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The determination of Fukushima-derived cesium-134 and cesium-137 in Japanese green tea samples and their distribution subsequent to simulated beverage preparation

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ABSTRACT

Health Canada's Radiation Protection Bureau has identified trace quantities of ^{134}Cs and ^{137}Cs in commercially available green tea products of Japanese origin. Referenced to March 11, 2011, the activity ratio (^{134}Cs/^{137}Cs) has been determined to be 1:1, which supports an origin from the Fukushima Dai-ichi Nuclear Power Plant accident. The upper limits of typical tea beverage preparation conditions were applied to the most contaminated of these green tea samples to determine the proportion of radiocesium contamination that would be available for human consumption. The distribution of radiocesium among the components of the extraction experiments (water, residual tea solid, and filter media) was determined by both conventional and Compton-suppressed gamma spectroscopy. The latter aided tremendously in providing a more complete radiocesium distribution profile, particularly for the shorter-lived ^{134}Cs. Cesium extraction efficiencies of 64 ± 7% and 64 ± 5% were determined based on ^{134}Cs and ^{137}Cs, respectively. Annual, effective dose estimates from ingestion of ^{137}Cs and ^{134}Cs (1.8–3.7 μSv), arising from the consumption of tea beverages prepared from the most contaminated of these samples, are insignificant relative to both total (~2.4 mSv) and ingested (~0.28 mSv) annual effective doses received from naturally occurring radioactive sources. As such, there is no health concern arising from the consumption of green tea beverages contaminated with radiocesium at the levels encountered in this study.

1. Introduction

Tea infusion is the second most popular beverage worldwide, behind drinking water (Dufrêne, 2012). Such popularity has been bolstered in recent years by numerous publications touting the potential health benefits associated with its relatively high polyphenol content (Carloni et al., 2013; Halliwell, 2006). Tea also represents a major dietary source of essential, minor, and trace elements owing to its efficient uptake of minerals from the acidic soil in which it flourishes, as evidenced by its relatively high inorganic content (4–9 wt%) (Karak and Bhagat, 2010; Tokahoğlu and Kartal, 2004). The mineral profile of tea leaves, made teas, and their subsequent infusions is therefore of considerable interest from both a nutritional and health risk perspective, especially given the potential for bio-accumulation of toxic elements (Chand et al., 2011; Karak and Bhagat, 2010; Szymczycha-Madeja et al., 2012). The tea plant's propensity for mineral uptake equally applies to anthropogenic radionuclides, and so the radio-analysis of tea is also a sensitive indicator for environmental impact assessment following a nuclear or radiological incident (Lalit et al., 1983; Topcuoğlu et al., 1997). Coupled with the popularity of tea beverage consumption worldwide, a well-informed determination of the radioactive content of infused tea preparations is important considering that a significant dose may arise from their ingestion, the restriction of which has been outlined by Health Canada (2000). In this regard, ^{134}Cs and ^{137}Cs are prominent owing to their relatively high fission yields, volatility, and chemical reactivity, all of which help to ensure their widespread environmental distribution (Avery, 1996).

From April 2011 to December 2012, Health Canada's Radiation Protection Bureau had performed radiological assessment of over

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500 domestic and imported foodstuff samples, the majority of which were collected as part of surveillance efforts stemming from the Fukushima Dai-ichi Nuclear Power Plant accident. Of these, 300 foodstuff samples imported from Japan were collected (October–December 2012) to supplement the domestic foodstuff items sampled for the 2012 Health Canada Food Basket Survey, which in that year was focused on Vancouver, British Columbia, Canada (Health Canada, 2009). From these Japan import samples, six green tea samples and one dried fish sample registered ^{137}Cs contamination. Four of these green tea samples and the one dried fish sample were shown to contain both ^{134}Cs ($t_{1/2} = 2.06$ y) and ^{137}Cs ($t_{1/2} = 30.2$ y). As a follow-up to this finding, ten additional Japanese green tea samples of various brands were purchased in Ottawa, Canada (February 2013) for analysis. One of these samples was shown to contain both ^{134}Cs and ^{137}Cs, as was a follow-up sample of the same brand.

To capitalize on the rare opportunity afforded by these samples, in light of the preceding discussion, the Radiation Surveillance Division of Health Canada's Radiation Protection Bureau has set out to firmly determine the quantities of ^{137}Cs and ^{134}Cs in these green tea samples and, more importantly, to convincingly determine the fraction of radiocesium in processed green tea that is made available for consumption under the upper limits of typical beverage preparation conditions. While the extraction of cesium from tea under various infusion conditions has been documented previously (Matsuura et al., 2000, 2001; Szymczycha-Madeja et al., 2012), the work presented herein constitutes a rare radiometric assessment that is further made unique considering the use of both conventional and Compton-suppressed gamma spectroscopy to provide a complete cesium distribution profile (Tagami et al., 2012).

