Journal of Environmental Radioactivity 133 (2014) 40–47

Contents lists available at SciVerse ScienceDirect

Journal of Environmental Radioactivity

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

# An estimate of the inventory of technetium-99 in the sub-tidal sediments of the Irish Sea

Stuart B. Jenkinson [a,1], David McCubbin [a,2], Paul H.W. Kennedy [b], Alastair Dewar [a], Rachel Bonfield [a], Kinson S. Leonard [a,*]

[a] Centre for Environment, Fisheries and Aquaculture Science, Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK
[b] Food Standards Agency, Aviation House, 125 Kingsway, London WC2B 6NH, UK

ARTICLE INFO

*Article history:*
Received 2 November 2012
Received in revised form
28 March 2013
Accepted 14 May 2013
Available online 10 June 2013

*Keywords:*
$^{99}$Tc
Technetium-99
Irish Sea
Inventory
Sediments

ABSTRACT

Published results from earlier studies have provided indications that measurable quantities of technetium-99 ($^{99}$Tc) have accumulated in the sub-tidal sediments of the Irish Sea. This is due to the enhanced discharges from the Sellafield nuclear reprocessing plant in Cumbria, UK (between 1994 and 2004). Depth distributions of $^{99}$Tc concentrations in sub-tidal sediments have been determined from a limited number of Irish Sea sites, following the collection of deep sediment cores (up to 2 m in depth), sampled in two research cruise surveys in 2005 and 2006. Vertical concentration profiles of $^{99}$Tc from a range of substrates in the Irish Sea are presented here and these have been used to produce an estimate of the total inventory of $^{99}$Tc residing in the sub-tidal sediments of the Irish Sea. Significant variation was observed between $^{99}$Tc concentrations in the sediment samples, as well as in the shape of individual depth profiles. As anticipated, concentrations tended to be greater on fine-grained (muddy) substrates and showed a general decrease with distance from Sellafield. Vertical concentration profiles of $^{137}$Cs, and $^{137}$Cs data from published work, have also been considered to evaluate the use of the relatively few $^{99}$Tc core data (upon which to determine the $^{99}$Tc inventory).

The inventories of $^{99}$Tc and $^{137}$Cs are estimated to have been of the order of 30 and 455 terabecquerels (TBq), respectively, or ∼2% of the total cumulative Sellafield discharge for each of the two radionuclides. The residence half-time of $^{137}$Cs in the sub-tidal sediments of the Irish Sea is estimated to be in the order of ∼16 years. Therefore, as the $K_d$ values for $^{99}$Tc and $^{137}$Cs are similar, this also provides an indicative value to predict future losses of $^{99}$Tc from the sediment reservoir.



## 1. Introduction

For over half a century, radionuclides in liquid effluent have been discharged, under Government permit (authorisation), from the nuclear reprocessing plant at Sellafield (Cumbria, UK) into the north-east Irish Sea. Overall, due to improved waste treatment procedures, significant reductions in the release of most radionuclides have occurred over the last few decades. However, in 1994, the quantities of technetium-99 ($^{99}$Tc) discharged in liquid wastes from Sellafield increased significantly to 72 terabecquerels (TBq) from an average of ∼5 TBq per year over the previous decade. $^{99}$Tc is a long-lived ($t^{½} = 2.13 \times 10^5$ years) pure β-emitter ($E_{\beta max}$ = 292 keV) (Lederer et al., 1967) and is the daughter product of $^{99}$Mo, which is produced as a fission and activation product. The increase in discharges was expected, following the commissioning of the Enhanced Actinide Removal Plant (EARP) (see e.g. Leonard et al., 1997). EARP was designed to reduce alpha and beta activity from effluents prior to discharge to allow the treatment of medium active waste (which previously had been accumulating on site). It was the treatment of these accumulated wastes that resulted in new discharges to the Irish Sea. The increased discharges had an immediate and well-recognised impact upon $^{99}$Tc concentrations in some items of seafood and seaweed (e.g. Hunt et al., 1998; Smith et al., 2001). The further introduction of new abatement technology, and diversion of some waste arisings into vitrification processes, permitted $^{99}$Tc discharges to be reduced. The new treatment used TPP (tetraphenylphosphonium bromide) to complex the $^{99}$Tc and to remove it from the liquid effluent. Consequently, in 2005 an overall reduction in liquid discharges of $^{99}$Tc was achieved from the

* Corresponding author. Tel.: +44 (0) 1502 524477; fax: +44 (0) 1502 513865.
*E-mail address:* kins.leonard@cefas.co.uk (K.S. Leonard).
[1] Present address: Montriond, France.
[2] Present address: Magnox Limited, Hinkley Point 'A' Site, Bridgwater, Somerset TA5 2PZ, UK.

