestion estimate distribution variance derived from many iterations of the model will

reflect the variability in soil ingestion estimates that would result from differences between the tracer concentration used in the study calculations and the soil actually ingested by the study subjects. One notable difference between this model and the model developed in Doyle et al. (2010) is the addition of a factor to simulate transit time misalignment (TT), where the mass transfer of tracer from food to feces food was randomly selected from a predetermined normal distribution with a mean transit time of 1 day (i.e., 1 iteration of the model) and a standard deviation of 0.35 day. The standard deviation is based on the approximate standard deviation in gastric clearance times reported by Madsen et al. (1992). 999 iterations of the model were run using data for the Al tracer. Al was chosen because it was considered the most reliable tracer in the Nemiah study by virtue of its low food/soil ratio.

The variance of the soil ingestion rate distribution calculated using the Monte Carlo model was used to calculate the minimum detectable quantity (δ) for a given sample size using Eq. (7.2) (Zar, 1999):

$$\delta^2 = {S^2}/{n} \times \left(t_{\alpha,v} + t_{\beta(1),v}\right)^2 \qquad (7.2)$$

where:

S^2 is the distribution variance

n is the number of samples

$t_{\alpha,v}$ is the t statistic for Type 1 error

$t_{\beta(1),v}$ is the t statistic for Type 2 error

Statistical manipulations and figures (i.e., distribution mean, standard deviation, median) were prepared using JMP® and Excel™ software.

Table 7.1
Parameter values for Monte Carlo simulation of soil ingestion rate calculated using uncertainty data for the Al tracer obtained from the soil ingestion study in the Nemiah Valley. SD means standard deviation

Parameter	Value Mean (SD)	Parameter Definition/Reference
E_{fc} (μg g^{-1})	1673 (33.5)	Mean concentration of Al in ashed feces reported in the Nemiah Valley soil ingestion study (Chapter 6). The standard deviation was based on the CV of 2% derived from multiple analyses of Al in a single sample by ICP/MS.
E_s (μg mg^{-1})	72.9 (5.4)	Mean concentration (standard deviation) of Al in soil. The mean and standard deviation was based on analyses of soils transecting the entire Nemiah Valley (Chapter 6).
W_{fd} (g)	32.4 (3.9)	Mean ashed weight (standard deviation) of food consumed per day per subject in the Nemiah Valley soil ingestion study. The standard deviation was determined from the average CV values derived from weighing multiple portions of smoked meat, ham, bread, apples, doughnuts, granola bars, cookies and eggs.
E_{fd} (μg g^{-1})	150.0 (3.0)	Mean concentration (standard deviation) of Al tracer in food. Based on median Al concentration in food in the Nemiah soil ingestion study. The median was selected to minimize the impact of 2 food items with high observed Al values. The standard deviation was based on the CV of 2% derived from multiple analyses of Al in a single sample by ICP/MS.
W_{fc} (g)	4.9 (0.1)	Mean ashed weight of daily fecal output from the Nemiah Valley soil ingestion study. The standard deviation was based on an assumed CV of 2% for the weighing of samples.
Transit Time	1 (0.35)	Dimensionless factor that simulates transit time misalignment of food derived tracers and tracers sampled in the feces. Based on average gastrointestinal tract clearance time variability reported by Madsen (1992).

7.3 Results and discussion

The output distribution derived from 999 iterations of the model using the parameters summarized in Table 7.1 is shown in Figure 7.1. The model output was showed significant deviation from a normal distribution (Shapiro-Wilks $W=0.98$, $p<0.0001$), with a mean value of approximately 46 mg d^{-1}, a median value of approximately 50 mg d^{-1}, and a variance of 1307 mg d^{-1}, or approximately 50% of the variance value of 2690 mg d^{-1} reported for soil ingestion estimates calculated with Al in the Nemiah Valley soil ingestion study. The

minimum detectable soil ingestion quantity, calculated as a function of the number of study subject days (i.e., number of daily soil ingestion estimates), was plotted based on the variance of the distribution shown in Figure 7.2. It was observed that the minimum detectable quantity using the Al tracer for the 43 estimates completed in the study was approximately 24 mg d^{-1}.

The mean soil ingestion rate, calculated with the Al tracer, observed in the Nemiah Valley soil ingestion study (Chapter 6) was approximately 37 mg d^{-1}, compared to a mean rate reported in the most recent study of adults of 12 mg d^{-1} (Stanek et al. 1997), and rates recommended for use in HHRAs in the order of 20-50 mg d^{-1}. This suggests that there may be insufficient power in the Nemiah Study to reliably detect the difference between the most recent mass balance studies of adults, and the values recommended for HHRAs. However, it is important to note that the variance of the model output was influenced by conservative assumptions. For example, the model input parameter for food weight was based on the measured variability of individual food portion measurements. However, the majority of mean food portion weights used in the soil ingestion study described in Chapter 6 were based on a measured total weight divided by the number of food portions served. In this case the variability in the mass of food has been consumed by the group, and hence the total tracer measured in food would be the uncertainty related to the analytical scale used, which is typically low. Consequently, each instance where a subject consumes a portion of food that is less than the weight used in the soil ingestion calculation is compensated by another subject consuming a portion of the same food that is too high. Under these circumstances, there is a "zero-sum" in food portion weight variability, where the variability in individual food portion weights will not be reflected in the variability in soil ingestion rate estimates for the entire study group. Similarly, the variability in transit time used in the model was based on the measured variability over several human subjects, and this value may overstate the variability in a single subject over the duration of a soil ingestion study. For example, in the Nemiah study, the total fecal output for each day of the study was collected for all subjects, and could be comprised of one or more samples delivered at any time during the day. Thus, the tracers measured in the fecal output from Day 2 of the study may represent a transit time greater than 24 hours if some of the sample where delivered later in the day.

The model was re-run to determine the minimum detectable quantity under extremely optimistic scenarios where the soil ingestion estimate variability is based only on sampling and analytical variability, and does not include variability resulting from variability in transit time misalignment. The resulting soil ingestion frequency distribution (Figure 7.3) was observed to be normally distributed (Shapiro-Wilks W=1.00, p=0.11), with the mean and median values of approximately 46 mg d^{-1} and a variance of 115 mg d^{-1}, or approximately an order of magnitude less than the variance of 1307 mg d^{-1} when transit time misalignment was considered. The minimum detectable soil ingestion quantity plotted using this distribution's variance against the number of subject-days is shown in Figure 7.4. The minimum detectable quantity for the 43 estimates completed in the study based on this distribution was observed to be 7 mg d^{-1}. This result illustrates how transit time misalignment amplifies the uncertainty in food tracer intake and soil ingestion estimates.

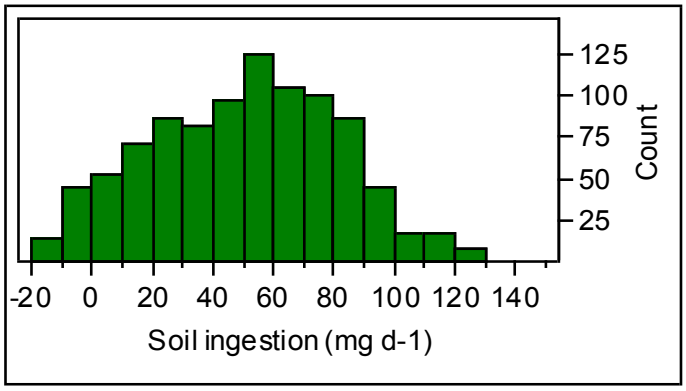

Fig. 7.1
Plot of soil ingestion estimates produced by 999 iterations of the Stella™ Model using the parameters provided in Table 7.1

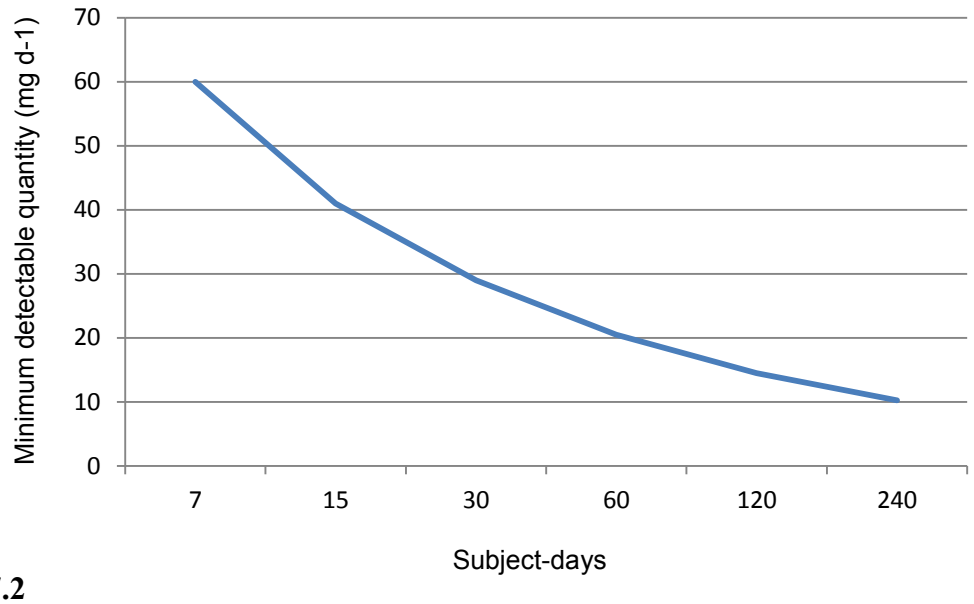

Fig. 7.2
Plot of minimum detectable quantity of soil ingested per day against the number of subject-days when transit time misalignment was included in the Stella™ Model simulation

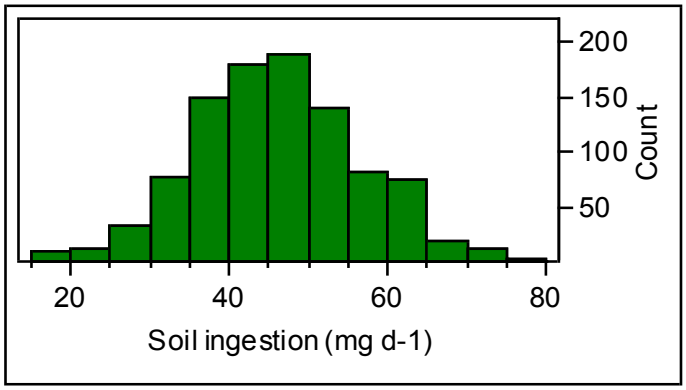

Fig. 7.3
Plot of soil ingestion estimates produced by 999 iterations of the Stella™ Model using the parameters provided in Table 7.1 for all parameters except food portion weight and transit time misalignment, where the CV of food portion weight is assumed to be 2% and there is no transit time misalignment

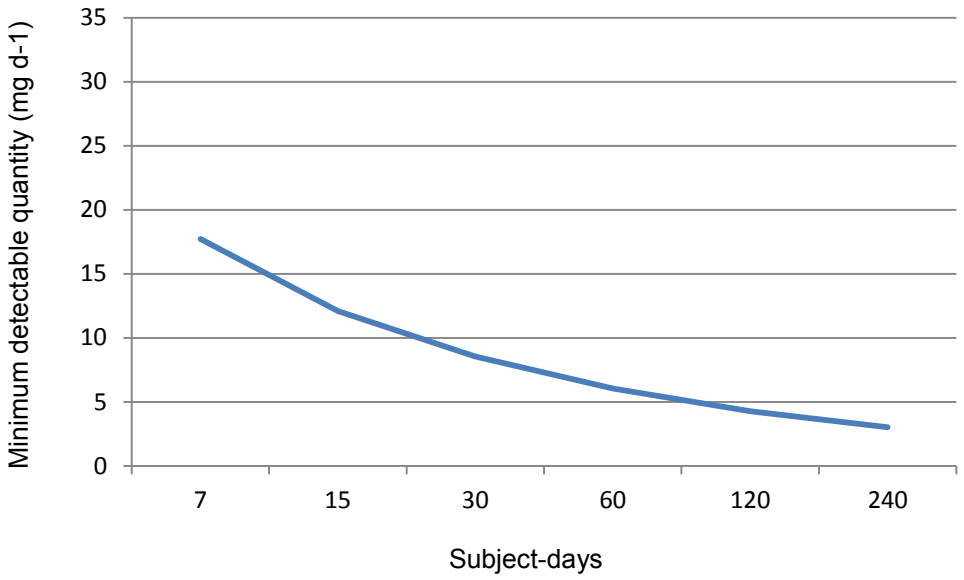

Fig. 7.4
Plot of minimum detectable quantity of soil ingested per day against the number of subject-days when transit time misalignment was not included in the Stella™ Model simulation

7.4 Conclusions

The results of the modeling exercise suggests that the minimum detection limit for the mass balance soil ingestion estimating method used in the Nemiah Valley study is at worst 24 mg d^{-1} and at best 7 mg d^{-1}. The modelling also reiterates the large contribution of transit time misalignment to variability in soil ingestion rate.