2. Experimental

2.1. Preparation of dry tea samples for gamma spectroscopy

The green tea samples (63–74 g) collected through the Health Canada Food Basket Survey were received dried and ground, requiring no further preparation before measurement by gamma spectroscopy (2 h) using an integrated gamma-ray spectrometry system (Gamma Analyst, Canberra, Meriden, CT). In addition to these, eleven green tea samples of Japanese origin were purchased at a local grocery store in Ottawa, February 2013. These dried tea samples (35–63 g) were used as received, without any further preparation. The ^{134}Cs and ^{137}Cs activities were decay corrected to the date of the Fukushima Dai-ichi incident (March 11, 2011) and the ^{134}Cs/^{137}Cs ratios were subsequently determined (Table 1).

2.2. Preparation of tea extract, residue, and filter samples for gamma spectroscopy

Extraction experiments simulating the preparation of tea beverages were performed on three replicate sub-samples of tea sample 4, which was found to contain the highest activity of ^{134}Cs and ^{137}Cs (Table 1). These replicate sub-samples are denoted as samples 4a, 4b, and 4c. Boiling water (200 mL, de-ionized, 18.2 MΩ cm) was added to each dried tea sample (4 g) and magnetically stirred (100 rpm) for 10 min giving a tea to water mass ratio of 0.02. These samples were then filtered (Whatman Grade 41 Quantitative Filter Paper, P/N 1441-125, 20 μm pore size) under vacuum, and the filtrate (130 mL) was added to a Parkway jar (58.0 × 66.6 mm clarified polypropylene container, Parkway Plastics, Inc. P/N A0700400PPC, C070C4SPLIW, Piscataway Township, NJ). The tea residue was collected from the filter paper, dried overnight at 80 °C, ground with a mortar and pestle, and added to a 51 × 5 mm plastic air filter holder and cap (Acron Plastics Ltd, P/N 4500261774, Box Hill, Victoria). The filter paper was also dried overnight at 80 °C, folded and placed in a 51 × 5 mm plastic air filter holder. The tea extracts, residues and filter papers were counted for 72 h by conventional non-Compton suppressed gamma spectroscopy (Table 2) and for 24 h by Compton-suppressed gamma spectroscopy (Table 3) to determine the radiocesium distribution. The ^{134}Cs/^{137}Cs activities of the dry tea samples used in the extraction experiments were decay corrected to the date of gamma measurement of the extract, residue or filter in order to calculate the distribution of radiocesium.

2.3. Gamma spectroscopy

The dried tea samples, and subsequent samples arising from their infusions, were measured on a Canberra Gamma Analyst gamma spectrometer equipped with a single crystal, high purity germanium (HPGe) coaxial detector (GX13022, crystal dimensions: 85.5 mm (diameter) x 87 mm (length), 130% relative efficiency), an aluminum end-cap and a copper crystal holder. Data from the extraction experiments was collected and processed using Genie 2k 3.0 software suite (Canberra, Meriden, CT). Data from the dried tea sample analysis was also collected using Genie 2k 3.0, but was further analyzed using the UniSampo-Shaman software suite (Baryon Oy Ltd, Finland). In both cases, cascade summation corrections for ^{134}Cs were handled by the analysis software. All dried tea samples were counted for 2 h. Store-bought tea samples with detectable ^{134}Cs/^{137}Cs were re-counted for 6 h. The aqueous extract, tea residue and filter samples obtained from the extraction experiments were counted for 72 h. The uncertainties reported in subsequent sections are at the 2σ level and were obtained from counting statistics, self-absorption, efficiency calibration and mass transfer.

The aqueous extract, tea residue and filter samples arising from the tea infusions were also counted for 24 h on a Compton-suppressed gamma spectrometer (ORTEC), previously described in detail by Zhang et al. (2012). Briefly, the spectrometer consists of an n-type (GMX) HPGe coaxial primary detector (crystal dimensions: 66.2 mm (diameter) x 69.0 mm (length), 25% relative efficiency), a carbon fiber end-cap, and a guard detector consisting of a 9″ x 9″ NaI(Tl) annulus with four photomultiplier tubes (PMT) and a 3″ x 3″ NaI(Tl) plug with one PMT.

Two different geometries were used to measure the tea samples. The dried tea samples and aqueous tea extracts (130 mL) were measured in 58.0 × 66.6 mm clarified polypropylene Parkway jars equipped with lids. The extracted tea residues and filters were analyzed in 51 × 5 mm plastic air filter holders and caps.

Certified, mixed radionuclide standards of identical geometry to the samples measured were used to determine the respective counting efficiencies on both gamma spectrometers. A standard consisting of simulated vegetation (0.6 g/cm^3) in a Parkway jar (Eckert and Ziegler Analytics, SRS: 80465-411) was used to approximate the counting efficiency of the original dry tea samples on the Gamma Analyst. A standard consisting of simulated water (1.15 g/cm^3) in a Parkway jar (Eckert and Ziegler Analytics, SRS: 79535-411) was used for the aqueous tea extract samples. The counting efficiencies applied to the tea residue and filter samples measured on the Gamma Analyst spectrometer were determined using a 50 × 5 mm polypropylene disk standard (National Physical Laboratory, X08215). The counting efficiencies applied to the tea residue and filter samples measured on the Compton-suppressed gamma spectrometer were determined using a 50 × 5 mm compressed filter disk standard (National Physical Laboratory, X11091).

