Tritium in the Aquatic Environment

Dr Gillian MacKinnon
SUERC

What is tritium (^3H)?

It is the radioactive isotope of hydrogen and decays to the stable isotope helium (^3He), emitting a beta particle (and a neutrino).

The beta particle has a maximum energy of 18.6 keV with a short range.

This means that tritium is not dangerous externally, but it is an internal radiation hazard when inhaled, or ingested via food or water, or absorbed through the skin.

As a form of hydrogen, it readily forms water molecules (HTO) and can be incorporated into organic molecules (OBT).

Sources of ^3H in the environment

Natural

Cosmogenic radionuclide continuously produced in the upper atmosphere
Annual production rate of ~ 7.4×10^4 TBq
Global inventory of ~9.6×10^5 TBq
12.43 y half-life
Low natural abundance

Manmade

Legacy of atmospheric nuclear weapons tests 1952-1962
Estimated 520 atmospheric tests mainly in the northern hemisphere, 1352 underground tests
Total ^3H production estimated at 1.86×10^8 TBq

Source: UNSCEAR Reports

Atmospheric ^3H sources

^3H released by nuclear explosions (HT and CH_3T)
^3H produced naturally in the upper atmosphere

Becomes rapidly oxidised to water (HTO)

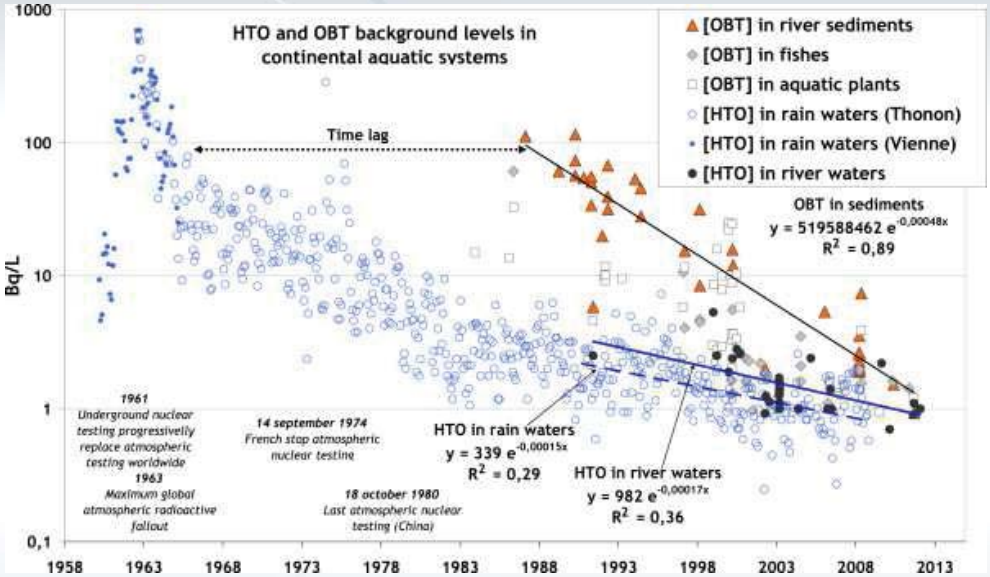
Transported to the earth's surface in precipitation events

In the early 1960's, ^3H concentrations X 1000 the natural background level

Since 1963, environmental ^3H levels have gradually decreased

Current precipitation and surface water concentrations of 1-2 BqL^{-1}

^{3}H background level over time



Time series acquired for HTO and OBT in components of the various continental aquatic systems investigated and in rain waters. All these characterise the background level over time.

From Eyrolle-Boyer et al., Journal of Environmental Radioactivity, Volume 136, 2014, 162 - 168

Current understanding of ^{3}H behaviour in the environment

Similar HTO levels in rainwater and river waters - with similar loss rates over the years illustrating the rapid kinetic exchange between water masses.

Significantly higher values of OBT in sediments, fish and aquatic plants than HTO.