7.5 References

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Chapter 8

Research summary and scientific contributions

8.1 Research summary and conclusions

The focus of the research described in this thesis was directed at determining if the lifestyles and living conditions typical of populations living in rural or wilderness areas resulted in increased inadvertent ingestion of soil. This focus emanated from a realization that the quantitative soil ingestion studies supporting human health risk assessment (HHRA) of contaminated sites were mostly derived from epidemiological studies (i.e., cohort studies) assessing soil ingestion in children, and restricted to populations living in urban or suburban areas of the United States, and to a lesser extent, Europe. Children were often selected as study subjects based on the underlying assumption that toddlers, aged between 7 months and 4 years of age, were more pre-disposed to soil ingestion than adults because they frequently display mouthing (i.e., placing hands or objects in their mouths) and soil pica behaviour. However, North American urban and suburban environments tend to be landscaped, and the populations in these areas spend much of their time indoors, and individuals are not typically in direct contact with the soil environment. Conversely, many populations, such as indigenous and Aboriginal peoples residing in rural and wilderness areas of North America and worldwide, live under subsistence conditions, practice traditional land uses that involve substantial periods of time spent outdoors, and participate in activities that increase the likelihood of direct contact with soil (e.g., ranching and agriculture, local foraging of foods, preservation and preparation of foods outdoors). Qualitative soil exposure assessments published to date suggest that very high soil ingestion rates (i.e., gram per day quantities) may occur in Aboriginal populations practicing a subsistence lifestyle, resulting in overall soil ingestion rates many times greater than those recommended by regulatory agencies for use in HHRAs. Accordingly, it was hypothesized that the potential for inadvertent soil ingestion is greater in populations following lifestyles typical of traditional land use in rural or wilderness areas in comparison with populations living in urban or suburban environments. Moreover, since populations in rural or wilderness areas often reside near sites contaminated with toxic substances released as a consequence of mining or other industrial

activities (e.g., tailings or mineral processing facilities). These populations may be vulnerable to exposure to toxic contaminants via the soil ingestion pathway.

Mass balance tracer methods have been used in a few key studies to quantify soil ingestion, and these studies form the scientific underpinnings of recommended soil ingestion rates for assessing the risks of adverse human effects from contaminated sites. The studies employed inorganic elements commonly found in soil (e.g., Al, Si, Ti, V) as tracers, where the mass of the tracers measured in excreta, the mass of tracers measured in food, and the concentration of the tracers measured in local soils were used to estimate daily soil ingestion. However, these methods have not been used to determine the soil ingestion rate for individuals living under conditions that would typically be encountered in a rural or wilderness area. Moreover, the soil ingestion estimates reported in the aforementioned studies are highly variable. Much of this variability is a result of sampling and analytical uncertainty in addition to the lack of a one-to-one correspondence between tracer levels measured in food items and tracer levels measured in feces (i.e., transit time misalignment), source error, and tracer uptake in the gastrointestinal tract. Therefore, the first phase of the research conducted for this thesis was directed at assessing the accuracy, precision and utility of tracer methods as they would apply to soil ingestion assessment of a population living in a rural and wilderness area.

Soil ingestion studies of populations inhabiting rural or wilderness areas present many challenges. For example, communities in rural and wilderness area are small and recruiting sufficiently large numbers subjects to participate in a cohort study of soil ingestion is difficult, with an attendant reduction in the power of the study. In addition, wilderness communities are often located a considerable distance from laboratory facilities, thus creating logistical challenges for sample collection, shipment, preservation and storage. It was also recognized that soil ingestion studies require a high degree of commitment on the part of study subjects and participation would likely diminish if study durations are lengthy. In contrast, previous studies of children had the advantage of parental oversight and/or controlled sampling conditions (e.g., soil sampling limited to the backyards of homes and excreta collected from diapers). The area and environmental conditions wherein soil could be ingested by people following a traditional wilderness lifestyle is likely to be large and

diverse. For example, a person could be fishing in one area, then travel tens of kilometres over unpaved roads to gather traditional foods and medicines in another area. Each activity represents a different potential for soil ingestion, and in possible contact with different surficial geology and tracer concentrations in soil. All of these factors could increase the variability of soil ingestion estimates determined using mass balance methods.

Naturally occurring primordial radionuclides of the ^{238}U and ^{232}Th decay series were identified as potential alternatives to elemental tracers for use in future mass balance soil ingestion studies with the view of improving the accuracy, precision and utility for ingestion assessments in rural and wilderness areas. These radionuclides were considered because they are ubiquitous in the environment at relatively constant concentrations, many of the daughter isotopes with both decay series are not readily absorbed in the gastrointestinal tract (GI), and they are amenable to non-destructive, simple measurement by gamma spectrometry. A Monte Carlo model was developed to simulate the variability and uncertainty associated with the collection and analysis of samples using a radionuclide tracer (^{226}Ra, as measured by the gamma spectrometric analysis of ^{214}Pb) to calculate soil ingestion. The model simulation showed that, based on sampling and analytical uncertainty alone, approximately 225 subject days would be required to detect a difference of 20 mg d^{-1} in soil ingestion (i.e., the soil ingestion rate for adults currently recommended by Health Canada). Given that the anticipated difficulties posed by community size and logistical constraints associated with evaluating traditional activities in a rural or wilderness setting would limit the duration and number of subjects participating in a soil ingestion study, it was anticipated that only relatively high soil ingestion rates could be reliably detected. Thus, it was concluded that studies of traditional lifestyles and land-use practices in a rural and wilderness areas should be focussed on the members of the community that are most likely to experience high levels of exposure, and moreover, assess specific activities that would increase the likelihood of contact with soil and fugitive dusts.

Methods were developed or modified to measure isotopes of the ^{238}U and ^{232}Th decay series by gamma spectrometry, and the accuracy and precision of gamma spectrometric analysis of the daughter isotopes were determined for various sample matrices. It was found that the ^{214}Pb of the ^{238}U decay series and ^{212}Pb of the ^{232}Th decay series, as determined by multiple

analyses of a reference standard sample, could be accurately and precisely measured with gamma spectrometry with coefficients of variability (CV) ranging between 3 and 8%. However, multiple analyses of elemental tracers (i.e., Al, Ba, Ce, La, Mn, Th, Si, Ti, U, Y and Zr) in one sample were more precise than measurements isotope tracers by gamma spectrometry, with CV values ranging between 1 and 5%. Specifically, the CV values for Al and Si, considered by other researchers to be very reliable mass balance tracers, were observed to be 2 and 1%, respectively. The combined ashing and high compaction of samples in preparation for gamma spectrometry was found to be the best method to reduce the detection limits in fecal samples, resulting in an approximately 8-fold concentration of fecal samples, and a 20-fold concentration of fish samples. There were no statistically significant differences in the gamma spectrometric analysis of samples prepared by ashing or compaction relative to samples with no pre-treatment. However, even after pre-treatment by ashing and compaction, the detection limits of the gamma spectrometer precluded reliable measurement of ^{214}Pb and ^{212}Pb in food samples. A procedure to extract ^{214}Pb and ^{212}Pb was developed in an attempt to detect these tracers at low levels in food; however, the observed recoveries were poor, and the level of effort required was deemed too high, and further development of the extraction procedure was abandoned. A procedure to increase the volume of sample being analysed by gamma spectrometry was also developed using Marinelli Beakers. A conversion factor to compensate for the loss of detector efficiency resulting from the change in the geometry of the sample in the spectrometer was developed by measuring the reference standard in the Marinelli Beaker, and comparing measured values with the reference values. A method was also developed to pre-concentrate water samples in a rotary evaporator, and the method validated against a reference standard. It was observed that multiple analyses of water samples spiked with a ^{226}Ra standard, and concentrated by a factor of 500 yielded results that were within <6% of the reference values. The measurement of tracers in various soil particle size fractions was also examined, and it was observed that there were statistically significant differences in isotope and elemental tracer concentrations for deceasing particle size fractions (i.e., ≥100 μm <250 μm, >63 μm ≥100 μm, and <63 μm). Enrichments in the order of 50% were observed for the isotope tracers and most of the element tracers in the smallest soil faction (<63 μm). Conversely, Si was observed to be depleted by ~25% in this fraction. Given that soil inadvertently ingested is generally <63 μm,

it was concluded that tracer concentrations from this fraction of soil should be used to calculate soil ingestion in future mass balance tracer studies.

The mass balance tracer methods using isotope tracers were validated in a pilot study involving a canine subject fed a known amount of tracer on a daily basis. The results of the study showed that the mean ^{214}Pb and ^{212}Pb activities measured in fecal samples were greater than what was contained in the soil inoculant ingested by the canine subject over the duration of the study, suggesting that the tracers were not being significantly absorbed in the GI tract. The mean daily soil ingestion rates, calculated after subtracting the contribution of tracers in the soil inoculant, were observed to be 3.9 g d^{-1} (standard deviation 3.5 g d^{-1}) using the isotope tracers, and 1.5 g d^{-1} (standard deviation 9.6 g d^{-1}) using the element tracers. However, this difference was not statistically significant. Further, there were no statistically significant differences between estimates calculated with ^{214}Pb and ^{212}Pb, suggesting that both tracers are behaving similarly as mass balance tracers.

The differences in the ^{226}Ra (as measured by ^{214}Pb) to ^{228}Th (as measured by ^{212}Pb) ratios measured in soil, food, and fecal samples obtained from the canine pilot study were used to develop a novel method to measure soil ingestion using isotopic mixing models (the Isotope Ratio Method). No statistically significant difference in the mean soil ingestion rate calculated using ^{212}Pb and the Isotope Ratio Method was observed. However, the Isotope Ratio Method was observed to positively bias the soil ingestion estimates by approximately 50%. As such, it was concluded that this method would be better suited for use as a confirmatory check of mass balance estimates rather than replacing them as the soil ingestion estimating method of choice.

The mass balance methods using isotope tracers were adapted to calculate sediment ingestion in a benthivorous fish, the Shorthead Redhorse Sucker (*Moxostoma macrolepidotum*). Several qualitative assessments have reported substantial sediment ingestion by benthivorous fish; however, no known quantitative mass balance sediment ingestion studies in fish have been published to date. Given the potential for hydrophobic organic contaminants to accumulate in aquatic sediments and enter aquatic food webs, a method to quantify sediment ingestion in wildlife species such as fish is warranted. Moreover, tools to quantify exposure

of wildlife to contaminated soils or sediments are also warranted considering the importance of fish and wildlife in the diets of Aboriginal people. The study found that the Shorthead Redhorse Suckers ingested considerable quantities of sediment, and sediment constituted approximately 46% of the contents of their gut. These results were compared to results derived from a method developed to calculate soil ingestion in wildlife based on the amount of acid insoluble residues in scat. No statistically significant difference was observed in the sediment ingestion estimates calculated using the two methods.

The next phase of the research involved a pilot soil ingestion study of a population following a traditional lifestyle in a rural or wilderness area. The selected subject community is located in the Nemiah Valley British Columbia, and an agreement was established with the Xeni Gwet'in First Nation Government to conduct a soil ingestion study in their community. Before initiating the study, an ethno-cultural survey of community members was completed to examine the types and extent of traditional activities. The survey confirmed that community members were engaged in activities typical of traditional or subsistence lifestyles, and as such, would be presumably susceptible to high rates of inadvertent soil ingestion. Further, the survey identified the activities practiced, and the traditional food items consumed that could be included in a soil ingestion study. The survey concluded that a significant portion of the Xeni Gwet'in practice a traditional lifestyle similar to the subsistence lifestyles of other indigenous communities, where soil exposure scenarios in the order of hundreds of mg d^{-1} have been proposed. Moreover, the survey results confirmed that a traditional lifestyle was important to the well-being of the community, and loss of traditional food sources due to contamination of wildlife, ingestion of contaminated soil from gathering or preparation of food, would negatively impact many community members. A preliminary assessment of traditional foods was also completed, and it was concluded that some traditional foods, specifically roots, may have substantial amounts of soil adhering to them.

A soil ingestion pilot study following 7 subjects over a 3-week period was conducted in the Nemiah Valley, British Columbia in August 2010. The study subjects participated in fishing, hunting and camping activities that were considered to result in moderate contact with soil. The mean soil ingestion rate calculated using the daily mean values of the 4 most reliable

tracers, based on the lowest food to soil (F/S) ratio, was observed to be approximately 74 mg d^{-1} (standard deviation ~91 mg d^{-1}), and 42 mg d-1 (standard deviation ~74 mg d-1) based on the combined estimates calculated with the Al and Si tracers. These mean values are significantly greater than those currently recommended for adults by regulatory agencies, which range from 20 mg d^{-1} to 100 mg d^{-1}. Further, the median values using the 4 most reliable tracers, Al, or Si were observed to be higher than those reported in most of the previous studies of adults. Moreover, the 90^{th} percentile of the soil ingestion distribution is in the order of 100 to 200 mg d^{-1}, which is much higher than the current regulatory guidelines for adults. Thus, the results from this study supports the hypothesis that members of a community living in rural and wilderness areas that practice a traditional lifestyle likely experience higher soil ingestion rates than adults living in suburban/urban environments. However, these estimates are much lower than those envisaged in qualitative assessments that proposed soil ingestion rates in the hundreds of mg d^{-1} for people following traditional subsistence lifestyles. It was further observed that the study design, involving a group of subjects living under the same environmental conditions and consuming the same array of food items for the duration of the study, reduced the variability of tracer intake in food, and hence reduced the variability of the soil ingestion estimates. Al and Si were found to be the most reliable tracers used in this study, based on their low F/S ratios, and the low variance of the soil ingestion rate estimate distributions. The low variance observed in these distributions confirms the utility of these elemental tracers in mass balance studies of soil ingestion.

