Journal of Environmental Radioactivity 151 (2016) 601–608

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Natural and anthropogenic radionuclide activity concentrations in the New Zealand diet

Andrew J. Pearson [a, b, *], Sally Gaw [b], Nikolaus Hermanspahn [c], Chris N. Glover [b]

[a] Ministry for Primary Industries, PO Box 2526, Wellington, 6140, New Zealand
[b] University of Canterbury, Private Bag 4800, Christchurch, 8140, New Zealand
[c] Institute of Environmental Science & Research Ltd, PO Box 29-181, Christchurch, 8540, New Zealand

ARTICLE INFO

Article history:
Received 10 February 2015
Received in revised form
15 May 2015
Accepted 25 May 2015
Available online 18 June 2015

Keywords:
Caesium
Polonium
Uranium
Dietary monitoring
Dietary radionuclide activity
New Zealand

ABSTRACT

To support New Zealand's food safety monitoring regime, a survey was undertaken to establish radionuclide activity concentrations across the New Zealand diet. This survey was undertaken to better understand the radioactivity content of the modern diet and also to assess the suitability of the current use of milk as a sentinel for dietary radionuclide trends. Thirteen radionuclides were analysed in 40 common food commodities, including animal products, fruits, vegetables, cereal grains and seafood. Activity was detected for ^{137}Caesium, ^{90}Strontium and ^{131}Iodine. No other anthropogenic radionuclides were detected. Activity concentrations of the three natural radionuclides of Uranium and the daughter radionuclide ^{210}Polonium were detected in the majority of food sampled, with a large variation in magnitude. The maximum activity concentrations were detected in shellfish for all these radionuclides. Based on the established activity concentrations and ranges, the New Zealand diet contains activity concentrations of anthropogenic radionuclides far below the Codex Alimentarius guideline levels. Activity concentrations obtained for milk support its continued use as a sentinel for monitoring fallout radionuclides in terrestrial agriculture. The significant levels of natural and anthropogenic radionuclide activity concentrations detected in finfish and molluscs support undertaking further research to identify a suitable sentinel for New Zealand seafood monitoring.

1. Introduction

Dietary surveys are an invaluable source of data for undertaking risk assessments for public health. Such surveys enable concentrations of contaminants and the impact of reduction programs to be identified over a number of years. In New Zealand, dietary surveys have been undertaken over a number of decades; the most comprehensive is the New Zealand Total Diet Study which has been run seven times from 1974 to the latest in 2009 (Vannoort and Thomson, 2009). These surveys have quantified estimates of health risk for the New Zealand population through exposures to a range of agricultural chemicals and contaminants in the diet.

Assessing radionuclide contamination in the diet is an important consideration in modern food safety. Radionuclides can originate from a variety of sources and processes; either those occurring naturally, such as primordial or cosmogenic formation, or through human activities, such as release from nuclear weapons testing or accidents (UNSCEAR, 2000). Understanding the range of radionuclides in the diet and their respective activity concentrations is necessary to be able to quantify the risk of exposure. Characterising the current background activity of radionuclides in the diet makes it possible to better identify future contamination incidents and emerging long-term trends, and it enables possible mitigation before increasing levels of contamination become a significant health risk.

Radionuclide monitoring in New Zealand foods has focused on determining activity concentrations of ^{137}Caesium (^{137}Cs), and up until 2000, ^{90}Strontium (^{90}Sr) in milk powders (Matthews, 1993). These data have been used to estimate the contribution of nuclear testing fallout radionuclides to the diet. Radionuclide activity concentrations in milk have declined following their peak at an average of 33 Bq/kg ^{137}Cs and 5.5 Bq/kg ^{90}Sr in 1965. The most

* Corresponding author. Ministry for Primary Industries, PO Box 2526, Wellington, 6140, New Zealand.
E-mail addresses: andrew.pearson@mpi.govt.nz (A.J. Pearson), sally.gaw@canterbury.ac.nz (S. Gaw), Nikolaus.Hermanspahn@esr.cri.nz (N. Hermanspahn), chris.glover@canterbury.ac.nz (C.N. Glover).

http://dx.doi.org/10.1016/j.jenvrad.2015.05.022

recent study of activity concentrations in milk, in 2010, reported ^{137}Cs levels of 0.4–0.8 Bq/kg dry weight (dw) (Hermanspahn, 2010). However, no comprehensive survey of the radionuclide activity concentrations in other food types in the New Zealand diet has been conducted. It is unknown if milk remains an appropriate sentinel for radionuclide activity concentrations in the New Zealand diet.

Following the Fukushima-Daiichi Nuclear Power Plant accident in March 2011, global awareness has focused on the entry of imported foods with elevated anthropogenic radionuclide activity concentrations into the diet. New Zealand has previously implemented targeted monitoring; for example to determine ^{90}Sr and ^{137}Cs levels in fish from the North Pacific following the marine release from Fukushima-Daiichi (MPI, 2013). This study identified activity ranges for ^{134}Cs of 1.45–2.23 Bq/kg and for ^{137}Cs of 1.93–3.23 Bq/kg in mackerel from Japan, with no detections in tuna from Japan and in mackerel from other North Pacific nations. However results from imported food monitoring have had to be interpreted in isolation as the current ranges of radionuclides in the full New Zealand diet have not been characterised.

The objective of this research was to establish current activity concentrations across a range of food types available to New Zealand consumers for a number of natural and anthropogenic radionuclides. This was a component of a wider programme of research that included examining inputs into the diet and assessing the ingested ionising radiation dose to the New Zealand public. Targeted radionuclides were selected based on several criteria such as those previously identified or suspected to be present in the New Zealand environment, and/or by reference to international regulatory limits established by Codex Alimentarius (CAC, 1993). Additionally where no occurrence data was available for a radionuclide in New Zealand prioritisation was made for inclusion based on the results from overseas dietary monitoring programmes such as the United States Food and Drug Administration total diet survey (US FDA, 2006) and the United Kingdom's Radioactivity in Food and the Environment reports (RIFE, 2013). Interpretation of levels and comparison to results from other countries provides a useful benchmark to establish the current radiological status of the New Zealand diet. Another objective was to assess the appropriateness of the current practice of using milk as a sentinel for radionuclide contamination of the New Zealand diet.

