Determination of Polonium-210 in various foodstuffs after microwave digestion

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INTRODUCTION

Natural radioactivity is associated with the vast mineral resources in South Africa in such concentrations that the radionuclides from the natural uranium and thorium decay series are found to pose concern for public exposure to communities living around these areas. The radiological impact of all operations is monitored as part of the license obligations, imposed by the South African National Nuclear Regulator Act. Two main pathways giving rise to significant exposures are of interest: (a) direct ingestion resulting from regular and continuous use of contaminated water for drinking purposes, and (b) regular consumption of fish and other food products harvested from and/or grown in contaminated areas. To measure the individual nuclides in foodstuffs at the required sensitivity level in order to evaluate the yearly dose due to an individual source at a screening level of 25 μSv/a, one is faced with a lower limit of determination (LLD) of 0.1 to 0.5 Bq/kg for certain foodstuffs. For some of the nuclides this LLD can only be obtained with radiochemical separation through acid destruction of dried foodstuffs followed by individual element separations.
In this study the digestion of foodstuffs in an open-vessel microwave system followed by the determination of ^{210}Po through radiochemical separation by spontaneous deposition onto silver discs and subsequent measurement by α-spectrometry, has been evaluated. The levels of ^{210}Po in a variety of foodstuffs were determined and the estimated dose for the adult age group, resulting from consumption was evaluated.

MATERIALS AND METHODS

A variety of food samples from the six categories cereals and grains, meat, seafood/fish, vegetables, roots and tubers, and fruit, were analysed. Most samples were collected in the vicinity of areas known to be influenced by mining and mineral processing industries. Samples were prepared as would apply, for human consumption. Samples were dissolved with concentrated nitric acid and hydrogen peroxide using an open vessel microwave digestion system (Milestone Ethos Touch). ^{209}Po was added as yield tracer in the initial stages of the dissolution. ^{210}Po was separated by spontaneous deposition of Polonium onto a silver disc and the alpha activities of ^{209}Po and ^{210}Po were then measured with α-spectrometry.

RESULTS AND CONCLUSION

Sample Dissolution

The main problems with the analytical method may occur in the steps of sample dissolution.
In samples digested with HNO_3/H_2O_2 on a hot plate for 4 - 6 hours at a low temperature organic residues persisted even though wet ashing appeared to be complete. Using the microwave with a combination of HNO_3 and H_2O_2, the latter being slowly added during the second phase of the digestion, a clear solution with little undissolved material was obtained.
A series of food test samples spiked with approximately 100 Bq/kg ^{210}Po, were analysed. The good chemical recoveries and spectral quality indicate that matrix effects do not interfere in the experimental procedure and that foodstuffs can be successfully digested with nitric acid

and hydrogen peroxide using microwave digestion.

Polonium-210 activity in food samples

Analytical results for the ^{210}Po activity of a number of dietary samples are presented in Table 1. The activity concentration of ^{210}Po in fish varied depending on the origin, with the highest values in the samples taken near the gypsum outlet of one of the mining and mineral processing plants. The high and dominant ^{210}Po concentrations in fish are to be expected, since ^{210}Po is known to accumulate in fish and seafood. Concentrations of other nuclides such as ^{232}Th and ^{226}Ra in fish were significantly lower than those of ^{210}Po. The activity concentrations of ^{210}Po in beef obtained from different sampling sites, were similar. The concentration in chicken was quite high. Concentrations in the liver and kidney samples were very high, which can be expected since internal organs are known to accumulate ^{210}Po; ^{226}Ra, ^{228}Ra and ^{228}Th were also dominant activities in these samples. Concentrations of ^{210}Po in milk and mushrooms were quite low.

