Mechanisms for accumulation and migration of technetium-99 in saltmarsh sediments

UNIVERSITY OF SOUTHAMPTON
FACULTY OF SCIENCE
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A thesis presented for the degree of
Doctor of Philosophy

By

Frank Wigley

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Abstract

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This thesis describes the development of analytical methods for both the bulk determination of ^{99}Tc, and determination of ^{99}Tc in sequential extracts from sediments. These methods have been used to collect data, which, along with trace and major element data have been used to interpret the mechanisms for ^{99}Tc input, migration and accumulation in saltmarshes. The inventory of ^{99}Tc stored in the Thornflatt Saltmarsh, Esk Estuary has also been determined.

The routine determination of ^{99}Tc in bulk samples uses ^{99m}Tc as a yield monitor. Samples are ignited stepwise to 550°C and the ^{99}Tc is extracted using 8M nitric acid. Many contaminants are precipitated with $Fe(OH)_3$ and the Tc in the supernant is pre-concentrated and further purified using anion-exchange chromatography. Final separation of Tc from Ru is achieved by extraction of Tc into 5% TnOA in xylene from 2M sulphuric acid. The yield is determined by γ-spectrometric analysis of ^{99m}Tc. Determination of ^{99}Tc is made by liquid scintillation counting. Typical recoveries are in the order of 70-95% and the method has a detection limit of 1.7 Bq/kg for a sample size of 10g. Determination of Tc in sequential extracts uses operationally defined procedures to extract: exchangeable Tc, reducible Tc and oxidisable Tc. An initial water wash is used to extract any occluded Tc and a final leach in 8 M nitric acid is used to dissolve any residual Tc. The isolation of ^{99}Tc uses TEVA resin for Extracts 1-4 and the decontamination procedure developed for bulk analysis for Extract 5. ^{99m}Tc was used as a yield monitor, and determination of ^{99}Tc is by liquid scintillation counting. Limits of detection were dependent on the amount of ^{99m}Tc tracer used but were found to be as low as 2.4 Bq/kg for a sample size of 2g.

A study was made of the mechanisms responsible for the accumulation and migration of Tc in estuarine sediments using sediments collected from saltmarshes at Thornflatt, Carlaverock and the Ribble Estuary. ^{99}Tc was present at determinable activities in all the sediment cores taken from these sites.

Good correlations between Tc and CaO as well as CO_3 concentrations and poor correlation between Tc and radionuclides adsorbed to inorganic detritus infer a direct input of ^{99}Tc to marsh sediments. Determination of ^{99}Tc in biota living on the marsh also showed that this was not a significant pathway for input of Tc to the sediments. Sequential extraction data imply sorption to an organic fraction of the sediment.

Stable element and sequential extraction data indicates that Tc is readily oxidised and remobilised before re-precipitation where redox conditions are favourable. Data indicate a reduction potential between those of the Mn^{IV} to Mn^{II} reaction and the Fe^{III} to Fe^{II} reaction is necessary for re-accumulation to occur, as suggested by published thermodynamic data. Data collected from reducing sediments imply that similar mechanisms are responsible for the accumulation of Mn (*e.g.* reduction by sulphate reducing bacteria) and the accumulation of Tc.

The inventory of ^{99}Tc held within the Thornflatt saltmarsh is proportionally less than that of ^{137}Cs or ^{241}Am when compared to discharges from Sellafield. However a higher proportion of ^{99}Tc is transferred from Sellafield and incorporated into saltmarsh sediments than is suggested by previously published standard distribution coefficient data. Saltmarsh sediments are therefore a more important sink of ^{99}Tc than extrapolations made from inventories of other radionuclides would suggest.

Acknowledgements

I would like to thank Dr Ian Croudace, Dr Phil Warwick and Dr Arthur Sanchez for their valued supervision, contribution, support, patience, and brain storming sessions on everything from technetium geochemistry to marketing policies for Uranopoo hair care products.

I would also like to thank the following people for their help during this study: Dr Bob Carpenter (AEA Technology) for support of the PhD; The Geosciences Advisory Unit, AEA Technology and The Institute of Terrestrial Ecology for funding the Project; Dr David Sanderson (SURRC) for the Carlaverock Samples and Dr Martin McCartney (SURRC) for the ^{99}Tc intercomparison standards.

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I would like to dedicate this thesis to my parents, without whose support and belief in me I would never have had the chance to undertake this work let alone complete it.

"Peu importe à la Science que ses serviteurs passionnés soient riches ou pauvres, heureux ou malheureux, sains ou malades. Elle sait qu'ils existent pour chercher et pour découvrir et qu'ils ne cesseront de chercher et de trouver que lorsque la source de leurs forces se tarira. Un scientifique est impuissant à lutter contre sa vocation: même les jours de dégoût ou de révolte, ses pas le ramènent inévitablement aux instruments de son laboratoire."

Marie Curie

What does it matter to Science if her passionate servants are rich or poor, happy or unhappy, healthy or ill? She knows they have been created to seek and discover, and that they will seek and find until their strength dries up at its source. It is not in a scientist's power to struggle against his vocation: even on his days of disgust or rebellion his steps inevitably lead him back to his laboratory apparatus.

Declaration

This study consists predominantly of research conducted by myself. However some data presented have resulted from collaboration with individuals working in the Environmental Geochemistry and Radiochemistry Research Group (School of Ocean and Earth Science). In all cases the interpretation of these data from the view of technetium input, accumulation and migration has been dominantly due to my intellectual input. Where collaborations have occurred, this is clearly stated in the text or in the list of authors on the paper, where the work has been published.

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Chapter 1

Scope of Thesis

Chapter 1. Scope of Thesis

1.1 Introduction

All isotopes of technetium are radioactive with half-lives ranging from 8 milliseconds to 4.2 million years. These half lives are short compared to the age of the Earth so all primordial technetium is considered to have decayed and technetium in the contemporary environment is derived from anthropogenic sources. Of the isotopes of Tc, ^{99}Tc is the most environmentally important due to its long half life and high fission yield. Most ^{99}Tc is produced primarily by fission of ^{235}U and ^{239}Pu in the nuclear fuel cycle and fallout from nuclear weapons' testing. Naturally occurring ^{99}Tc has been determined at trace levels as the result of spontaneous fission of uranium in uranium rich mineral deposits.

The commissioning of the Enhanced Actinide Removal Plant (EARP) led to subsequent increases in ^{99}Tc discharges from the Sellafield site in 1994 as the result of the processing of previously stockpiled Medium Active Concentrates (MAC) wastes. Public awareness of ^{99}Tc has increased principally due to the recent high discharges from EARP and the reported accumulation of ^{99}Tc at high levels in seafood. Technetium as pertechnetate (TcO_4^-), the dominant chemical form of technetium in aerobic environments, acts conservatively in seawater and so is extremely mobile. Technetium also readily accumulates in some marine and freshwater biota and terrestrial plants, introducing ^{99}Tc into the human food chain. The combination of these factors has prompted the expansion of ^{99}Tc monitoring programmes as well as research into the interaction of technetium in marine organisms.

1.2 Problem definition

Why study the accumulation of ^{99}Tc in saltmarsh sediments?

^{99}Tc discharges to the environment increased tenfold after the commissioning of the EARP Plant in 1994 and the processing of stored wastes. As a result of this a dramatic rise in the activities of ^{99}Tc in shellfish and *fucoid* seaweeds has been documented.

The most likely pathway for marine discharges of radioactive waste to land and into the human food chain via terrestrial pathways is through incorporation into sediments, particularly in tide washed pastures and grazed salt-marshes (Sanchez *et al.* 1999). Given the recent high discharges of technetium from the EARP plant, this pathway has become potentially significant. There has, however, been little study of the geochemical behaviour of technetium in sediments since these have not been regarded as important sinks for technetium. This is because pertechnetate acts conservatively in marine waters and so is unlikely to accumulate in aerobic sediments. These hypotheses have been based on a limited number of laboratory based experiments and a small number of observations of technetium accumulation in sediment samples. However, a detailed understanding of the geochemical behaviour of technetium in sediments is important when considering the burial and storage of nuclear waste due to the mobility and long half life of ^{99}Tc.

Previous research into the behaviour of Tc with sediments leaves a number of questions unanswered:

1. **Does ^{99}Tc accumulate in saltmarsh sediments?**

If so:

2. **Are there any geochemical constraints on accumulation?**

3. **What are the input mechanisms of ^{99}Tc to saltmarsh sediments?**

4. **What proportion of discharged ^{99}Tc is being held in saltmarsh sediments?**

1.3 Research Approach

The study of the interaction of Tc with sediments requires a range of methods. The approaches used in this thesis include:

- Low level bulk determination of ^{99}Tc from a range of sample matrices.
- The determination of sediment geochemistry.
- The determination of mineralogical and other associations of Tc, inferred from sequential extraction studies.

Suitable determination must be made to characterise the sediments so that the chemical behaviour of Tc in the sediments can be deduced. A study must also be made of the input mechanisms (physical, mineralogical, organic transports) of Tc to a saltmarsh environment. Finally an inventory of ^{99}Tc in a saltmarsh should be made and compared to other radionuclides to see if ^{99}Tc accumulation is higher or lower than is expected from data derived from reported laboratory based distribution coefficient experiments.

The remainder of the thesis is organised as follows:

Chapter 2 is dedicated to a review of the discovery, chemistry, input and environmental behaviour of technetium. The input from different sources are reviewed. An examination of the previous work on Tc in sediments is made, the radiological considerations of Tc accumulation in sediments and pathways into the human food chain are presented.

Chapter 3 is a review of previously published methods for the determination of ^{99}Tc. This includes a review of: possible yield monitors, sample preparation, decontamination of samples and also the various methods of final determination.

Chapter 4 deals with the search for a reliable, cost effective and user-friendly method for the determination of ^{99}Tc in environmental samples, including sediments. This method has been published as an "Optimised method for the routine determination of ^{99}Tc in environmental samples by liquid scintillation counting" Analytica Chimica Acta (1999) **380,** 73-82.

Chapter 5 represents the development of an optimised method for the sequential extraction of ^{99}Tc from sediments. This chapter acknowledges the limitations of sequential extraction procedures, and is dedicated to the development of an operationally-defined sequential extraction procedure, decontamination of the samples and final determination.

Chapter 6 is a study of the chemical behaviour of Tc in saltmarsh sediments. Radionuclide activity depth variations are investigated in sediment core profiles taken from the Thornflatt saltmarsh, Carlaverock saltmarsh and the Ribble Estuary. An explanation of the variations in the ^{99}Tc activity profiles is made by comparison with discharge from Sellafield and the post-depositional diagenetic processes occurring in the sediment cores. Tc-sediment associations are clarified using sequential extraction data.

Chapter 7 deals with the spatial accumulation of ^{99}Tc in the Thornflatt saltmarsh. The ^{99}Tc activities, trace and major element concentrations and physical parameters in the top 50cm of the marsh are determined in 27 cores. Data are contoured using a block meaning technique. Possible inputs to the marsh by vegetation are studied. Correlation between ^{99}Tc activities and other core components are made using Pearson's product-moment coefficient of correlation so that inferences about the accumulation mechanism can be made. This chapter also discusses the inventory of ^{99}Tc in the Ravenglass saltmarsh. The inventory is calculated from homogenised cores which were collected to a depth of 50 cm. The inventory for each core is calculated allowing for variations in sediment density and water loss. Ordinary kriging is used to allow spatial prediction of the data over the area and the inventory for the whole marsh is estimated. Comparisons are made for different radionuclides and their relative distribution coefficients are considered. Potential pathways for contamination of the human food-chain are also discussed.

Chapter 8 concludes the thesis and provides a general discussion of the accumulation mechanisms of Tc. Mechanisms are related to input and diagenetic processes.