Variation of OBT/HTO ratio in sediments:
~ 45 in the mid-1980's, to ~ 5 in 2005 and close to 1 in 2013.

Reflect the long-term persistence of tritium in terrestrial biomass contaminated by past nuclear fallout.

The persistence of OBT forms in terrestrial biomass has resulted in a substantial time lag between the source term (organic matter from catchments) and OBT appearance in the aquatic environment.

Current understanding of ^{3}H behaviour in the environment continued

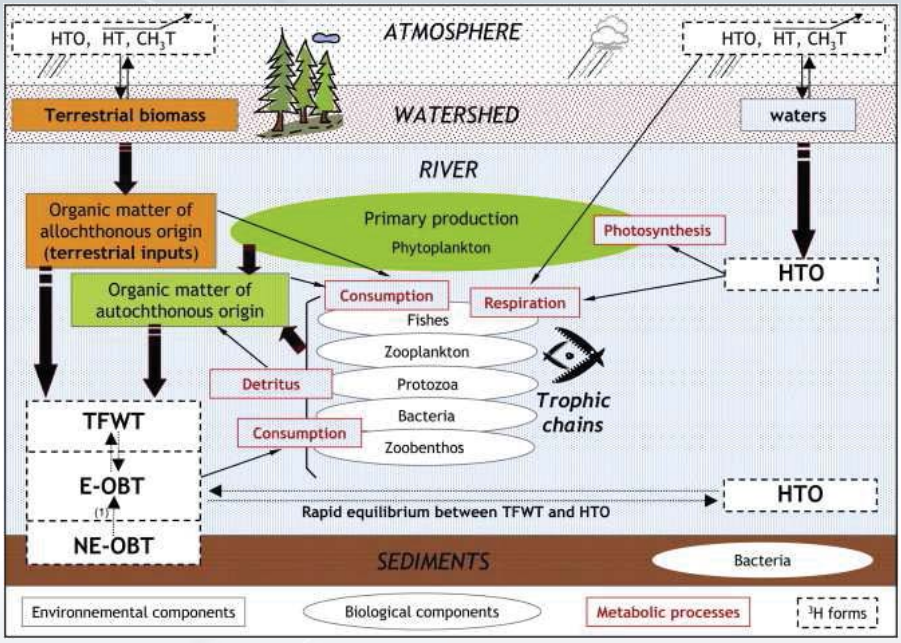
It is well established that ^{3}H as HTO cannot accumulate in the natural environment.
It is not clear whether or not ^{3}H can be accumulated in the form of OBT, which exists in the environment.

If the living organism was exposed to higher environmental ^{3}H concentrations in the past than in the present, past contamination may remain in some of its tissue.

This is one of the reasons for the high OBT/HTO ratios in nature.

IAEA tritium working group definition:
"OBT is carbon-bound and buried tritium formed in living systems through natural environmental or biological processes from HTO. Other types of organic tritium (e.g. tritiated methane, pump oil, radiochemicals and so on) should be called tritiated organics, which can exist in any chemical or physical form".

^{3}H behaviour in the environment



HT (3H gas or 3H hydride); CH3T (methyl 3H gas); HTO (tritiated water or 3H oxide); TFWT (Tissue Free Water 3H); E-OBT (Exchangeable Organically Bound 3H); NE-OBT (Non Exchangeable Organically Bound 3H)

From Eyrolle-Boyer et al., Journal of Environmental Radioactivity, Volume 136, 2014, 162 - 168

Nuclear Power Generation

Reactor Type	UNSCEAR 1993 (for year 1985)	Reactor Type	UNSCEAR 2000 (for year 1997)
HWR		HWR	
Bruce 1-4, Canada	600	Bruce 1-4, Canada	600
PWR		PWR	
Diablo Canyon, US	17	Diablo Canyon 1 & 2, US	55
AGR		AGR	
Hinkley Point B, UK	12	Hinkley Point B, UK	18.7
BWR		BWR	
Wurgassen, Germany	2	Phillipsburg, Germany	1.6

Tritium (HTO) releases (gaseous & liquid) from various reactor types, TBq y^{-1}

Tritium is produced during the operation of all nuclear reactors.