Isotopes of the ^{238}U and ^{232}Th decay series were deemed not to be reliable as mass balance tracers for soil ingestion studies of human populations. The isotopic tracers used (^{226}Ra measured by ^{214}Pb, and ^{228}Th measured by ^{212}Pb) were found to have prohibitively high F/S ratios, and were excluded from the soil ingestion calculations. Moreover, the levels of ^{214}Pb and ^{212}Pb in food samples were frequently below the detection limits of the gamma spectrometer, even after ashing and compaction in Marinelli Beakers. Based on this pilot study, it was concluded that the isotopic tracers evaluated are not suitable for use in mass balance studies of human populations where soil ingestion rates are low and the accurate and precise quantification contribution of tracers in food is vital to the reliability of the estimate. However, radionuclide tracers are still a viable option for estimating soil ingestion in wildlife since tracers in food are derived from plants and animal in the area, and intake of tracers

accumulated in plant and animal food items can be determined from the database of soil to biota, sediment transfer factors, and concentration ratios developed by the nuclear industry. Furthermore, differences in $^{212}Pb/^{214}Pb$ ratios in feces, food, and soil may, with additional work, provide values for a viable independent method to confirm soil ingestion estimates from future mass balance tracer studies.

Finally, the mass balance estimating method and the tracers used to measure soil ingestion, were evaluated in a Monte Carlo soil ingestion model, adapted to simulate the sampling and analytical variability observed in the pilot human study, modified to account for uncertainty related to transit time misalignment. The minimum detectable quantity calculated by the model using sampling and analytical variability for Al alone (i.e., not including transit time uncertainty) was 7 mg d^{-1}, compared to a measured soil ingestion rate of approximately 37 mg d^{-1} (standard deviation ~52 mg d^{-1}). However, the minimum detectable quantity calculated by the model using sampling and analytical variability for Al and accounting for transit time uncertainty, was 24 mg d^{-1}. This finding emphasizes the need to maintain, to the extent possible, consistently low levels of tracer intake via food.

8.2 Scientific contributions of the research and future directions

Soil ingestion rate is as important in HHRAs for determining soil quality guidelines and cleanup criteria for contaminated sites as contaminant toxicity or bioavailability. Yet, the last reliable quantitative soil ingestion study was conducted in the mid 1990's, and there remains considerable uncertainty in the soil ingestion estimates developed in these studies and their applicability to populations living in close contact with their environmental surroundings, or practicing lifestyles that would enhance soil ingestion. Further, an understanding of soil ingestion in wildlife species, such as fish, to support ecological risk assessment (ERA) is underdeveloped, and the provision of new tools to estimate soil and sediment ingestion in wildlife species is certainly warranted. Thus, the research in this thesis has made a substantive contribution to our understanding regarding the ability to use radionuclide and elemental tracers to assess soil or sediment ingestion, and moreover the level of soil ingestion that might be expected for an Aboriginal population practising a subsistence lifestyles in a remote, wilderness area. Moreover, the contributions dramatically enhance the quantitative understanding of soil exposure via inadvertent ingestion, a metric that has been called the

weakest and most problematic metric employed in HHRAs of contaminated sites. Hopefully, this contribution will rekindle an interest in enhancing the accuracy and precision of soil ingestion studies, thus strengthening the scientific foundations of HHRAs and ERAs of contaminated sites.

The data from this research will be useful for regulators developing cleanup guidelines for contaminated sites in rural or wilderness areas. The soil ingestion study represents the first quantitative soil ingestion study of a Canadian population, the first of a population following a traditional aboriginal lifestyle, and one of only a few studies of adults. Further, the ethno-cultural survey of the subject community reinforces the need for future soil ingestion studies of people following traditional subsistence lifestyles, such as indigenous and Aboriginal peoples of the Americas, and also reinforces the need to not only to assess soil ingestion related to traditional activities, but also the exposure of wildlife consumed as traditional foods. To this end, the quantification of sediment ingestion by fish represents a new tool that can be used to quantify the exposure of wildlife to particle-bound contaminants in aquatic systems.

The research also developed several improvements to the mass balance methods used to determine soil ingestion. Notable improvements include:

a) Measurements of tracer concentrations in the smallest particle size fractions (i.e., <63 μm). This modification eliminates a positive bias in the order of approximately 50% for most tracers (i.e., isotopic tracers, element tracers except Si), and a negative bias of approximately 25% for Si.

b) A simple, but effective method to pre-concentrate water samples for analysis by gamma spectrometry.

c) A novel method to estimate soil ingestion based on differences in ^{238}U and ^{232}Th series isotopes. The method could serve to confirm the soil ingestion results from mass balance studies using elemental tracers.

d) Focussing of small soil ingestion studies on specific high soil ingestion activities representative of the most exposed members of a population, as an alternative to large cohort studies that assess soil ingestion in the population at large.

e) Control of tracer intake via food by eliminating processed foods with additives that contain relatively large amounts of tracer elements. This reduces the variability of soil ingestion estimates.

f) A method to estimate the minimum detection limit of the mass balance soil ingestion approach.

The results of the Nemiah Valley soil ingestion study are still preliminary, and the soil ingestion estimates are indicative of levels that should be expected for subjects involved in activities that likely result in a moderate level of contact with soil. Future studies should also assess high contact activities, such as root digging and ranching, which would be expected to generate large quantities of dust and/or direct contact with soil. Future studies should also include more rigorous assessments of direct soil ingestion via consumption of soil particles adhered to traditional food items, and the indirect exposure to contaminants in traditional foods resulting from the ingestion of contaminated soil consumed by fish and wildlife.

The work described in this thesis involved substantial contributions from collaborators and several of the chapters provided in this thesis have been published or have been submitted for publication. The contributions of collaborators to the research described herein and to papers published or earmarked for publication are detailed in Appendix J.

Appendix A

Radium Extraction/Pre-concentration Protocol

A method used to pre-concentrate samples was developed to selectively extract either or both ^{214}Pb and ^{212}Pb and/or their precursors from large volume samples prior to measurement with gamma spectrometry. The method developed is summarized in Figure A1. The purpose of the method was to easily measure the radionuclide tracers by gamma spectrometry in samples where the ^{214}Pb and ^{212}Pb concentrations are anticipated to be very low (e.g., food samples). In order to achieve volume reduction, radium was co-precipitated out of the supernatant via barium sulphate formation. Radium ions behave similarly to barium ions, and any radium in solution should precipitate out when barium does, forming $Ba(Ra)SO_4(s)$ (Decaillon et. al. 2004). Based on equilibrium calculations made in PHREEQ (United Stated Geological Survey software), ^{228}Ra, ^{226}Ra, and ^{224}Ra will be precipitated as a sulphate. Further thoranite (ThO_2) will be precipitated. Thus, the parent nuclides to measure both ^{214}Pb and ^{212}Pb will be precipitated and available for measurement with gamma spectrometry. The precipitation procedure used in this study was adapted from methods used to isolate radium for alpha spectrometry (Rodriguez-Alvarez, 1995). However, the method does not require purification steps to remove U and Th isotopes because these isotopes will not interfere with the gamma spectrometric analysis of ^{214}Pb and ^{212}Pb.

Fish samples were chopped then ground, spiked (if required) with a reference soil or liquid, freeze-dried, and ground to a powder in a mortar and pestle before digestion. For these method development samples, the size of fish samples digested were limited to approximately 250 g dry weight, representing a potential concentration factor of only 20-30. However, it is assumed that by increasing the mass of sample digested, concentration factors of ~50 can be attained using this method.

Recoveries of ^{214}Pb and ^{212}Pb, when corrected for tracers measured in un-spiked samples of fish, ranged from 16-78%. The poor recoveries may be due to a large proportion of the isotopes of interest being held within the mineral matrix rather than sorbed to the surface of the reference soil, and therefore unavailable for dissolution in HCl alone. Moreover, some

samples varied substantially between repeated analyses of the same sample. This latter variability is attributed to analytical variability near the lower detection limit of the gamma spectrometer for these samples. Variability between samples may be the result of differential application of the extraction method. Specifically, temperature control problems were encountered during the digestion of ashed samples using a water bath and hot plate, and all samples may not have had an equivalent and/or sufficient duration for digestion at the desired temperature. Isotope recoveries may also be improved by increasing the number of washes of the centrifuged digested sample pellet from 3 to 4.

The procedure was observed to be time intensive, requiring several extraction steps in addition to the preparation work for gamma spectrometry. Considerable development work would be required to improve the method sufficiently for use in mass balance tracer methods, and other approaches may be more suitable for analysis of these samples. Given that the objective of the procedure was to easily and reliably pre-concentrate analytes in food samples, this extraction method was abandoned.

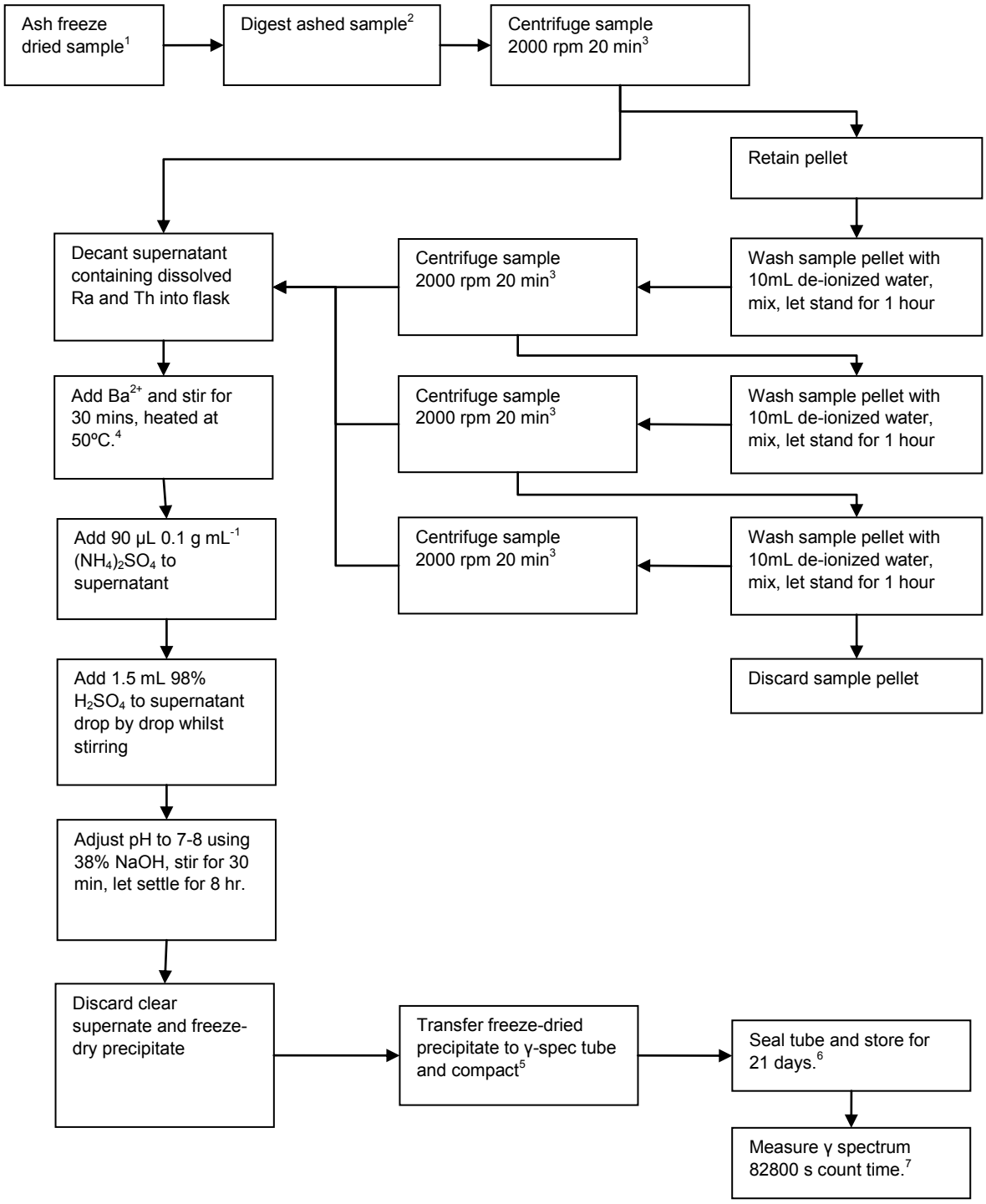


Figure A1: Flow diagram for digestion and co-precipitation of radium extraction method to pre-concentrate solid samples for gamma spectrometry

[1]Ashed in muffle furnace ramped to 550°C (ramped up over 7 hours, hold at 550°C for 6 hours).
[2]Add 10mL HCl per 5 g sample; (Fisher omnitrace 36.5-38%), let stand 1 hr. then cover and heat overnight in waterbath at max 90°C.
[3]Swing bucket centrifuge Corning #430921 50mL polypropylene centrifuge tube (falcon tube).
[4]Add 0.8 mL of $BaCl_2$ stock solution (1516 mg $BaCl_2$ dissolved in 100 mL de-ionized? water)
[5]Sarstedt #55.523 8 mL polypropylene centrifuge tube filled to approximately 75% height.
[6]Precipitate isolated in tube with Teflon septum then sealed with ~1cm epoxy resin/hardener.
[7]Ortec DSPEC high purity germanium well detector.