To add accuracy in the determination of the coincidence

Table 1
^{134}Cs and ^{137}Cs activities and ^{134}Cs/^{137}Cs ratio determination for dried green tea samples.

Sample	Nuclide	Measured activity (Bq/kg)	Decay corrected activity (Bq/kg)	^{134}Cs/^{137}Cs ratio
1[a]	^{134}Cs	4.6 ± 0.8	7.9 ± 1.4	1.0 ± 0.2
	^{137}Cs	7.9 ± 1.1	8.2 ± 1.1	
2[a]	^{134}Cs	12.5 ± 2.1	22.6 ± 3.7	1.1 ± 0.2
	^{137}Cs	19.8 ± 1.8	19.9 ± 1.9	
3[a]	^{134}Cs	14.4 ± 1.3	24.9 ± 2.2	0.9 ± 0.1
	^{137}Cs	26.1 ± 1.6	27.1 ± 1.7	
4[a]	^{134}Cs	48.5 ± 3.8	87.9 ± 6.9	1.0 ± 0.1
	^{137}Cs	80.4 ± 8.0	83.8 ± 8.4	
5A[b]	^{134}Cs	4.7 ± 0.5	8.9 ± 0.9	1.1 ± 0.1
	^{137}Cs	8.0 ± 0.7	8.4 ± 0.7	
5B[b]	^{134}Cs	4.6 ± 0.6	8.6 ± 1.2	1.0 ± 0.2
	^{137}Cs	8.3 ± 0.7	8.6 ± 0.8	
6A[b]	^{134}Cs	4.6 ± 0.4	8.7 ± 0.8	1.1 ± 0.1
	^{137}Cs	7.6 ± 0.7	8.0 ± 0.8	
6B[b]	^{134}Cs	5.9 ± 0.6	11.2 ± 1.1	1.2 ± 0.1
	^{137}Cs	8.9 ± 0.8	9.3 ± 0.8	

Note that only samples with detectable ^{134}Cs and ^{137}Cs activity are shown.
The data was decay corrected to the date of the Fukushima Dai-ichi nuclear disaster (March 11, 2011).
The reported uncertainties are at the 2σ level.
[a] Food basket samples (2 h count time).
[b] Store bought samples (same brand), each with two sub-samples, A and B (6 h count time).

spectrum efficiencies, a complex Monte-Carlo simulation of the Compton-suppressed gamma spectrometer was employed using the Geant4 Toolkit. It consisted of a detailed detector geometry definition along with the definition of the physical processes that occur within the system. For each radioactive decay event, each of the gamma rays produced were tracked and the subsequent deposition in each detector volume was recorded, allowing for the creation of coincidence and anti-coincidence spectra. Previous studies have shown that these spectra closely match those produced by the experimental setup (Agostinelli et al., 2003). With the known number of decays for the specified radioisotope and the resulting simulated spectra, the efficiency values needed to perform the activity calculations were determined.

3. Results and discussion

3.1. ^{134}Cs/^{137}Cs ratio determination

The Fukushima Dai-ichi nuclear accident released approximately equal quantities of ^{134}Cs and ^{137}Cs into the environment, with estimates of 1 × 10^{16} Bq and 3.5 × 10^{15} Bq of each into the atmosphere and the ocean, respectively (IAEA, 2012; Stohl et al., 2012; TEPCO, 2012). Since the Fukushima Dai-ichi nuclear accident, the ^{134}Cs–^{137}Cs ratio measured in soil (Tagami et al., 2011; Yamaguchi, 2011), water (Buesseler et al., 2012; Honda et al., 2012; Kamenik et al., 2013; Sakaguchi et al., 2012) and atmosphere has been consistently shown to be 1:1 (Friese et al., 2013;

Table 2
Conventional gamma spectroscopic results (72 h counts) from the analysis of tea extract, residue and filter.

Sample	Type	Nuclide	Measured activity (mBq)	Initial activity of dry tea sub-sample (mBq)[a]	Activity recovered (%)[b]
4a	Extract	^{134}Cs	70.1 ± 9.3	175 ± 14	40.2 ± 6.2
		^{137}Cs	192 ± 36	325 ± 33	59 ± 13
	Residue	^{134}Cs	n.d.	174 ± 14	n.d.
		^{137}Cs	47 ± 25	325 ± 32	14.3 ± 7.8
	Filter	^{134}Cs	n.d.	174 ± 14	n.d.
		^{137}Cs	7 ± 13	325 ± 32	2.0 ± 4.1
	^{134}Cs total recovery				**40.2 ± 6.2**
	^{137}Cs total recovery				**75 ± 15**
4b	Extract	^{134}Cs	67 ± 12	169 ± 13	39.6 ± 8.0
		^{137}Cs	168 ± 16	320 ± 32	52.4 ± 7.2
	Residue	^{134}Cs	n.d.	168 ± 13	n.d.
		^{137}Cs	45.0 ± 5.9	320 ± 32	14.1 ± 2.3
	Filter	^{134}Cs	n.d.	165 ± 13	n.d.
		^{137}Cs	22.0 ± 5.4	321 ± 32	6.9 ± 1.8
	^{134}Cs total recovery				**39.6 ± 8.0**
	^{137}Cs total recovery				**73.3 ± 7.8**
4c	Extract	^{134}Cs	88 ± 14	166 ± 13	53.0 ± 9.3
		^{137}Cs	181.7 ± 3.8	320 ± 32	56.9 ± 5.8
	Residue	^{134}Cs	n.d.	166 ± 13	n.d.
		^{137}Cs	32 ± 13	320 ± 32	10.0 ± 4.1
	Filter	^{134}Cs	n.d.	166 ± 13	n.d.
		^{137}Cs	2 ± 16	321 ± 32	0.7 ± 4.9
	^{134}Cs total recovery				**53.0 ± 9.3**
	^{137}Cs total recovery				**67.5 ± 8.6**