Heavy Water Reactors

Heavy water reactors discharge far more ^{3}H than other reactor types because they use heavy water (deuterium) as coolant and moderator.

During reactor operation, deuterium is activated by fission neutrons to form ^{3}H.

Heavy water volume in Candu nuclear reactors = >3 million litres

Heavy water losses from the cooling water circuits = 3% of their inventory per year

Heavy water losses from the moderator circuits inside the reactor = about 0.1% of their inventory per year

Tritium Reduction Facility (TRF)

Before 1990, ^{3}H contaminated heavy water was released and replaced with ^{3}H -free heavy water = higher ^{3}H discharges.

In early 1990 a TRF at Darlington was started up which extracted ^{3}H from tritiated heavy water.

In this facility, ^{3}H atoms on water molecules are transferred to deuterium gas molecules by means of catalytic exchange at 200°C.

Then the tritiated deuterium (i.e., tritium gas) is separated from deuterium gas by cryogenic distillation at -250°C and then stored.

Ontario's reactors contain ~10 million litres of moderator and coolant heavy water.

It is estimated to take 4 -5 years for this large inventory to be treated once through the TRF.

UK Sources of Radioactive Waste Disposal

Dounreay, Highland

Chapelcross, Dumfries and Galloway

Sellafield, Cumbria

Sizewell, Suffolk

Amersham, Cardiff

Harwell, Oxfordshire

Culham, Oxfordshire

Aldermaston, Berkshire

Hinkley Point, Somerset

Winfrith, Dorset

Contributors of ^{3}H

Nuclear Power Production

e.g. Chapelcross, Dumfries and Galloway – 4 Magnox reactors

Hinkley Point, Somerset – 2 Magnox reactors and 2 AGR's

Sizewell, Suffolk – 2 Magnox reactors & 1 **PWR**

Nuclear fuel production and processing

e.g. Sellafield, Cumbria
Reprocessing of fuel cladding

Other i.e. radiochemical industry

e.g. Amersham, Cardiff

Research Establishments

e.g. Harwell, Oxfordshire – 5 research reactors of various

Culham, Oxfordshire – JET experimental fusion reactor

Dounreay, Highland –development of research reactors

Winfrith, Dorset
At various times there have been nine research and d e v e l o p m e n t reactors including a **Steam Generating Heavy Water Reactor (SGHWR)**

Defence

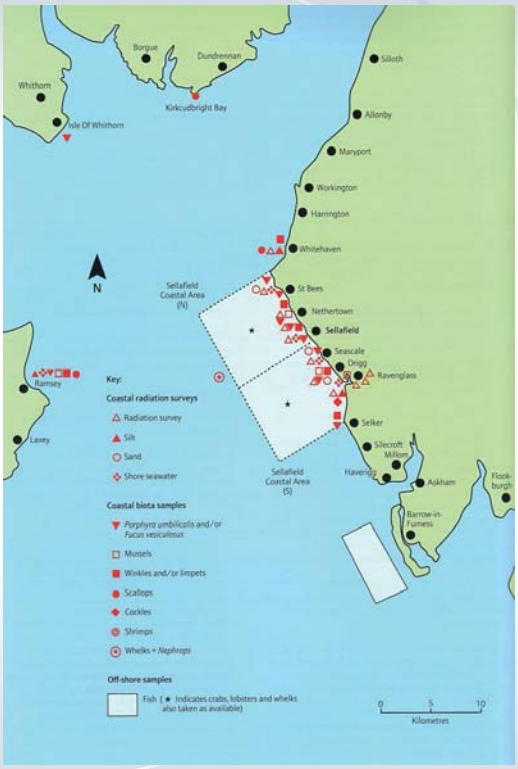
e.g. Aldermaston, Berkshire

Sellafield, Cumbria

Annual ^{3}H liquid discharge in TBq from the Sellafield pipeline to the Irish Sea

