The effect of chemical speciation on the impact of ^{129}I discharges to atmosphere from BNFL Sellafield, Cumbria

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Abstract. ^{129}I is produced through neutron-induced fission of ^{235}U and neutron capture reactions with the fission products ^{128}Te and ^{130}Te in the cores of nuclear reactors. This typically constitutes about 1% of the total fission products, depending on fuel burn-up. Whilst ^{129}I is not released in routine discharges from nuclear power plants it is released during reprocessing. The ability to model ^{129}I behaviour (important for prospective assessments) has been relatively poor. This is due both to variability in the reported behaviour of iodine, which may be related to abundance and physico-chemical form, and to the relative paucity of data for ^{129}I. The primary aims of this study are to measure environmental concentrations of ^{129}I around Sellafield; to establish whether the chemical species of iodine in air differs as a function of the source term, and; to determine concomitant values for model parameters defining ^{129}I transport through the environment. Some differences in the environmental transport of ^{129}I are observed, albeit slight, apparently related to source term. These findings suggest that a source-specific approach may be appropriate. The critical group dose arising from ^{129}I is estimated to be about 1.4 µSv a^{-1} to adults and 3.2 µSv a^{-1} to infants.

1. INTRODUCTION

Anthropogenic ^{129}I is produced through neutron-induced fission of ^{235}U and neutron capture reactions with the fission products ^{128}Te and ^{130}Te. Typically, ^{129}I makes up about 1% of the total fission products, depending on fuel burn-up. ^{129}I is not released in routine discharges from nuclear power plants but is released along with other volatile waste products when reprocessing of the fuel is undertaken. Iodine may be emitted to the atmosphere in organic, inorganic or particulate forms and the proportions of iodine present in these different forms are likely to vary with the type of nuclear facility.

Aerial discharges of ^{129}I from the nuclear fuel reprocessing works at Sellafield, Cumbria, have remained relatively constant since the early 1980s at around 20 to 30 GBq per annum [1]. Atmospheric emissions of other radionuclides have declined over this period, with the introduction of new plants with improved clean-up of aerial discharge streams, and consequently the ^{129}I proportion of the total dose received by critical group members around Sellafield has increased. Nonetheless, the actual incurred critical group dose arising from ^{129}I is currently estimated to be only 1.4 µSv a^{-1} to adults and 3.2 µSv a^{-1} to infants.

The environmental behaviour of iodine is not fully understood [e.g. 2]. The present work aims to define, for the Sellafield site, parameter values for modelling terrestrial food consumption exposure pathway of ^{129}I, encompassing the effects of a change in the source of ^{129}I from Magnox fuel reprocessing dominated discharge to oxide fuels.
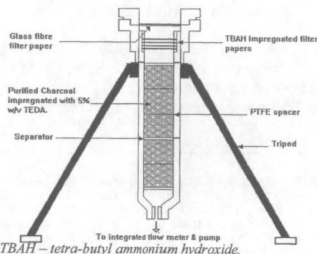
2. STUDY SITE

A field site approximately 2 km from Sellafield was established. This has been used previously by Westlakes [3, 4]. The site is sufficiently far away to receive maximum ground concentration, given that the main ^{129}I discharges are from stacks over 80 m tall, but is not constricted by severe changes in terrain (hillocks and valleys) nor substantially affected by local features such as woodland and buildings. For comparison, a control site was established at the Silwood Park site of Imperial College in Berkshire, UK. This site has also been used for control purposes in a number of previous studies and is not known to receive measurable inputs of ^{129}I from any source.

3. EXPERIMENTAL SET-UP

Crops growing in the area around Sellafield receive ^{129}I from direct interception of material deposited from atmosphere and from root uptake of material previously deposited onto soil. Other pathways, such as soil splash onto external surfaces may be relevant but are not considered here.

A multi-stage air sampler was employed, to determine separately the organic, inorganic and particulate phases ^{129}I in air. The sampler consists of 3 different types of sampling media, illustrated in Figure 1. In trials, Birch *et al.* [4] and Gravett and Collins [5] concluded that the efficiency and

reproducibility of sample collection is very high, although it is recognised that individual sample results may be associated with some unquantified uncertainty.