The reported uncertainties are at the 2σ level.
n.d. = not detected.
[a] The expected activity of the original dry tea sample (4 g) on the day of measurement of the extract, residue or filter.
[b] The reported uncertainties are combined uncertainties.

Table 3
Compton-suppressed gamma spectroscopic results (24 h count) from the analysis of tea extract, residue and filter.

Sample	Type	Nuclide	Measured activity (mBq)	Initial activity of dry tea sub-sample (mBq)[a]	Activity recovered (%)[b]
4a	Extract	^{134}Cs	93 ± 20	167 ± 13	56 ± 13
		^{137}Cs	219 ± 24	324 ± 32	68 ± 10
	Residue	^{134}Cs	39.1 ± 8.2	165 ± 13	23.6 ± 5.3
		^{137}Cs	67 ± 11	323 ± 32	20.6 ± 3.9
	Filter	^{134}Cs	n.d.	164 ± 13	n.d.
		^{137}Cs	53 ± 11	323 ± 32	16.3 ± 3.8
	^{134}Cs total recovery				**79 ± 14**
	^{137}Cs total recovery				**105 ± 11**
4b	Extract	^{134}Cs	110 ± 21	165 ± 13	67 ± 14
		^{137}Cs	188 ± 24	320 ± 32	58.8 ± 9.6
	Residue	^{134}Cs	n.d.	164 ± 13	n.d.
		^{137}Cs	66 ± 12	320 ± 32	20.6 ± 4.2
	Filter	^{134}Cs	n.d.	163 ± 13	n.d.
		^{137}Cs	47 ± 11	320 ± 32	14.6 ± 3.7
	^{134}Cs total recovery				**67 ± 14**
	^{137}Cs total recovery				**94 ± 11**
4c	Extract	^{134}Cs	115 ± 20	165 ± 13	70 ± 13
		^{137}Cs	211 ± 28	319 ± 32	66 ± 11
	Residue	^{134}Cs	48.9 ± 8.8	163 ± 13	30.0 ± 5.9
		^{137}Cs	74 ± 11	319 ± 32	23.0 ± 4.1
	Filter	^{134}Cs	n.d.	162 ± 13	n.d.
		^{137}Cs	37.2 ± 9.7	320 ± 32	11.6 ± 3.2
	^{134}Cs total recovery				**100 ± 14**
	^{137}Cs total recovery				**101 ± 12**

The reported uncertainties are at the 2σ level.
n.d. = not detected.

[a] The expected activity of the original dry tea sample (4 g) on the day of measurement of the extract, residue or filter (n.d. = not detected).

[b] The reported uncertainties are combined uncertainties.

Lozano et al., 2011; Manolopoulou et al., 2011; Masson et al., 2011; Paatero et al., 2012).

The four green tea samples with detectable levels of both ^{134}Cs and ^{137}Cs collected through Health Canada's Food Basket Survey are listed in Table 1. The most active tea sample (4) was found to contain 48.5 ± 3.8 Bq/kg of ^{134}Cs and 80.4 ± 8.0 Bq/kg of ^{137}Cs on the date of measurement. Only one of ten store-bought tea samples (Table 1), duplicate sub-samples 5A and 5B, had detectable quantities of ^{134}Cs and ^{137}Cs (6 h counting time). As a follow-up to this finding, a second sample of the same brand was purchased, and it also showed detectable quantities of ^{134}Cs and ^{137}Cs (Table 1, duplicate sub-samples 6A and 6B). The measured ^{134}Cs/^{137}Cs activity ratios for the dried tea samples (Table 1), determined with decay correction to March 11, 2011, consistently approached unity in all cases. This finding strongly suggests that the found radiocesium in these samples originated solely from the Fukushima Daiichi nuclear incident.