Source: Gray *et al.*, 1995, MAFF & RIFE Reports

Routine monitoring around UK nuclear establishments



Sampling includes:

Terrestrial sampling of:

- Rainwater
- Foodstuffs i.e. milk, vegetables, soft fruits, meat, cereal crops and grass/sillage

Transfer of radionuclides from sea to land

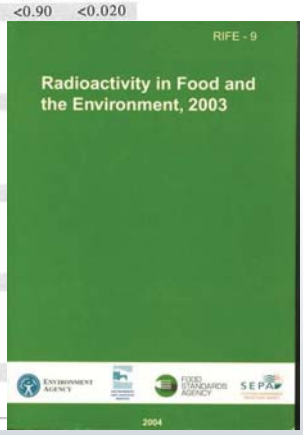
Coastal radiation surveys
Sediment – sand/silt
Seawater sampling
Coastal biota samples such as:

- seaweeds
- mussels, winkles, cockles, scallops
- shrimps, crabs, lobster
- fish

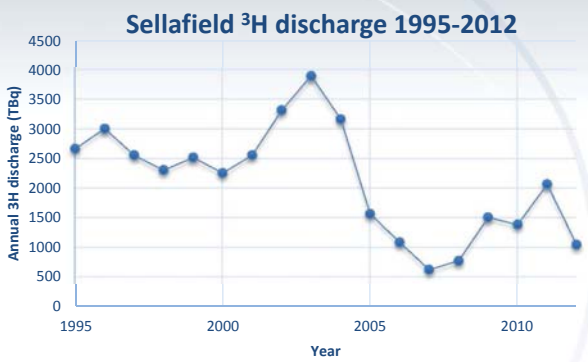
Example data from Radioactivity in Food and the Environment Report (RIFE) for terrestrial food and the environment near Sellafield, 2004.

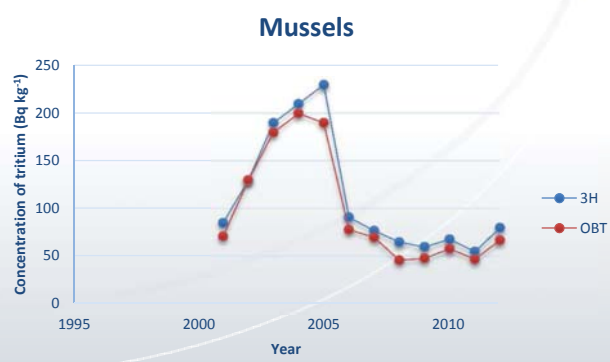
Table 3.15. Concentrations of radionuclides in terrestrial food and the environment near Sellafield, 2004