Note: TEDA – triethylene diamine; TBAH – tetra-butyl ammonium hydroxide.

Figure 1:   Multi-stage air sampler design

Trays of perennial ryegrass (*Lolium perenne*) grown in Preston, Lancashire, away from any significant sources of atmospheric [129]I contamination, were used to collect [129]I deposition during the air sampling period. Samples of field grass were also taken periodically from fields in which cows had previously been grazing. Spot milk samples were taken from the farm bulk tank.

In a second experimental regime, soil from the Sellafield area was homogenised and put into large containers, which were placed at the study site near Sellafield and at Silwood Park, and plants grown in them. Under this regime, plants at Sellafield receive [129]I both from the plume and from the soil. Crops grown in the containers at Silwood Park exclusively derive their [129]I from that already present in the soil.

4. ANALYTICAL METHODS

Various approaches to measuring iodine were tested during the course of these studies. Analytical values presented here were determined primarily using radiochemical neutron activation analysis (RNAA), largely developed by Parry *et al.* [6]. Iodine is wet extracted from the sample (using 2M KOH) and sorbed onto an anion exchange resin (Bio-Rad AG1-X8), which is then dried and irradiated for 7 hours using a thermal neutron flux of 1×10^{12} n cm^{-2} s^{-1}. After irradiation the iodine is extracted off the anion resin, precipitated as AgI solid and counted on a pure Ge detector gamma spectrometer.

5. RESULTS AND DISCUSSION

5.1 Aerial discharges of [129]I from Sellafield

A summary of the annual discharges of [129]I from Sellafield during 1992-1999 is presented in Figure 2, from data in the BNFL Annual Reports [1]. Discharges from Thorp commenced in 1994 with active commissioning trials and increased through 1995 to 1997 with fuel throughput. The main Magnox discharge from the dissolver, which is emitted through the B204 stack, was offline during the first half of 1997 due to routine maintenance.
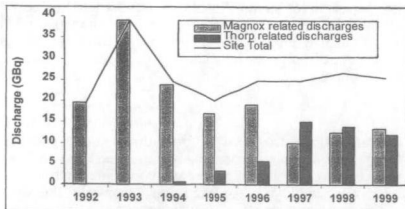

Figure 2:   Discharges of [129]I from Sellafield 1992-1999

It has been suggested in the past, based on sampling campaigns undertaken by BNFL, that discharges of ^{129}I from the Magnox fuel reprocessing waste streams are largely organic in nature. By contrast the Thorp plant was designed to minimise ^{129}I discharge from organic solvent areas and it is probable that the main species of gaseous discharge are inorganic in nature.

5.2 Speciation in the environment

Air samplers were run continuously from April to December 1997, apart from change-over periods at the end of each month and the period 7 July 1997 to 17 July 1997, when the electrical supply was interrupted. Results are presented in Table 1.

Table 1:   Atmospheric ^{129}I concentration and speciation April to December 1997

Sampling period	n	Total ^{129}I in air (Bq m^{-3})	Distribution between fractions		
			% ^{129}Ip	% ^{129}Ii	% ^{129}Io
April	2	2.0×10^{-5}	13.7	26.0	60.3
May	2	6.8×10^{-6}	7.1	18.1	74.8
June & July	2	1.0×10^{-5}	31.6	9.2	59.2
August	2	8.5×10^{-6}	6.3	12.5	81.2
September	2	1.9×10^{-5}	17.8	27.6	54.6
Oct – Dec	2	1.2×10^{-5}	19.2	34.7	46.1
mean ± std dev		$1.3 \times 10^{-5} \pm 6.5 \times 10^{-6}$	16 ± 10	21 ± 12	63 ± 16

^{129}Ip - particulate; ^{129}Ii - inorganic; ^{129}Io – organic. Results given as the mean of 2 air samplers

Proportions of ^{129}I associated with particulate material are highly variable and it is uncertain whether these arise from attachment to atmospheric particles in transit or at source. Nonetheless, comparison may be made to results obtained during 1993-1995 [3]. Values appear to be broadly similar in both studies at 9±12% in 1993-1995 and 16±10% in 1997. By contrast, there is evidence of an increase in the proportion of inorganic ^{129}I collected at the study site in 1997 (21±12%), when discharges from Thorp were significantly higher than those from the Magnox reprocessing plant, compared with the proportion measured over 1993–1995 at sites around Sellafield (2.9±4.5%). It thus appears that the form of ^{129}I in air is affected by the discharge source, although other factors may also be involved.