Appendix B

Supporting documentation provided to the subject community

MEMORANDUM OF AGREEMENT TEMPLATE: RESEARCH PROTOCOL

Between:

The Participant Community

And:

Principal Investigator,

University of Ottawa,

30 Marie Curie Ave.

Ottawa, Ontario K1N 6N5

WHEREAS:

A. **The student**, under the supervision of **the Principal Investigator and the University of Ottawa**, will carry out fieldwork to quantify soil ingestion rates in people following traditional lifestyles, in the Xeni Gwet'in Caretaker Area within the Chilcotin District, Cariboo Region, BC, Canada (Summary Proposal, attached as Schedule "A" and Plain Language Summary attached as Schedule "B");

B. The **Participant Community** is within that part of the traditional territory of the Tsilhqot'in for which the Xeni Gwet'in are caretakers;

This Research Protocol Agreement (the "Agreement") records the mutual understandings of the Parties, as of the day and year recorded below.

1. The Xeni Gwet'in agree that **the student** and any other researchers he uses (the "Researchers"), under the supervision of the **Principal Investigator and the University of Ottawa,** may undertake the work set out in the attached Summary Proposal (Schedule A).

Communication Protocol

2. The Researcher will comply with the research intent, methodology and timeframe as set out in the attached Summary Proposal (Schedule A).

3. After the collection and analysis of data, a presentation on the research may be made to the Xeni Gwet'in and their community, should the Xeni Gwet'in wish it, at a location chosen by the Xeni Gwet'in.

4. The information and data gained about wild horses and any other plant and wildlife species will be made available to the Xeni Gwet'in for review and approval prior to public distribution.

5. A copy of the final thesis and a summary report of data will be provided to the Xeni Gwet'in for review and approval prior to public distribution.

Research Conduct and Knowledge

6. All research activities associated with this study, including the handling, storage and publication of data, shall be conducted according to the **University of Ottawa** Research Ethics Approval and guidelines.

7. The Researcher shall keep the identity of individual participants and interviewees anonymous in all published documents and public research presentations, except where permission to identify an individual is explicitly granted by that individual, either in writing or by verbal consent on an audio recording.

8. Raw interview data shall be kept confidential by the Researchers. Interview transcripts will be sent to interviewees for their review and approval, with the opportunity for interviewees to clarify or change wording, to ensure that their intended meaning has been communicated and correctly interpreted.

9. Interview recordings will be kept in confidence by the Researcher for seven years after the research has been conducted. After that time, the audio recordings and transcripts will be provided to the Xeni Gwet'in First Nation, should they wish it.

Publication and Research Results

10. It is understood and recognized that the people of the Xeni Gwet'in First Nation and the Tsilhqot'in (Nation) are the owners and keepers of their traditional knowledge about the wild horses, other wildlife, plants, and all other aspects of their land use and management and cultural practices. The Researcher will explicitly recognize First Nations ownership of this knowledge in all publications of research results.

11. It is understood by all parties that any interpretations, analysis, and opinions regarding research results and data expressed in the thesis and other published documents reflect views held by the Researcher.

12. The Xeni Gwet'in understand that data gathered as part of this study may be summarized in report form by the Researcher, for use in the thesis, publications, and presentations for

academic and professional purposes. Direct narrative quotations from interviews may be used after interviewees have reviewed and approved the interview transcripts.

13. The Xeni Gwet'in will be notified and consultation will be undertaken regarding any popular media (i.e. television, radio, or journalistic print publication) exposure that occurs with respect to the study.

14. It is understood by all parties that the research results, in the form of a doctoral thesis, academic publications, and public presentations, will be publicly available and accessible in accordance with university practices.

15. This Agreement is intended to support the efforts of the Xeni Gwet'in and the Researcher in their common objective of understanding the wild horses, plants and wildlife and conserving habitat in the Xeni Gwet'in Caretaker area; and

    a. Nothing in this Agreement shall abrogate or derogate from any aboriginal title or aboriginal rights of the Xeni Gwet'in or Tsilhqot'in people;

    b. Nothing in this Agreement shall be taken to mean that the Xeni Gwet'in First Nation or the Tsilhqot'in Nation has in any way abandoned or given up its title and rights.

16. This Agreement may be signed in counterpart.

The parties have signed below to witness entering into this Agreement,

this _____ day of _____, 2009.

Chief **Witnessed and co-signed by:**
for the Participant Community

Principal Investigator **Witnessed and co-signed by:**
Professor, University of Ottawa

SCHEDULE "A" - SUMMARY PROPOSAL

Purpose of the Research Project

The soil ingestion rate is a key component in Human Health Risk Assessment (HHRA) and the development of soil quality guidelines to guide the remediation of contaminated sites in Canada and internationally. Further, knowledge of soil ingestion rates and exposure to soil is required to determine the potential environmental effects of proposed projects assessed pursuant to the *Canadian Environmental Assessment Act* (CEAA).

However, the relatively few quantitative studies completed to date have focused on assessing soil ingestion in children living in urban/suburban areas in the United States as a basis for developing ingestion rates for the population at large. A weakness of these studies is that they do not account for the degree of urbanization, social/economic status, regional and ethnic variation in behaviors, land cover (e.g., grass) or seasonality (Calabrese and Stanek, 1994). Moreover, although initial qualitative soil exposure assessments suggest that people following traditional lifestyles may ingest considerably more soil than people living in an urban/suburban environment, there are no published quantitative assessments of soil ingestion of traditional lifestyles. Given this, it is not clear if current regulatory recommended soil ingestion rates for use in HHRA are adequately protective of people following traditional lifestyles.

The purpose of the research is to quantify soil ingestion rates in people following traditional lifestyles to determine if soil ingestion estimates currently used in risk assessments of contaminated sites are adequately protective. The proposed research will make several important contributions to the science underpinning soil exposure estimates used in HHRA and the methods used in studies to estimate soil ingestion rates in people.

First, the research will provide quantitative soil ingestion estimates for people following traditional lifestyles that currently do not exist and thus improve HHRA of northern contaminated sites and/or environmental assessment of projects proposed in areas where traditional lifestyles are practiced.

Second, the research will provide the means to measure the amount of local soil adhering to foods and quantitative estimates of the contribution of preservation, preparation and consumption of traditional foods to overall soil ingestion. Quantification of ingestion of soils adhering to traditional foods will improve the estimation of dietary exposure to contaminants in HHRA and provide insight to enable the development appropriate mitigation strategies to reduce contaminant exposure to people consuming traditionally preserved and prepared foods.

Research Objectives

The objective of proposed research is to determine if participating in traditional activities and consuming traditional foods collected, preserved and prepared will result in higher contaminant exposure from soil ingestion than the majority of the population living in urban/suburban environments.

The proposed research has been separated into two parts and sub-hypotheses: one part to assess soil ingestion related to participating in traditional activities; and a second part to assess soil ingestion related to soils adhering to traditionally collected, preserved and prepared food.

To assess soil exposure related to traditional activities, individual studies will be directed at comparing the rate of soil ingestion estimated for specific high ingestion rate activities identified in qualitative assessments of traditional lifestyles, with chronic ingestion rates typical of people living in an urban/suburban environment. These studies will be developed in accordance with the following generic hypothesis:

> *"people participating in traditional activity X (e.g., rodeos, root gathering days) will ingest more soil than would normally be ingested based on regulatory soil ingestion rates recommended for risk assessment".*

If the qualitative soil ingestion exposure estimates of traditional activities are true, then the minimum detectable quantity required to distinguish between high ingestion rate activities from what would normally be expected will be in the order of hundreds of milligrams rather than in tens of milligrams. Accordingly, study designs with fewer subjects and/or focused on specific short-term high ingestion rate activities can be used that will have sufficient power to evaluate differences in soil ingestion rate statistically.

Exposure related to the consumption of soil adhering to traditional food items collected and gathered locally, and preserved, prepared and consumed in a traditional manner, will also be assessed. Studies to assess exposure to soils adhering to traditional food will be developed in accordance with the following generic hypothesis:

> *"people consuming traditional food items collected and gathered locally, and preserved, prepared and consumed in a traditional manner ingest more local soil than people consuming store-bought food that is prepared in a manner typical of urban/suburban lifestyles".*

Methodology

Quantifying Soil Adhering to Food

This work will provide an evaluation of the extent that soil adheres to traditionally preserved, prepared and consumed foods. Fish are a staple food item of many people following

traditional northern lifestyles in Canada. Traditional preservation techniques for fish include drying and smoking outdoors and are vulnerable to contamination with airborne dust and soils. As such, fish has been selected as the food item for study.

Samples of fresh (i.e., untreated) and preserved (i.e., air dried outdoors) fish will be purchased from local sources identified through the Xeni Gwet'in First Nations Government. It is anticipated that the fish obtained will be fresh and dried sockeye salmon from the Chilko River west of Williams Lake British Columbia. Although the research will focus on assessing fish samples, other traditional food items (e.g., Caribou) will be assessed if they are readily available. Local soil samples (in the vicinity of where traditional foods are preserved or prepared) will also be obtained. Samples will be ground in a commercial grade meat processor, ashed and the isotopes of interest extracted chemically, transferred to 8 ml centrifuge tubes, sealed with epoxy and stored for at least 21 days to allow for the ^{214}Pb to reach secular equilibrium and then analyzed in the University of Ottawa Ortec DSpec gamma-spectrometer. Soil adhesion will be estimated in traditionally prepared and preserved foods by quantifying the ^{214}Pb and ^{212}Pb tracers (naturally found in all soils) in the food items and measuring the concentration of these tracers in local soils. The tracer levels in preserved and prepared foods will be compared to fresh samples to determine differences in the amount of soil adhering to food as a result of traditional preservation and preparation techniques. This data will then be used to quantify annual soil ingestion rates based on a survey of traditional food consumption rates for the community.

Quantifying Soil Ingestion from Traditional Activities

The research will ultimately result in a study(s) of soil ingestion of people following traditional lifestyles using a mass balance estimating approach. The design of these studies (e.g., activities, duration and number of subjects) will require consultations with Xeni Gwet'in First Nations Government from which volunteers for the study will be obtained. Extensive pre-study planning and discussions to obtain research ethics review and applicable approvals will also be required. Study subjects will be compensated at a pre-agreed to rate for their participation in the research.

At this time the work envisages includes the following:

- Identification of a representative traditional activity (e.g., rodeo participation, hunting or fishing, community gatherings) conducted over a 3-4 day period,
- Selection of 3-4 subjects that will participate in the study,
- Preparation of pre-weighed and analyzed food portions for the study team,
- Recording all food and beverages consumed over the duration of the study,
- Collection of fecal samples for the duration of the study,
- Collection of soil samples in the area where the activities were conducted.

All food will be provided to the study subjects for the duration of the study. Personal commodes and special sample containers will be provided to all participants to ensure privacy and confidentiality in the provision of fecal samples. Fecal samples will either be flash frozen or ashed immediately after being submitted, then stored in an appropriate or secure manner.

Ashed samples will be transferred to 8 ml centrifuge tubes, sealed with epoxy and stored for at least 21 days to allow for the ^{214}Pb to reach secular equilibrium and then analyzed by gamma-spectrometry at the University of Ottawa. Soil ingestion per day will be calculated quantifying the ^{214}Pb and ^{212}Pb tracers (naturally found in all soils) in the fecal samples and measuring the concentration of these tracers in local soils. Soil ingestion rates will be adjusted to exclude the contribution of tracers measured in fecal samples that would have originated from food.

This data will then be used to quantify annual soil ingestion rates resulting from participating in traditional activities based on a survey of traditional activities for the community and similar studies published in the literature.