3.2. ^{134}Cs and ^{137}Cs infusion results

3.2.1. General

The extractability of radiocesium from processed green tea leaves was investigated using the most contaminated sample (4, Table 1). The extraction efficiency of minerals is dependent on the infusion conditions (Welna et al., 2012). In these experiments, a tea to water mass ratio of 0.02 was selected to be consistent with both common practice and those literature reports which have examined cesium extraction from green tea (Matsuura et al., 2000; Tagami et al., 2012). The other conditions, consisting of infusion duration (10 min), infusion temperature (100 °C), physical form of the tea (powder), and agitation were selected to be conducive to mineral extraction within the limits of practical application. The proportion of activity found in the extract may be of primary interest to most since it is the component available for human consumption. Nevertheless, a full account of the radiocesium distribution (extract, residue, and filter) was made for both ^{134}Cs and ^{137}Cs as this provides a degree of redundancy, and hence, opportunity for validation while showcasing the analytical limitations and strengths of the methods employed. In addition, a complete activity account also assigns a proportionate degree of confidence to the activity distribution data.

The individual recoveries were calculated by dividing the measured activity for the extract, residue and filter by the initial activity of the dry tea sub-sample used in the extraction experiment. These values were summed to give a total recovery for each individual sample (Tables 2 and 3). The average total recovery was calculated from the sum of the average recoveries of the three components (extract, residue, filter) from the three replicate extraction experiments (Table 4). A “non-detected” (n.d.) result means that there was no discernable ^{134}Cs/^{137}Cs signal in the counting time of the experiment to give an analytically significant result. Therefore, the n.d. results did not enter into the calculations.

3.2.2. Conventional gamma spectroscopy

Representative examples of the conventional gamma spectra for

Table 4
Average ^{134}Cs and ^{137}Cs recoveries from both conventional (Table 2) and Compton-suppressed (Table 3) gamma spectroscopic analysis of the triplicate extraction experiments.

	Nuclide	Average recovery (%)	
		Conventional (72 h)	Compton-suppressed (24 h)
Extract	^{134}Cs	44.2 ± 7.6	64.2 ± 7.5
	^{137}Cs	56.1 ± 3.4	64.2 ± 4.8
Residue	^{134}Cs	n.d.	18 ± 16
	^{137}Cs	12.8 ± 2.4	21.4 ± 1.4
Filter	^{134}Cs	n.d.	n.d.
	^{137}Cs	3.2 ± 3.3	14.2 ± 2.4
Total	^{134}Cs	44.2 ± 7.6	82 ± 17
	^{137}Cs	72.1 ± 4.1	99.8 ± 5.4

The reported uncertainties are standard deviations from three measurements (1σ).
n.d. = not detected.

the original dry tea sample, along with those of its subsequent extract and residue samples, are shown in Fig. 1. From these, it is qualitatively apparent that, despite a prolonged counting time of 72 h, the characteristic emission lines of highest abundance in the extract and residue samples are significantly diminished relative to those in the parent sample spectra, particularly for the shorter-lived ^{134}Cs. This is due, in large part, to the fact that the sub-sample size (4 g) is only about 5% of the sample 4 that was counted before extraction. The consequence of a significantly diminished signal-to-noise ratio is reflected in Tables 2 and 4, which present the conventional gamma spectrometric results for each of the three replicate extraction experiments and their averages, respectively. Minimal detectable concentration (MDC) values for ^{134}Cs and ^{137}Cs were calculated using the Currie method (Currie, 1968). For ^{134}Cs, typical MDC values for 72 h counting times of the aqueous extract (~130 g), residual tea solids (~1.9 g), and filter media (~0.6 g) were found to be in the ranges of 0.2–0.4 Bq/kg, 12.2–13.6 Bq/kg, and 35.3–39.5 Bq/kg, respectively. For ^{137}Cs, typical MDC values for 72 h counting times of the aqueous extract, residual tea solids, and filter media were found to be in the ranges of 0.2–0.5 Bq/kg, 8.2–10.8 Bq/kg, and 22.1–34.3 Bq/kg, respectively. While results for recovered activity were comparable between the three replicate experiments, there was a consistent failure to fully account for the activity content of the original tea sample, as reflected by the average total activity recoveries of 44.2 ± 7.6% and 72.1 ± 4.1% for ^{134}Cs and ^{137}Cs, respectively. While this data, particularly for the longer-lived ^{137}Cs, shows that the radiocesium is localized to a large extent in the aqueous extract (average based on ^{137}Cs is 56.1 ± 3.4%), no firm conclusions can be made without a full account of the initial radiocesium content. This is where Compton-suppressed gamma spectrometric measurement provided significant refinement, without the need for unwieldy sample sizes or sample concentration.

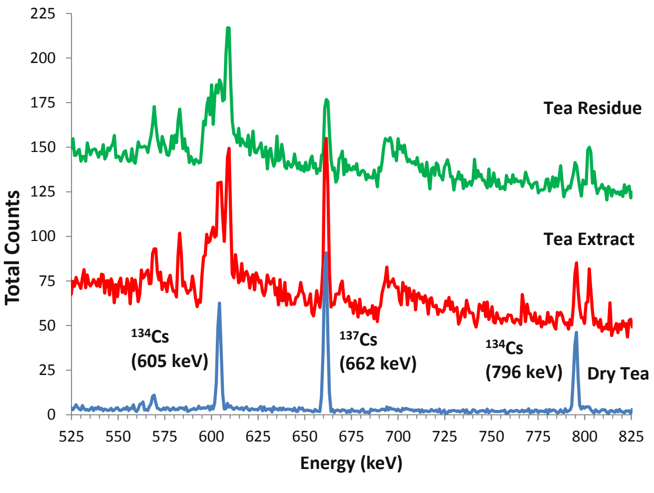

Fig. 1. Gamma spectra of the dry tea sample 4 (2 h count, bottom blue) and subsequent extract (72 h count, middle red) and residue (72 h count, top green) of sub-samples (~4 g) illustrating the characteristic ^{134}Cs and ^{137}Cs emissions obtained by conventional gamma spectroscopy (Gamma Analyst). The spectra have been offset for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