5.3 Deposition to ground and interception fraction to grass

The current study also sought to determine whether there would be any change in i) flux to ground, ii) interception fraction to grass and iii) concentration in pasture and milk. As for the air samplers, sampling began in April 1997 and continued monthly until the end of December 1997.

Literature values for deposition velocities of iodine thought to be largely in an inorganic form tend to cluster around 10^{-2} m s^{-1}. Organic iodides (e.g. methyl iodide) have much lower rates of deposition. Recently, for the purposes of modelling, Simmonds et al. [7] recommended representative values for dry deposition velocity of 10^{-2} m s^{-1} and 10^{-5} m s^{-1}, respectively, for inorganic and organic gaseous iodine to the ground, and 10^{-3} m s^{-1} for radionuclides associated with particulate material of the order of 10 µm diameter. Similarly, the Food Standards Agency has recommended that the deposition velocities for elemental and particulate iodine should be taken as 10^{-2} m s^{-1}, and for organic iodine as 10^{-5} m s^{-1} [8]. Based on the fractional speciation recorded at the study site (Table 1), this would imply a mean deposition velocity to the ground of ca. 2×10^{-3} m s^{-1} for ^{129}I. This is an order of magnitude lower than the measured value (Table 2). However, this latter is based on the sum of dry and wet deposition, calculated using mean concentrations and fluxes for each of the sampling periods.

Table 2:   Calculated deposition velocities for ^{129}I, April to December 1997

Parameter	Mean Monthly Values						Mean	Std Dev'n
	April	May	Jun-Jul	Aug	Sept	Oct-Dec		
Atmos. Conc'n (Bq m^{-3})	1.9×10^{-5}	7.9×10^{-6}	8.5×10^{-6}	2.2×10^{-5}	1.9×10^{-5}	1.3×10^{-5}	1.5×10^{-5}	6.0×10^{-6}
Flux to Grass (Bq m^{-2} s^{-1})	2.0×10^{-8}	1.4×10^{-8}	2.9×10^{-8}	2.0×10^{-7}	7.9×10^{-8}	-	6.8×10^{-8}	7.7×10^{-8}
Flux to Coll. (Bq m^{-2} s^{-1})	9.1×10^{-8}	1.9×10^{-7}	1.9×10^{-7}	1.2×10^{-6}	1.9×10^{-7}	4.0×10^{-7}	3.8×10^{-7}	4.2×10^{-7}
Vg (grass) (m s^{-1})	1.0×10^{-3}	1.8×10^{-3}	3.4×10^{-3}	9.2×10^{-3}	4.2×10^{-3}	-	3.9×10^{-3}	3.2×10^{-3}
Vg (collector) (m s^{-1})	4.7×10^{-3}	2.4×10^{-2}	2.2×10^{-2}	5.5×10^{-2}	1.0×10^{-2}	3.2×10^{-2}	2.5×10^{-2}	1.8×10^{-2}
Flux Grass/Flux Coll.	2.2×10^{-1}	7.4×10^{-2}	1.5×10^{-1}	1.7×10^{-1}	4.1×10^{-1}	-	2.0×10^{-1}	1.2×10^{-1}

There are several processes involved in deposition, including sedimentation, impaction on vegetation and other surfaces, Brownian diffusion to surfaces, chemical reactions at surfaces, deposition under

electrical or thermophoretic forces and washout in cloud droplets or by occult deposition. For aerosols, the relative importance of the processes depends on the particle size, with the first two processes being of major importance when the aerodynamic diameter exceeds 10 μm. For gases and vapours, deposition is mainly by chemical reactions at surfaces and is controlled by the nature and rate of these reactions and the available surface area, together with the rate of re-supply of contaminant to the surface by diffusion.