Research Outputs

The research will provide a set of data quantifying soil ingestion in people following traditional lifestyles. The results of the study will first be presented to the Xeni Gwet'in community in a manner agreed to with the Xeni Gwet'in First Nations Government (e.g., presentation to community elders, council, poster preparation etc.). The data will also be published in scientific journals, conference proceedings and presentations. Confidentiality of the study subjects will be strictly guarded and all data relating subjects to the data will be destroyed after 2 years.

Agreements and Protocols

Final study design and protocols will be agreed to in advance with the Xeni Gwet'in First Nations Government. Approval of the study design and protocols will also require approval by the University of Ottawa Research Ethics Board prior to proceeding with the research studies planned.

Timeframe

The research studies are tentatively planned for the summer and fall of 2010. However, the actual timing of the research would be determined after discussions with the Xeni Gwet'in First Nations Government.

Cultural Employment Opportunity (Land Keepers Program)

No cultural employment opportunities are planned.

Not only are the traditional or subsistence lifestyles practiced by Aboriginal peoples in North America important to the economic well-being of Aboriginal communities, they also provide the basis for Aboriginal cultural existence and survival. The traditional and subsistence lifestyles followed by Aboriginal peoples are an inseparable part of Aboriginal cultural and spiritual identity and are vital to the maintenance of individual and community health and well-being. For example, the harvesting, sharing and preparation of traditional foods embodies Aboriginal cultural values and reflects a spiritual relationship to the land and its resources.

A traditional or subsistence lifestyle is lived close to the land and relies on land use practices, such as agriculture, hunting, and gathering that require a high level of contact with soil, which may be inadvertently ingested. Traditional activities are often conducted outdoors over larger geographical areas in environmental settings that may further enhance the likelihood of soil intake.

Many contaminated sites requiring clean-up, such as abandoned mine tailings, smelting operations and radar sites, are located in rural and wilderness regions potentially used by people following traditional hunting and gathering lifestyles. The cleanup levels prescribed for these contaminated sites are based on an assessment of both the health risk posed by the contaminants found at the site and the potential for people to be exposed to the contaminants. An important route by which people are exposed to contaminants is through the ingestion of soil. Regulators use recommended soil ingestion rates provided by Health Canada, the United States Environmental Protection Agency, and other agencies to develop cleanup criteria for contaminated sites. If a low soil ingestion rate is assumed in the assessment of a contaminated site, then the cleanup criteria developed for that site will allow higher levels of contamination than if a higher soil ingestion rate is assumed.

More importantly, many projects planned for rural and wilderness areas have the potential to contaminate soils. For example, mines and smelters produce tailings and airborne emissions that have the potential to release contaminants in the environment that will ultimately end up in local soil and water. Projects that may impact the environment and require involvement of a federal agency must be assessed under the *Canadian Environmental Assessment Act* (CEAA). CEAA states that proposed projects must not have significant adverse effects on "the current use of lands and resources for traditional purposes by aboriginal persons". Projects approved in areas where traditional hunting and gathering lifestyles are practiced must ensure that soils are not contaminated as to pose a health risk or that would constrain First Nations peoples to participate in traditional activities or consume traditional foods.

The soil ingestion rates recommended by regulators in Canada and the United States to assess the health risks posed by contaminated soil are based on soil ingestion studies of people

living in urban/suburban environments and are not necessarily representative of people living a traditional and/or subsistence lifestyle. In fact, some reports suggest that the amount of soil that would be inadvertently ingested following traditional or subsistence lifestyles may be many times greater than what has been measured in the soil ingestion studies conducted to date.

Proposed projects requiring environmental assessment under CEAA must demonstrate that their activities will not interfere with the use of lands for traditional purposes. It is important that the soil ingestion rates used in these assessments are representative of the rates experienced by people following traditional lifestyles and not soil ingestion rates typical of people living in suburban or urban areas. For areas where soil contamination already exists, soil ingestion studies that more accurately reflect rates expected from participating in traditional activities could support a case to for more stringent clean up requirements for these contaminated sites in areas where these traditional activities occur.

The purpose of our research is to determine if soil ingestion estimates currently used in risk assessments of contaminated sites are adequately protective of people following traditional or subsistence lifestyles. The long-term objective is to conduct a study of people engaging in traditional activities in rural or wilderness areas to determine if they inadvertently ingest larger amounts of soil than what has been measured in people living in urban or suburban environments.

Methods specifically designed to estimate soil ingestion of people following traditional lifestyles through the measurement of tracers normally found in soils.

Our first objective is to quantify how much soil adheres to traditionally preserved and prepared foods. For example, tracer levels measured in traditional preserved and prepared fish (e.g., dried or smoked fish) will be compared with tracer levels measured in fresh fish (e.g., freshly caught) and store bought fish to determine how much soil adheres to the food as a result of traditional preservation and preparation methods..

Our second objective is to quantify soil ingestion that may result from participating in traditional activities. This study include the participation of a few community members for several days in a traditional activity, during which soil ingestion will be determined by measuring tracers in the stool of study participants.

All studies would not be started unless consultation with community representatives and/or elders has been completed and their support for the objectives and scope of the research work has been obtained.

Participant Consent Form Template

Estimating soil ingestion rates using naturally-occurring mass balance tracers

The Student and the Principal Investigator*, Department of Biology, Faculty of Science, (613) 562-5800)*

Invitation to Participate: Volunteers will be invited to participate in the abovementioned research study conducted by the Student and the Principal Investigator; six volunteers for the soil ingestion study and 15 volunteers for the ethno-cultural survey.

Purpose of the Study: The purpose of the study is to determine how much soil is ingested by people following traditional lifestyles and that live in rural or wilderness areas.

Participation: My participation will consist essentially of providing daily fecal samples for radiochemical analysis. Volunteers participating in the soil ingestion study will be provided food rations during the study (rations will be provided by the researcher).

Risks: No physical or emotional risks are anticipated from this research.

Benefits: My participation in this study will improve soil ingestion rate measurements and contribute to better estimates of soil exposure in areas where soil contamination is a concern.

Confidentiality and anonymity: I have received assurance from the researcher that the information I will share will remain strictly confidential. I understand that the contents will be used only for research purposes and that my confidentiality and anonymity will be protected by removing my name from any publications, and by keeping results securely in the possession of the two investigators.

Conservation of data: The data collected (fecal samples, analytical results, responses to interview questions) will be kept in a secure manner by storing in the offices of the two investigators until publication within 5 years (i.e. until 2015).

Compensation: There will be compensation for the participant of this study that has been negotiated with the Participant Community.

Voluntary Participation: I am under no obligation to participate and if I choose to participate, I can withdraw from the study at any time and/or refuse to answer any questions, without suffering any negative consequences. If I choose to withdraw, all data gathered until the time of withdrawal will be destroyed.

Acceptance: I, (participant), agree to participate in the above research study conducted by the Student, whose research is under the supervision of the Principal Investigator.

If I have any questions about the study, I may contact the researcher or his supervisor.

If I have any questions regarding the ethical conduct of this study, I may contact the Protocol Officer for Ethics in Research, University of Ottawa, Tabaret Hall, 550 Cumberland Street, Room 159, Ottawa, ON K1N 6N5

Tel.: (613) 562-5841

Email: ethics@uottawa.ca

There are two copies of the consent form, one of which is mine to keep.

Participant's signature: Date:

Researcher's signature: Date:

Appendix C

Fecal Sample Preparation Safe Work Protocol (SWP)

Scope:

The objective of this SWP is to prepare human fecal samples collected for soil ingestion study analysis with gamma spectrometry. The individual samples will be contained in 19" X 25" biohazard bags closed with a zip tie (sample bags). Several individual samples will be bagged within a larger biohazards bag closed with a zip tie (secondary containment bag). The larger bags will be contained within a regular plastic camping cooler. The samples should be frozen.

Hazards and Precautions

Safety precautions must be taken in order to guard against the risk of infection from pathogens that may be present in un-sterilized feces. Wear personal protective equipment (PPE) as required by the procedure. Duct tape sleeves closed over gloves. Dispose of gloves, wipes etc. in a regular plastic bag (disposal bag), and dispose of this bag in regular garbage can.

Wash hands with antibacterial soap and rinse well with water after working with these samples. Wipe down all equipment that could have been exposed to samples with an antibacterial soap solution and then wiped down with 70% ethanol.

Follow all existing lab and Emergency Response Procedures as required.

Personal Protection Equipment (PPE) Required:

- Lab coat
- Safety glasses
- Dust mask
- Nitrile gloves and duct tape
- Biohazard disposal

Materials

- Biohazard bags
- Tie wraps
- Plastic disposal bags
- Analytical balance
- Evaporation dishes
- Oven in fume hood
- Crucibles and tongs
- Muffle furnace
- Mortar and pestle
- Falcon tubes
- 8mL centrifuge tubes
- Teflon septa
- Epoxy and epoxy gun or syringe
- Gamma spectrometer

Procedure:

In laboratory

	Initial
1. Unseal outer container (camping cooler) and check for abnormalities (i.e., leaks in containment). If leak observed stop work and obtain guidance.	
2. Transfer secondary containment bag with the individual samples into freezer – if required, unseal outer containment bag to deflate the bag to permit the bag to fit in the freezer.	
3. Leave samples in freezer for at least 24 hours to allow samples to fully freeze.	
4. Transfer samples to fume hood as required.	

In fume hood

5. Remove sample bags from the secondary containment bag and reseal secondary containment with tie wrap. Put empty secondary containment bag into disposal bag when empty.	
6. Weigh each sample bag and record weight and sample number.	
7. Remove tie wrap from sample bag and place sample bag on pre-tared evaporation dish, folding bag over sides to allow moisture to evaporate from sample. Note: be careful when folding bag to avoid having sample exposed outside of evaporation dish.	
8. Weigh each dish with sample; record wet weight and sample number.	

9. Transfer evaporation dish into drying oven.	
10. Dry sample for 3 days at 110°C.	
11. Weigh each dish with sample record dry weight and sample number.	
12. Transfer dry sample to pre-tared large crucibles with the help of paintbrush (this may require the sample to be divided up into smaller chunks (~20g) and record dry weights, crucible and sample numbers.	
13. Wipe down all exposed surfaces (ie. Balance) with 1:10 anti-bacterial soap and water solution, dry with paper towel and then re-wipe with 70% ethanol.	

In laboratory

14. Transfer crucibles to muffle furnace and ash at 550°C using program 4 *Note: always verify that program has not been changed: ramp to 200°C in 5 hrs, ramp to 550°C in 6 hours, dwell for 9hrs, end.*	
15. Remove crucibles, cool and record ash weights, crucible and sample numbers.	
16. Lightly de-aggregate ashed sample with glass pestle and transfer (using paintbrush specific to ashed fecal matter) to pre-tared falcon tubes labeled with sample number.	
17. Weigh falcon tubes and record ashed weight and sample number.	
18. Store ashed fecal sample.	
19. Compact into 8mL centrifuge tube up to 4cm height. Subsample if necessary.	
20. Record weight of sample and height.	
21. Seal with a Teflon septum and ~1mL epoxy.	
22. Record sealing and equilibrium dates on spreadsheet. Allow to reach secular equilibrium over 21 days.	
23. Analyze on gamma spectrometer for 23h when equilibrated (after 21 days).	

Appendix D

Table summarizing the number of food portions recorded for each subject for each meal/day/week of the Nemiah soil ingestion study. The size of each portion is also provided for each food type.