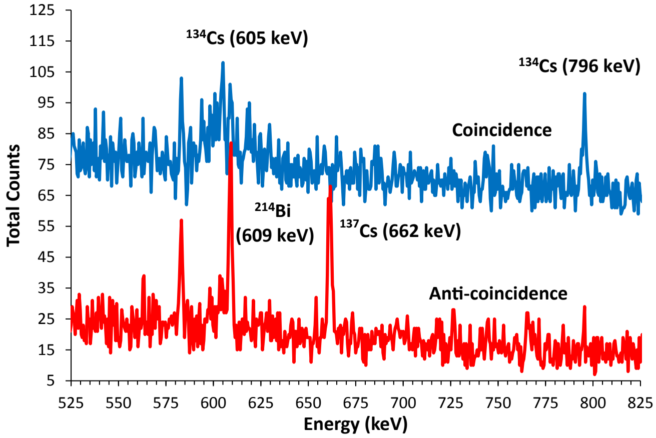

Fig. 2. Coincidence (top, blue) and anti-coincidence (bottom, red) Compton-suppressed gamma spectra of the tea extract for sub-sample 4a (24 h count). The coincidence spectrum has been offset for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2.3. Compton-suppressed gamma spectroscopy

The Compton-suppressed gamma spectrometer was simultaneously operated in anti-coincidence and coincidence mode to measure ^{137}Cs and ^{134}Cs, respectively. Examples of the anti-coincidence and coincidence spectra for the extract of tea sub-sample 4a are shown in Fig. 2. The principles of operation have been described extensively elsewhere (Zhang et al., 2012). Briefly, in anti-coincidence mode, the Compton interactions in the primary detector (HPGe) are rejected on the basis of simultaneous detection of scattered gamma photons in the peripheral guard (NaI) detector. Photoelectric events in the primary detector are not affected, leading to suppression of the Compton continuum. As a result, the ^{137}Cs peak (662 keV) is enhanced in the anti-coincidence spectrum (Fig. 2, bottom) since Compton events and emission from other nuclides with complex decay schemes are effectively screened out. Nuclides with complex decay schemes, such as ^{134}Cs, may emit several coincident gamma photons. It is therefore possible that two gamma photons from the same disintegration will be detected by both detectors simultaneously. Such occurrences, in anti-coincidence mode, will be misinterpreted, and subsequently rejected as Compton events, leading to reduced photopeak efficiency. To resolve this problem, a coincidence counting mode was employed, whereby an energy window is defined such that only the primary detector events that are in coincidence with a selected energy event in the guard detector are recorded. Consequently, for nuclides characterized by coincident photon emission, using this approach leads to high photopeak efficiency with concomitant suppression of the Compton scatter background. Unfortunately, however, such defined specificity also precludes multi-nuclide analysis in this counting mode. The coincidence spectrum (Fig. 2, top) of sub-sample 4a shows enhancement of the major coincident ^{134}Cs peaks at 605 keV and 796 keV. The ^{137}Cs (662 keV) and the ^{214}Bi peak (609 keV), a spectral interference of the ^{134}Cs peak at 605 keV, were rejected and therefore not present in the coincidence spectrum.

With Compton-suppressed gamma spectroscopy, the typical MDC values for ^{134}Cs (24 h counting time) of the aqueous extract (~130 g), residual tea solids (~1.9 g), and filter media (~0.6 g) were found to be in the ranges of 0.01–0.02 Bq/kg, 0.66–1.59 Bq/kg, and 2.10–5.05 Bq/kg, respectively. For ^{137}Cs (24 h counting time), the typical MDC values for of the aqueous extract, residual tea solids, and filter media were found to be in the ranges of 0.01–0.03 Bq/kg, 0.71–1.83 Bq/kg, and 2.23–5.80 Bq/kg, respectively. Compared to the MDC values obtained for ^{134}Cs and ^{137}Cs using conventional gamma spectroscopy (72 h counting time, Section 3.2.2), the MDC values observed using Compton-suppressed detection were substantially reduced even though the samples were counted for one-third of the time (24 h). The enhanced detection limits offered by Compton-suppressed detection are consistent with the noted background suppression described in the literature (Zhang et al., 2013).