Over the summer of 1997, the mean deposition velocity to grass at the study site was $3.9 \pm 3.2 \times 10^{-3}$ m s^{-1}. This value is higher than that reported for 1993-1995 (2.7×10^{-3} m s^{-1} [3]) although the uncertainties involved mean that this difference cannot be considered statistically significant. Furthermore, the value calculated by Birch [3] is based on a mixture of dry and bulk deposition measurements. These values were not significantly different in that study, but may provide a partial explanation for the lower value calculated relative to that presented here. However, Wershofen and Aumann [9] measured an average dry deposition velocity to grass of $5.8 \pm 2.6 \times 10^{-3}$ m s^{-1} from air with a similar ^{129}I speciation to that reported here. Notwithstanding the variability in these measured values (although it should be noted that the range for the three mean values is only a little over two-fold), it seems that dry deposition dominates the fraction intercepted by grass. The mean deposition velocity to the total deposition collector in 1997 was $2.3 \pm 1.8 \times 10^{-2}$ m s^{-1}.

Currently, emissions of ^{129}I from the Magnox and Thorp waste-streams are treated in models as having the same deposition velocity to ground of 10^{-2} m s^{-1}. This is a generic value, derived from the literature, and takes no account of the possible differences in deposition behaviour due to the differing speciation of ^{129}I in the two waste-streams from Sellafield. The atmospheric speciation data obtained during 1993–1995 and 1997 suggest that the commissioning of Thorp has led to an increase in the proportion of reactive inorganic ^{129}I in the atmosphere, which may be expected to lead to an increase in the overall V_g of ^{129}I.

As noted, data obtained over 1993–1995 gave a bulk V_g (wet and dry deposition processes) for Magnox ^{129}I deposition to grass of 2.7×10^{-3} m s^{-1}. Whilst data were not obtained for the bulk V_g to ground during that study, some short-term experiments suggested an interception fraction of 0.66.

Caution must be exercised in using the figures in Table 3 to estimate a comparable value for the interception fraction to grass during 1997, as the collection efficiency of the rainfall deposition collector may differ from that for grass plus underlying soil. Nonetheless, an implied interception fraction of 0.2 (flux grass/flux collector) can be derived.

If it is assumed that the average interception fraction over this period lies between 0.2 and 0.66 then a range for the Magnox ^{129}I V_g to ground can be estimated as:

$$0.0027/[0.2 \text{ to } 0.66] = 0.0041 \text{ to } 0.0135 \text{ m s}^{-1}. \quad (1)$$

The data obtained in 1997 give a bulk V_g of 2.3×10^{-2} m s^{-1} for combined Magnox (9.3 GBq) and Thorp (15.3 GBq) emissions, considerably higher than the range estimated for Magnox emissions alone. These figures suggest that the contribution of emissions from Thorp has resulted in an increase in the total V_g of ^{129}I. Given the higher proportion of inorganic iodine in atmospheric samples measured in 1997 than in the period 1993–1995, this increase in the overall deposition velocity is in line with expectation.

Using the 'Magnox V_g' and the 'Magnox + Thorp V_g', an estimate of the V_g of ^{129}I from Thorp can be made. Using discharge data for 1997, the relative contributions of Magnox and Thorp emissions to air concentrations at the study site are estimated (allowing for distance of plume travel from the respective stacks) to be roughly equal. Thus:

$$(0.5 \times \text{Magnox } V_g) + 0.5 \times (\text{Thorp } V_g) = \text{Total 1997 } V_g \quad (2)$$

which can be rearranged to give:

$$\text{Thorp } V_g = (2 \times \text{Total 1997 } V_g) - \text{Magnox } V_g \quad (3)$$

Substituting in the appropriate values in equation (3), Thorp V_g is derived as 0.032 to 0.042 m s^{-1}. It must be emphasised that this calculation is quite crude. It does not differentiate between the effects of wet and dry deposition, and takes no account of weathering losses or the uncertainties associated with the measured values for V_g and the pasture interception fraction. Moreover, it is critically dependent on the relative contributions from Magnox and Thorp discharges in air at the study site.