Chapter 2

Review of the chemistry, sources and environmental behaviour of technetium

Chapter 2 Review of the chemistry, sources and environmental behaviour of technetium

2.1. Discovery of element No. 43

The publication of the Periodic Table reported gaps for elements 43 and 75 which were predicted to be filled by analogues of manganese (Mendeleev 1869). The missing elements were temporarily named eka-manganese (element 43) and dwi-manganese (element 75) and were anticipated to have atomic weights of approximately 100 and 190 respectively (Mendeleev 1869).

Many of the claims to the discovery of element 43 prior to Mendeleev's report were in fact compounds of approximately mass 100 which had similar chemical properties to technetium. Osan claimed to have found "polinium" in 1828 which he extracted from platinum ores. This actually proved to be impure iridium (Kuroda 1993). In 1846 Herman claimed to have found "ilmenium" from ores containing niobium and tantalum. On further analysis ilmenium proved to be a mixture of titanium, niobium and tantalum (Kuroda 1993).

After the publication of Mendeleev's report there was a surge of activity to fill the gaps in his periodic table. Kern in 1877 found "davyum" which was thought to belong more appropriately to the platinum group elements. As davyum had a mass of 154 it was too heavy to be an isotope of element 43. Barrière separated "lucium" from a monzanite sand in 1896, which actually proved to be mainly yttrium mixed with a few other rare earth elements. Ogawa claimed the discovery of "nipponium" in 1908, which he extracted from sulphides obtained from the radioactive mineral Thorianite (Ogawa 1908). Evans also reported the detection of an element with the same chemical properties in the same year. The next claim to the discovery of the missing group 7B elements was made by concentration of 7B elements from likely minerals (Noddack *et al.* 1925). Rhenium was separated from Sperrylite ($4[PtAs_2]$), as platinum is replaced by other platinum group elements including rhenium in platinum group minerals. Efforts were made to separate both rhenium and masarium (as they named element 43) from Gadolinite, $2[Be_2 Fe Yt_2 Si_2 O_{10}]$, and from Columbite ($4[(Fe,Mn)(Nb,Ta)_2O_6]$). Columbite was thought to be a likely source of other Group 7B elements. However in spite of a number of reports from 1925 to 1927 the Noddacks' masarium claim was never accepted (Boyd 1959).
Element 43 was first obtained in 1937 as the isotopes ^{95m}Tc and ^{97m}Tc as ^{94}Mo (d,n) and ^{96}Mo (d,n) reaction products respectively, and so became the first element obtained artificially (Perrier and Segre 1937[1], Perrier and Segre 1939). Element 43 was named Technetium after the Greek word *technos* (τεχηos), meaning artificial in 1946 (IUPAC 1946). After the discovery of uranium

fission in 1939, ^{99m}Tc was found among the fission products (Segré and Wu 1940) and by the late 1940s nuclear reactors were producing macroscopic amounts of ^{99}Tc which was finally detected amongst fission products and neutron-irradiated fission products in 1946 (Sullivan 1951).

2.2. Chemistry

Most technetium-99 is produced as a result of neutron induced fission of uranium-235, with approximately a 6% yield for ^{99}Tc (Equation 2.1, Figure 2.2.1). Technetium-99 is also produced by dueteron irradiation of ^{98}Mo (Equation 2.2). Although primordial Tc is considered to have completely decayed on Earth (Hidaka *et al.* 1993), ^{99}Tc has been found naturally in minute quantities in pitchblende, a uranium rich ore, at concentrations of between 0.25 – 0.31 parts per trillion (Kenna and Kuroda 1964). This is the result of the spontaneous fission of ^{235}U. The action of cosmic rays on Mo, Nb, Ru, and Zr may also produce naturally occurring ^{99}Tc (Attrep *et al.* 1971). No other isotopes of technetium exist naturally.

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \xrightarrow{\text{Fission yield 6\%}} {}^{99}_{42}\mathrm{Mo} \xrightarrow{t_{1/2}\ 67\ \text{hrs}} {}^{99m}_{43}\mathrm{Tc} + \beta \qquad [2.1]$$

$$^{98}_{42}\mathrm{Mo} + \mathrm{d,n} \longrightarrow {}^{99}_{43}\mathrm{Tc} \qquad [2.2]$$

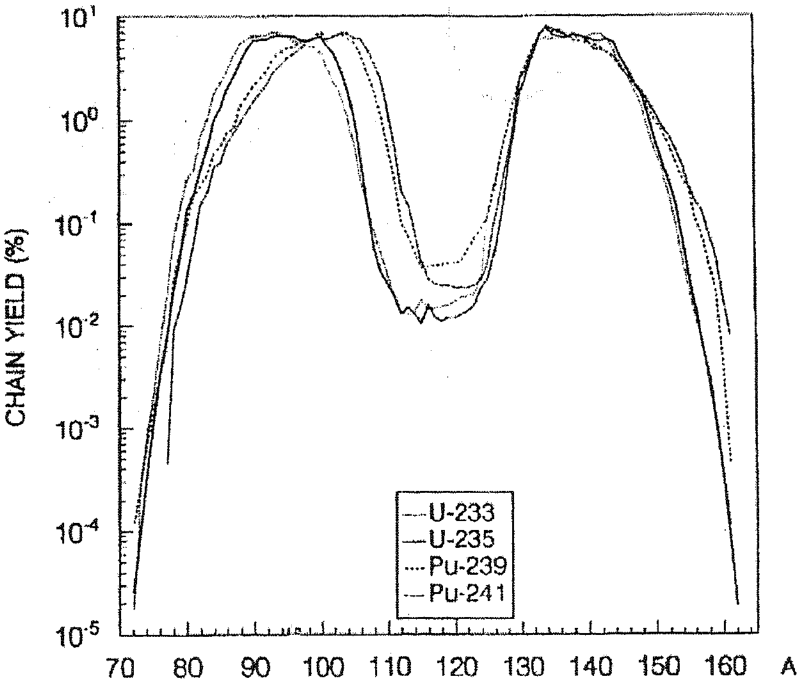

Figure 2.2.1. Yield of fission products according to mass (Choppin *et al.* 1996).

Technetium is a transition metal falling in Group 7B of the periodic table, with a ground state electron configuration of $[Kr]4d^5 5s^2$. The closest chemical analogues of technetium are manganese and rhenium, and to a lesser degree the neighbouring elements molybdenum and ruthenium. Rhenium has the most similar properties but is distinctly different with respect to redox behaviour and substitution lability of the lower oxidation states (Deutsch *et al.* 1986).

2.2.1. Nuclear properties of Technetium Isotopes

Technetium has an atomic number of 43, an atomic mass ranging from 87-111, and is the lightest element without any stable isotopes (Browne and Firestone 1986).

There are 21 known isotopes of technetium (^{90}Tc to ^{110}Tc) and 7 nuclear isomers (^{93m}Tc, ^{94m}Tc, ^{95m}Tc, ^{96m}Tc, ^{97m}Tc, ^{99m}Tc and ^{102m}Tc). All isotopes are radioactive, most having relatively short half lives ranging from 0.82 seconds (^{110}Tc) to 61.2 days (^{97m}Tc), with the exception of three long lived isotopes: ^{97}Tc ($t_{½}$ = 2.6 x10^6 years), ^{98}Tc ($t_{½}$ = 4.2 x10^6 years), and ^{99}Tc ($t_{½}$ 2.14 x 10^5 years) (Browne and Firestone 1986).

2.2.2. Oxidation States of Technetium

Technetium has oxidation states ranging from –I to VII, and a wide variety of co-ordination chemistry related to each of these states. Pertechnetate $[Tc^{VII}O_4]^-$ is among the most environmentally important species formed by this element. Unlike MoO_4^-, pertechnetate has little tendency to form isopolyanions (Davidson and Jones 1982). Pertechnetate is a much weaker oxidizing agent than permanganate, and is reduced by HCl (Davidson and Jones 1982). The VI oxidation state of Tc is dominated by the $[Tc^{VI}N]^{3+}$, $[Tc^{VI}N(O)TC^{VI}N]^{4+}$, and $[Tc^{VI}N(\mu\text{-}O)_2Tc^{VI}N]^{2+}$ cores, which contain the Tc≡N bond (Baldas 1996). The electronic structure of the $Tc^VO_2^+$ core renders this kinetically inert in ligand substitution reactions (Omori 1996). A variety of monomeric Tc^{IV} and dimeric (bis) μ-oxo $Tc^{III}Tc^{IV}$ and $Tc^{IV}Tc^{IV}$ species have been reported (Schwochau and Pleger 1993, Baldas 1994). Tc^{IV} (d^3) complexes are generally considered to be chemically inert (Baldas 1996). A considerable number of binuclear Tc^{II} and Tc^{III} compounds containing Tc_2^{4+}, Tc_2^{5+}, and Tc_2^{6+} cores as well as monomeric Tc^{II} and Tc^{III} species have also been characterized (Schwochau and Pleger 1993, Baldas 1994). A considerable variety of stable, mostly six coordinate, Tc^I complexes have also been prepared in aqueous media (Holman *et al.* 1987). Tc^0 has also been characterized as the $Tc^0_2(CO)_{10}$ dimer (Bailey and Dahl 1965). Tc^{-1} is only known to exist in the $Tc^{-1}(CO)_5^-$ form and is the rarest oxidation state of Tc (Hileman *et al.* 1962).

2.2.3. Aqueous Chemistry

The Eh-pH diagram of Tc in aqueous solutions, calculated from thermodynamic data, indicates areas in which the various oxidation states of Tc are expected to predominate (Figure 2.2.2.) (Torstenfeld 1981). Since TcO_2 remains insoluble in most aqueous conditions found in the natural environment, TcO_2 formation will be an important factor in the accumulation of Tc and any further diagenetic movement.

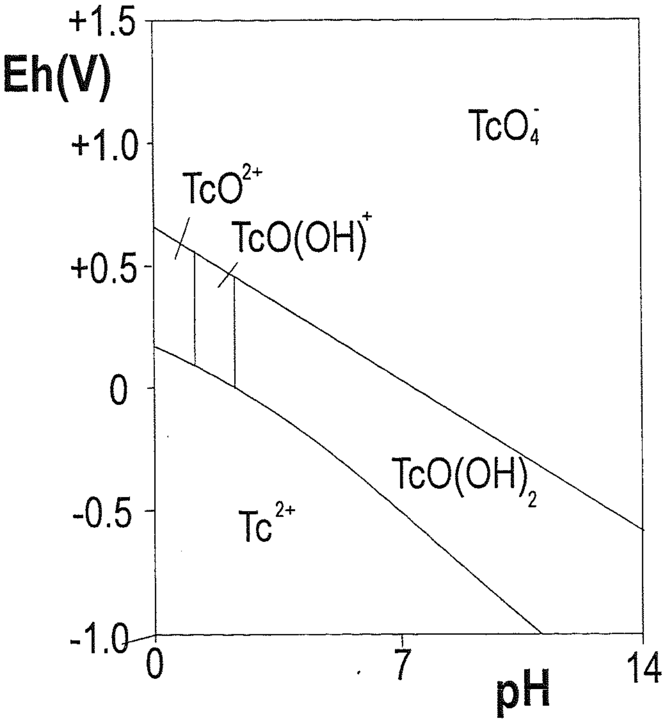

Figure 2.2.2. Eh-pH diagram of Tc in the absence of complexing agents, determined using thermodynamic data compiled by Torstenfeld 1981.