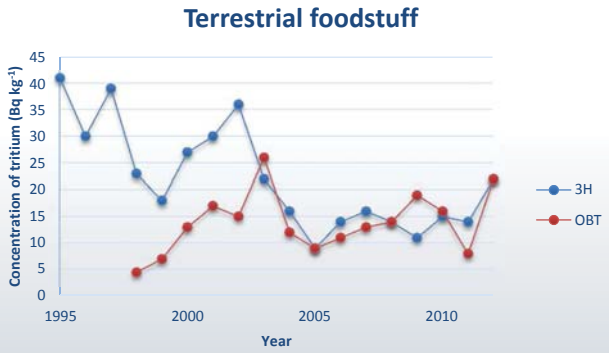
Material	Selection[a]	No. of sampling observ-ations[c]	Mean radioactivity concentration (wet)[b], Bq kg^{-1}								
			Organic ^{3}H	^{3}H	^{14}C	^{60}Co	^{90}Sr	^{99}Tc	^{106}Ru	^{125}Sb	^{129}I
Milk[d]		16	<3.9	<5.1	17	<0.31	0.091	<0.0035	<2.2	<0.64	<0.016
Milk[d]	max		<4.8	<6.5	22	<0.34	0.25		<2.4	<0.71	<0.033
Apples		2	<9.5	<8.5	17	<0.30	0.23	0.026	<2.2	<0.60	<0.019
Apples	max		<13	13	19		0.41		<2.7	<0.70	
Barley		1		<6.0	110	<0.30	1.3		<2.3	<0.80	<0.047
Blackberries		3	<4.3	<8.7	16	<0.33	1.4		<2.4	<0.70	<0.036
Blackberries	max		<6.0	16	17	<0.40	3.5		<2.8	<0.90	<0.054
Bovine kidney		1	<8.0	8.0	31	<0.30	0.38	<0.025	<1.8	<0.90	
Bovine liver		1	9.0	16	38	<0.30	0.015	<0.030	<2.3	<0.60	<0.055
Bovine muscle		1	<7.0	6.0	32	<0.40	0.013	<0.027	<2.2	<0.60	<0.035
Broccoli		1	<4.0	<4.0	<3.0	<0.30	0.19		<2.2	<0.60	<0.024
Cabbage		1	<4.0	<4.0	<3.0	<0.30	0.22		<1.8	<0.60	<0.021
Carrots		1	<4.0	<4.0	10	<0.40	0.21	<0.017	<2.4	<0.70	<0.019
Cauliflower[e]		1	<4.0	<4.0	8.0	<0.30	0.12		<2.0	<0.60	<0.019
Eggs		1	<4.0	<4.0	34	<0.20	0.049		<2.3	<0.90	<0.020
Elderberries		1	<9.0	9.0	20	<0.20	0.52		<1.6		
Honey		1		<6.0	94	<0.20	0.059		<1.8		
Mushrooms		1	2.0	6.0	<4.0	<0.40	0.71		<1.4		
Onions		1	<6.0	<4.0	10	<0.30	0.24		<2.5		
Ovine kidney		1	5.0	13	<9.0	<0.20	1.4	<0.055	<2.3		
Ovine liver		1	<12	10	15	<0.30	0.34	<0.032	<2.1		
Ovine muscle		3	<6.3	8.3	35	<0.37	0.056	<0.021	<2.1		
Ovine muscle	max		<9.0	9.0	36	<0.40	0.077	<0.034	<2.6		
Ovine offal		2	<6.5	<6.0	28	<0.25	0.32	0.034	<2.2		
	max		<7.0		36	<0.30	0.36	0.041	<2.3		
Pheasants		1	<6.0	<5.0	25	<0.30	<0.012	<0.016	<1.8		
Potatoes		1	1.0	5.0	18	<0.30	<0.010		<2.3		
Rabbit		1	1.0	7.0	21	<0.30	0.026	<0.016	<1.9		
Runner beans		1	<8.0	7.0	11	<0.50	0.25		<3.4		
Sprouts		1	<4.0	4.0	20	<0.30	0.20		<2.3		
Swede		1	<5.0	<4.0	8.0	<0.20	0.73		<2.1		
Turnips		1	<4.0	<4.0	9.0	<0.50	0.57		<2.9		
Wheat		1		<7.0	70	<0.40	0.77		<1.2		
Grass		5				<0.40		<0.018	<1.8		
Grass	max							<0.024	<2.4		
Soil		3				<0.43			<1.4		
Soil[f]	max					0.80			<1.5		