2. Materials and methods

2.1. Sample description

Forty foods were chosen for sampling (Table 1). The majority of foods were domestically produced. Approximately 25% were seasonally imported and exclusively imported foods. Foods were selected based on prominence in the diet as determined from the New Zealand Total Diet Study (Vannoort and Thomson, 2009). Other considerations such as potential for concentrating radionuclides and potential sentinels for specific types of agriculture or aquaculture were taken into account. For example bottled water was selected over tap water due to the potential for higher activity concentrations of naturally occurring radionuclides in bore and artesian sources (EFSA, 2009). The foods tested were classified as fruits, vegetables, cereal grains, animal products, seafood, beverages and other foods.

Samples were obtained from a range of local supermarkets and wholesalers in the Christchurch and Wellington areas of New Zealand, with the exception being wild pork samples, which were sourced from the North Canterbury area of New Zealand. Where possible, food samples were chosen from across important domestic production regions. For example wine samples were selected so as to cover important viticulture regions of New Zealand, and shellfish and salmon obtained from regions with aquaculture. Sampling was undertaken through the year of January 2013 to January 2014. Perishable samples were collected fresh during this period according to seasonal availability. Four samples of each food type were obtained. Pooled samples of fruit and vegetables consisted of 400–600 g of individual pieces. Meat and fish sample sizes were approximately 300 g and liquid samples were approximately 500–1000 ml. Cereal and miscellaneous foods were obtained pre-packed at various weights.

Samples were prepared by removing inedible components, for example peels, hulls, stones and shells. Non-liquid samples were then homogenised, prior to separation of portions for individual radiochemistry assays. Exceptions to this preparation were coffee which was freshly extracted, through an espresso machine, at a ratio of 1 g of beans to 10 ml water; and tea which for the beta and alpha emitter assays was prepared as the brewed drink at a ratio of 1 g of tea leaves to 100 ml water. All liquid samples, with the exception of olive oil, were acidified with 69% nitric acid to 0.1M to prevent sorption losses to container walls.

2.2. Gamma emitters

All food samples were screened for gamma emitting radionuclides using gamma spectroscopy. Samples were prepared in either a 400 ml cylindrical container or a 400–600 ml Marinelli beaker and analysed using CANBERRA high purity germanium (HPGe) semiconductor detectors. Samples were counted for a minimum of 172,000 s. All spectra were analysed using Genie 2000 software to derive activity levels for ^{40}Potassium (^{40}K), ^{131}Iodine (^{131}I), ^{134}Caesium (^{134}Cs) and ^{137}Cs. A proportion of the CANBERRA HPGe detectors were also calibrated to quantify activity levels of ^{60}Cobalt (^{60}Co) and ^{241}Americium (^{241}Am).

Table 1
Sampling regime for dietary survey of radionuclides sorted by food classes.

Fruits	Vegetables	Cereal grains	Animal products	Seafood	Beverages	Other
Apple (D)	Beans (D)	Breakfast cereal (M)	Beef steak(D)	Lemonfish (Rig shark) (D)	Beer (D)	Chocolate (M)
Banana (I)	Broccoli (D)	Flour (M)	Chicken breast(D)	Salmon (D)	Coffee (I)	Olive oil (M)
Kiwifruit(D)	Lettuce(D)	Oats, rolled (M)	Chicken egg(D)	Shellfish (D)	Tea (I)	Peanut (I)
Orange (M)	Mushrooms(D)	Pasta (I)	Honey(D)	Tuna (M)	Water, bottled (D)	Spice mix (I)
Peach (D)	Potato(D)	Rice (I)	Cow's milk (D)			
Strawberry (D)	Pumpkin(D)		Lamb's liver(D)			
Wine (D)	Sweetcorn (D)		Pork chop (D)			
	Tomato(D)		Wild pork(D)			

(D) Samples of New Zealand origin.
(I) Samples of imported origin.
(M) Samples of New Zealand and imported origin.

2.3. Beta emitters

A pooled sample of all four replicates of each food type was analysed for the beta emitter ^{90}Sr. Samples were ashed at 500 °C, prior to acid digestion with a mixture of 69% nitric acid and 35% hydrochloric acid. Radiochemical separation was performed with an Eichrom Technologies Sr resin using the extraction chromatography principles in the ISO 18589-5, 2009 standard method. The samples were then analysed by Liquid Scintillation using a QUANTULUS low-background liquid scintillation counter (LSC).

Stable strontium was used to gravimetrically estimate method recovery, by addition of 5 mg strontium in the form of strontium nitrate prior to acid digestion. Method precision was confirmed with a 95% recovery over five blank spike repeats.

2.4. Alpha emitters

2.4.1. ^{210}Polonium

All samples were analysed for ^{210}Polonium (^{210}Po), with the exception of a single tuna sample. Perishable foods were dried at 80 °C prior to digestion using *aqua regia*, with addition of H_2O_2. Digestion of olive oil was preceded by saponification utilising saturated sodium hydroxide solution and 1 ml methanol to ensure even uptake of the yield tracer. Difficult matrices underwent a microwave digestion stage. The polonium isotopes were extracted from the digests by autodeposition onto silver disks. Plated disks were counted for 23 h using Passivated Implanted Planar Silicon (PIPS) detectors in a CANBERRA alpha spectrometer. ^{209}Polonium was used as a yield tracer to estimate method recovery. Sample recovery, background counts and decay corrections were applied to back-calculate ^{210}Po activity on the date of sample collection. Sample preparation and analysis was undertaken within a month of sample collection to reduce the influence of ^{210}Po ingrowth resulting from ^{210}Lead (^{210}Pb) decay.