In aqueous solutions, TcO_4^- is stable under oxidizing conditions, whereas reduction to Tc (IV) occurs under reducing conditions, forming TcO^{2+}, TcO(OH) or $Tc(OH)_4$, depending on the pH (Figure 2.2.2). The oxidation states +5 and +4 can be stabilized by complex formation, and have a high affinity for sulphur donor ligands (Torstenfeld 1981). Complexes containing Tc in the 3+ oxidation state are also known but are easily oxidisable in aerobic conditions (Gmelin 1983). The aqueous chemistry and immobilization of Tc particularly as TcO_2 is important in considering Tc association with particulate matter and incorporation of Tc into sediments.

2.2.3.1. Dissolution of Tc with equilibrium as the limiting factor

TcO_2 (aq) is the Tc^{IV} species in equilibrium with solid TcO_2 (s) *e.g.* $TcO(OH)_2$ or $Tc(OH)_4$. If no oxidation takes place , the concentration of Tc in solution / aqueous phase will be determined by the solubility of TcO_2 under the given conditions. This solubility is expected to be very small and of similar magnitude to the solubility of other metal dioxides like MnO_2, ReO_2, ZrO_2, ThO_2, UO_2,

NpO_2, MoO_2, and others (Lieser *et al.* 1993). For the solubility products (K_s) of $TcO_2.H_2O$ and $TcO(OH)_2$, the following values have been estimated: log K_s = -31 (Allard *et al.* 1979), log K_s = -33 (Rard 1983) for $TcO_2.H_2O$ and log K_s=-24.2 (Srivastava *et al.* 1977) for $TcO(OH)_2$. Tc^{IV} is easily oxidized in neutral aerobic conditions (Figure 2.2.2). Therefore, in the presence of air, dissolution of TcO_2 (s) according to the solubility equilibrium [2.3] will be followed by oxidation of the dissolved Tc^{IV} to Tc^{VII}.

$$TcO_2\ (s) \overset{H_2O}{\rightleftharpoons} TcO_2\ (aq) \qquad [2.3]$$

$$TcO_2\,(aq) + O_2 \rightleftharpoons TcO_4^- \qquad [2.4]$$

This oxidation may take place via Tc^V and Tc^{VI}. In the absence of strongly complexing agents for Tc^V, TcO_4^- is the only stable oxidation state of Tc in the presence of oxygen. Tc^V as well as Tc^{IV} disproportionate quickly into Tc^{VI} and Tc^{VII} (Rard 1983). If the solubility equilibrium according to equation [2.3] is established, the rate of formation of TcO_4^- according to equation [2.4] will be the rate-determining step of dissolution. It will not depend on the mass or the specific surface area of TcO_2 (s), but only on the equilibrium concentration of TcO_2 (aq) and the concentration of oxygen in solution. Although the equilibrium value is independent of the surface area, the rate of dissolution (*i.e.* the time taken to reach equilibrium) is dependent on the surface area of the TcO_2 (s).

2.2.3.2. Dissolution of Tc with oxidation as the limiting factor

$$TcO_2\ (s) \overset{O_2}{\rightleftharpoons} (Tc^V,\ Tc^{VI},\ Tc^{VII}) \overset{H_2O}{\rightleftharpoons} TcO_4^- \qquad [2.5]$$

In this case the solubility equilibrium of TcO_2 (s) is not established. Oxidation may proceed via the oxidation states +5, +6, to +7. However the final oxidation product, in the absence of complexing agents is TcO_4^- (Lieser 1993). The rate of dissolution will be proportional to the rate of oxidation and that will depend on the specific surface area and on the chemical properties of the surface. The rate of dissolution may also be expected to be proportional to the concentration of oxygen in the solution. Laboratory based experiments showed that in solutions of low salinity the oxidation of TcO_2 by molecular oxygen is the rate limiting step of dissolution and that the dissolution rate is proportional to the concentration of oxygen (Figure 2.2.3) (Lieser *et al.* 1987).

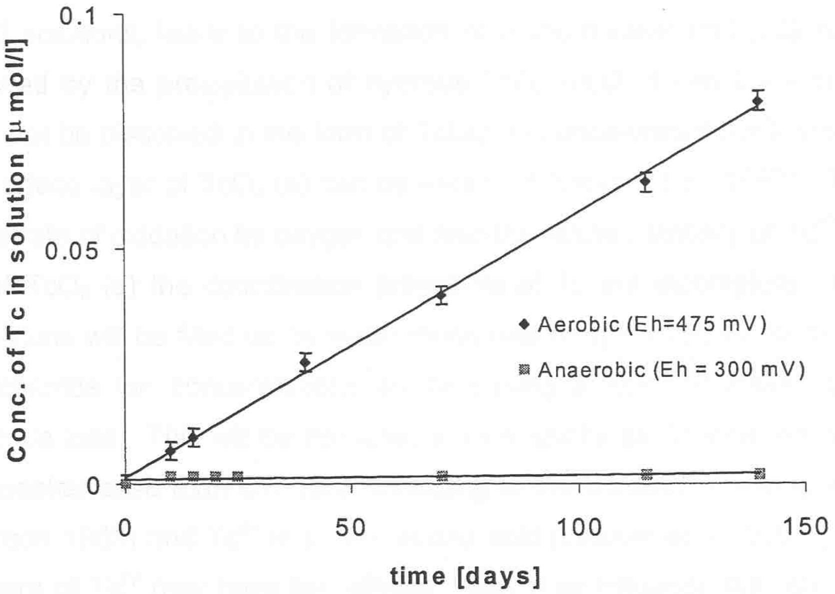

Figure 2.2.3. Dissolution of TcO_2 under anaerobic and aerobic conditions. >99% of dissolved Tc was found as TcO_4^- (Lieser *et al.* 1987).

2.2.3.3. Dissolution of TcO_2 in NaCl solutions

At high concentrations of halide ions Tc^{IV} forms complexes of the type TcX_6^{2-} (X= halide) (Gmelins 1982, Rard 1983). The solubility of various salts of $TcCl_6^{2-}$ and of $TcBr_6^{2-}$ in HCl and HBr solutions vary in the range between 10^{-4} to 10^{-2} mol/l (Vinogradov *et al.* 1974). Tc^{IV} and Tc^{V} are stabilized by the formation of these halide complexes. As a consequence of the relatively high stability of the chloro complexes pertechnetate is reduced by concentrated HCl solutions to give $TcOCl_5^{2-}$ as an intermediate and $TcCl_6^{2-}$ as a final product (Cotton *et al.* 1979). Two oxy-halides of Tc^V, $TcOCl_5^{2-}$ and $TcOCl_4^-$have been isolated as solid compounds as their reduction to $TcCl_6^{2-}$ is relatively slow (Cotton *et al.* 1979).

If the salinity is decreased and the acidity maintained then substitution of the chloride ions by water molecules occurs, equations [2.6], [2.7] (Koyama *et al.* 1968).

$$TcCl_6^{2-} + H_2O \longrightarrow Tc(H_2O)Cl_5^- + Cl^- \quad [2.6]$$

$$Tc(H_2O)Cl_5^- + H_2O \longrightarrow Tc(H_2O)_2Cl_4 + Cl^- \quad [2.7]$$

$TcCl_6^{2-}$ is stable in the dark and substitution only proceeds when stimulated by light (visible or UV). If the chloride ion concentration is maintained and the acidity is decreased then hydrolysis occurs, equation [2.8] (Koyama *et al.* 1968).

$$Tc(H_2O)Cl_5^- \longrightarrow Tc(OH)Cl_5^- + H^+ \quad [2.8]$$

Simultaneous decrease of chloride ion concentration and of acidity, *e.g.* by dilution of concentrated HCl solutions, leads to the formation of mono-nuclear and poly-nuclear hydroxo complexes, followed by the precipitation of hydrous $TcO_2.2H_2O$. It can therefore be assumed that TcO_2 (s) will not be dissolved in the form of $TcCl_6^{2-}$ in concentrated NaCl solutions and that changes in the surface layer of TcO_2 (s) can be expected (Lieser *et al.* 1987). These changes may influence the rate of oxidation by oxygen and also the relative stability of Tc^{VII} and Tc^{IV}.

At the surface of TcO_2 (s) the coordination polyhedra of Tc are incomplete. In contact with water, ligand positions will be filled up by water molecules or by hydroxyl groups, depending on pH. At higher chloride ion concentrations an increasing amount of these positions will be occupied by chloride ions. This will be favoured at high acidity as Cl^- ions are a stronger base than H_2O but a weaker base than OH^- ions according to the concept of strong and weak acids and bases (Pearson 1963) and Tc^{4+} is a very strong acid (Liesser *et al.* 1987). Cl^- ions in the coordination sphere of Tc^{IV} may have two effects: they may influence the rate of oxidation by molecular oxygen and if present in high ratios of Cl^- : Tc^{IV} at the surface they may stabilize Tc in the +4 oxidation state.

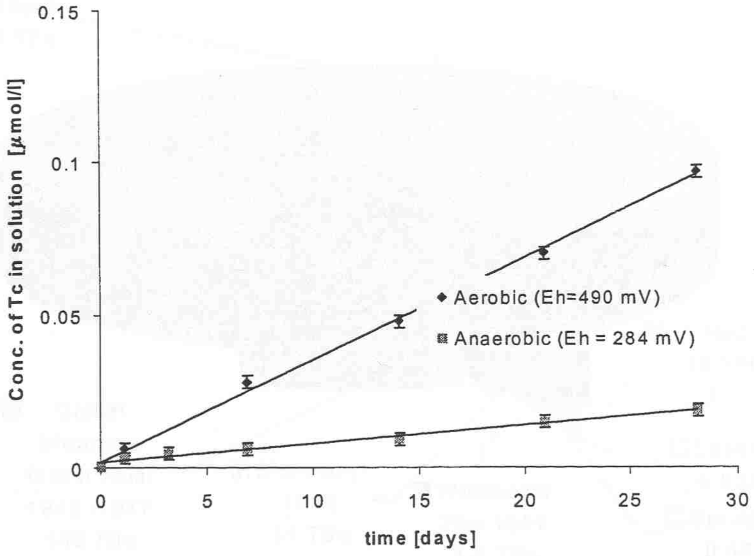

Figure 2.2.4. Dissolution of TcO_2 under aerobic and anaerobic conditions in saturated NaCl solution (Liesser *et al.* 1987)

Therefore under anaerobic conditions an appreciable dissolution rate is observed from high salinity solutions, due to the influence of radiolytic effects in NaCl solutions (Figure 2.4) (Lieser *et al.* 1987). Whilst radiolysis may be important when explaining laboratory based experiments using substantial activities, radiolysis is less likely to be such an important consideration in comparison with other factors affecting environmental behaviour.

2.3. Sources and discharge of ^{99}Tc into the environment

Waters around the British Isles have a number of possible sources of contamination of ^{99}Tc. These are from the reprocessing of spent nuclear fuel, which contributes by far the greatest input of ^{99}Tc to the environment (Figure 2.3.1). The two principal points of discharge in waters around the UK are Sellafield (formerly Windscale) which has been discharging into the Irish Sea since 1952 and La Hague in north west France which has been discharging into the English Channel since 1966 (GueguenIat *et al.* 1993). Sellafield has been dominant both in the quantities of waste discharged and in the impacts of its releases (Kershaw and Baxter 1995). Other less significant inputs have come from the isotope separation plant at Springfields and from nuclear accidents (Chernobyl and the Windscale fire) as well as from weapons' testing. Trivial amounts of ^{99}Tc have been introduced to the environment from the medical use of ^{99m}Tc (Luykx 1986) as well as natural ^{99}Tc which is formed by the spontaneous fission of ^{235}U in uranium ores.