Serving size		1 mL	1 mL	30 g	17 g	88 g	44 g	100 g	110 g	110 g	52 g	36 g	8 g	34 g	20 g	300 g	400 g	125 g	50 g	75 g	125 g	50 g	50 g	10 g	45 g	38 g	50 g
ID	Meal	Water , coffee/tea	5-Alive/ pop	Sandwich bread	Garlic bread	smoked meat - dinner	smoked meat - sandwich	Fish - salmon	roast beef /steak	Whole Ham	eggs	sausage	bacon	ham - sandwich	cheese	spaghetti sauce	pasta	Potato - dinner	Potato - breakfast	sauerkraut	salad	apple/ oranges	plum/ peach	cookie	doughnut	granola bar	pancakes
Week 0			Number of portions consumed																								
F0-0	Bkfst	1000		4									5														
	Lunch			2																0.5		1	2			1	
	Dinner									2																	
	Snack	2000																2			1.8						
F0-1	Bkfst	1000									2																
	Lunch		200	2										3							0.3		2			1	
	Dinner																				1.8						
	Snack	1750																									
F0-2	Bkfst	250									2	5							1		0.3						
	Lunch		200	2										3							0.3		2				
	Dinner															0.7	0.7										
	Snack	1750																									

F0-3	Bkfst	1000		2									2								0.3							
	Lunch			2										3							0.3	1						
	Dinner															0.3	0.3										1	
	Snack																											
G0-0	Bkfst	500		2																								
	Lunch		300						0.8													0.4						
	Dinner	500																			2	2						
	Snack																											
G0-1	Bkfst	750		2											2													
	Lunch		200	2										2	2													
	Dinner	750		3										3	2													
	Snack		200																									
G0-2	Bkfst	750		2							2		5															
	Lunch													2								1						
	Dinner	250	200					0.7	0.4												1							
	Snack		750																									
G0-3	Bkfst	750									3			3					1				1					
	Lunch		600																									
	Dinner								1									0.3										
	Snack		1500																									
Week 1			Number of portions consumed																									
A1-0	Bkfst							1											2					2				
	Lunch	250		2										2	1						0.33							
	Dinner	500	200			2								2				1.5		1								
	Snack		300																						2			
A1-1	Bkfst	500									2	4							1									
	Lunch		200	2			1																			1		

	Dinner	750			5										0.5	1	1				1						
	Snack	250																						8	1		
A1-2	Bkfst	750										3		3										4			3
	Lunch		500	2			1								1								1			1	
	Dinner	250	200		5				1									1.5			1						
	Snack																							5			
B1-0	Bkfst								1																		
	Lunch	500		2			3															1					
	Dinner	500				2												1		1	1						
	Snack		200																						1		
B1-1	Bkfst	500									2	3							1								
	Lunch			2			1								1						0.5	1	1				
	Dinner	250			2										0.5	1	1				1						
	Snack	250																						4	1	1	
B1-2	Bkfst	750										4		2													5
	Lunch		1	2			1								1												
	Dinner				1				1									1			1		1				
	Snack	500																				1				1	
C1-0	Bkfst	500									2		5														
	Lunch		300	2											1							1		4			
	Dinner	250	200			2												1		1	1						
	Snack																								1		
C1-1	Bkfst	250									2	5							1								
	Lunch		400	2			1															1	1			1	
	Dinner	500			5										0.5	1	1										
	Snack	250																						2	1		
C1-2	Bkfst	250										3															3
	Lunch		600	2			1								1								1			1	

	Dinner	500			3				1									3			1							
	Snack																									1		
D1-0	Bkfst	250	300																1									
	Lunch			2							1																	
	Dinner		200			2												1			1							
	Snack																											
D1-1	Bkfst	250									2	3							1									
	Lunch		400	2			1															1				1		
	Dinner		400		4										0.5	1	1				1							
	Snack														1													
D1-2	Bkfst	250										3																2
	Lunch		400	2										2	1							1	1					
	Dinner	250			4				2									1			1			2				
	Snack																											
E1-0	Bkfst	500																										
	Lunch	500		2							2	3							1									
	Dinner	500				2.5												0.5		1	2							
	Snack																								1.5	1		
E1-1	Bkfst	500									2	3							2									
	Lunch		200	2			1																			1		
	Dinner	250			6										0.25	0.5	0.5				2							
	Snack																					1	1	3	1			
E1-2	Bkfst	750										3																3
	Lunch			1			0.5								1								2			1		
	Dinner	250							1									1			1							
	Snack	250	200																					6				
F1-0	Bkfst																											

	Lunch																										
	Dinner																										
	Snack																										
F1-1	Bkfst																										
	Lunch																										
	Dinner																										
	Snack																										
F1-2	Bkfst																										
	Lunch																										
	Dinner																										
	Snack																										
G1-0	Bkfst	500																									
	Lunch	250		1						1.3	2																
	Dinner					2												1		1	1						
	Snack	250																									
G1-1	Bkfst	1000					0.25				2	3							1	1							
	Lunch						1															1				1	
	Dinner	750			2										0.5	1	1										
	Snack		200																					3			
G1-2	Bkfst	750					0.75					3		3													2
	Lunch			2			2								1												
	Dinner	250							1									1			1						
	Snack	250																						4			
Week 2			Number of portions consumed																								
A2-0	Bkfst			2							1				1												
	Lunch			2					0.5																		
	Dinner	500					3											2		1	1						
	Snack																								1		

A2-1	Bkfst	500									2	3							1									
	Lunch		800	2			1																1			1		
	Dinner				5											1	1				1							
	Snack																								1			
A2-2	Bkfst	500											6															3
	Lunch		500	2			1																2	6		1		
	Dinner		200						2									2			1							
	Snack	500																						12				
B2-0	Bkfst							1										1		1				4				
	Lunch			2										3	1													
	Dinner	750				2												2		1	1							
	Snack																					1	1		1			
B2-1	Bkfst	250									2	3							1						1			
	Lunch		400	2			1								1							1	1	3				
	Dinner	500			2										0.5	1	1				1							
	Snack																							3				
B2-2	Bkfst	500											5											3				3
	Lunch		200	2			1																1	4				
	Dinner								2									1		1	1							
	Snack																											
C2-0	Bkfst																											
	Lunch		300																1									
	Dinner	750				2												2			1			3				
	Snack																											
C2-1	Bkfst	500									2	4							1									
	Lunch		500	2			1								1								1			1		
	Dinner	500			5											1	1							1	1			
	Snack																											

C2-2	Bkfst	500											6														2
	Lunch		200	2											1							1	1			1	
	Dinner								2									2			1						
	Snack	500																						4			
D2-0	Bkfst		300																1								
	Lunch			2							1																
	Dinner	750				2.5												2			1						
	Snack																										
D2-1	Bkfst	500									2	3							1								
	Lunch	750	200	2	2		1								1							1		3	1		
	Dinner	750	200													1	1				1						
	Snack																										
D2-2	Bkfst	500											6														2
	Lunch		200	2			1								1											1	
	Dinner		200						3									2			1						
	Snack	500																						4			
F2-0	Bkfst											3															
	Lunch		200	2																			1				
	Dinner	500				1.5												1.5		1	1						
	Snack																								1		
F2-1	Bkfst	1500									2	4							1								
	Lunch		200	2			1															1					
	Dinner	1000			2											1	1				1			2			
	Snack																										
F2-2	Bkfst	1500											5														2
	Lunch		400	2			1																1			1	
	Dinner	500							2									2		1	1						
	Snack																										

G2-0	Bkfst	750		2				1																			
	Lunch																										
	Dinner		200			2.5													2		1	1					
	Snack	250																									
G2-1	Bkfst	1000										4							0.5								
	Lunch		400	2			1																			2	
	Dinner				2												1	1				1					
	Snack	750																							3		
G2-2	Bkfst	1000					0.2						4														3
	Lunch	250		2			1								1						1						
	Dinner								2										2		1	1					
	Snack	750																							3		1	

Appendix E

Calculated daily intake of tracers in food by subjects during the Nemiah soil ingestion study

		Nuclides (Bq)		Metals (ng)										
Subject/ Day		214Pb	212Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
Week 0														
F0-0	Day 0	0.167	0.005	8544391	433555	4588	2109	2337645	13512837	731	11683309	17788	1991	17881
F0-1	Day 1	0.171	0.005	5086962	211671	2537	1091	1175747	8438666	1303	11362898	2732	534	12700
F0-2	Day 2	0.087	0.003	5274154	477105	3849	1674	2399103	14807686	1463	448733	3170	845	13833
F0-3	Day 3	0.073	0.002	5297133	343583	2419	1129	1906633	8869861	376	11387598	1432	653	11177
G0-0	Day 0	0.148	0.005	1146212	306594	2156	929	1239068	7169465	1737	125418	2081	388	9972
G0-1	Day 1	0.034	0.001	4816186	481189	4416	1866	2259565	20472018	2523	622434	4389	1008	16941
G0-2	Day 2	0.082	0.009	3861116	343911	4651	1789	714732	11918702	5108	295425	5257	463	24671
G0-3	Day 3	0.018	0.001	4072663	438141	7958	2820	544985	6730058	10739	374021	13660	670	38761

Week 1														
A1-0	Day 0	0.102	0.013	6635731	583310	5532	2551	2609710	33370084	3340	61353998	14057	2795	28195
A1-1	Day 1	0.131	0.004	6069679	855026	4082	1935	4715790	43353187	1600	41857227	5406	1310	19438
A1-2	Day 2	0.104	0.003	8569826	577579	5758	2501	2818778	38235398	4130	11557619	14052	2028	26222
B1-0	Day 0	0.140	0.004	1777862	419788	2442	1386	1136461	12942896	1397	30568487	5240	1313	14119
B1-1	Day 1	0.161	0.005	5770608	809150	3222	1612	4221281	33185131	597	41858297	4224	1239	16781
B1-2	Day 2	0.107	0.004	8561557	413121	3079	1560	1682750	21128031	608	11454902	8631	2045	16773
C1-0	Day 0	0.121	0.004	2039816	431079	3270	1529	1458187	17248805	2886	30615524	7416	1278	17443
C1-1	Day 1	0.070	0.002	6152330	822855	4597	2090	4106342	40374891	2570	41866412	5658	1271	22461
C1-2	Day 2	0.108	0.003	8607900	584157	4767	2159	2671346	31277066	3549	22455363	19040	2267	24287
D1-0	Day 0	0.076	0.002	1596067	308131	2932	1354	1030885	9497316	2742	122829	8016	812	11858
D1-1	Day 1	0.127	0.004	5970366	884057	5509	2357	3977455	36727096	4511	11461659	7250	763	25670
D1-2	Day 2	0.095	0.003	4807023	424219	3896	1683	1528602	28483508	2460	376142	7921	1432	17369
E1-0	Day 0	0.192	0.006	4408347	490263	2368	1375	2721574	25567066	505	56914007	6868	1602	15398
E1-1	Day 1	0.177	0.006	5281639	672206	3631	1732	3483707	40592082	1563	41796585	6607	1417	18681
E1-2	Day 2	0.092	0.003	5577872	341501	2342	1120	1774580	16858604	1362	11282303	9320	1285	13103
G1-0	Day 0	0.117	0.004	4383389	269387	2762	1394	861360	12917393	429	375125	9238	1140	10366
G1-1	Day 1	0.096	0.003	5383739	802003	3268	1558	3653477	29645164	1489	11385328	4979	671	17039
G1-2	Day 2	0.087	0.003	5183149	322136	2848	1433	1352976	13017268	476	386002	5768	1459	11295

Week 2														
A2-0	Day 0	0.125	0.004	1877416	377475	2104	1154	1554021	10807564	394	30599051	7919	1734	8695
A2-1	Day 1	0.129	0.004	6058341	816256	5630	2410	4054337	37905125	4522	41836262	7086	1246	26680
A2-2	Day 2	0.100	0.003	6362324	629197	4556	1997	3244835	22952905	4016	11330110	17784	1791	23286
B2-0	Day 0	0.185	0.015	6070807	624021	4042	2096	3068392	36645084	855	30882645	15121	2602	18500
B2-2	Day 1	0.125	0.004	3920521	777761	4217	1886	3901038	30124738	2529	30779187	5177	1190	18270
B2-3	Day 2	0.129	0.004	3586208	409778	2415	1168	1658569	14622990	1392	176650	8314	1394	12207
C2-0	Day 0	0.075	0.002	1597945	301227	2381	1176	1216669	11840506	1777	119002	11433	1134	8638
C2-1	Day 1	0.068	0.002	5972553	794946	4741	2114	3978466	39998480	3025	41857639	5759	1241	22530
C2-2	Day 2	0.095	0.003	5128692	460519	2637	1240	1964513	18044242	1420	11302077	12319	1526	14929
D2-0	Day 0	0.081	0.002	1956731	360990	2814	1427	1315129	12536522	1828	145831	10940	1251	10021
D2-1	Day 1	0.124	0.004	3807617	742702	4130	1840	3630614	27535555	2499	30754268	4398	1174	17928
D2-2	Day 2	0.094	0.003	5355032	521873	3340	1525	1981171	19354094	2412	11322046	12833	1552	18787
F2-0	Day 0	0.122	0.004	1961331	284825	2383	1189	1173372	12292699	1349	30582015	7220	1445	11085
F2-1	Day 1	0.120	0.004	3734958	683634	3456	1600	3480592	24481152	1434	299977	3198	677	12247
F2-2	Day 2	0.130	0.004	5181149	446856	3224	1477	1697249	15180117	2391	11271521	12419	1579	17296
G2-0	Day 0	0.130	0.014	3193384	363099	2757	1477	1247165	22287206	1450	164238	8889	1223	12201
G2-1	Day 1	0.122	0.004	7391051	755918	4064	1857	4280948	29043895	2450	22452887	5660	617	20268
G2-2	Day 2	0.171	0.005	5671751	471696	2224	1203	2013594	20507371	451	11289341	11223	1890	12268

Appendix F

Calculated daily tracer concentrations in subject's feces during the Nemiah soil ingestion study