Quality control of the ^{210}Po method was confirmed through the use of tracer blanks and a traceable ^{210}Pb solution containing ^{210}Po in secular equilibrium. A tenth of the samples were analysed in duplicate for quality control assessment.

2.4.2. $^{234,\ 235,\ 238}$Uranium and ^{239,240}Plutonium

Uranium and plutonium isotopes were analysed in pooled samples comprised of the four samples of each of the food types. Samples were ashed and acid digested. Digests then underwent radiochemical separation following the protocol specified in Eichrom Technologies method ACW 16 VBS prior to undergoing counting for 23 h using PIPS detectors in a CANBERRA alpha spectrometer. ^{232}Uranium and ^{242}Plutonium were utilised as yield tracers to estimate method recovery.

2.5. Data analysis

Quality assurance of the radioanalytical methods was provided through the laboratory's participation in proficiency test exercises organised by the IAEA and the UK National Physical Laboratory (IAEA, 2013; Dean et al., 2014). Background counts were obtained monthly for each analytical instrument. Additional steps included use of scintillant blanks in each batch run of the LSC and reagent and matrix spikes to validate methods for the alpha spectrometry. Alpha spectrometry assays resulting in peak interference were repeated to obtain clearly defined peak counts.

Results for grains and spice mix are reported as Bq/kg dw. All other samples are reported as Bq/kg wet weight (ww) unless otherwise specified. Minimum Detectable Concentrations (MDCs) were calculated for each assay according to the method defined by Currie (1968).

For most of the assays a high proportion of non-detected results were determined. To provide estimates of the likely activity range all means were reported as upper-bound, where the calculated MDC was taken as the result for a non-detect and lower-bound, where zero activity was assumed for a non-detect. For gamma spectroscopy any indicative trace activities above the qualitative determination limit but below the MDC have been reported.

3. Results & discussion

3.1. Anthropogenic gamma-emitting radionuclides

All 160 individual food samples were analysed through gamma spectroscopy. The resulting spectra were interpreted to derive activity concentrations and MDC for a range of gamma-emitting radionuclides. Of primary interest were the fission products ^{131}I, ^{134}Cs and ^{137}Cs which due to their volatility are environmental contaminants and human health risks in the short to medium term duration following a nuclear release. Activity concentrations for ^{60}Co and ^{241}Am were also reported due to their potential health significance if present in the diet, as evidenced by both having established Codex Alimentarius Guideline Limits in food (CAC, 1995). Data on the occurrence of either radionuclide in the New Zealand diet was also absent through which to indicate if contamination resulting from their use in non-nuclear applications was a concern.

The gamma emitting anthropogenic radionuclide ^{134}Cs was not detected in any of the 160 samples analysed (MDCs were in the range of 0.07–0.41 Bq/kg). As the Fukushima-Daiichi nuclear accident was the only large scale emission of ^{134}Cs in recent times, any detection of this isotope can be assumed to have come from Fukushima with almost certainty. For example in Pacific bluefin tuna tested in the Eastern Pacific following the accident ^{134}Cs was detected with a mean activity of 4 Bq/kg dry weight (dw) (approximately 1 Bq/kg ww) (Madigan et al., 2012).

Activity of ^{137}Cs was quantified in five samples and indicative trace activity was reported in a further 19 samples covering all food classes but with highest frequency for seafood. The sampled marine fish included different fish stocks that are available to the New Zealand market with two Pacific Bluefin tuna of central Pacific origin, a single Southern Bluefin tuna of Southern Ocean origin and a locally caught Skipjack tuna. All the lemonfish were caught in New Zealand coastal waters. The occurrence of ^{137}Cs activity concentrations in all the marine fish samples from different stocks, coupled with the absence of ^{134}Cs activity concentrations suggests the detected ^{137}Cs activity concentrations are not of Fukushima-Daiichi origin. Consistent with this assertion the ^{137}Cs results for tuna are comparable to activity concentrations reported prior to the Fukushima-Daiichi accident. For example, ^{137}Cs activity concentrations of 1.4 Bq/kg dw (approximately 0.35 Bq/kg ww) were reported in Pacific Bluefin tuna sampled in the Eastern Pacific in 2008 (Madigan et al., 2012). The reported levels of ^{137}Cs in fish for the current survey are also in similar ranges to those reported in surveys from other ocean bodies, including the Arabian Gulf and North Atlantic Ocean (Goddard et al., 2003; Carvalho et al., 2011).

Activity concentrations of ^{137}Cs reported in land-based agriculture produce were all at trace levels, falling below the calculated MDCs for the assay (Table 2). These results indicate that no significant terrestrial contamination is present. The pork and wild pork samples were all domestically raised or caught and as such the indicated activity concentrations of 0.05–0.16 Bq/kg likely represent the current residual level of ^{137}Cs in the New Zealand food chain from historical global fallout. Similar trace values for sweetcorn, potato and tomato, which were all domestically grown, also indicate a trace presence of ^{137}Cs in New Zealand soils. The presence of detectable ^{137}Cs in two milk samples is consistent with milk

Table 2
Detected wet weight activity concentrations and assay MDCs for ^{137}Caesium in a survey of 160 foods from the New Zealand diet.

Food sample	Assay MDC (Bq/kg)	Reported activity concentration (Bq/kg)
Banana	<0.15	0.09
Cereal	<0.26 (dw)	0.20 (dw)
Lamb's liver	<0.13	0.07
Lemonfish	<0.11	0.17
Lemonfish	<0.19	0.16
Lemonfish	<0.28	0.36
Lemonfish	<0.11	0.13
Milk	<0.15	0.08
Milk	<0.13	0.07
Peanut	<0.26	0.15
Pork	<0.08	0.05
Potato	<0.14	0.07
Spice mix	<0.30 (dw)	0.18 (dw)
Spice mix	<0.23 (dw)	0.12 (dw)
Sweetcorn	<0.12	0.06
Tea	<0.36 (dw)	0.27 (dw)
Tea	<0.36 (dw)	0.21 (dw)
Tomato	<0.15	0.09
Tuna	<0.12	0.10
Tuna	<0.38	0.44
Tuna	<0.17	0.15
Tuna	<0.16	0.27
Wild pork	<0.20	0.16
Wild pork	<0.12	0.06

monitoring data for New Zealand collected over the last decade which indicates a trace presence from historical fallout (Hermanspahn, 2010).