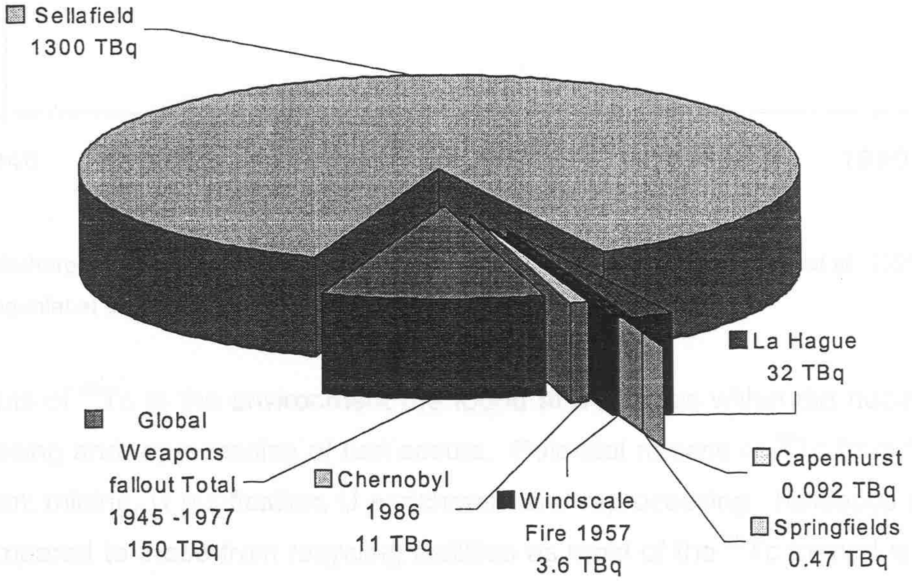

Figure 2.3.1. Sources of ^{99}Tc into the UK environment (Crick and Linsley 1984, INSAG 1986, BNFL Reports 1983-1998, Gray *et al.* 1995, Guegeniat *et al.* 1993, UNSCEAR 1977). The total discharge represented by the pie is 1500 TBq.

2.3.1. Technetium discharges from the nuclear fuel cycle

The main sources of ^{99}Tc are nuclear reactors. A modern nuclear reactor contains about 100 tons of U with an initial ^{235}U enrichment of about 3% (Lieser 1993). After 2 to 3 years the fuel elements are exchanged for fresh ones although approximately 93% of spent fuel is still U (Lieser *et al.* 1987). This corresponds to a production of about 40kg of ^{99}Tc per reactor per year (Lieser *et al.* 1987).

There are four sources of ^{99}Tc discharged to waters around the UK (Figure 2.3.2). Discharges of ^{99}Tc from La Hague declined rapidly in the early 1990s to levels similar to those of BNFL Springfields. The discharges from BNFL Springfields and BNFL Capenhurst are several orders of magnitude smaller than those from Sellafield.

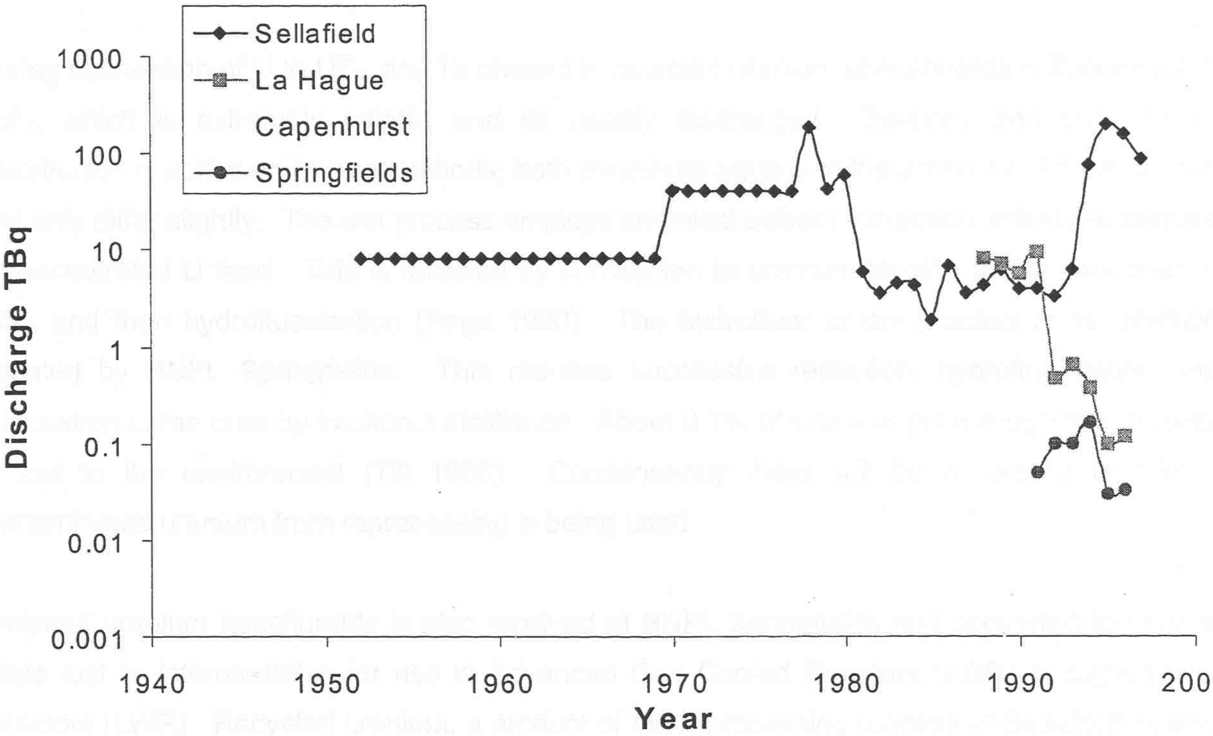

Figure 2.3.2. Discharge profile from ^{99}Tc discharging plants around the British Isles (Gray *et al.* 1995, BNFL reports 1983-1997, Guegeniat *et al.* 1997)

Potential inputs of ^{99}Tc to the environment are found at all stages within the nuclear fuel cycle where processing and reprocessing of fuel occurs. Potential release of ^{99}Tc from the fuel cycle may arise from: mining, U purification, U enrichment and reprocessing. Releases from reactors are small compared to those from recycling facilities as most of the ^{99}Tc formed is contained in the fuel. Discharge of ^{99}Tc from nuclear power stations during normal operation is of the order of 1 MBq/year per power station. 25% of this is thought to be released directly to the atmosphere although this is dependent on power production and reactor type (Holm 1993).

2.3.1.1. Mining and milling

There are currently no mining operations for uranium minerals in the UK. As Tc exists in uranium ores in trace amounts, it is assumed that release of ^{99}Tc to the environment will be negligible worldwide.

2.3.1.2. Discharge from U purification

BNFL Springfields, situated near Preston in Lancashire, produces fuel and immediate fuel products for the UK nuclear industry. Uranium ore concentrates are received on site and are processed to either uranium metal for use in Magnox reactors or as uranium hexafluoride, which is then sent for enrichment at BNFL Capenhurst. ^{99}Tc may be present in recycled U supplied for fluorination as Tc can be extracted along with U during the Purex process (Till 1986).

During fluorination of U to UF_6, any Tc present in recycled uranium concentrates is fluorinated to TcF_6, which is extremely volatile and so readily discharged (Beasley and Lorz 1986). Fluorination is achieved by two methods; both contribute equally to the amount of UF_6 produced and only differ slightly. The wet process employs chemical solvent extraction, initially to prepare a concentrated U feed. This is followed by conversion to uranium trioxide (UO_3), reduction to UO_2, and then hydrofluorination (Page 1980). The hydrofluor or dry process is the method adopted by BNFL Springfields. This requires successive reduction, hydrofluorination and fluorination of the ores by fractional distillation. About 0.1% of uranium put through this process is lost to the environment (Till 1986). Consequently there will be a release of ^{99}Tc if contaminated uranium from reprocessing is being used.

Enriched uranium hexafluoride is also received at BNFL Springfields and converted to provide oxide fuel or intermediates for use in Advanced Gas Cooled Reactors (AGR) or Light Water Reactors (LWR). Recycled uranium, a product of the reprocessing process at Sellafield, is also received and processed. This is the main source of ^{99}Tc to the plant and so is responsible for the output to the environment.

Discharges of ^{99}Tc are likely to have occurred since the plant has handled recycled uranium. However routine monitoring of ^{99}Tc discharge has only been performed at BNFL Springfields since 1991 (Figure 2.3.2). Whilst the Irish Sea will be dominated by the discharges from Sellafield, the discharges from BNFL Springfields may have an important impact on the Ribble estuary and the surrounding area. Compared to recent discharges from Sellafield, discharges from Springfiels are small, but are only slightly lower than those of the La Hague reprocessing plant.

2.3.1.3. Discharge from U enrichment.

Two methods have been used for the enrichment of U to fuel grade in the UK. These are enrichment by the gaseous diffusion process or enrichment by gas centrifugation. The gaseous diffusion process works on the principle that the velocities of gas molecules at a given temperature are based on their masses (Till 1986). By passing UF_6 through a series of porous barriers, the flow of lighter isotopes of uranium is faster than heavier isotopes, thus creating a greater concentration of ^{235}U in the final product than in the feed. The maximum theoretical enrichment in a single stage is a factor of 1.0043, therefore approximately 1200 stages are required to produce U enriched to 4% which is necessary to sustain a chain reaction in a reactor. 13.2% of the total U in the source is recycled back into the fuel system (Till 1986). The centrifuge process also relies on the principle that volatile gasses can be separated by mass. Enrichment of uranium to fuel grade in the UK is now carried out by centrifuge, which has replaced the gaseous diffusion process.

U enrichment in the UK is carried out at the BNFL Capenhurst plant, Ellesmere Port. The site consists mainly of centrifuge plants, a redundant gaseous diffusion plant and a small tritium processing facility. BNFL Capenhurst is the principal source for enriched uranium, and the main uranic storage facility for the UK nuclear industry. Residual uranium from the enrichment process is either sent for further enrichment or is discarded as depleted uranium. Again, during the enrichment process it is possible for volatile TcF_6 to be lost to the environment.

Discharges of ^{99}Tc from the Capenhurst site result from the decommissioning of the old gaseous diffusion plant (Figure 2.3.2.) (BNFL 1996). The total amount of ^{99}Tc released by the plant is small and is only likely to affect the areas immediately surrounding the discharge sites and the mouth of the Riverace Brook, where it enters the Mersey.

2.3.1.4. Discharges from Reprocessing

Sellafield on the Cumbrian coast, near Seascale, is the site of BNFL's plant for reprocessing spent nuclear fuel and the conditioning of radioactive wastes for safe long-term disposal. In France the La Hague reprocessing plant is responsible for reprocessing and conditioning of radioactive wastes in France. Reprocessing is carried out in the Thermal Oxide Reprocessing Plant (THORP), which was completed in 1992. Recovery of fuel from spent fuel rods is achieved using a chemical technique known as the Purex process. The fuel is stored for 150 days to allow short-lived isotopes to decay before dissolution in nitric acid. The fuel solution is then processed through a series of solvent extraction stages which consist of extraction of the U and Pu from the nitric acid solution into tri butyl-posphate (TBP) in kerosene (Till 1986). The Purex process produces a purified UO_2 solution which is then returned to the Springfields Plant for re-conversion to UF_6 (Till 1986).

Dissolution of spent nuclear fuel is in general incomplete. A certain amount of small metallic particles containing Mo, Tc, Ru, Rh and Pd is not dissolved and is removed for storage as highly active waste (HAW) (Bramman *et al.* 1969, Jenkins *et al.* 1984, Huber *et al.* 1986). In the first extraction cycle of the Purex process a part of the TcO_4^- is extracted together with U, Equation 2.9.

$$UO_2(NO_3)_2(TBP) + TcO_4^- \rightleftharpoons UO_2(NO_3)(TcO_4)(TBP) + NO_3^- \quad [2.9]$$

As TcO_4^- is bound in the complex more strongly than NO_3^-, appreciable amounts (approximately 30%) of the total Tc accompanies U, even at high concentrations of NO_3^- (Lieser *et al.* 1981). Tc that is not extracted with the U goes with the main part of the other fission products and the actinides into the highly active waste where it is further treated in the Enhanced Actinide Removal Plant (EARP). The remainder of the separation of U and Pu, and their purification, comprise further reduction and extraction processes (Lieser 1987). Depending on the conditions, Tc extracted together with the U may be reduced to Tc^{IV} and go with the Pu stream. If no precautions are taken Tc could then be found in all products and the waste stream. Most of these wastes are classified as Low Active wastes and so may be discharged.