0265-931X/$ – see front matter Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jenvrad.2013.05.004

Sellafield site by ~90% compared with 2002 levels. These reductions in discharges of $^{99}$Tc (<10 TBq per year since 2005) have led to concentrations returning to their pre-EARP levels in the immediate Sellafield area, although far-field effects of the enhanced discharges are still being observed (Environment Agency et al., 2011).

Under the declining discharge regime, remobilisation of $^{99}$Tc from Irish Sea sediments is likely to become an increasingly significant source term to the waters of the Irish Sea. Previous research has indicated that the sediment/seawater distribution coefficient ($K_d$ value) of $^{99}$Tc in the Irish Sea may be as high as $2 \times 10^3$ (McCubbin et al., 2006), an order of magnitude greater than the value of $10^2$ presently recommended by the IAEA (2004). This implies that a greater proportion of the $^{99}$Tc released from Sellafield may be associated with sub-tidal sediments, and theoretically available for remobilisation and re-dissolution into the water column, than predicted by modelling using the lower $K_d$ value. The higher $K_d$ value for $^{99}$Tc is also similar to that derived for caesium-137 ($^{137}$Cs) in the Irish Sea (~$10^3$, Kershaw et al., 1992). This suggests that, despite their dissimilar biogeochemical characteristics, any re-dissolution of $^{99}$Tc may follow the pattern observed for $^{137}$Cs after its discharge reduced in the mid-1980s. For $^{137}$Cs, remobilisation became the primary source term to the water column in the Irish Sea (Poole et al., 1997; Leonard et al., 1998; MacKenzie et al., 1998; McCubbin et al., 2002; Hunt et al., 2013) and has been estimated to outweigh the $^{137}$Cs discharged from Sellafield by around a factor of four since then (Poole et al., 1997; McCubbin et al., 2002). Information providing the $^{99}$Tc inventory, associated with seabed sediments, is likely to be useful in helping to determine the future potential risk from the legacy of elevated $^{99}$Tc discharges, resulting in the future remobilisation/re-dissolution into seawater and uptake in seafood.

The work here reports the analysis of 16 deep sediment cores for $^{99}$Tc, from sites in the Irish Sea selected to cover all the major surface sediment substrates. Sample intensity was greatest on muddy material close to Sellafield, as previous surveys indicated that the bulk of radionuclide inventories were located in this area (Poole et al., 1997; Kershaw et al., 1999). Depth concentration profiles for $^{99}$Tc were obtained at each sample site, and these formed the basis of the sub-tidal $^{99}$Tc inventory calculations. Due to the limited number of sediment cores obtained, results are necessarily extrapolated across large areas of sub-tidal seabed. In an attempt to estimate the likely error associated with this approach, the sediment cores were also analysed for $^{137}$Cs, and the inventory obtained from this method of calculation was compared to $^{137}$Cs inventory calculations using data from a previous, more extensive survey of the Irish Sea (Poole et al., 1997). Like $^{99}$Tc, $^{137}$Cs ($t^{½} = 30$ years) is considered to exhibit conservative behaviour due to its low particle reactivity in the oxic marine environment (e.g. McCubbin et al., 2002). The inclusion of the $^{137}$Cs core and inventory data is a useful parameter to assess the possible sampling error of the estimated $^{99}$Tc inventory value (due to limited availability of $^{99}$Tc core data) and, by comparison, the potential for future loss of $^{99}$Tc from Irish Sea sediments.