The detection of ^{137}Cs trace activity in two of the spice mixture samples and in two tea leaf samples, all of which were imported, are likely to be a factor of the degree of concentration of the ingredients in these foods and the potential for higher background ^{137}Cs in the northern hemisphere countries of origin. All of the detections reported for ^{137}Cs were, however, below the Codex Alimentarius guideline level of 1000 Bq/kg (CAC, 1995).

Trace activity of ^{131}I was reported in a shellfish sample. The validity of this result was confirmed with analysis of a follow-up sample from the same aquaculture site, which also reported trace ^{131}I activity. Due to the short half-life of this isotope (8.02 days) the presence of this radionuclide is unlikely to have originated from sources outside New Zealand. Other surveys from overseas have reported similar detections of ^{131}I in seafood (Goddard et al., 2003). A study in Australia confirmed that ^{131}I passes through wastewater treatment plants and is taken up by algae growing near the outfalls, with the majority of the ^{131}I present attributed to nuclear medicine patients (Veliscek Carolan et al., 2011). ^{131}I is used in New Zealand for radiotherapy (Beach, 2005), including in the region of the shellfish sampling site. As the shellfish sampling site was in close proximity to a wastewater discharge, medical origin is the probable source for the presence of trace levels of this radionuclide. The detected activity concentration of ^{131}I in the shellfish sample was less than 1% of the Codex Alimentarius guideline level of 100 Bq/kg (CAC, 1995).

^{60}Co and ^{241}Am were analysed for in 82 samples. No detections were recorded. The MDC ranges for these two radionuclides were 0.10–0.49 Bq/kg and 0.05–0.27 Bq/kg respectively. Absence of any reported activity for ^{60}Co and ^{241}Am is consistent with other surveys, for example the US Food and Drug Administration Total diet survey (US FDA, 2006).

All the gamma spectra for the analysed food samples showed activity concentrations for ^{40}K. These ranged from bottled water at 1–6 Bq/L to tea leaves and spice mixes that had 300–1000 Bq/kg.

3.2. Beta emitters

Forty composite food samples were analysed for ^{90}Sr activity. ^{90}Sr was included in the survey as an important fission product for which historical monitoring in New Zealand indicated that terrestrial deposition occurred following global nuclear testing (Matthews, 1993). ^{90}Sr has an established Codex Alimentarius Guideline Limit in food (CAC, 1995).

Method recovery was calculated at 80–100% for all except the bottled water composite sample. For bottled water a 1.6 L composite sample was used for analysis leading to lower recovery but greater method sensitivity. MDCs for ^{90}Sr ranged from 0.01 to 0.46 Bq/kg, and ^{90}Sr activity was absent in 39 of the assayed samples. Activity of ^{90}Sr was detected in only a single composite spice mix sample and the average of a duplicate assay on this sample gave an activity concentration of 0.46 Bq/kg.

Current New Zealand milk monitoring does not include ^{90}Sr as it had depleted to levels below the MDC at the start of the millennium (Hermanspahn, 2010). Its absence in all domestically produced samples from this survey reinforces this approach and indicates that fallout ^{90}Sr may have become bound in soils or leached below the root zone and is therefore unavailable for uptake into the food chain.

The single detect in the imported spice mix composite is likely to be a factor of the concentrated nature of the ingredients in this food, a consequence of drying. Additionally, due to the origin of all the spice mix samples from Northern Hemisphere countries it may reflect higher backgrounds of ^{90}Sr due to the greater global fallout in the northern hemisphere (UNSCEAR, 2000). For example, the presence of trace ^{137}Cs activity in two of the individual spice mix samples would support that the presence of ^{90}Sr is as a fission product from residual nuclear fallout. Absence of ^{90}Sr in most food samples and the low level of ^{90}Sr detected in the spice mixture support the current practice of not monitoring for this radionuclide.

3.3. Alpha emitters

3.3.1. ^{210}Polonium

^{210}Po was selected for analysis based on consideration of its high dose conversion coefficient (ICRP, 2012) and a deficit of data on its magnitude in the New Zealand food chain. Additionally reports from overseas have indicated elevation of ^{210}Po can occur in the food chain from anthropogenic sources (McCartney et al., 2000). A total of 159 samples were analysed for ^{210}Po. One tuna sample was unavailable for ^{210}Po assay as it had been ashed to improve gamma spectroscopy sensitivity. Method recovery varied between samples from 10 to 85%, dependent on the difficulty of acid digesting the sample. Average recovery across all foods analysed was 54%. The mean relative standard deviation for duplicate samples was 27.5%. This value is dominated by counting statistics.

^{210}Po activity was absent in 56 of the analysed samples. There was no detection of ^{210}Po in any of the beer, broccoli, chicken, coffee, milk or pork samples. Calculated MDCs for bottled water were <0.0004 Bq/L, and for all other samples analysed ranged from <0.0045 to <0.1 Bq/kg dependent on sample volume and calculated recovery.

^{210}Po activity was determined in 103 of the analysed samples which encompassed a large variety of the foods (Table 3). There was also considerable variation between the different food types, with activity concentrations ranging over five orders of magnitude; most detected activity concentrations were, however, within the range of 0.005–0.05 Bq/kg. Of the samples sourced from terrestrial agriculture the highest ^{210}Po activity concentrations were determined in spice mix (1.3–5.6 Bq/kg). As with ^{90}Sr and ^{137}Cs these activity concentrations are likely to result from the high degree of

Table 3
Upper-bound mean radionuclide activity concentrations from analysis of 159 samples for ^{210}Po and mean activity concentrations for 40 composite food samples for ^{234}U and ^{238}U.