Clean up of the waste stream before effluent discharge is carried out in a number of treatment plants, which include: the Enhanced Actinide Removal Plant (EARP), the Site Ion Exchange Effluent Plant (SIXEP), the Solvent Treatment Plant (STP), and the Waste Packaging and Encapsulation Plant (WPEP).

The SIXEP plant is designed to remove a wide range of alkali earth and rare earth element isotopes by ion exchange extraction onto clinoptilolite, a natural zeolite. Sand filters and a carbonating tower are used to maintain the plant's efficiency. Any Tc present will be as the TcO_4^- oxyanion which will not be extracted by the cation exchange process used to remove alkali earth and rare earth element isotopes.

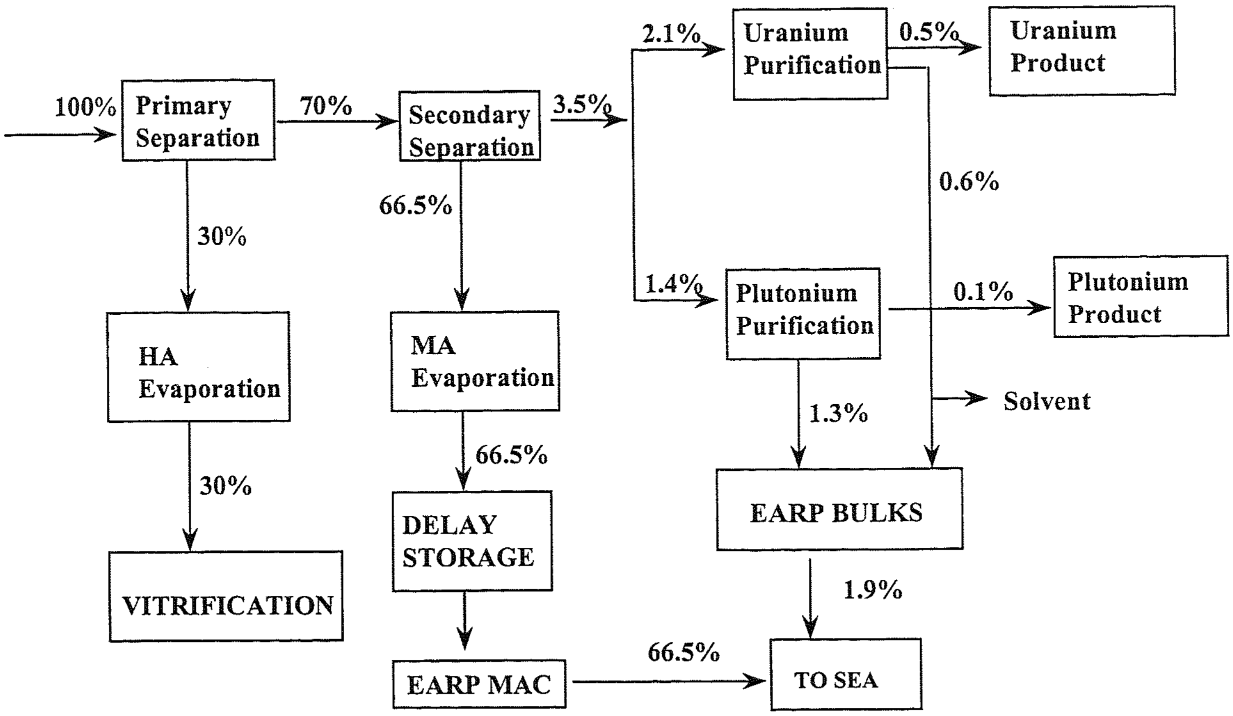

Figure 2.3.3. Distribution pathways of ^{99}Tc during the Purex process (After Edgar. Pers comm.)

The EARP plant is designed to remove alpha emitting radionuclides and reduce beta emitting radionuclides from current reprocessing effluents and a stockpile of historical wastes. The wastes consist of: 1) Low volume medium active concentrate (MAC) streams arising from current production, 2) Low volume historical MAC streams stored in tanks on site and 3) High volume low active bulk effluent streams. The EARP plant neutralises the iron rich acid wastes originating from the Purex process with NaOH to produce an iron hydroxide floc. The precipitation process removes actinides and most transition elements from solution. Again Tc will be present as TcO_4^- as the effluent is a nitric acid solution. Tc will therefore not be co-precipitated with the iron hydroxide. Consequently 66% of the total ^{99}Tc inventory is discharged to sea. Of the remaining 35%, 5% is included in the U and Pu products and the remaining 30% goes to vitrification (Figure 2.3.3.). A proportion of the ^{99}Tc included in the U product is also discharged during fluorination of the recycled U at Springfields.

Sellafield discharges of ^{99}Tc have been significant since the plant's commissioning in the late 1950s (Figures 2.3.1, 2.3.3, 2.3.4) and were of similar activities to those of ^{241}Am in the 1970s. An annual discharge of 40TBq / year of ^{99}Tc from Sellafield in the 1970s and early 1980s was estimated from concentrations of ^{99}Tc in *fucoid* seaweeds on the Norwegian Coast (Aarkrog *et al.* 1983). There has been a significant increase in the amount of ^{99}Tc released to the environment since the commissioning of EARP and the processing of previously stockpiled Medium Active Concentrate (MAC) wastes as EARP is currently unable to remove Tc from the effluent (Figure 2.3.4).

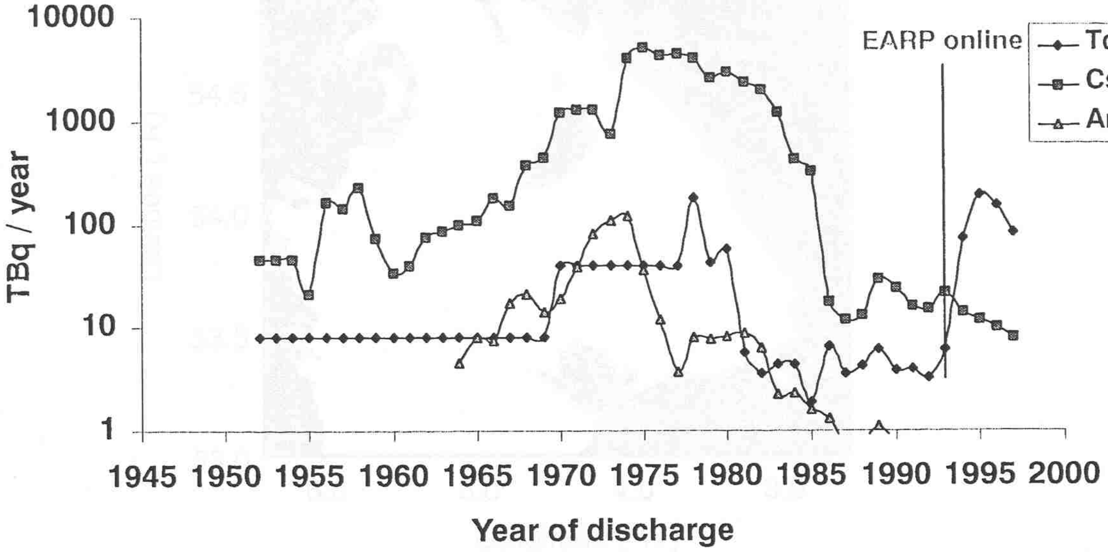

Figure 2.3.4. The annual mean discharge of ^{99}Tc ^{137}Cs and ^{241}Am from Sellafield

The La Hague reprocessing plant is also an important source of ^{99}Tc to the UK environment (Figure 2.3.1). Discharges from the La Hague plant travel eastwards to the North Sea to join those of Sellafield (Figure 2.3.6) (Dahlgaard *et al.* 1993, Masson *et al.* 1995). Discharges of ^{99}Tc have been reduced recently (Figure 2.3.2) despite the fact that the La Hague plant also uses the Purex process for reprocessing spent fuel.

2.3.1.5 Dispersion of discharged ^{99}Tc to the environment

Discharges of ^{99}Tc from Sellafield to the Irish Sea have been approximately two orders of magnitude higher than the global accumulated fallout and as the point of input is certain. ^{99}Tc is a useful marine tracer as there is a characterized point source discharge and TcO_4^- is conservative in behaviour. Consequently pulses of ^{99}Tc activity created following sudden changes in ^{99}Tc discharge from both Sellafield and La Hague have been used as such a tracer (Aarkrog *et al.* 1983; Dahlgaard *et al.* 1993; Leonard *et al.* 1997). It was found that the water containing elevated activities of ^{99}Tc moved parallel to the Cumbrian coast (Figure 2.3.5.). The elevated ^{99}Tc activities had reached the North Channel in less than three months and had reached the northern North Sea within nine months of the initial elevated discharge (Leonard *et al.* 1997).

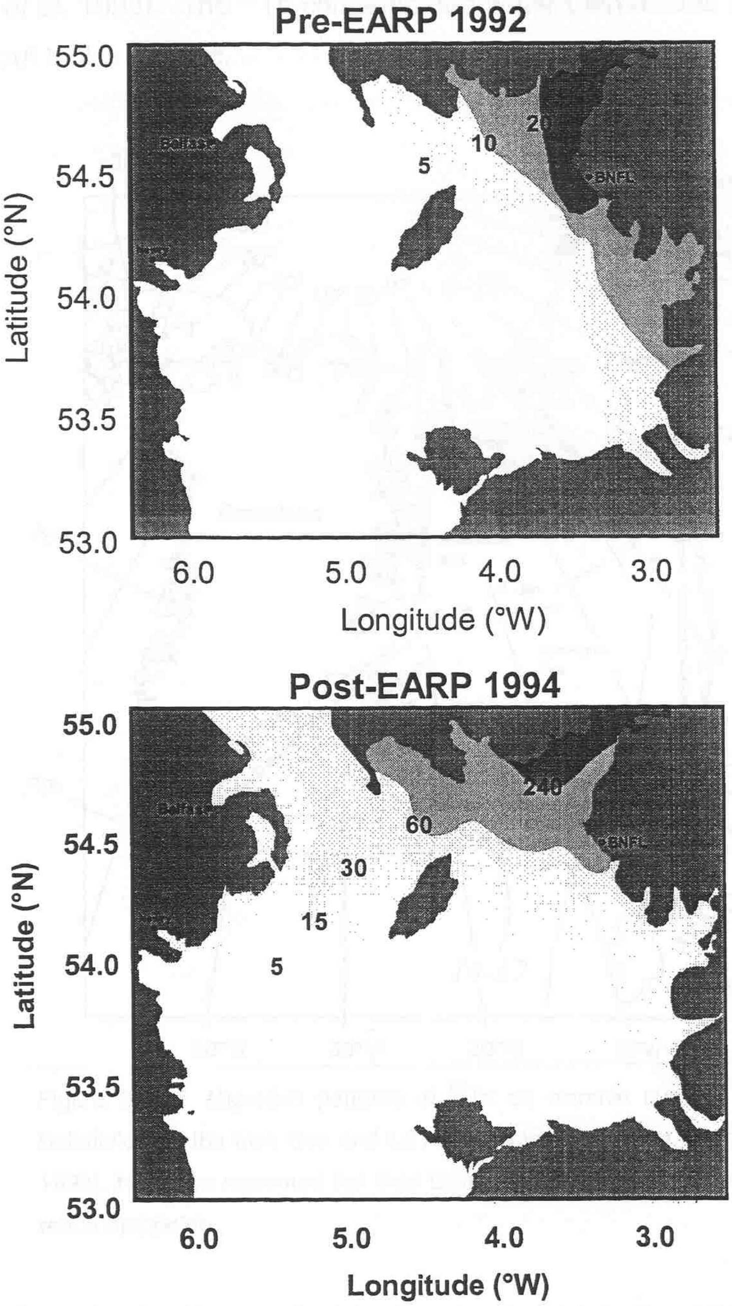

Figure 2.3.5. Contour maps of ^{99}Tc activity (mBq/l) distribution in the North Irish Sea (Leonard *et al.* 1997)

Pre-EARP levels of ^{99}Tc are essentially uniform at concentrations between 1 - 4 mBq / litre for most of the Irish Sea (Leonard *et al.* 1997). This is due to the relatively constant discharges during the preceding months and can be described as 'the residual concentration of a well-mixed system' (Leonard *et al.* 1997). Post-EARP concentrations of ^{99}Tc along the coast of Cumbria and the Solway Firth are an order of magnitude higher than measured in the remainder of the Irish Sea, and are most likely to be the result of transient heterogeneity before full mixing is achieved. After leaving the North Sea, water containing elevated levels of ^{99}Tc flows into the

North Sea and up along the Norwegian coast to the Arctic (Figure 2.3.6), (Aarkrog *et al.* 1983, Dahlgaard *et al.* 1993). The ^{99}Tc-contaminated water then moves along the Eastern Greenland coast and out to the Atlantic.