The Compton-suppressed gamma spectroscopy results from the three replicate extraction experiments, and their averages relative to those obtained by conventional gamma spectroscopy, are presented in Tables 3 and 4, respectively. The total activity recovered for both ^{134}Cs and ^{137}Cs has been much improved compared to that determined by conventional means. Total activity recoveries for ^{134}Cs and ^{137}Cs were, respectively, 44.2 ± 7.6% and 72.1 ± 4.1% as determined by conventional gamma spectroscopy. Employing Compton-suppressed gamma spectroscopy resulted in total activity recoveries of 82 ± 17% and 99.8 ± 5.4% for ^{134}Cs and ^{137}Cs, respectively. The longer-lived ^{137}Cs activity recovery is more complete and its partitioning is more consistent between replicate extractions compared to that for ^{134}Cs. The activity partitioning of ^{134}Cs in the tea residue showed more variability, while it was not detected at all on the filter medium.

The drastic improvement in total activity recovered is due, in large part, to detection of a significant fraction of radiocesium on the filter medium and tea residue that remains from the extraction process. Under the conditions employed in this study, based upon ^{137}Cs, 21.4 ± 1.4% and 14.2 ± 2.4% of the radiocesium from tea leaves is associated with the residual tea solids and filter medium, respectively (Table 4). This is not surprising given that both materials are capable of binding charged, metallic species.

The filter media is polysaccharide (cellulose) based which, even in a textile format, will interact with solubilized metals electrostatically (ion exchange) or, for the heavier non-alkali metals in particular, by ligand-metal complex formation (Öztürk et al., 2009). However, relative to the number of ^{134}Cs and ^{137}Cs atoms represented in the 4 g sub-sample, there is an overwhelming excess of stable cesium and other closely related metals, such as potassium, which are extracted to a large extent (Matsuura et al., 2000, 2001; Szymczycha-Madeja et al., 2012). The high mineral content of the infusion provides for strong competitive displacement of the cesium activity that would otherwise bind to the cellulose of the filter paper. As such, any activity associated with the filter paper is most likely due to retention of fine particulates of the solid tea residue. This has been supported by visual inspection, in this case. For this reason, the activity associated with the filter medium should not be added to the content of the aqueous extract.

The chemical composition of tea solids is very complex, and much of it is well-suited to bind charged metallic species in a similar fashion (Dekker, 1995; Polar, 2002; Welna et al., 2012). While many of the chemical compounds (largely polyphenolic) in tea are water soluble and therefore extracted to a significant extent into the aqueous phase during infusions, a myriad of insoluble and/or non-solubilized compounds persist on the tea solids, including polyphenolics (Astill et al., 2001; Lakenbrink et al., 2000; Welna et al., 2012). These immobilized compounds impart a significant metal binding capacity (ion exchange and ligating) to the residual tea solids, to such an extent that they have been proposed as an abundant and cost-effective means to remove toxic metals associated with industrial waste from natural waters (Wasewar, 2010).

Compton-suppressed results for the partitioning of ^{134}Cs and ^{137}Cs into the aqueous extract showed excellent agreement (64.2 ± 7.5% $_{\text{(avg.)}}$ and 64.2 ± 4.8% $_{\text{(avg.)}}$, respectively, Table 4) and were larger than those determined by conventional gamma measurement (44.2 ± 7.6% and 56.1 ± 3.4% for ^{134}Cs and ^{137}Cs, respectively, Table 4). It is worth comparing these results to other studies which have directly examined the extraction efficiency of cesium from green tea infusions, of which there are only three, to date. The first, a report from Japan's Radioactive Waste Management Center (1994), reported contradictory cesium extraction efficiencies of 7% and 50% based on radiocesium (^{137}Cs and ^{134}Cs) and stable cesium, respectively. The second study by Matsuura et al. (2000) involved non-radiometric analysis (ICP-AES/ICP-MS) of green tea solids (leaves) before and after infusion (tea to water mass ratio of 0.02, 100 °C, 5 min, no agitation) and found cesium extraction efficiencies of 55–60%. The third, and most recent report, by Tagami et al. (2012) described gamma spectroscopic (^{134}Cs and ^{137}Cs) analysis of green tea solids (leaves) before and after infusion (tea to water mass ratio of 0.02, 90 °C, 1 min, no agitation) that yielded extraction efficiencies ranging from 50 to 70% (60 ± 9% $_{\text{(avg)}}$). Relative to the results of these previous reports, the extraction efficiency obtained here (64.2 ± 4.8% $_{\text{(avg.)}}$ based on ^{137}Cs, Table 4) is fairly consistent despite having employed infusion conditions that should enhance aqueous extraction efficiency within reasonable beverage preparation limits (i.e. longer extraction time of 10 min, the use of powdered tea sample to increase surface contact, and the use of mechanical agitation). The agreement between literature results and the results of this study is testament to the fact that the system equilibrates quickly. The water soluble components (i.e. radiocesium) are extracted efficiently and quickly during the tea preparation process. Given that we have selected infusion conditions that are conducive to greater cesium extraction efficiency, within practical limits, we propose that the extraction efficiency determined here could be used toward establishing an upper limit (or worst case scenario) for internal dose estimation stemming from the consumption of radiocesium contaminated green tea preparations.