Food	Radionuclide activity concentration (Bq/kg)		
	^{238}U	^{234}U	^{210}Po
Apple	0.005	<0.006	0.088
Banana	0.004	<0.004	0.018
Beans	0.005	0.005	0.012
Beef steak	0.024	0.024	0.031
Beer	0.003	<0.008	<0.010
Breakfast cereal	0.011 (dw)	0.011 (dw)	0.080 (dw)
Broccoli	0.007	0.005	0.013
Chicken breast	0.043	0.051	<0.015
Chocolate	0.014	0.014	0.093
Coffee[a]	0.015	<0.010	<0.009
Corn	0.003	<0.005	0.043
Drinking water	0.001	0.002	0.001
Egg	0.006	<0.012	0.040
Flour	<0.002 (dw)	<0.005 (dw)	0.029 (dw)
Honey	<0.065	<0.090	0.029
Kiwifruit	0.004	<0.008	0.025
Lamb's liver	0.067	0.087	0.643
Lemonfish (Rig shark)	0.014	0.008	0.044
Lettuce	0.013	0.018	0.018
Milk	0.001	0.006	<0.009
Mushrooms	0.004	<0.005	0.039
Oats, rolled	0.010 (dw)	<0.005 (dw)	0.026 (dw)
Olive oil	0.002	<0.005	0.042
Orange	<0.002	<0.004	0.020
Pasta	0.068 (dw)	0.078 (dw)	0.049 (dw)
Peaches	<0.003	<0.004	0.091
Peanut	0.006	0.004	0.101
Pork chop	0.021	0.016	<0.016
Potato	<0.005	<0.008	0.011
Pumpkin	<0.003	<0.005	<0.009
Rice	0.007 (dw)	<0.006 (dw)	0.076 (dw)
Salmon	0.013	0.012	0.068
Shellfish	0.171	0.194	25.673
Spice mix	0.250 (dw)	0.300 (dw)	2.486 (dw)
Strawberries	0.005	<0.006	0.019
Tea[a]	<0.002	<0.007	0.028
Tomato	<0.003	<0.005	0.026
Tuna	0.040	0.041	3.659
Wild pork	0.016	0.018	0.182
Wine	0.011	0.033	0.013

[a] Analysed as prepared beverage.

concentration of the dried ingredients in these mixes. Levels in all other foods were below 1 Bq/kg.

Activity concentrations of ^{210}Po detected in New Zealand plant-derived foods were consistent with those reported overseas (Meli et al., 2014) (RIFE, 2013) (Salahel Din, 2011). The ^{210}Po activity ranges for cereals, fruits and vegetables all were comparable to the reference values of 0.06, 0.04 and 0.1 Bq/kg stated by UNSCEAR (2000).

An interesting comparison between farm-raised pork and wild pork can be made. The farm-raised pork had no detectable activity concentrations of ^{210}Po whereas the wild pork had activity concentrations in the range of 0.063–0.43 Bq/kg. Similar differences have been found overseas with a comparative study of Italian wild and raised species (Meli et al., 2013). The authors hypothesised that higher levels in wild pork may be a result of increased deposition of ^{210}Po in forests and higher transfer through the diet. Both factors are also likely to be relevant for the difference in activity concentrations noted in the present study between the New Zealand wild and domestic pigs.

The highest activity concentrations of ^{210}Po were found in shellfish with all four samples being in the range of 20.8–29.4 Bq/kg. These levels were likely to occur as a result of accumulation of ^{210}Po- and ^{210}Pb-rich particulates by these filter feeders. Levels of this magnitude are common for bivalve molluscs and correspond to the ranges of levels detected in shellfish from other studies in Croatia, India, Slovenia, Taiwan and the United Kingdom (Rozmaric et al., 2012; Sunith Shine et al., 2013; Štrok and Smodiš, 2011; Lee and Wang, 2013; Young et al., 2002). Amongst the other aquatic species tested, activity concentrations of ^{210}Po varied. Tuna muscle had activity concentrations of 2.2–6.4 Bq/kg, and lemonfish and salmon showed activity concentrations of 0.03–0.1 Bq/kg in muscle tissue.

3.3.2. *$^{234, 235, 238}$Uranium*

As uranium is naturally present in New Zealand soils at levels between 1 and 3 mg/kg (eqv. 12–37 Bq/kg ^{238}U) (Schipper et al., 2011), detection of activity concentrations in various commodities in the diet was expected. This study is presenting the first data on uranium content of New Zealand food.

Composite samples of each food-type, and individual shellfish samples, were analysed for alpha emissions corresponding to activity of the uranium isotopes ^{234}U, ^{235}U and ^{238}U. Of all analysed samples, 81% had detectable activity concentrations of ^{238}U and 54% had detectable activity concentrations of both ^{234}U and ^{238}U. Eight composite samples did not have any reported uranium isotope activity concentrations including peaches, tomato, oranges, pumpkin, potato, honey, flour and tea (Table 3). Recoveries commonly ranged from 50 to 90% for uranium. High sugar content in samples, for example in honey and wine, decreased the method recovery; in these samples recoveries of uranium ranged between 30 and 50%.

As ^{234}U is a daughter nuclide of ^{238}U, its activity in soils increases until equal to its parent; a state termed secular equilibrium (Rieppo, 1978). However, in water a phenomenon whereby variation of the activity ratio of ^{234}U: ^{238}U, towards ^{234}U, is often seen. This occurs as the initial decay of ^{238}U releases sufficient recoil to dislodge the daughter nuclide from the rocks in aquifers. The daughter nuclide and its further decay nuclides may become mobile in ground water due to this dislodgment and a change in the oxidation state of the daughter nuclide (Suksi et al., 2006). With use of ground water for irrigation the altered ratio is transferred to foods crops. Examples where ^{234}U: ^{238}U disequilibrium was evident in New Zealand-sourced foods for the current study include bottled water (2.1 ^{234}U/^{238}U), lettuce (1.4 ^{234}U/^{238}U), lamb's liver (1.3 ^{234}U/^{238}U) and chicken breast (1.2 ^{234}U/^{238}U).