5.4 Uptake by plants from soil and atmospheric deposition

Potato, turnip, leaf beat and cabbage were grown in a "large-pot" experimental set-up. There are three disadvantages in growing crops in containers rather than in the field: i) roots grow in a confined volume, ii) watering has to be controlled to avoid water-logging, iii) if grown singly, competition between adjacent plants will be dissimilar to field conditions. These were overcome by the use of large containers capable of growing several specimens and by careful watering. Soil for the pots was collected from an

arable field near the study site and passed through a 13 mm mesh sieve, to remove large stones and debris.

Potato and cabbage crops grew successfully in tubs at both sites and potatoes were also grown in two arable fields near to the study site. Turnips grew successfully only at the study site and leaf beet grew only at the control site. Results of analyses are presented in Table 3, together with calculated concentration ratios.

Table 3: Availability of ^{129}I in crops and soils from study site and Silwood Park

Crop, location	^{129}I in crop (Bq kg^{-1} fw)	^{129}I in soil (Bq kg^{-1} dw)	Concentration ratio (CR)
potato, CS	0.0011	0.367	0.003
potato, SS	0.0385	0.636	0.061
potato, SS, field 1	0.0006	0.478	0.0026
potato, SS, field 2	0.0032	0.787	0.0041
cabbage hearts, CS	0.0014	0.343	0.0041
cabbage hearts, SS	0.0386	0.525	0.074
cabbage leaves, SS	0.0736	0.525	0.14
turnip, SS	0.0286	0.474	0.060
leaf beet, CS	0.0066	0.407	0.016

CS = control site, SS = Study Site

The expression of CR values is calculated as:

$$CR = \frac{\text{Concentration in crop (Bq kg}^{-1}\text{ fw)}}{\text{Concentration in soil (Bq kg}^{-1}\text{ dw, to 20 cm)}}$$

The mean ^{129}I concentrations in soil collected from the control and study site tubs were 0.37±0.03 and 0.58±0.07 Bq kg^{-1} dw, respectively, at the termination of the experimental period. Given a total deposition of *ca.* 6 Bq m^{-2} over the study period in the area around Sellafield an additional 0.02 Bq kg^{-1} or so would have been added to the concentration in the study site soil. This is not sufficient to account for the higher concentrations noted in soil from the study site, although it may represent one factor.

In a review of literature values, Coughtrey *et al.* [2] recorded considerable variability in concentration ratios, but averaging about 0.035 for root vegetables, 0.03 to 0.08 for the inner leaves of LGV and 0.2 to 0.46 for outer leaves. The averaged values determined in this study are 0.024 for root vegetables, 0.039 for the inner leaves of cabbage and 0.14 for the outer leaves.

For two crops (potatoes and cabbage hearts), direct comparison can be made in the present study between apparent concentration ratios for the control and study sites. It is notable that the values are up to an order of magnitude higher in the study site, suggesting that deposition from atmosphere is an important source of ^{129}I at this site and may be more readily available for uptake.

5.5 Uptake from pasture to milk

Another parameter which has received attention is the grass-to-milk transfer factor (F_m), defined as:

$$Fm = \frac{\text{activity per litre of milk}}{\text{activity ingested per day}}$$

The activity ingested by the cow per day is the ^{129}I concentration on grass, or other feed, multiplied by the consumption rate. Generic advice suggests a mean ingestion rate for grass and silage of 14.25 kg d^{-1} dw. In West Cumbria the consumption rates for dairy herds, based on advice from ADAS, are higher, averaging 18 kg d^{-1} dw over the year. In this study, values for F_m are calculated using 14.25 kg d^{-1} dw and the more region specific consumption rate of 18 kg d^{-1} for samples of matched pasture and milk collected in April, July and September 1997 (see Table 4).

The value for F_m currently recommended for modelling purposes is 5×10^{-3} d l^{-1} [7] and is thought to be largely independent of chemical form of intake, provided that the diet is not iodine deficient. Values of F_m calculated in this study were nearly 10 times lower than the generic advice.