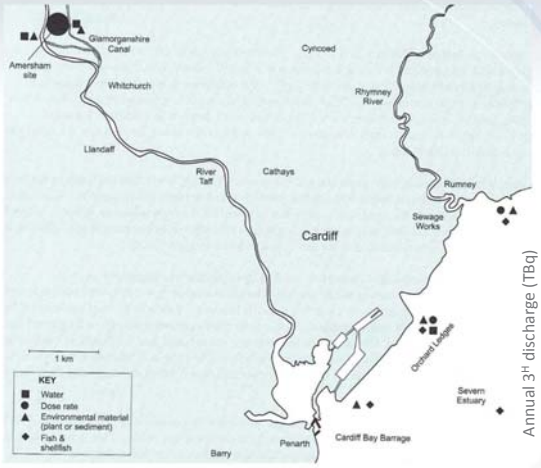
^{3}H and OBT time series at Sellafield

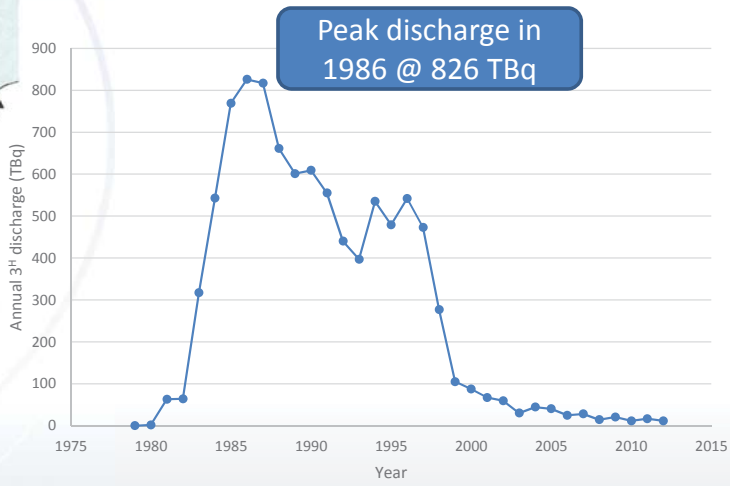






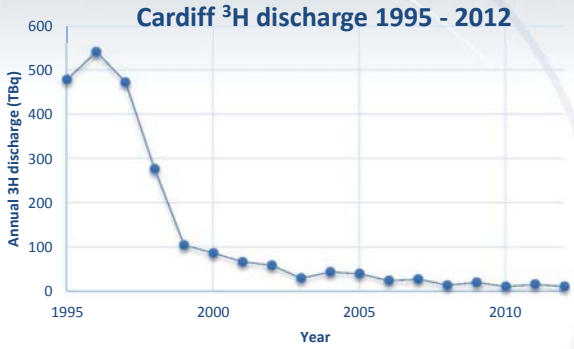
Amersham, Cardiff

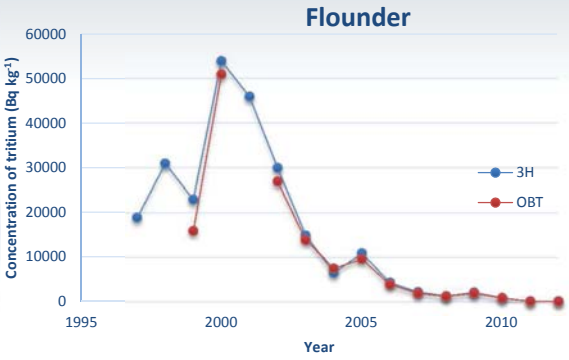


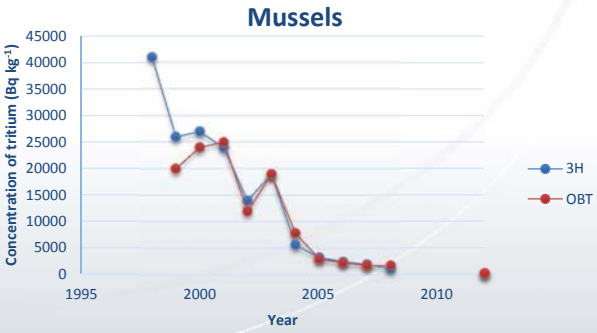


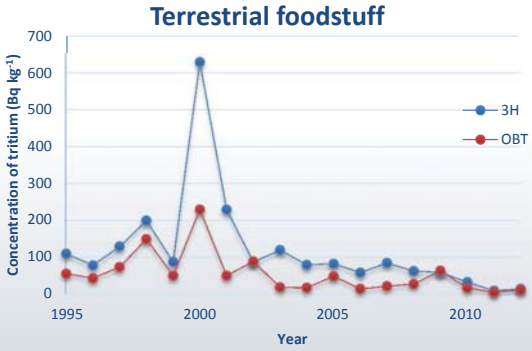
Annual ^{3}H liquid discharge in TBq from the Amersham radiochemical plant to the Severn Estuary