^{235}U was only been detected in samples with the highest ^{238}U activity. Three samples of the 43 analysed had detectable activity concentrations of ^{235}U. These were spice mix, little-neck clams and lamb's liver.

In New Zealand the range of activity concentrations for ^{238}U in fruit were <2.3–11 mBq/kg, and in meat 16.2–67.1 mBq/kg; higher than the UN reference values of 3 and 2 mBq/kg respectively (UNSCEAR, 2000). As ^{238}U is naturally occurring this variation may be due to regional geological differences in uranium abundance. Another consideration is that many agricultural phosphate sources can contain significant uranium levels as a contaminant; as such heavily fertilised agricultural soils could accumulate higher uranium levels. However research on New Zealand soils, considering the potential for uranium contamination from phosphate applications, has indicated that annual accumulation is very low (Schipper et al., 2011).

The highest activity concentrations for the uranium isotopes, as for ^{210}Po, were reported in the shellfish samples, with one sample having 0.588 Bq/kg ^{234}U and 0.417 Bq/kg ^{238}U. The levels measured in shellfish are consistent with international data for uranium isotopes in seafood. For example, monitoring of mussels at sites around the coast of the United Kingdom identified levels of up to

0.841 Bq/kg, 0.028 Bq/kg and 0.758 Bq/kg for ^{234}U, ^{235}U and ^{238}U, respectively (Young et al., 2002).

Drinking water, in particular mineral water, can be a significant source for uranium dietary exposure (EFSA, 2009). The 1 mBq/L ^{238}U activity reported for the composite sample of New Zealand bottled waters is equal to the UN reference value for drinking water (UNSCEAR, 2000).

3.4. ^{239,240}Plutonium

The plutonium isotopes ^{239}Pu and ^{240}Pu are a concern as dietary contaminants as they have high ingestion dose conversion coefficients (ICRP, 2012). A degree of atmospheric deposition from global fallout of ^{239}Pu and ^{240}Pu has been reported in New Zealand (Hancock et al., 2011) although transfer into the food chain has not been previously reported.

Composite samples of each food-type, and individual shellfish samples, were analysed for alpha emissions corresponding to activity of the plutonium isotopes ^{239}Pu and ^{240}Pu. Recoveries commonly ranged from 80 to 100% for plutonium, although as with the uranium assay high sugar content foods decreased the method recovery. In these samples plutonium recoveries were 55–70%. No $^{239+240}$Pu activity was detected in any of the food types analysed in this survey.

3.5. Activity concentration ranges

The developed upper-bound and lower-bound means and medians for radionuclides in the New Zealand diet are summarised in Table 4. Comparison to the Codex Alimentarius guideline levels for radionuclides indicates that dietary activity concentrations of anthropogenic radionuclides are orders of magnitude below those considered as a risk to health (CAC, 1995).

The low frequency and magnitude of anthropogenic radionuclides detected in domestically produced foods is a likely reflection of several factors. Firstly historical nuclear fallout to the Southern hemisphere has been lower than that to the Northern hemisphere resulting in lower activity concentrations of anthropogenic radionuclides (UNSCEAR, 2000). Similarly, with no nuclear industry in New Zealand and very few nuclear power facilities in the Southern hemisphere, contamination from local releases, either permitted or accidental, has not been significant for New Zealand.

However, while there is no nuclear power industry there is use of radionuclides in other fields, such as ^{131}I in medicine, ^{60}Co in irradiation facilities and finally ^{241}Am in home smoke detectors. By assigning expected ranges to all of the anthropogenic radionuclides it is possible to determine for future survey programs if additional sources or increased levels of contamination are present in the New Zealand food chain.

Of the naturally occurring radionuclides ^{238}U and its decay series daughters can be influenced by anthropogenic factors and be concentrated in certain regions due to a range of industrial processes. The derived activity ranges provide a benchmark from which to analyse for long-term trends of naturally occurring radionuclides in the food chain.

3.6. Sentinel foods

New Zealand monitoring for radionuclides in the diet has historically focused on milk, generally obtained in the powder form, as a sentinel. Activity concentrations have shown a consistent decrease from peak fallout from nuclear testing in the 1960's into the 2000's, with ^{90}Sr activity no longer being detectable. That no new contribution to activity has entered into New Zealand agriculture is consistent with the absence of significant fallout onto New Zealand since 1965 (Matthews, 1993) (Tinker and Pilviö, 2000).

Milk analysed in the current study identified two samples with trace activity concentrations of ^{137}Cs, values consistent with the last New Zealand environmental monitoring report (Ministry of Health, 2013). Of the domestically sourced terrestrial agriculture samples only wild pork had a similar number of samples with measurable activity. No further anthropogenic radionuclides or ^{210}Po activity concentrations were detected in the milk samples, although a trace ^{238}U activity of 0.7 mBq/L was detected.

Milk has many benefits as a sentinel. Firstly, it is consumed in significant volumes by the New Zealand population (Vannoort and Thomson, 2009) making any radionuclide present more relevant to the ingested dose. Secondly, it is produced in significant volumes throughout a large part of New Zealand and through a large part of the year, making obtaining monitoring samples simple; in contrast many of the foods sampled in this survey were only seasonally available. Finally, in comparison to many of the samples, milk is simple to process for the radiochemical analysis and good method recoveries were obtained for all of the assays. Milk in the form of powder also has a long shelf-life making retention of samples easier, and as a concentrate it gives lower MDCs than many fresh foods. The results of this current work suggest milk remains a useful sentinel for ^{137}Cs, it is therefore appropriate to maintain it as part of the New Zealand monitoring programme.

A number of imported foods in this survey had detectable activity concentrations of ^{137}Cs, including tea and spice mix. The spice

Table 4
Activity concentration ranges for radionuclides in a survey of 40 New Zealand food types, with comparison to relevant Codex Alimentarius Guideline Levels (CAC, 1995).