Table 4: F_m values measured at study site

Month	^{129}I in grass (Bq kg^{-1})	^{129}I in milk (Bq l^{-1})	F_m (@14.25 kg d^{-1}) (d l^{-1})	F_m (@18 kg d^{-1}) (d l^{-1})
April	1.024	0.012	8.22E-04	6.51E-04
July	0.596	0.004	4.71E-04	3.73E-04
September	0.964	0.011	8.01E-04	6.34E-04
		Mean ± std dev	6.98E-04 ± 1.97E-04	5.53E-4 ± 1.56E-4

Given the narrow sampling period, these results alone cannot be used to calculate an annual mean value for F_m nor to determine any seasonal bias. A review of all the available data on F_m values obtained during experimental studies conducted at Westlakes suggests that values in the range $5x10^{-4}$ to $5x10^{-3}$ (mean $3x10^{-3}$) d l^{-1} may be appropriate.

6. CONCLUSIONS AND RECOMMENDATIONS

Speciation of ^{129}I in atmosphere 2 km from Sellafield was determined during 1997 and found to be dominated by the organic fraction. This is similar to findings in previous years and to stable iodine speciation measured around the world. Nonetheless, there may be some advantage in deriving, and applying, site (and source term) specific factors to describe the uptake and distribution of ^{129}I.

Values recommended for use in defining the distribution and uptake of ^{129}I around Sellafield are summarised below.

Parameter	Broad range, from literature	Recommended values, this study
Deposition velocity to ground, V_g (m s^{-1}):		
Magnox	$10^{-3} - 10^{-1}$	$4.1\times10^{-3} - 1.4\times10^{-2}$
Thorp		$3.2\times10^{-2} - 4.2\times10^{-2}$
Interception fraction	$0.1 - 1.0$	$0.20 - 0.66$
Plant:soil concentration ratio, CR		
Pasture	$ca.$ 0.1 – 0.4	nm
LGV outer leaves	$0.2 - 0.46$	0.14
LGV inner leaves	$0.03 - 0.08$	0.039
Root veg	up to 0.04	0.06
Pasture:milk transfer coefficient, F_m, (d l^{-1})	$5\times10^{-4} - 5\times10^{-3}$	$3x10^{-3}$

It is noted that the recommended values encompass the qualitative uncertainties expressed in this study, and are relevant only to Sellafield.

References

[1] BNFL (1978-2000) Annual Report on Discharges and Monitoring of the Environment, 1977-1999. BNFL, Risley.

[2] Coughtrey PJ, Jackson D & Thorne MC (1983) Radionuclide distribution and transport in terrestrial and aquatic ecosystems: a critical review of data. Volume Three. AA Balkema, Rotterdam.

[3] Birch CP (1997) The behaviour of I-129 in the vicinity of a nuclear reprocessing plant. PhD Thesis, Imperial College of Science, Technology & Medicine, University of London.

[4] Birch CP, Fulker MJ, Parry SJ & Bennett BA (1994) I-129 in the vicinity of the Sellafield reprocessing plant: the development of an experimental method to examine the atmospheric behaviour of I-129. In: Nimmo-Scott W & Golding J (eds) Proceedings of the 17th IRPA regional congress, Portsmouth, p 265-268. Nuclear Technology Publishing.

[5] Gravett A and Collins C (1998) Validation of the Westlakes iodine speciating air filter. Report from IC Consultants Ltd, London.

[6] Parry SJ, Bennett BA, Benzing R, Lally AE, Birch CP & Fulker MJ (1995) The determination of I-129 in milk and vegetation using neutron activation analysis. *Sci Tot Environ* **173/174** 351-360.

[7] Simmonds JR, Lawson G & Mayall A (1995) Methodology for assessing the radiological consequences of routine releases of radionuclides to the environment. Radiation Protection 72, EUR 15760EN, CEC.

[8] FSA (2000) Guidance For Assessing the Potential Impact of Radionuclide Discharges to the Environment. Food Standards Agency, London.

[9] Wershofen H & Aumann DC (1989) Iodine-129 in the environment of a nuclear fuel reprocessing plant: VII. Concentrations and chemical forms of I-129 and I-127 in the atmosphere. *J Environ Radioact* **10** 141-156.