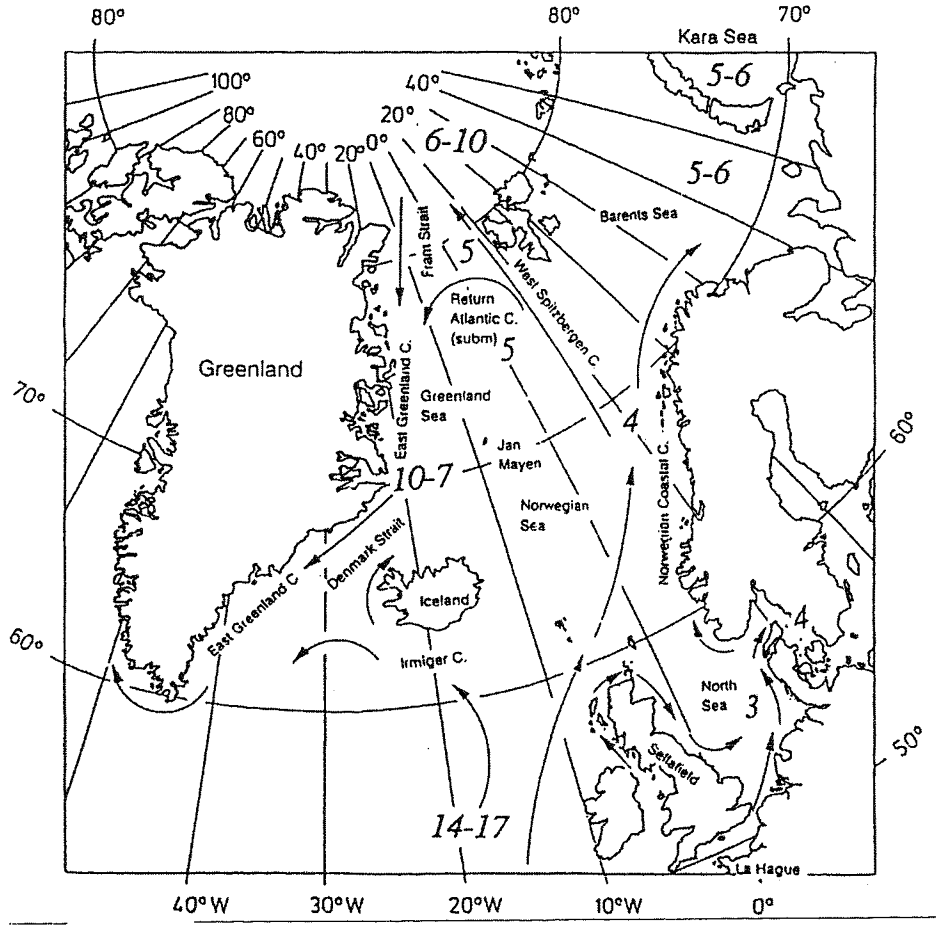

Figure 2.3.6. Migration patterns of ^{99}Tc on oceanic currents after discharge from Sellafield into the Irish Sea and La Hague into the English Channel (Dahlgaard *et al.* 1993). Numbers represent the time taken in years for the ^{99}Tc contaminated water to reach that point.

Discharge from the La Hague plant is dispersed out into the Atlantic and also up the English Channel into the North Sea. Approximately 2% of the discharge reaches as far as the Cattegat (Masson *et al.* 1995, Holm *et al.* 1986) (Figure 2.3.6).

Weapons' Fallout

The contribution of ^{99}Tc from weapons' fallout to the global inventory is quite considerable (Figure 2.3.1) as weapons undergoing fission have a yield of 6% ^{99}Tc. Most testing has, however, been carried out underground (Table 2.3.2), particularly after the signing of the Partial Test Ban Treaty on 8 August 1963. Fission products released underground are thought to be vitrified into the surrounding rock and so immobilized and will therefore make little contribution to the environmental inventory of ^{99}Tc (Kennish 1997).

Table 2.3.2. Estimated total number of nuclear explosions 16 July 1945 to 31 December 1998 (after Ferm 1993).

Country	Atmospheric	Underground	Total
U.S.	217	725	942
U.S.S.R.	165	465	630
U.K.	21	23	44
France	48	141	189
China	23	15	38
India	0	4	4
Pakistan	0	3	3

Atmospheric weapons' testing in the 1950s and early 1960s produced the most fallout in the mid-latitudes of the Northern Hemisphere, with ^{99}Tc concentrations decreasing substantially towards the equator and the North Pole (Livingston 1995). Radionuclide input to the Arctic Ocean has been restricted, but a larger input has been made to the North Atlantic and Northern Pacific Oceans, resulting in a semi-heterogeneous global dispersion of ^{99}Tc. Concentrations of ^{99}Tc in the air have decreased since the signing of the Partial Test Ban Treaty in 1963 when atmospheric testing was curtailed (Figure 2.3.7) (Ferm 1993). Minor inputs of ^{99}Tc to the atmosphere continued due to atmospheric testing by nations which did not sign up to the Partial Test Ban Treaty, these tests have now finished. The decline in ^{99}Tc activities is thought to be due to the continuing transfer of ^{99}Tc-contaminated particles from air to ground (Thomas 1978). Concentrations of ^{99}Tc in rainwater have decreased progressively from a high of 0.06 mBq/l in 1962, the most intense period of weapons' testing. This relatively long time period has meant that there has been significant mixing and therefore dilution of ^{99}Tc worldwide.

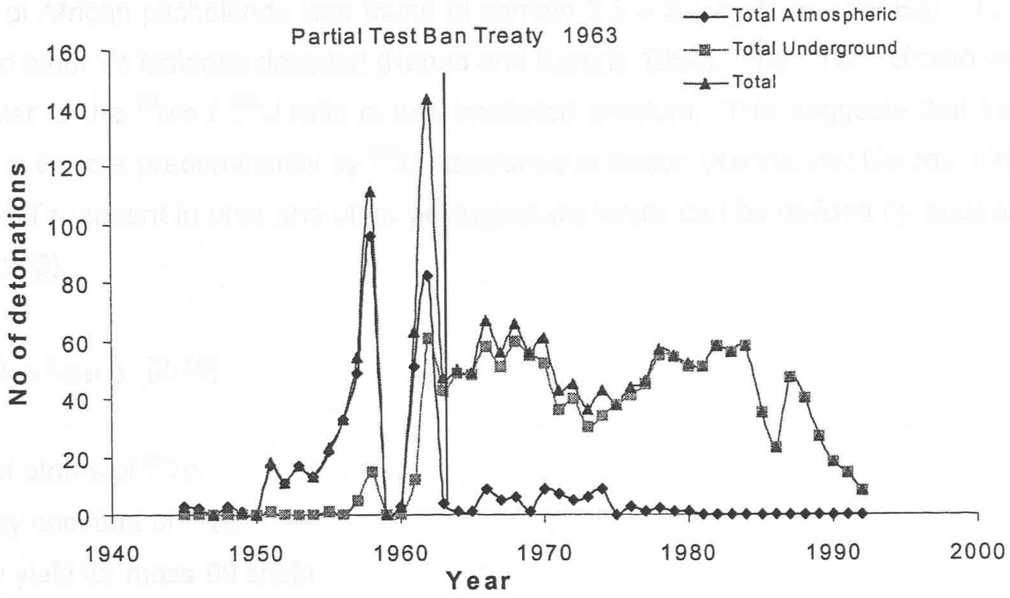

Figure 2.3.7. Detonations of atomic weapons by nuclear powers (Ferm 1993).

2.3.2. Chernobyl

Radionuclide emissions from the Chernobyl fire in 1986 were high (Figure 2.3.1) and declined considerably with increasing distance from the source.

Table 2.3.3. ^{99}Tc/^{137}Cs ratios in seawater from major environmental inputs.

Input	^{99}Tc/^{137}Cs ratio	Reference
Weapons fallout	2×10^{-4}	Holm *et al.* 1986, Aarkrog *et al.* 1987
Chernobyl	1.01×10^{-5}	Aarkrog *et al.* 1988
Fuel Reprocessing Discharge	*1.9×10^{-2}	Dahlgaard *et al.* 1993

* Data are based on ratios in 1988 after decay correction.

Measurement of the ^{99}Tc/^{137}Cs ratio allows an identification of the source of the ^{99}Tc in the environment. ^{99}Tc concentrations from fallout prior to the Chernobyl incident were comparatively much lower than that of ^{137}Cs. Part of the radioactive releases from the Chernobyl accident reached the stratosphere and have been measured worldwide after the incident (Jaworowski and Kowonaka 1988, Aoyama 1988, Whitehead *et al.* 1988, Higuchi *et al.* 1988). Up to 40% of the ^{99}Tc fallout over Japan in 1987 originated from Chernobyl, with the remaining 60% from global weapons' testing (Aoyama *et al.* 1991). As for the ^{99}Tc input from weapons' testing the discharge from Chernobyl has been dispersed over Northern Europe and is small in comparison to the discharge of ^{99}Tc from reprocessing close to the point of discharge.