Radionuclide	Mean activity concentration (LB-UB) (Bq/kg)	Median activity concentration (LB-UB) (Bq/kg)	Codex Alimentarius guideline level[a] (Bq/kg)
^{40}Potassium	96.56	73.63	n/a
^{90}Strontium	0.01–0.12	0–0.06	100
^{131}Iodine	0.001–0.13	0–0.12	
^{60}Cobalt	0–0.17	0–0.15	1000
^{134}Caesium	0–0.16	0–0.14	
^{137}Caesium	0.02–0.14	0–0.13	
^{210}Polonium	0.82–0.83	0.023–0.025	n/a
^{234}Uranium	0.043–0.047	0.0044–0.0077	n/a
^{235}Uranium	0.0008–0.007	0–0.0037	n/a/100[b]
^{238}Uranium	0.037–0.039	0.0064–0.0066	n/a
$^{239+240}$Plutonium	0–0.0052	0–0.0034	Infant food: 1, Other food: 10
^{241}Americium	0–0.12	0–0.11	

[a] Guideline levels apply to the sum of activities from representative radionuclides, Guideline levels are not set for naturally occurring radionuclides.
[b] ^{235}U is only considered against the 100 Bq/kg guideline level when present from technologically enriched sources; levels at the natural environmental ratio are not considered.

mix sample also had a detected activity for ^{90}Sr. However the compliance of the detected activity concentrations in the imported foods with the Codex Alimentarius guideline levels (CAC, 1995), indicates they do not represent a radiological risk. A specific sentinel for imported foods is not seen as necessary, however monitoring can be targeted to certain types of imported food where a risk of contamination exists. For example monitoring of tea from Japan for ^{137}Cs was undertaken in New Zealand following the Fukushima-Daiichi accident (MPI, 2013).

3.7. Future research

Based on the derived activity concentrations for the radionuclides in this work a comprehensive dietary burden estimate is being undertaken. Through the use of New Zealand food intake values this will assign the current baseline dose from dietary radionuclides to the New Zealand population and determine the contribution from anthropogenic and natural sources.

A noted gap in the New Zealand monitoring programme has been highlighted by the detection of a range of radionuclides, both anthropogenic (^{131}I and ^{137}Cs) and natural (^{210}Po and Uranium isotopes), in New Zealand seafood. Activity concentrations of ^{137}Cs were consistently detected in large fish species and ^{210}Po and Uranium isotope activity levels were higher than those in terrestrial foods. This indicates that seafood may be a significant source of dietary radionuclides for the New Zealand population. Following the release of anthropogenic radionuclides from Fukushima-Daiichi into the North Pacific Ocean and the potential for local release into the coastal environment of radionuclides, as demonstrated by the presence of ^{131}I in shellfish, seafood may have a greater risk of being contaminated by radionuclides than terrestrially-grown food.

New Zealand has a large coastline and a range of different ecological niches in its marine environment. Some radionuclides may be more prevalent in certain regions and seafood species. This could result in large variation in results from a monitoring programme. As the present work has only sampled a limited number of species and has little information on their catch locations, it is not possible to make a recommendation of a suitable sentinel species for New Zealand seafood. Further work has been undertaken to examine variations in some radionuclides in the different fishing regions to provide greater confidence in assigning a sentinel species and sample location for monitoring (Pearson et al. this issue).

The radionuclides targeted in the present work did not include the full range of radionuclides that could potentially enter food chains. In particular other natural radionuclides in the uranium and thorium decay series, such as radium isotopes may also be significant in the New Zealand diet. Further work is planned to consider inputs of radium through fertilisers and determine crop transfer factors in New Zealand conditions.

4. Conclusion

This survey of 160 food samples composing 40 food types common in the New Zealand diet has established activity ranges for different radionuclides of both natural and anthropogenic origin.

Levels of the natural isotopes of uranium (^{234,235,238}U) and ^{210}Po showed the largest variation. Activity concentrations of uranium and ^{210}Po in shellfish were orders of magnitude above other food types and further studies could be undertaken to better determine inter-species, temporal and regional variability. ^{238}U and ^{210}Po were also the most frequently detected radionuclides across the foods sampled. In contrast, detection of anthropogenic radionuclides in the New Zealand diet is infrequent and of low activity, with the absence of many anthropogenic radionuclides an indicator of the isolation of New Zealand from nuclear activities. Milk, in the form of powder, remains a suitable sentinel for anthropogenic radionuclides in New Zealand terrestrial agriculture.

The activity concentrations of radionuclides in the New Zealand food supply appear equal to, or less than, that of other countries. Full dietary modelling on the activity concentrations using New Zealand food intake values will establish the baseline ingestion dose to sections of the New Zealand public.

Acknowledgements

This work was funded by the Ministry for Primary Industries operational research programme.

References

Beach, K., 2005. Nuclear Medicine Practice and Patient Doses in New Zealand in 2005. National Radiation Laboratory, Christchurch.

Carvalho, F.P., Oliveira, J.M., Malta, M., 2011. Radionuclides in deep-sea fish and other organisms from the North Atlantic Ocean. IECS J. Mar. Sci. 68 (2), 333–340.

CAC, 1995. General Standard for Contaminants and Toxins in Food and Feed. Codex Stan 193–1995. Codex Alimentarius. http://www.codexalimentarius.org/download/standards/17/CXS_193e2015.pdf.

Currie, L.A., 1968. Limits for qualitative detection and quantitative determination, application to radiochemistry. Anal. Chem. 40, 586–593.

Dean, J., Ivanov, P., Collins, S., Miranda, M.G., 2014. Environmental Radioactivity Proficiency Test Exercise 2013. NPL Report IR 32. National Physical Laboratory, United Kingdom.

EFSA, 2009. Scientific opinion of the panel on contaminants in the food chain on a request from German federal institute for risk assessment (BfR) on uranium in foodstuff, in particular mineral water. EFSA J. 1018, 1–59.