Sample Number	Pb-214 (Bq kg^{-1})	Pb-212 (Bq kg^{-1})	Al (ug g^{-1})	Ba (ug g^{-1})	Ce (ug g^{-1})	La (ug g^{-1})	Mn (ug g^{-1})	Th (ug g^{-1})	Ti (ug g^{-1})	V (ug g^{-1})	U (ug g^{-1})	Y (ug g^{-1})	Zr (ug g^{-1})	Si (ug g^{-1})
Week 0														
F0-1	13.05	7.13	3500	210	2.6	1.4	3400	0.47	3200	6	0.57	0.57	3.7	14000.00
F0-2	11.93	4.62	1800	200	1.1	0.62	2600	0.27	2200	3	0.35	0.35	2.4	5800.00
F0-3	16.39	5.05	1700	130	1.0	0.48	1900	0.12	2000	3	0.25	0.25	2.1	4500.00
F0-4	13.52	3.92	2100	130	0.94	0.50	2000	0.11	1800	2	0.21	0.21	1.9	4400.00
G0-1	5.4	3.73	2200	160	0.82	0.45	960	0.13	540	5	0.44	0.44	4.4	8500.00
G0-2	5.55	3.59	1800	170	0.78	0.43	1100	0.12	1100	4	0.42	0.42	5.5	9100.00
G0-3	9.69	5.47	1000	140	0.68	0.46	670	0.11	600	3	0.19	0.19	4.4	5700.00
G0-4	11.96	6.91	1100	140	0.64	0.41	670	0.08	270	5	0.18	0.18	4.1	6100.00

Week 1														
A1-1	11.7	4.9	3700.0	150.0	1.0	0.5	760.0	0.2	20000.0	12.0	0.6	0.6	8.4	
A1-2	12.7	4.5	2000.0	190.0	1.1	0.7	1000.0	0	7300	8	0	1	5.2	
A1-4	13.1	6.4	1600.0	210.0	1.1	0.6	1200.0	0	5500	5	0	1	14.0	
B1-2	7.77	4.64	1400	180	0.89	0.49	1200	0.65	6300	3	0.28	0.38	3.9	6700.00
B1-3	8.86	4.45	2000	180	0.89	0.47	1200	0.28	6700	4	0.34	0.52	5.0	7000.00
B1-6	10.26	5.95	2300	210	1.9	1.1	960	0.30	14000	6	1.5	0.62	8.0	12700.00
C1-2	13.02	7.08	1000	200	0.94	0.60	850	0.17	1600	4	0.37	0.36	5.0	6800.00
C1-5	11.11	5.58	980	210	1.00	0.66	1100	0.17	2400	3	0.30	0.41	3.5	6100.00
C1-6	9.73	4.66	1100	140	0.68	0.47	870	0.12	2000	2	0.25	0.34	2.7	4000.00
D1-1	17.39	4.45	2300	200	6.3	2.7	1200	0.28	310	14	0.57	0.85	4.2	17100.00
D1-2	18.84	10.43	2800	250	3.2	1.8	1400	0.25	1900	6	0.42	0.72	4.5	11500.00
D1-3	18.6	8.33	1600	210	1.6	1.1	1300	0.17	2600	4	0.39	0.73	5.0	10400.00
E1-2	9.84	4.73	890	180	0.94	0.59	1900	0.15	2800	8	0.46	0.76	3.6	7800.00
E1-5	9.84	4.73	1300	200	1.1	0.64	1600	0.17	4100	5	0.40	0.68	3.4	
E1-6	6.99	3.95	1400	160	0.94	0.56	1200	0.14	4800	4	0.35	0.52	3.4	7400.00
G1-2	7.5	4.63	940	130	0.87	0.48	670	0.14	330	6	0.42	0.43	5.4	8000
G1-3	9.95	4.46	1000	160	0.93	0.52	980	0.12	3000	3	0.34	0.42	5.5	8100
G1-4	10.26	5.95	1200	140	0.73	0.4	980	0.11	2100	3	0.25	0.37	5.1	6600

Week 2														
A2-1	10.4	5.76	2200	160	1.3	0.68	870	0.26	2000	4	0.54	0.7	4.2	--nss
A2-2	11.58	6.37	1500	210	1.1	0.6	1100	0.3	2500	3	0.38	0.53	3.6	--nss
A2-3	14.34	6.57	1500	230	1.1	0.55	1400	0.35	2300	2	0.3	0.42	3.6	--nss
B2-1	12.05	6.84	2200	180	1.0	0.57	1100	0.33	4300	3	0.34	0.49	3.2	3700.00
B2-3	23.93	17.63	2600	210	1.2	0.64	1400	0.69	3800	2	0.26	0.54	3.3	5900.00
B2-4	11.03	5.66	1700	190	0.94	0.51	1300	0.48	1100	3	0.26	0.47	2.8	4300.00
C2-1	7.34	5.31	1100	150	1.1	0.54	860	0.17	330	8	0.36	0.56	3.6	--nss
C2-3	8.06	4.62	1100	150	0.93	0.48	930	0.27	1800	3	0.21	0.4	3.1	--nss
C2-4	11.1	5.87	1500	180	0.89	0.46	1300	0.4	3300	2	0.23	0.4	3.6	--nss
D2-1	14.73	5.16	1300	190	2.9	2.5	1200	0.33	5600	6	0.40	2.1	5.3	13600.00
D2-4	15.59	9.84	1600	260	2.4	1.6	1500	0.44	1600	4	0.34	1.0	4.5	11000.00
F2-1	6.99	3.95	1600	210	1.2	0.89	1600	0.33	950	5	0.44	0.55	5.8	5800.00
F2-3	17.81	12.33	2000	220	1.2	0.82	2000	2.4	1600	2	0.81	0.59	4.0	5500.00
F2-4	9.36	6.59	1900	180	1.0	0.57	1600	0.37	2300	2	0.36	0.47	3.1	3800.00
G2-1	5.29	5.32	930	130	0.97	0.49	810	0.16	670	7	0.44	0.44	3.5	--nss
G2-2	8.59	3.92	1300	110	0.69	0.35	910	0.32	2300	2	0.28	0.35	3.5	--nss
G2-3	11.02	6.68	1200	160	0.85	0.53	1100	0.22	3300	3	0.45	0.48	4.1	--nss

Appendix G

Calculated mass of tracers in subject's daily fecal output during the Nemiah soil ingestion study

Fecal Sample	Day	Ash Wt (g)	Nuclides (Bq)		Metals (ug)										
			214Pb	212Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
Week 0															
F0-1	Day 1	1.4	0.019	0.010	4967	298	3.7	2.0	4825	19868	0.7	4541	8.5	0.8	5.3
F0-2	Day 2	6.4	0.076	0.029	11455	1273	7.0	3.9	16546	36909	1.7	14000	19.1	2.2	15.3
F0-3	Day 3	1.9	0.031	0.009	3167	242	1.9	0.9	3540	8383	0.2	3726	5.6	0.5	3.9
G0-1	Day 1	3.5	0.019	0.013	7794	567	2.9	1.6	3401	30112	0.5	1913	17.7	1.6	15.6
G0-2	Day 2	3.8	0.021	0.014	6860	648	3.0	1.6	4192	34681	0.5	4192	15.2	1.6	21.0
G0-3	Day 3	8.3	0.080	0.045	8287	1160	5.6	3.8	5552	47235	0.9	4972	24.9	1.6	36.5
Week 1															
A1-1	Day 1	5.0	0.058	0.024	18454	748	5.0	2.7	3791		0.9	99754	59.9	3.1	41.9
A1-2	Day 2	4.5	0.057	0.020	9072	862	5.0	3.0	4536		0.8	33112	36.3	2.0	23.6
A1-4	Day 3	6.7	0.087	0.043	10703	1405	7.4	4.2	8027		1.0	36792	33.4	2.5	93.7
B1-2	Day 1	2.8	0.022	0.013	3953	508	2.5	1.4	3388	18917	1.8	17787	8.5	0.8	11.0
B1-3	Day 2	3.4	0.030	0.015	6762	609	3.0	1.6	4057	23665	0.9	22651	13.5	1.1	16.9
B1-6	Day 3	4.1	0.042	0.025	9479	865	7.8	4.5	3956	52339	1.2	57697	24.7	6.2	33.0
C1-2	Day 1	4.1	0.054	0.029	4112	822	3.9	2.5	3495	27961	0.7	6579	16.4	1.5	20.6
C1-5	Day 2	4.7	0.053	0.026	4643	995	4.7	3.1	5211	28900	0.8	11371	14.2	1.4	16.6

Fecal Sample	Day	Ash Wt (g)	Nuclides (Bq)		Metals (ug)										
			214Pb	212Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
C1-6	Day 3	5.5	0.054	0.026	6077	773	3.8	2.6	4806	22098	0.7	11049	11.0	1.4	14.9
D1-1	Day 1	2.4	0.042	0.011	5550	483	15.2	6.5	2896	41264	0.7	748	33.8	1.4	10.1
D1-2	Day 2	3.4	0.064	0.036	9539	852	10.9	6.1	4770	39178	0.9	6473	20.4	1.4	15.3
D1-3	Day 3	3.2	0.059	0.027	5094	669	5.1	3.5	4139	33110	0.5	8277	12.7	1.2	15.9
E1-2	Day 1	6.4	0.063	0.030	5712	1155	6.0	3.8	12193	50057	1.0	17969	51.3	3.0	23.1
E1-5	Day 2	4.9	0.048	0.023	6370	980	5.4	3.1	7840		0.8	20090	24.5	2.0	16.7
E1-6	Day 3	5.6	0.039	0.022	7839	896	5.3	3.1	6719	41436	0.8	26878	22.4	2.0	19.0
G1-2	Day 1	8.6	0.064	0.040	8066	1115	7.5	4.1	5749	68644	1.2	2832	51.5	3.6	46.3
G1-3	Day 2	5.2	0.051	0.023	5162	826	4.8	2.7	5059	41816	0.6	15487	15.5	1.8	28.4
G1-4	Day 3	5.7	0.058	0.034	6828	797	4.2	2.3	5577	37556	0.6	11950	17.1	1.4	29.0
Week 2															
A2-1	Day 1	4.2	0.044	0.024	9240	672	5.5	2.9	3654		1.1	8400	16.8	2.3	17.6
A2-2	Day 2	3.1	0.036	0.020	4709	659	3.5	1.9	3453		0.9	7849	9.4	1.2	11.3
A2-3	Day 3	4.8	0.069	0.031	7183	1101	5.3	2.6	6704		1.7	11014	9.6	1.4	17.2
B2-1	Day 1	3.0	0.036	0.020	6538	535	3.0	1.7	3269	10996	1.0	12779	8.9	1.0	9.5
B2-3	Day 2	5.9	0.142	0.105	15455	1248	7.1	3.8	8322	35071	4.1	22588	11.9	1.5	19.6
B2-4	Day 3	2.4	0.026	0.013	4025	450	2.2	1.2	3078	10180	1.1	2604	7.1	0.6	6.6
C2-1	Day 1	2.8	0.020	0.015	3028	413	3.0	1.5	2367		0.5	908.3	22.0	1.0	9.9
C2-3	Day 2	2.9	0.023	0.013	3173	432.6	2.7	1.4	2682		0.8	5192	8.7	0.6	8.9
C2-4	Day 3	7.1	0.079	0.042	10643	1277	6.3	3.3	9224		2.8	23415	14.2	1.6	25.5

Fecal Sample	Day	Ash Wt (g)	Nuclides (Bq)		Metals (ug)										
			214Pb	212Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
D2-1	Day 1	3.5	0.052	0.018	4578	669	10.2	8.8	4226	47898	1.2	19723	21.1	1.4	18.7
D2-4	Day 2	2.2	0.035	0.022	3593	584	5.4	3.6	3369	24703	1.0	3593	9.0	0.8	10.1
F2-1	Day 1	6.0	0.042	0.024	9606	1261	7.2	5.3	9606	34821	2.0	5703	30.0	2.6	34.8
F2-3	Day 2	5.5	0.098	0.068	11047	1215	6.6	4.5	11047	30378	13.3	8837	11.0	4.5	22.1
F2-4	Day 3	2.9	0.027	0.019	5556	526	2.9	1.7	4679	11112	1.1	6726	5.8	1.1	9.1
G2-1	Day 1	10.3	0.055	0.055	9606	1343	10.0	5.1	8367		1.7	6920	72.3	4.5	36.2
G2-2	Day 2	7.7	0.066	0.030	995	843	5.3	2.7	6969		2.5	17613	15.3	2.1	26.8
G2-3	Day 3	6.6	0.072	0.044	7894	1053	5.6	3.5	7237		1.4	21710	19.7	3.0	27.0