2.3.4. Naturally occurring technetium

A sample of African pitchblende was found to contain 2.5 – 3.1 ng (1.5 – 1.9 Bq) ^{99}Tc per g of ore with no other Tc isotopes detected (Kenna and Kuroda 1964). The ^{99}Tc/^{238}U ratio was found to be similar to the ^{99}Mo / ^{238}U ratio in non irradiated uranium. This suggests that the ^{99}Tc is produced in the ore predominantly by ^{238}U spontaneous fission (Kenna and Kuroda 1964). The activity of ^{99}Tc present in ores and other geological materials can be defined by equation [2.10] (Kuroda 1993).

$$N_{99}\lambda_{99} = N_{238}\,\lambda_{238f}\; y \quad [2.10]$$

N_{99} = no of atoms of ^{99}Tc.
λ_{99} = decay constant of ^{99}Tc
y = fission yield for mass 99 chain
N_{238} = no of atoms of ^{238}U
λ_{238f} = spontaneous decay fission constant of ^{238}U (8.04 x10^{15} years)

The behavior of ^{99}Tc in the Oklo 'natural reactors' in the Republic of Gabon, Africa has been inferred from the study of fissionogenic ^{99}Ru (Hidaka *et al.* 1993). Both Tc and Ru form water soluble oxidizing compounds such as RuO_4 and Tc_2O_7 under oxidizing conditions, which migrate more easily than other compounds. However, the free oxygen tends to be limited in U ores as these tend to accumulate under reducing conditions. A depth profile of ^{99}Ru suggested that ^{99}Tc was enriched near to the boundary layer of the reactor core, but had traveled further than the corresponding ^{99}Ru. Naturally occurring ^{99}Tc has been determined in routine geological standards (Canadian reference Mtl. BL-5. Uranium Ore) and was found to contain 0.6 pg / g (3.8 x 10^{-4} Bq) of ^{99}Tc (Dixon *et al.* 1998), however, no study into its geochemical behaviour was made. The total activity of ^{99}Tc contained in 'natural reactors' and in standard geological materials is minute, and as the highest concentrations are stabilized in reducing conditions the input of ^{99}Tc from these sources to the environment will be negligible.

2.3.6 Technetium used in Medicine

Technetium-99m, a metastable isomer of ^{99}Tc, is used for imaging a variety of organs including the brain, kidneys, lungs, thyroid, spleen and gastrointestinal tract. It is obtained from a generator source containing ^{99}Mo in activities up to 20 GBq (Amersham 1976). Given that ^{99m}Tc has a specific activity of 1.5x10^{17} Bq/g (Browne and Firestone 1986) its decay is rapid and will only generate 38 Bq of ^{99}Tc daughter for every 20 GBq ^{99m}Tc source. On the basis of relative half lives, the resulting ^{99}Tc in the environment will be negligible (Luykx 1986).

2.4. Environmental Implications

2.4.1. Geochemistry

The increased input of ^{99}Tc into the marine environment has generated some concern about the potential accumulation of ^{99}Tc in the food chain. Although significant amounts of laboratory based experimental work have been carried out on the nature of ^{99}Tc – sediment interactions, little study has been made of ^{99}Tc in samples collected from different sedimentary environments.

2.4.1.1. Chemical Forms

The principal form of Tc entering the environment from fuel processing plants is as TcO_4^- (Till *et al.* 1979), with indirect evidence from the Irish Sea supporting this (Pentreath *et al.* 1980).

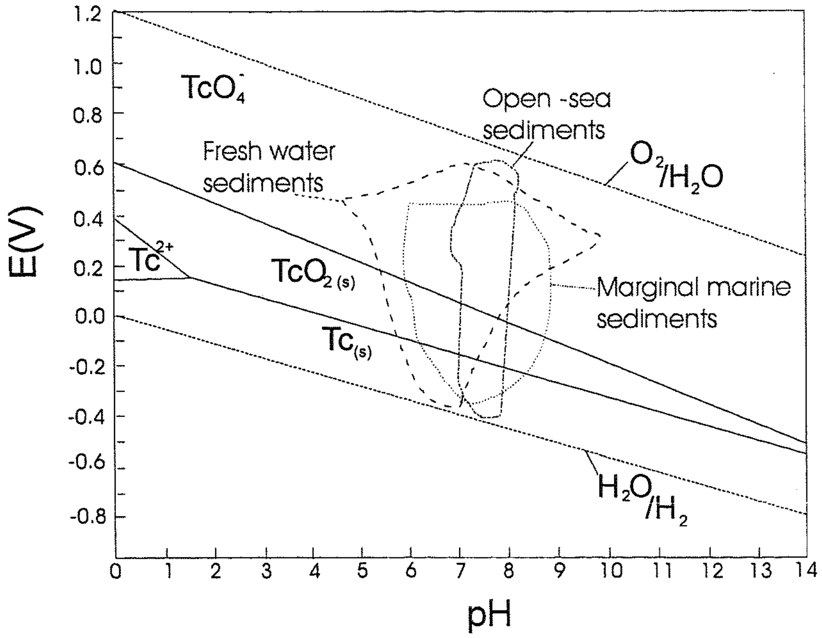

Figure 2.4.1. Stability diagram of the various chemical forms of Tc under different environmental conditions of E_h and pH. For well oxgenated seawater, E_h = 0.4 V and pH = 8, after Beasley and Lorz (1986). Eh – pH fields for sedimentary environments after Bass Becking *et al.* (1960).

The calculated stability relationships expected for the various chemical forms of Tc at different environmental values of E_h and pH are shown (Figure 2.4.1). In oxygenated seawater where E_h and pH are assigned values of 0.40 V and 8.0 respectively (Bass Becking *et al.* 1960), the most stable form of Tc would be as pertechnetate, the negatively charge anion. As E_h decreases, reduced species can be formed which could include TcO_2 (s). It is also possible that in seawater intermediate species such as $TcO(OH)_2$ and $TcCl_6^{2-}$ would be present (Anders 1960). However, stability diagrams are derived purely from thermodynamic data and so provide no information on the rates of transformation between species on the effect of complexation.

Tc transfer in marine and terrestrial environments has been investigated in laboratory experiments and data imply that Tc remains as TcO_4^- as long as the seawater remains oxygenated (Masson *et al.* 1989). Various agents may reduce Tc to Tc^{IV}, but when transferred to seawater 90% of Tc^{IV} returns to Tc^{VII} after a few hours. Similar results are obtained when pertechnetate is reduced with hydrazine sulphate (Fowler *et al.* 1981). Approximately 10% of the reduced species can remain in lower oxygenation states for appreciable periods of time (longer than 14 days).

Technetium as TcO_2 complexes readily with humic acids to form a Tc-HA compound that is precipitated readily in a reducing acid environment (Sekine *et al.* 1993). This precipitate could be dissolved again by raising the pH. However, it could not be re-dissolved as the Tc-HA complex, but as pertechnetate. Further stiochiometric analysis of the Tc-HA formation yield against the amount of reductant added suggested a valence state of Tc^{III}. These experiments indicate that in the presence of humic acid, Tc will be precipitated preferentially under anaerobic conditions.

Distribution coefficients for TcO_4^- between aerobic sediments which are poor in organic matter, and seawater are very low, and the k_D for sediments from the North East Atlantic Abyssal Plain never exceed 3.5 (Fowler *et al.* 1983). The distribution coefficients are not significantly different for Tc^{IV} and Tc^{VII}. This suggests that Tc^{IV} is oxidized to TcO_4^- during the experiments (Aston *et al.* 1984). Tc should therefore be highly mobile under the oxic conditions that are prevalent in pelagic environments and the upper layers of many sediments, and should become fixed on interaction with reducing conditions (Scoppa *et al.* 1983). Technetium was found to accumulate in the reducing zone during experiments, immobilized as insoluble $TcO_2.H_2O$ or as Tc^{IV} sulphides or co-precipitated with iron sulphides (Wildung *et al.* 1979). In such cases the distribution coefficient may reach as high as 1000.

2.4.1.2. Sorption experiments to inorganic particulate

Fine sediments or muds can act as sinks for heavy metals and radionuclides in the marine environment (Masson *et al.* 1989). The effectiveness of sediments as sinks for ^{99}Tc can be assessed by the determination of the k_D of each sediment type. The distribution coefficient is defined in equation [2.4.1].

$$k_D = \frac{\text{Concentration of } ^{99}\text{Tc adsorbed to sediment Bq/kg}}{\text{Concentration of } ^{99}\text{Tc in solution Bq/L}} \qquad [2.4.1]$$

Most of the k_D studies dealing with the interaction of the different chemical forms of Tc with inorganic particulate matter have been laboratory-based experiments. A series of experiments have been conducted (Masson *et al.* 1981, 1989) in which both ^{99}Tc and ^{95m}Tc were added to marine sediments with differing concentrations of organic material including petroleum hydrocarbon residues. Little or no fixation onto the sediments was observed for oxidized calcareous sediments. Data from further experiments showed that the k_D for Tc in aerobic sediments rarely exceeds 1 – 4 (Fowler *et al.* 1981, Beasley and Lorz 1986). Reduced forms of Tc added to these sediments when exposed to oxygenated seawater displayed rapid loss of Tc from the solid phase, indicating efficient oxidation of reduced Tc species to pertechnetate (Fowler *et al.* 1983).

Reducing sediments rich in organic matter showed K_Ds as high as 1500 in sediments containing 7% organic material over a 50 day equilibration period (Aprosi and Masson 1981, Masson *et al.* 1981). Over the first 8 days the k_D was extremely low but then increased sharply with time. In organic-rich sediments where anaerobic conditions with an Eh < -150 mV were allowed to develop, Tc was seen to disappear slowly from seawater after a lag of eight days. Tc precipitation from the aqueous phase in aerobic conditions with an Eh > 250 mV was not observed (Masson *et al.* 1981). In the presence of reducing sediments low in organic matter, TcO_4^- appeared to be either reduced to insoluble tetravalent compounds (*e.g.* TcO_2) or co-precipitated with sulphides in sediments or precipitated as Tc_2S_7. This was thought to be a result of bacterial accumulation of Tc by reduction of TcO_4^- to lower valence states, which were then adsorbed to sediments.

When sediments contaminated with Tc were returned to flowing seawater, two results were observed (Masson *et al.* 1989):

- In reducing sediment approximately half the Tc was transferred to solution within 24 hours; the remaining Tc desorbed only after the addition of concentrated nitric acid.
- In an oxidizing sediment containing organic carbon the sediment-Tc bonds are highly unstable and Tc is quickly desorbed with circulating water, within 3 days (Masson *et al.* (1989)).

Loss of Tc from labelled sediments was observed when added as either TcO_4^- or as reduced Tc (IV) when the sediment was placed into oxygenated seawater (Fowler *et al.* 1983).

2.4.1.3. Bio accumulation into sediments

Bacterial fixing

Aerobic bacteria have no effect on TcO_4^-, neither accumulating Tc nor modifying its chemical form (Henrot 1989). Anaerobic bacteria exhibited high bioaccumulation and reduced TcO_4^- with concentration factors as high as 600 (Henrot 1989). Accumulation of the reduced Tc is thought to be the result of one of the following: reducing conditions in the growth media and Tc accumulation associated with organics, namely the bacteria themselves (Carlsen *et al.* 1984), or a metabolic process (Henrot 1989). The most likely mechanism for the reduction of TcO_4^- to a lower valence state by bacteria is that in the absence of oxygen the TcO_4^- ion is used as an electron acceptor in anaerobic respiration.

Sulphate reducing bacteria (*Desulphovibrio sp.*) also effectively removed Tc from solution and promoted its association with organic material, with up to 70% of the total available Tc in the growth media either bioaccumulated or precipitated. The pertechnetate ion is not considered to be reduced during sulphate-reduction, but rather by some other reducing agent released in the growth medium (Henrot 1989).

Role of marine organisms

The uptake of Tc by marine organisms is well researched in: phytoplankton (Gormov 1976, Fischer 1982), macroalgae (Pentreath *et al.* 1980, Masson *et al.* 1981, Aarkrog *et al.* 1983, Masson *et al.* 1989, Holm 1986) and marine fauna (Masson *et al.* 1989). The main method of inclusion into the sediment column is by incorporation of dead matter, which is contaminated with Tc. However, inputs are likely to be low as marine phytoplankton only has a distribution coefficient of less than 10 (Fowler *et al.* 1983). Organic matter already present in a sediment also appears to be an important sink for Tc by sorption (Bondetti and Garten 1985). Marine fauna are also likely to promote migration of Tc in the sediment column by bioturbation and mixing of the contaminated sediment.