Trends from vegetable crops were not consistent. In general, the ^{210}Po activity was low (<0.5 Bq/kg) for most of the vegetables, but differed between sites. The ^{210}Po concentrations in the "background" samples were not significantly lower than those in vegetables from other sites. The spinach and carrot samples from Site C had very high ^{210}Po activity. These two samples also had measurable levels of ^{238}U, ^{226}Ra and ^{228}Ra, whereas for most of the vegetables the concentrations of the other radionuclides were below the LLD, which was as high as 10 Bq/kg for some samples. Concentration of radionuclides in the above-ground parts of the plants, are expected to be higher than in the roots. This was not found as a definite trend in the samples analysed in this study. Although the concentration in beetroot was lower than in spinach, carrots had a higher concentration. In general spinach had higher ^{210} Po activity than cabbage, which suggests dominance of leaf deposition of ^{210}Po from the atmosphere. Spinach requires minimal preparation prior to cooking, whereas the outer leaves of cabbage are usually removed, resulting in lower concentrations.

The very high ^{210}Po concentrations found in oats and rye samples from Site B is a cause of concern. The measured gross activities of these samples were also high, with high ^{238}U, ^{232}Th, ^{226}Ra and ^{210}Po concentrations. The high results may be partly due to adhesion of soil particles to the leaves. For some above ground crops such as cereals, the edible portion is protected by inedible plant parts and the activity concentration in the edible parts will not be affected by direct deposition; this can explain the low activity values found for maize, relative to that of oats and rye.

Committed effective dose

Intake via ingestion depends on the dietary habits of the affected groups and/or individuals (which is also age related), and the concentration of the radionuclides concerned. The annual intake was estimated by multiplying the ^{210}Po level present in the individual food by the amount of food consumed per year. Doses were evaluated using the dose conversion factor for ingestion exposure for ^{210}Po (1.2×10^{-6} Sv/Bq). Results for adults are reported in Table 1. Default consumption values for foodstuffs as applied by the South African National Nuclear Regulator (NNR) were used. These consumption values are conservative values for use in screening assessments that will ensure that all critical groups are covered, and apply to broad categories of food.

Table 1. Sample activity of ^{210}Po in Bq/kg wet weight and Committed Effective dose for adult age group (μSv/a)
Note: Number of samples in brackets; Sampling sites A-E refer to gold mining areas

Category	Sampling Site	^{210}Po (Bq/kg)	Consumption (kg/a)	Dose due to ^{210}Po intake (μSv/a)	Overall dose (μSv/a)
Grains/Cereals					
Maize	Background	0.281 ± 0.141	150	50	1645
Maize	Consumer	0.531 ± 0.211	150	95	-
Oats	Site A	1.39 ± 0.339	150	250	420
Oats	Site B	5.64 ± 0.36	150	1015	21 554
Rye	Site B	9.55 ± 0.93	150	1719	4854
Lucerne	Site C	0.498 ± 0.083	150	90	7290
Vegetables					
Cabbage	Site B	0.054 ± 0.020	55	4	196
Spinach [2]	Site B	0.435 – 0.648	55	29 – 43	118 – 493
Spinach	Site C	1.96 ± 0.16	55	130	2205
Barley Asparagus	Background	0.375 ± 0.110	55	25	208
	Site A	0.213 ± 0.084	55	14	30
Roots and Tubers					
Spring Onion	Site A	0.600 ± 0.101	55	40	100
Turnip	Site B	< 0.14	170	15	55
Beetroot [2]	Site B	0.255 – 0.281	170	52 – 57	162 – 991
Carrot	Site C	2.78 ± 0.31	170	566	11 572
Fruit					
Lemon	Site C	0.136 ± 0.038	75	12	1931
Mushrooms	Consumer	0.010 ± 0.005	55	1.6	33
Fish					
Marine [4]	Background	1.15 – 3.17	25	34 – 95	128 – 330
Marine [5]	Gypsum outlet	2.21 – 8.08	25	66 – 242	91 – 209
Fresh [4]	Phosphate mines	0.627 – 1.65	25	19 – 50	30 – 138
Fresh [3]	Site D	0.431 – 0.775	25	13 – 23	23 – 82
Meat					
Chicken	Site D	1.63 ± 0.314	75	147	723
Beef [6]	Sites B, D, E	0.115 – 0.250	100	14 – 30	112 – 244
Liver	Site D	13.1 ± 0.75	100	1568	2667
Liver	Site E	6.93 ± 0.516	100	831	1165
Liver [2]	RA Waste site	0.532 ± 0.639	100	64 – 76	906 – 1370
Kidney [2]	RA Waste site	3.04 ± 13.2	100	365 – 1582	1669 – 5132
Milk	Site B	0.162 ± 0.075	350	68	460

