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A pilot study to assess the feasibility of using naturally-occurring radionuclides as mass balance tracers to estimate soil ingestion

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ABSTRACT

The relatively few soil ingestion studies that have been conducted to date to support soil ingestion rate values used for contaminated site human health risk assessments (HHRAs) typically have measured mass balance elemental tracers (e.g., Al, Si, Ba, Ce, Mn, Ti, V, Zr), found in soil to estimate soil ingestion. This pilot study, involving a canine subject fed a known amount of tracer on a daily basis, assessed the use of alternative mass balance tracers, specifically naturally occurring radionuclides of the ^{238}U and ^{232}Th decay series, to estimate soil ingestion. A novel method of estimating soil ingestion via difference in isotopic ratios between the two decay series in food and soil was also assessed. 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, 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 3.9 g d^{-1} (standard deviation 3.6 g d^{-1}) for the isotope tracers, and 1.9 g^{-1} (standard deviation 2.1 g d^{-1}) for the 3 most reliable elemental tracers. The differences were not statistically significant and further evaluation of isotopic tracers for soil ingestion studies is warranted. Similarly, soil ingestion estimates calculated using the Isotope Ratio Method were not significantly different than when calculated using ^{212}Pb; however, the Isotope Ratio Method was observed to positively bias the soil ingestion estimates by approximately 50%.

1. Introduction

Relatively few soil ingestion studies have been conducted to date to support the development of soil ingestion rates for contaminated site human health risk assessments (HHRAs) by regulatory agencies in North America and Europe. These studies that have been conducted typically measured elemental mass balance tracers (e.g., Al, Si, Ba, Ce, Mn, Ti, V, Zr), commonly found in soil, in excreta to estimate soil ingestion. Moreover, of the studies completed to date, few experimental validation studies of the mass balance tracer approach to estimate soil ingestion have been conducted. Two pilot studies of adults were conducted at the University of Massachusetts, Amherst to validate the soil ingestion mass balance estimating methodology used in 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 three 1-week periods. To validate their methodology, the study subjects received daily doses 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 was measured in subjects' feces. 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 of 10–20 g d^{-1}, or several hundred-fold higher than soil ingestion rates observed in children.

The soil ingestion estimates reported in the aforementioned studies are highly variable and the use of naturally-occurring radionuclides from the ^{238}U and ^{232}Th decay series as alternative, less variable mass balance tracers was proposed by Doyle et al. (2010). The ^{238}U and ^{232}Th decay series isotopes were identified as candidates as mass balance tracers in soil ingestion studies because they are not readily absorbed in the gastrointestinal tract, are ubiquitous in soils and are not common ingredients in foods or consumer products, which reduces the potential for biasing soil ingestion estimates through unaccounted ingestion of tracers (i.e., source error). Moreover, they are easily measured non-destructively by gamma spectrometry. Specifically, ^{226}Ra (determined by the measurement of ^{214}Pb assuming secular equilibrium between

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the two ^{238}U series isotopes has been achieved) and ^{228}Th (determined by the measurement of ^{214P}b assuming secular equilibrium between the two ^{232}Th series isotopes has been achieved) were used as mass balance tracers in this pilot study.

The ^{238}U and ^{232}Th series are commonly found together in environmental samples at a proportion of approximately 1:1, and deviations from this proportion may be indicative of differences in soil composition and soil properties (Navas et al., 2005). 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. Thus, 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 amount of soil 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 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 ensure that a measurable soil ingestion signal would be achieved during the study and to confirm that the radionuclide mass balance tracers were not significantly absorbed in the gastrointestinal tract relative to elemental tracers. Moreover, the use of secular disequilibrium and/or fractionation in the ^{238}U and ^{232}Th series, measured with gamma spectrometry, was assessed as an alternative and novel method of estimating soil ingestion.

2. Methods

A 1-year old 29 kg Golden Retriever was identified as the subject for the pilot study. 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. Approval to proceed with the study was obtained from the University of Ottawa Animal Care Committee (approval ♯BL-230) on April 16, 2009.

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 of dry dog food and 1 g inoculant mixed with a small amount of wet dog food was fed to the canine subject twice daily. 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. In accordance with the study approvals, the inoculant samples were ashed to ensure that no pathogens were ingested by the canine subject. Two 500 mg glucosamine capsules were also given to the canine subject at each feeding to treat a hip ailment. A measured volume of water was provided 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 (i.e., one between the front of the cottage and a road and two between the back of the cottage and the lake) with 4 replicate samples, one sample for each corner of a 1 m^2 square, being collected from each location. Daily fecal output was collected from Day 2 to Day 8 of the study and stored in pre-weighed plastic containers in a cold box until transported to the laboratory, where they were freeze dried, weighed and stored until analysis. The canine subject normally provided a fecal sample within 30 min 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 being deposited on the grass covered lawn. Although contamination of the sample cannot be ruled out, dirt was not normally observed to be adhering to the fecal samples. Any debris adhering to collected fecal samples was removed.

Food and fecal samples were ashed before analysis. Approximately 1 g subsamples 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. 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 and hydrofluoric acid using microwave heating). Digested samples were then analyzed 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). 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 evaporated and total dissolved solids were compacted in 8 mL centrifuge tubes and sealed with epoxy resin. All samples to be analyzed 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 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 (Appleby, 2001):

$$A = \frac{N}{\in YCT} \tag{1}$$

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 (s).

^{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.

The daily soil ingestion for each subject was calculated from:

$$S_a = \frac{(F_c \times F_a) - (I_c \times I_a) - (D_c \times D_a)}{S_c} \tag{2}$$

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 g of soil into the mass of the tracer element ingested from food over a 1-day period.

The mathematical model employed to calculate soil ingestion via Isotope Ratio Method is provided in Eqs. (3) and (4). 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

$$S_p = \frac{R_f - F_r}{S_r - F_r} \tag{3}$$

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

$$S_a = \frac{(F_c \times F_a) \times S_p}{S_c} \tag{4}$$

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}), statistical analyses of the data (i.e., means, standard deviations, paired t-test ANOVA, Welch ANOVA, linear regression, and power analysis) were calculated using JMP® software.

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 1, with all results well above the analytical minimum detection limit for each parameter. 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 2. It was noted that some of