Appendix H

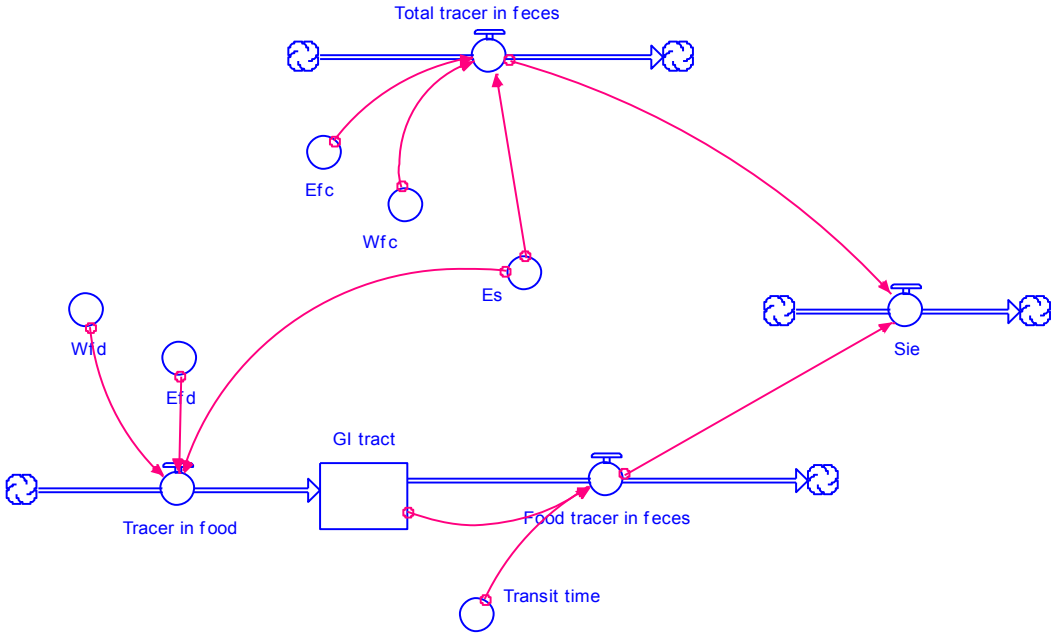
Daily soil ingestion rate calculated for each subject during the Nemiah soil ingestion study

Week and subject	Soil ingestion (mg d^{-1})												
	^{214}Pb	^{212}Pb	Al	Ba	Ce	La	Mn	Si	Th	Ti	V	U	Zr
Week 0													
F0-0	-968.71	714.07	-49	-315	-37	-11	3195	26	-30	-2074	-88	-1197	-334
F0-1	3063.96	2612.85	87	2468	186	253	19741	116	194	766	156	1716	68
F0-2	65.11	-381.16	-29	-546	-83	-69	1465	-26	-578	952	23	-384	-262
F0-3	3414.49	2185.02	82	826	110	138	11361	60	101	-497	89	483	-25
G0-0	-80.96	123.40	92	457	28	55	1965	100	-412	344	149	1186	99
G0-1	-657.14	-241.30	28	292	-53	-19	1757	62	-666	687	104	601	71
G0-2	3017.34	-1237.67	61	1432	36	169	4398	154	-1354	899	187	1126	207
G0-3	-253.36	-5707.88	-19	-167	-237	-151	997	36	-3401	55	-13	-232	-504
Week 1													
A1-1	931.9	-1599.9	177	330	-23	13	1205		-1129	10323	445	270	368
A1-2	855.5	278.0	45	14	38	98	-184		-391	-2351	300	582	112
A1-3	3466.8	1564.3	32	1654	67	159	5315		-1475	6783	188	467	1813
B1-1	-560.1	-735.2	33	177	3	0	2298	25	206	-3436	31	-475	-84
B1-2	-523.3	572.1	15	-401	-9	-2	-168	-40	165	-5163	90	-81	3
B1-3	1154.9	2518.9	14	905	200	275	2320	130	297	12431	156	3760	435
C1-1	957.2	368.6	31	783	25	87	2078	44	-1031	-6461	88	222	84
C1-2	769.3	279.2	-23	344	6	96	1128	-48	-833	-8198	83	137	-158
C1-3	1550.7	-147.0	-38	379	-42	41	2179	-38	-1361	-3066	-78	-805	-252
D1-1	1500.4	-1288.1	59	349	516	478	1903	132	-975	168	250	513	-46
D1-2	1338.6	-296.8	53	-65	227	350	808	10	-1726	-1341	128	607	-278
D1-3	2373.7	1140.5	4	489	50	168	2663	19	-905	2124	47	-173	-39

E1-1	1228.3	2262.7	20	1330	154	223	9665	102	216	-10469	432	1227	207
E1-2	631.6	1163.5	16	616	74	130	4445		-344	-5835	174	494	-54
E1-3	1234.7	1328.0	34	1109	123	187	5046	102	-273	4192	127	614	160
G1-1	2002.4	3921.7	55	1692	198	252	4987	231	364	660	410	2240	967
G1-2	402.6	151.7	-3	48	64	104	1434	51	-410	1103	102	985	305
G1-3	2553.4	3649.5	25	949	55	78	4310	102	71	3109	110	-33	476
Week 2													
A2-1	743.8	2023.6	110	589	141	158	2143		329	-5967	86	485	240
A2-2	-408.4	-2229.9	-20	-314	-91	-49	-613		-1689	-9136	23	-48	-413
A2-3	2504.5	-113.2	12	944	30	59	3530		-1104	-85	-80	-323	-163
B2-1	-1231.6	-509.2	7	-178	-45	-37	205	-107	59	-4867	-60	-1447	-242
B2-2	6781.2	10193.2	173	941	123	178	4511	21	742	-2202	65	323	36
B2-3	-333.6	-338.4	7	80	-8	4	1448	-18	-121	653	-12	-708	-150
C2-1	535.5	15.2	21	223	27	29	1174		-617	212	103	-130	34
C2-2	-1127.9	-1772.0	-42	-725	-87	-68	-1323		-1059	-9856	28	-577	-365
C2-3	3799.5	3665.2	83	1633	155	187	7408		669	3256	18	97	285
D2-1	2031.8	393.6	39	616	311	683	2971	147	-314	5263	99	143	232
D2-2	-111.4	-61.8	-3	-318	53	162	-267	-12	-713	-7301	45	-373	-210
F2-1	962.8	1179.4	114	1952	203	385	8605	94	298	-6688	221	1088	638
F2-2	4086.5	6562.7	109	1063	133	271	7720	24	5576	2295	76	3452	265
F2-3	-324.1	-579.6	6	159	-13	18	3042	-17	-617	-1222	-64	-478	-221
G2-1	1141.5	3659.7	96	1959	305	332	7265		96	1816	616	3020	644
G2-2	2108.9	518.8	38	173	51	76	2743		0	-1301	94	1388	176
G2-3	1843.6	3622.6	33	1162	142	211	5330		470	2801	83	973	395

Appendix I

Monte Carlo conceptual model, and model equations, developed in Stella™ (includes variability resulting from transit time misalignment)



GI_tract(t) = GI_tract(t - dt) + (Tracer_in_food - Food_tracer_in_feces) * dt
INIT GI_tract = 0
INFLOWS:
Tracer_in_food = (Efd*Wfd)/Es
OUTFLOWS:
Food_tracer_in_feces = GI_tract*Transit_time
UNATTACHED:
Soil ingestion (Sie) = Total_tracer_in_feces-Food_tracer_in_feces
UNATTACHED:
Total_tracer_in_feces = ((Efc*Wfc)/Es)
Efc = NORMAL(1673,33.5,7828)
Efd = NORMAL(150,3,10250)
Es = NORMAL(72.9,5.400,12224)
Transit_time = NORMAL(1,.35,22244)
Wfc = NORMAL(4.9,0.1,17088)
Wfd = NORMAL(32.4,3.9,23686)

Appendix J

Statement of Collaborator Contributions

Jules Blais (University of Ottawa) and Paul White (Health Canada) established the initial research concept to examine mass balance soil ingestion estimating methods to support HHRA using naturally occurring radionuclides and coordinated funding to support the work. Funding was largely provided by the Contaminated Sites Division of Health Canada under the direction of Luigi Lorusso and Mark Richardson. Jack Cornett (Defense Research Development Canada) and Ed Calabrese (University of Massachusetts, Amherst) provided input to the research objectives throughout the program of study as members of the author's Ph.D. committee. James Doyle developed the specific research objectives, approach and hypotheses for the research and as described in Chapter 1.

The work described in Chapter 2 was a collaborative effort involving James Doyle, Jules Blais (University of Ottawa), ad Paul White (Health Canada). James Doyle completed the review of the literature, developed the mass balance soil ingestion estimating model and power calculations, and formulated conclusions. Paul White and Jules Blais provided review and input to the conclusions. Chapter 2 was formatted for submission and published in Science of the Total Environment in 2010. Co-authors include the aforementioned collaborators in the following order: James Doyle, Paul White and Jules Blais.

The work described in Chapter 3 was a collaborative effort involving James Doyle, Rachelle Gendron (University of Ottawa), Linda Kimpe (University of Ottawa), Jules Blais, and Paul White. James Doyle was the principal investigator in the development of the sampling, pre-concentration and analytical methods to be used in the research program. He also designed, planned and executed validation studies, and analysed and interpreted all results from these studies. Paul White and Jules Blais provided input on experimental design and assisted with interpretation of results. Rachelle Gendron provided substantial input to the development of pre-concentration methods for radioisotope analysis and helped write safe work protocols for methods developed in support of the research. Linda Kimpe was responsible for the management of the Blais laboratory facilities, provided advice on the operation of the gamma

spectrometer and input to the interpretation of gamma spectrometric analyses and sample preparation methods throughout the entire research period. The research methods developed also benefitted from contributions of others. Herve Beaudoin provided advice and fabricated purpose-built dies for the compaction of samples for gamma spectrometry. Weihua Zhang (Health Canada) provided valuable input into the development of methods to analyze samples in Marinelli Beakers. Sections 3.5 and 3.6 were consolidated into a paper submitted to Ecotoxicology and Environmental Safety in 2011, which is currently under review, with the co-authors in the following order: James Doyle, Jules Blais and Paul White.

The work described in Chapter 4 was a collaborative effort involving James Doyle, Ahmed Al-Ansari (University of Ottawa), Rachelle Gendron (University of Ottawa), Paul White, and Jules Blais. James Doyle conceived the research objectives, designed and planned the experiments/studies, developed the methods, and interpreted the results of the studies. Ahmed Al-Ansari, Paul White and Jules Blais provided input to the development of research objectives, and reviewed the manuscript. Rachelle Gendron provided input to the development of the study methods, analyzed the samples and reviewed the manuscript. The study also benefitted from contributions of others. W. Nelson Beyer (united States Geological Survey) provided input to the initial development of research objects during a conversation at the Society of Toxicology and Environmental Chemistry North American meeting in 2008 and Don Mackay (Trent University) provided useful advice on the applicability of the approach to environmental modeling. Gilbert Cabana provided the research vessel used to collect the fish samples and Ahmed Al-Ansari collected and preserved the fish samples for later analysis. Chapter 4 was formatted for submission and published in Aquatic Toxicology in 2011. Co-authors include the aforementioned collaborators in the following order: James Doyle, Ahmed Al-Ansari, Rachelle Gendron, Paul White and Jules Blais.

The work described in Chapters 5 and 6 was a collaborative effort involving James Doyle, Jules Blais, Richard Holmes (University of Northern British Columbia), and Paul White. James Doyle conceived the research objectives, obtained requisite approvals, designed the subject interviews, executed all aspects of the field work and subject interviews, analysed all

fecal samples and interpreted the study results. Paul White and Jules Blais provided input to the research objectives, helped secure research ethics approvals and the Memorandum of Understanding with the subject community, and provided input to the interpretation of results and composition of the manuscript. Richard Holmes acted as an interface with the subject community in the Nemiah Valley during the initial planning phases of the work, provided input to the selection of field activities to be assessed and provided substantial logistical support during the field work. The study also greatly benefitted from contributions of others. The cooperation of Chief Marilyn Baptiste, Council and the Elders of the Xeni Gwet'in community was essential the success of the study. Nancy Oppermann helped forge the contractual agreements with the community and Pam Quilt recruited and coordinated the participation of the study subjects. Conway William and Dinah Lulua provided translation to and from English and Tsilhqot'in, when required, during interviews with Elders. Rachelle Gendron provided substantial support analyzing food and water samples and assisting the preparation and analysis of samples by gamma spectrometry as well as verifying the accuracy of equation transcription in spreadsheets used to calculate daily soil ingestion estimates. SGS Laboratories in Peterborough, Ontario analyzed all samples for metals and Si. Paddy Smith (Cariboo Envirotech Ltd.) provided field supervision of the workers participating in the traditional fishery work. The results of Chapter 5 were formatted for publication and submitted to Science of the Total Environment in 2011, and is currently under review, with the co-authors in the following order: James Doyle, Jules Blais and Paul White. The results of Chapter 6 were also formatted for publication separately from Chapter 5 and submitted to Science of the Total Environment in 2011, and currently under review, with the co-authors in the following order: James Doyle, Richard Holmes, Jules Blais and Paul White.

The work described in Chapter 7 was a collaborative effort involving James Doyle, Paul White, and Jules Blais. James Doyle conceived the research objectives, designed the soil ingestion model, analysed and interpreted all results. Paul White and Jules Blais provided input on experimental design and assisted with interpretation of results and composition of manuscript. Chapter 7 is also earmarked for publication, pending a review of recently published data and meta-analyses of past soil ingestion studies of children and adults.