3.3. Effective dose estimates

The Health Canada recommended action levels for food contaminated with ^{134}Cs or ^{137}Cs are 100 Bq/kg for public drinking water, 300 Bq/kg for fresh liquid milk and 1000 Bq/kg for other commercial foods and beverages, including tea (Health Canada, 2000). Thus, the detected quantities of ^{134}Cs and ^{137}Cs in the dried tea samples presented in Table 1 (4–80 Bq/kg) do not constitute a health concern. To prove this point further, the effective dose estimates arising from ingestion of the most contaminated green tea sample (Table 1, sample 4) are presented in Table 5 using the dose coefficients for internal exposure via ingestion for adults, as recommended by the International Commission on Radiological Protection (ICRP, 2012). These dose estimates have been determined by applying the extraction efficiency of 64.2 ± 4.8% (Table 4) under matching conditions, i.e. a 4.0 g quantity of dried tea infused in 0.2 L of water. The ^{134}Cs and ^{137}Cs activity levels used for dose calculation were those originally measured (Table 1, sample 4) in the dried tea samples. Note that these dose estimates assume there is no ingestion of the tea leaves (i.e. it is representative of a beverage preparation using bagged-tea), that the physical form of bagged, commercially available tea very closely resembles the dried tea that was used for these experiments, and that the dose estimates are based upon a serving size of 0.2 L.

According to a report prepared for Agriculture and Agri-Food Canada, the annual per capita consumption of tea in Canada is about 80 L (Serecon, 2005). The consumption rate applied here for internal dose estimation (0.2 L–0.4 L/day) yields an annual, per capita consumption of 73–146 L with a corresponding effective dose of 1.8–3.7 μSv (Table 5), making this a very conservative approximation. By comparison to international averages for effective dose reported by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), the total (external + internal) annual effective dose arising from naturally occurring radiation sources is 2.4 mSv y^{-1}, while the annual effective dose due to the ingestion of naturally occurring radionuclides (U and Th decay series plus ^{40}K) is 0.28 mSv y^{-1} (UNSCEAR, 2000). It is clear, then, that the contamination levels of Fukushima-

Table 5
Effective dose estimation (adults) from consumption of the most contaminated green tea sample (sample 4, Table 1) assuming 4.0 g tea per 0.2 L serving.

	Activity Bq (4.0 g green tea)	Dose coefficient nSv/Bq	Effective dose, µSv (4.0 g, 0.2 L serving)	Effective dose µSv (0.2 L/day for a year)	Effective dose µSv (0.4 L/day for a year)
^{134}Cs	0.124 ± 0.012	19	0.0024 ± 0.0002	0.86 ± 0.08	1.72 ± 0.17
^{137}Cs	0.206 ± 0.022	13	0.0027 ± 0.0003	0.98 ± 0.10	1.95 ± 0.21
Sum			0.0051 ± 0.0007	1.84 ± 0.25	3.67 ± 0.54

derived ^{134}Cs and ^{137}Cs in the tea products encountered in this study pose no health risk.

4. Conclusion

The Radiation Surveillance Division has identified four green tea products of Japanese origin through Health Canada's 2012 Food Basket Survey which contain measurable quantities of ^{134}Cs and ^{137}Cs. As a follow-up, eleven additional green tea products were purchased in Ottawa, two of which showed measurable quantities of ^{134}Cs and ^{137}Cs. Corrected to the Fukushima Dai-ichi nuclear accident of March 11, 2011, the ^{134}Cs/^{137}Cs ratio in all cases was found to be consistent with the established ^{134}Cs/^{137}Cs ratio (1:1) at the time of the accident. This finding strongly indicates that this contamination originates solely from the Fukushima Dai-ichi nuclear accident. Sub-samples taken from the most contaminated green tea product were used to simulate upper limits of typical infusion conditions for beverage preparation and consumption (100 °C, 10 min, homogenous tea powder, tea/water mass ratio of 0.02). Both conventional and Compton-suppressed gamma spectroscopy were employed to determine the ^{134}Cs and ^{137}Cs activity distribution amongst the components of the extraction experiments. For the small sub-samples used for these experiments (~4 g), the 72 h counting times by conventional gamma spectroscopic means proved to be insufficient in providing a complete and reliable activity profile for these nuclides, particularly for the relatively shorter lived ^{134}Cs. However, with 24 h counting times, Compton-suppressed spectroscopic analysis aided greatly in providing a more complete and accurate activity distribution profile, underscoring its utility for environmental sample measurement. As a result, excellent agreement was obtained for aqueous extraction efficiencies based on ^{134}Cs (64.2 ± 7.5%) and ^{137}Cs (64.2 ± 4.8%), and these results are, in turn, consistent with analogous literature reports despite variation in infusion conditions. For the most contaminated, commercially available sample encountered by Health Canada, at consumption rates that greatly exceed per capita dietary habits of Canadians, this amounted to an annual effective dose (1.8–3.7 µSv) that is dwarfed by the effective doses received from naturally occurring radioactive sources. As such, there is no health risk posed to Canadians who consume tea beverages contaminated with radiocesium at the levels encountered in this study.

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