^{3}H and OBT time series at Cardiff









Behaviour of ^{3}H in Surface Waters

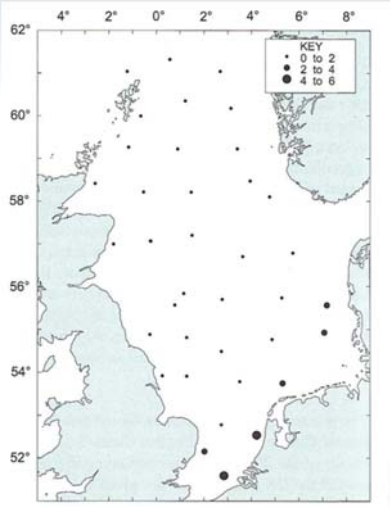


Figure 9.4 Concentrations (Bq l⁻¹) of tritium in surface water from the North Sea, August-September 2004

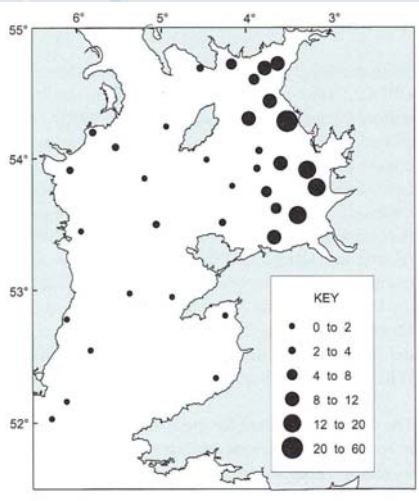


Figure 9.4 Concentrations (Bq l⁻¹) of tritium in surface seawater from the Irish Sea, August-September 2003

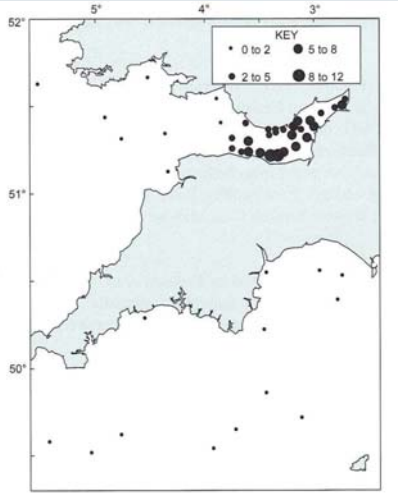


Figure 9.5 Concentrations (Bq l⁻¹) of tritium in surface water from the Bristol Channel and western English Channel, September-October 2003

Concentration (Bq L^{-1}) of ^{3}H in filtered sea water from the Irish Sea and Bristol Channel, 2003 and the North Sea, 2004.

Aquatic Food Chain Models

AQUATRIT – a dynamic ^{3}H transfer in the aquatic food chain model

OURSON – Tool for Environmental and Health Risk Assessment Model

These models are based on the assumption that the OBT specific activity in fish is directly linked with the HTO in water or the OBT in fish food.

Assuming this the concentration factor (CF) in fish must ≤ 1.

$$CF = \frac{\text{Conc. per unit mass of biota at equilibrium}}{\text{Dissolved conc. per unit volume in ambient water}}$$

CF's for Sellafield and Cardiff examples

		Sellafield	
Year	Fish	Mussel	Terrestrial*
2000	8	ND	7
2004	13	22	6
2012	17	11	11

*2 Bq L^{-1} natural background for rainwater value used

Sellafield marine biota CF 8 – 22

Sellafield terrestrial biota CF 6-11

		Cardiff	
Year	Fish	Mussel	Terrestrial*
1999	2286	2857	102
2003	1169	1215	9
2012	11	8	6

Cardiff marine biota CF 8 – 2857

Cardiff terrestrial biota CF 6 – 102

All CF's > 1

CF = OBT concentration/ ambient seawater ^{3}H concentrations

Is ^{3}H a radiological hazard ?