The natural radionuclides such as uranium (^{238}U, ^{235}U); thorium (^{232}Th, ^{228}Th), radium (^{228}Ra and ^{226}Ra), were also measured for most of the samples. Non-destructive techniques such as INAA and gamma spectrometry were used. A conservative approach has been followed to obtain the possible yearly dose. Equilibrium with the respective mother/daughter nuclides were assumed for those radionuclides not analysed for. For the short-lived nuclides such assumptions are acceptable, but for nuclides such as ^{227}Ac and ^{231}Pa these assumptions are not entirely accurate. Assumed equilibrium between ^{210}Po and ^{210}Pb will result in an underestimation of the dose for those foodstuffs with ^{210}Po:^{210}Pb ratios much lower than 1. By ignoring the contribution of radionuclides measured lower than the LLD, especially where the LLD is quite high, the dose may be underestimated. Therefore values lower than the LLD is taken as LLD/2 in the dose calculations. However, if the radionuclides are not measured with

the necessary sensitivity, the dose will most likely be overestimated. The concentration of ^{40}K was excluded from the dose calculation since potassium is under homeostatic control in the body, and so doses from ^{40}K are independent of the amount of activity ingested.

For the specific marine fish source(s), given the conservative approach mentioned above, the overall dosage for adults varied between 90 and 330 μSv per annum, with the dominant contribution from ^{210}Po (40-70%). The contribution of ^{210}Po to the overall dose for vegetables, beef and chicken was about 10 - 20%; other contributors to the dose were ^{228}Ra, ^{226}Ra, ^{230}Th and ^{210}Pb; contributing not because of actual high measured values but mainly because of the high dose conversion factors of these nuclides and the poor sensitivity of the measurement techniques. For liver, dose was dominated by ^{210}Pb and ^{210}Po, with ^{210}Po contributing up to 60% of the overall dose. The high doses from liver and kidney arise from the unrealistic high consumption rate of 100 kg per annum used in the dose assessment.
Consumption of oats and rye from Site B will result in doses of higher than 1 mSv/a due to intake of ^{210}Po only, and doses as high as 20 mSv/a if all nuclides are considered. However, it is debatable whether they will be used as such for human consumption. It is more likely that they will be used as fodder and accordingly the pathways to milk and meat would be a better option to evaluate the dose to humans. The high overall dose for some samples (e.g. maize, oats, rye, lucerne) are probably overestimated due to the "insensitivity" of the analytical method used (LLD ~ 10 Bq/kg).

If oats and rye are considered as fodder rather than human food, and liver and kidney samples are excluded because of the unrealistic high consumption rate of 100 kg, the annual effective dose from ^{210}Po varied between 4 and 250 μSv/a.

Conclusions
The analytical method proved to be an appropriate methodology for determining ^{210}Po in foodstuffs at low concentrations. The levels of ^{210}Po in food clearly indicate that the ingestion of food is an important route for acquisition of body-burdens of the nuclide. In general ^{210}Po is lower in meat, milk and vegetables than in cereals, and higher in fish and liver. The largest intake of ^{210}Po was from fish (appr 0.5 Bq/day). From this study, it seems that public exposure could accumulate up to a few mSv per year, if these food sources are part of the food sources available to the communities living in and around the specific area. This is of obvious concern and further investigation is mandatory. To calculate the actual yearly dose and potential radiological impact on the public the following needs to be considered: (a) Analysis of food consumed by the general public purchased from local markets and retailers, (b) Determination of more accurate consumption/intake values and (c) Improvement of the lower limit of determination in order to evaluate the yearly dose due to an individual source at a screening level of 25 μSv/a as required by the South African National Nuclear Regulator.