Goddard, C.C., Mathews, C.P., Al Mamry, J., 2003. Baseline radionuclide concentrations in Omani fish. Mar. Pollut. Bull. 46 (7), 914–917.

Hancock, G.J., Leslie, C., Everett, S.E., Tims, S.G., Brunskill, G.J., Haese, R., 2011. Plutonium as a chronomarker in Australian and New Zealand sediments: a comparison with ^{137}Cs. J. Environ. Radioact. 102 (10), 919–929.

Hermanspahn, N., 2010. Environmental Radioactivity in New Zealand and Rarotonga. NRL-F/90. National Radiation Laboratory, Christchurch.

IAEA, 2013. ALMERA Proficiency Test: Determination of Natural and Artificial Radionuclides in Soil and Water. IAEA, Vienna.

ICRP, 2012. Compendium of dose coefficients based on ICRP Publication 60. ICRP Publication 119. Ann. ICRP 41 (Suppl. I.).

ISO 18589-5, 2009. International Standard, 2009. Measurement of Radioactivity in the Environment – Soil – Part 5: Measurement of Strontium 90.

Lee, H.W., Wang, J.J., 2013. Annual dose of Taiwanese from the ingestion of ^{210}Po in oysters. Appl. Radiat. Isot. 73, 9–11.

Madigan, D.J., Baumann, Z., Fisher, N.S., 2012. Pacific bluefin tuna transport Fukushima-derived radionuclides from Japan to California. PNAS 109 (24), 9483–9486.

Matthews, K.M., 1993. Radioactive Fallout in the South Pacific: a History, Part 3: Strontium-90 and Caesium-137 Deposition in New Zealand and Resulting Contamination of Milk. National Radiation Laboratory, Christchurch.

McCartney, M., Davidson, C.M., Howe, S.E., Keating, G.E., 2000. Temporal changes in the distribution of natural radionuclides along the Cumbrian coast following the reduction of discharges from a phosphoric acid production plant. J. Environ. Radioact. 49, 279–291.

Meli, M.A., Cantaluppi, C., Desideri, D., Benedetti, C., Feduzi, L., Ceccotto, F., Fasson, A., 2013. Radioactivity measurements and dosimetric evaluation in meat of wild and bred animals in central Italy. Food Control 30 (1), 272–279.

Meli, M.A., Desideri, D., Roselli, C., Feduzi, L., 2014. Assessment of ^{210}Po in Italian diet. Food Chem. 155, 87–90.

Ministry of Health, 2013. Environmental Radioactivity in New Zealand and Rarotonga: Annual Report 2011. Ministry of Health, Wellington.

MPI, 2013. Radionuclide Testing in Imported Foods Survey, Imported Foods Monitoring Programme. Technical Paper No: 2013/26. Ministry for Primary Industries, Wellington.

Pearson, A.J., Gaw, S., Hermanspahn, N., Glover, C.N., 2015. Activity concentrations of ^{137}Caesium and ^{210}Polonium in seafood from fishing regions of New Zealand and the dose assessment for seafood consumers (This issue).

Rieppo, R., 1978. A method to investigate the secular equilibrium of natural radioactive series. Geoexploration 16 (3), 177–183.

RIFE, 2013. Radioactivity in Food and the Environment, 2012. Environment Agency, Food Standards Agency, Northern Ireland Environment Agency, Scottish Environment Protection Agency, United Kingdom.

Rožmarić, M., Rogić, M., Benedik, L., Štrok, M., Barišić, D., Ivšić, A.G., 2012. ^{210}Po and ^{210}Pb activity concentrations in Mytilus galloprovincialis from Croatian Adriatic coast with the related dose assessment to the coastal population. Chemosphere 87 (11), 1295–1300.

Salahel Din, K., 2011. Determination of ^{210}Po in various foodstuffs and its annual effective dose to inhabitants of Qena city, Egypt. Sci. Total Environ. 409, 5301–5304.
Schipper, L.A., Sparling, G.P., Fisk, L.M., Dodd, M.B., Power, I.L., Littler, R.A., 2011. Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer. Agric. Ecosyst. Environ. 144 (1), 95–101.
Štrok, M., Smodiš, B., 2011. Levels of ^{210}Po and ^{210}Pb in fish and molluscs in Slovenia and the related dose assessment to the population. Chemosphere 82 (7), 970–976.
Suksi, J., Rasilainen, K., Pitkänen, P., 2006. Variations in ^{234}U/^{238}U activity ratios in groundwater—A key to flow system characterisation? Phys. Chem. Earth, Parts A/B/C 31 (10–14), 556–571.
Sunith Shine, S.R., Feroz Khan, M., Godwin Wesley, S., 2013. Occurrence of ^{210}Po in periwinkle (Littorina undulata, Gray, 1839) collected from Kudankulam (Gulf of Mannar (GOM), Southeast coast of India). Mar. Pollut. Bull. 75 (1–2), 276–282.
Tinker, R.A., Pilviö, R., 2000. Environmental Radioactivity in New Zealand and Rarotonga. NRL-F/78. National Radiation Laboratory, Christchurch.
UNSCEAR, 2000. Sources and Effects of Ionising Radiation. United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations, New York.
U.S. Food and Drug Administration, 2006. Total Diet Study Statistics on Radionuclide Results. Center for Food Safety and Applied Nutrition, College Park, MD.
Vannoort, R.W., Thomson, B.M., 2009. 2009 New Zealand Total Diet Survey. Agricultural Compound Residues, Selected Contaminants and Nutrient Elements. Ministry of Agriculture and Forestry, Wellington.
Veliscek Carolan, J., Hughes, C.E., Hoffmann, E.L., 2011. Dose assessment for marine biota and humans from discharge of ^{131}I to the marine environment and uptake by algae in Sydney, Australia. J. Environ. Radioact. 102 (10), 953–963.
Young, A.K., McCubbin, D., Camplin, W.C., 2002. Natural Radionuclides in Seafood. Environment Report RL 17/02. Food Standards Agency, United Kingdom.