1. ^{3}H's unique properties of extremely high mobility, exchangeability, and binding with organic materials are not properly recognised by official dose models.
2. Because of the short range of ^{3}H's beta particle, ^{3}H's damage depends on its exact location in the cell.
3. ^{3}H is often described as a "weak" beta-emitter, but in radiation biology, so-called "weak" beta particles are more effective than energetic ones.
4. Much evidence indicates that ^{3}H's effectiveness (in radiation biology terms) is 2-3 times that recognised by the ICRP.
5. Little official recognition is given to ^{3}H's ability to incorporate in organic molecules to high levels as a result of 'chronic exposures'.
6. Official dose models for OBT therefore significantly underestimate its doses.

So would increasing ^{3}H dose factors make a difference?

Environmental Assessment Models

Evaluating the radiological impact of actual and potential releases of radionuclides to the environment.

The ICRP recommends two main metabolic models to estimate the dose from compounds that contain ^{3}H.
The HTO model – intake of tritiated water or other tritiated compounds that partially convert to HTO
The OBT model – applies to inhalation of ingestion of organically-bound tritiated compounds which yield a dose per unit intake about double those of tritiated water.

The Taylor HTO biokinetic model (2003) accounts for the different ways that OBT deposits in organs vs tissues but only applies to adults.

Further developments of OURSON have been reported taking seasonality into account and adding a metabolic model for the OBT biological loss rate in fish as well as a first attempt to consider the Cardiff case of tritiated organics.

IAEA have updated this model but it has not yet been released in the open literature.

Conclusions

Gaps do exist in ^{3}H environmental science but they are not significant for people or the biosphere at current low levels of exposure.

^{3}H has a complex behavior once released into the environment.

The processes involved in ^{3}H transfer have timescales as short as minutes (for HTO equilibration with TFWT in biota) or as long as 10's of years (for non-exchangeable OBT in organic material).

^{3}H can be effectively incorporated into biological systems including the human body as OBT.

^{3}H is transferred through the environment and through food chains.

Recommendations – for discussion

Use this unique opportunity to study the environmental half-life of ^{3}H surrounding other, non-accident nuclear power plants in Japan to better understand the environmental behavior and persistence of ^{3}H.

OBT measurements provide a better indication of the level of environmental ^{3}H contamination however methodological clarification, within an international framework, is required to improve confidence and reliability.

OBT inter-comparison programmes

1988 – Akita University School of Medicine, Japan – intercomparison of 6 labs for swine liver and polished rice
1998 – study to develop a vegetation standard reference material and carryout an intercomparison of OBT was initiated at Chalk River Laboratories, Canada.
2008 – two studies conducted in Canada – HTO concentrations in agreement, OBT differed considerably
2009-2010 – CETMA, French analytical laboratories intercomparison of grass samples.

Analytical method ?
Instrumentation – LSC vs mass spectrometry?
Background ^{3}H concentrations?
High Coefficients of Variation?
Differences between sample matrices?

Even though OBT measurement and prediction are associated with high uncertainty, OBT should not be ignored in ^{3}H dose estimates.

Recommendations – for discussion continued

Observed concentrations in the environment rather than model predictions should be used as a starting point in the calculation of doses to members of the public.

Fully characterize the ^{3}H contaminated stored water in order to assess whether abatement technology would be appropriate prior to discharge i.e. destroying organic matter present, catalytic exchange and cryogenic distillation prior to storage (TRF).

If disposal to sea is deemed necessary, **proceed with caution** and implement small test releases of ^{3}H contaminated stored water to well chosen and well characterized aquatic sites and carry out full scale monitoring of the environment.