## 2. Materials and methods

### 2.1. Sampling strategy

The radionuclide distributions in Irish Sea sediments are greatly influenced by the type of sediment substrate, and distance from Sellafield, with the activity being greatest on fine-grained material close to the Sellafield pipeline (Poole et al., 1997; Kershaw et al., 1999). Muddy sediments are confined to two main areas (Fig. 1): a belt of sandy muds and muddy sands parallel to the Cumbrian coast, extending into Morecambe Bay in the south and partly across

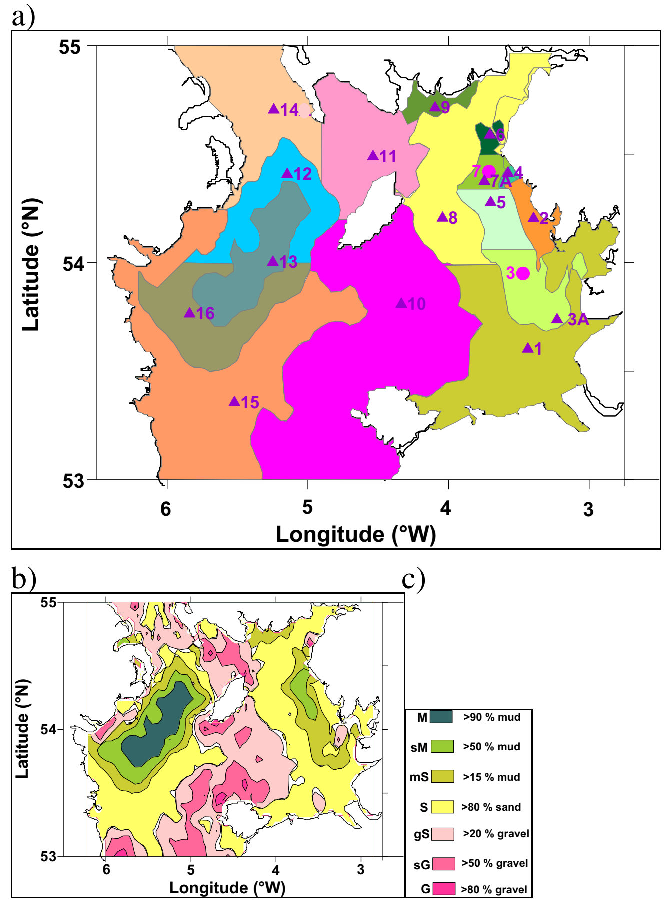


**Fig. 1.** Sampling locations and composition maps (Irish Sea). a) Sectioning of Irish Sea sub-tidal sediments into sixteen operational sectors. Circles and triangles indicate core locations; Cory 3/05 and CEnd 13/06, respectively. b) Seabed composition from grain sizes supplied by the British Geological Survey. c) Legend indicating seabed composition in Fig. 1b.

the mouth of the Solway Firth in the north; and a relatively deep (~100 m) basin between the Isle of Man and Ireland. Both areas coincide with zones of relatively weak tidal currents (Kershaw et al., 1992). Elsewhere, the surface sediments are coarser grained. Gravelly material, representing glacial lag deposits, predominates in the central Irish Sea to the north and south of the Isle of Man (and in St. Georges Channel) grading into mobile sands in the east and south-west.

The core sampling design was established from previous investigations (in 1978, 1988 and 1995) that estimated the inventories of $^{137}$Cs, $^{239+240}$Pu and $^{241}$Am in the sub-tidal sediments of the Irish Sea (Poole et al., 1997; Kershaw et al., 1999). The most recent sub-tidal sediment inventory survey, prior to the present study, was undertaken over a period of ~10 days in June 1995, and involved the collection of over 100 cores using a dedicated research vessel. In an attempt to reduce the uncertainty resulting from sampling error, a large number of cores were collected in the muddy sediments close to Sellafield. The distribution of sampling sites by operationally defined sectors in the present study (Table 1; Fig. 1) covers all the major surface sediment substrates. Sediment substrate in individual sectors of the Irish Sea (Fig. 1) was assessed by contouring raw data, supplied by the British Geological Survey (BGS), for surface particle size distribution using a commercial software package (SURFER™). The output (Fig. 1) shows general agreement with a more detailed finer scale map published elsewhere (Holmes and Tappin, 2005). Surface areas of each sector