2.4.1.4. Diffusion of Tc within the sediment column

As yet no data have been reported which relate to the post-depositional behaviour of Tc in sediment cores from either the deep ocean or from coastal low-level waste discharge sites. This is mainly due to the low levels of activity anticipated. Some laboratory experiments have been made using smectite-rich deep-sea sediments (with low organic content) in contact with atmospheric oxygen. These show diffusion coefficients in the order of 3×10^{-6} cm^2/s (Schriener *et al.* 1981), a value comparable to those predicted for the sulphate ion in a temperature range of 0-12°C (Li and Gregory 1974). Under anoxic conditions in these sediments TcO_4^- appears to undergo slow reduction with a concomitant decrease in the diffusion coefficient to a value near 1×10^{-8} cm^2/s.

This evidence implies that the association of pertechnetate with organic particulate matter in oxygenated seawater is slight. At the sediment-water interface of organic-rich sediments and particularly in anoxic basins some removal of TcO_4^- to the underlying sediments could occur, especially if the bottom water transport is sufficient to produce intense nepheloid layers where particle populations are high.

2.4.1.5. Analogues for the geochemical behaviour of Tc

Re has been suggested as an analogue for the study of the behaviour of Tc in sediments (Colodner *et al.* 1993) as both elements are in group 7b of the periodic table and share a similar chemistry (Colton 1965). Re also behaves conservatively in seawater and has been reported to accumulate in reducing sediments (Colodner *et al.* 1993). The transfer of Re to the sediment occurs below the sediment/ water interface, although the scavenging mechanisms for Re by various surfaces as well as differences in adsorption behaviour between Re and other oxyanions are still unclear and require further study (Colodner *et al.* 1993).

Evidence from cores taken from the Sea of Japan, Pakistan Margin, Black Sea and Saanich Inlet implies that Re is reduced and enriched as ReO_2 in suboxic conditions (absence of O_2 and H_2S) (Crusius *et al.* 1996). Accumulation of Re occurs at depths below observed decreases in solid phase Mn and also below decreases in the Fe/Al ratio and increases in solid phase U. These data imply that Re is reduced from $Re^{VII}O_4^-$ to Re^{IV} at depths below the permeation of pore-water oxygen (Crusius *et al.* 1996) inferred from geochemical trends of Mn, Fe and U (Frolich *et al.* 1979; Klinkhammer and Palmer 1991).

The sulphidic zone also shows evidence of Re enrichment but not to the same levels as the suboxic zone (Crusius *et al.* 1996). Given that the area of suboxic sediments is an order of magnitude larger than the area of sulphidic sediments (Emmerson and Huested 1991), Re removal into suboxic sediments is the most important oceanic sink (Crusius *et al.* 1996).

While laboratory experiments have implied that Tc would accumulate in reducing sediments, reported work on the behaviour of Re implies that Tc accumulation will occur predominantly in suboxic sediment and around the same depth as the reduction of Fe^{III} species and accumulation of solid phase U. Initial accumulation of Tc, if Re is used as an analogue, will therefore be directly from pore-water either sorbed to the sediment or precipitated as Tc^{IV} species.

2.4.2. Environmental Implications

2.4.2.1. Possible transfer mechanisms

The interactions of radionuclides in marine and estuarine systems are the result of a complex mixture of physical, chemical and biological controls. Radionuclides behave in the same manner as their stable counterparts and so are extensively used as tracers to study metal movement. As radionuclides enter an estuarine system they are subject to turbulent and molecular diffusion, with dispersion lowering their concentration away from the effluent source. Many radionuclides are easily adsorbed to particulate minerals, usually clay minerals, though Tc has a particularly low distribution coefficient in aerobic seawater and so tends to behave conservatively (Edington and Nelson 1986). Once the sediments, with radionuclides attached, are deposited in an estuarine environment, there is greater potential for the interaction of these radionuclides with the surrounding terrestrial environment and a greater chance for them to enter the local ecosystem (Figure 2.4.2).

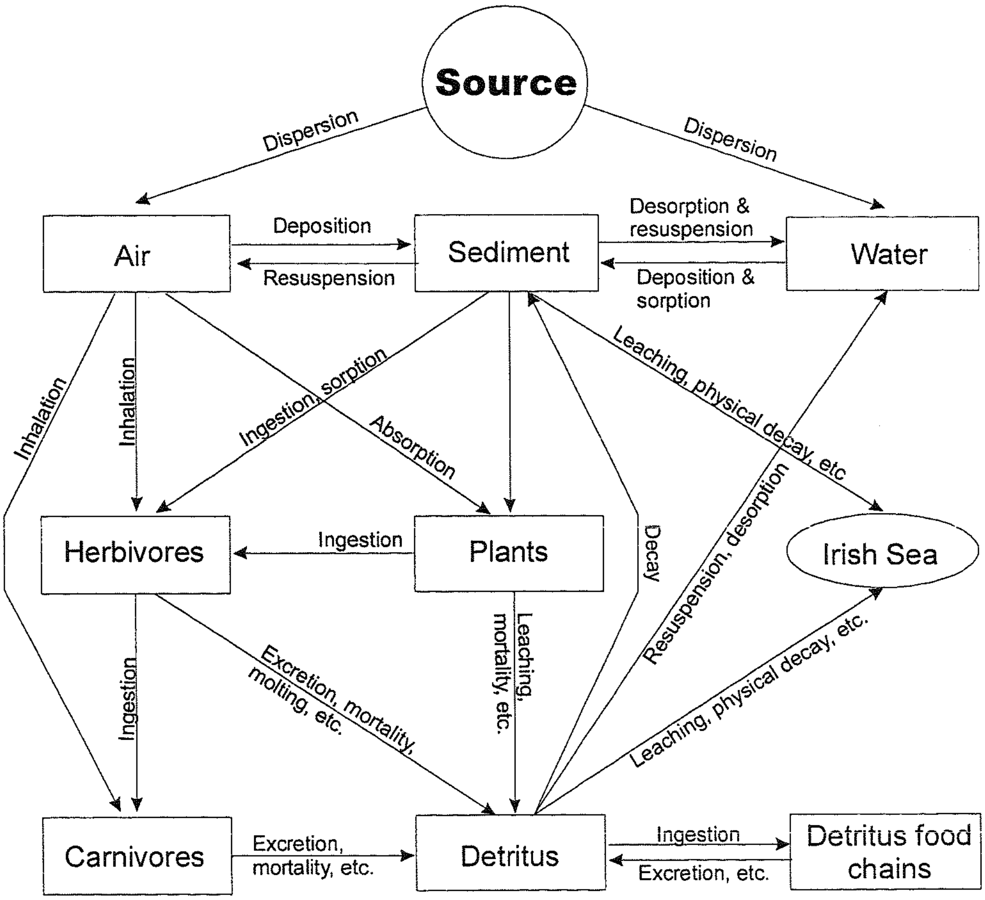

Figure 2.4.2. General transport processes operating on radionuclides in ecosystems. Boxes define the ecosystem components and arrows depict the flow of the materials through functional processes (after Whicker and Schultz 1982).

Uptake of radionuclides by organisms may be from sediments, directly from seawater or by ingestion of other organisms. Marine algae and autotrophs obtain radionuclides directly from seawater as well as sediments. ^{99}Tc is particularly well taken up in *fucoid* seaweeds (Aarkrog *et al.* 1983). In food webs, herbivores will accumulate ^{99}Tc principally from the consumption of primary producers. Omnivores and carnivores in turn will accumulate ^{99}Tc by consuming prey and other organisms that already contain high ^{99}Tc activities. They will also assimilate some ^{99}Tc from the water and sediments. If ^{99}Tc is found to be accumulating in sediments these sediments could provide a temporary storage for ^{99}Tc contamination. However as the distribution coefficient for Tc in aerobic sediments is so low, it would be easily remobilized and so present a renewed contamination problem. Some of the ^{99}Tc that has accumulated in estuarine sediments will therefore be incorporated into the human food chain through farming of tidally inundated areas. ^{99}Tc held in the sediments will be transferred into pasture or crops. Grazing of these pastures would then result in a transfer of ^{99}Tc to livestock.

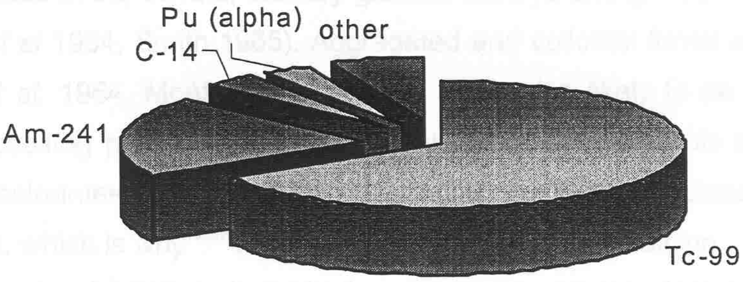

Figure 2.4.3. Radiation doses to the St Bees-Selker critical group from the consumption of crustacea (MAFF 1997). Total dose from consumption of crustacea = 0.03 mSv. Total dose to consumers of all seafood is less than 0.11 mSv

The other main entrance of ^{99}Tc into the human food chain is via the consumption of contaminated marine fauna. Lobsters (*Homarus gammarus*) have a particularly high concentration factor for ^{99}Tc (Masson *et al.* 1989). The radiation dose to a theoretical group of people who live around the Sellafield area and eat seafood frequently has been calculated (Figure 2.4.3). ^{99}Tc comprises the highest dose from any of the discharged radionuclides. This is due to the currently high activities being discharged by Sellafield and since the emissions from the reprocessing plant are now declining, the corresponding activities in seafood will also be reduced.

2.4.2.2. ^{99}Tc in Humans

^{99}Tc dose could be received by direct radiation, inhalation of ^{99}Tc contaminated material or by ingestion of ^{99}Tc contaminated food. External radiation dose is unlikely to be significant as ^{99}Tc is a relatively weak pure β-emitter. A substantial direct dose is unlikely to members of the public and risk of inhalation of ^{99}Tc is slight and only likely within close proximity to a nuclear facility. Dose from the inhalation of contaminated sediments could be more substantial if the sediments were contaminated with significant amounts of ^{99}Tc. Such an effect could be significant at a distance from a nuclear facility after accumulation of ^{99}Tc under favorable conditions. The greatest risk comes from the ingestion of contaminated foods. Approximately 95% of Tc is absorbed on ingestion from the small intestine, with a biological half life of 2 days (Beasley *et al.* 1966) (Table 2.4.1).

Table 2.4 1. Fraction of ^{99}Tc transferred to source tissues from human body fluids (Kendall *et al.* 1987)

Tissue	**Fraction transferred**
Thyroid	0.04
Liver	0.03
Stomach wall	0.01
Rest of body	0.83

TcO_4^- concentrates in the thyroid, salivary glands, kidneys and gastrointestinal tract (Beasley *et al.* 1966, Harper *et al* 1964, Smith 1965). Aggregated and colloidal forms of Tc tend to localize in the liver (Harper *et al.* 1964, McAfee *et al.* 1964). Tc is also likely to be reduced by the low pH of stomach acid causing precipitation as TcO_2 which is insoluble. This would account for the high doses to the gastrointestinal tract. Numerous other chemical complexes of Tc will accumulate in discrete tissues, which is why ^{99m}Tc is widely used in nuclear medicine. However, as pertechnetate is the stable form in which Tc is found in the oxic environment pertechnetate, is the most important form for dose implications.

Table 2.4.2. Committed doses to selected organs by ingestion of ^{99}Tc contaminated material Sv/Bq (Kendall *et al.* 1987).

	CEDE	Thyroid	Liver	L.L.I.*	R.B.M.**	Ovaries / Testes	Stomach	Rest
Adult	3.5×10^{-10}	1.6×10^{-9}	8.2×10^{-11}	1.1×10^{-9}	6.0×10^{-11}	6.0×10^{-11}	3.4×10^{-9}	7.0×10^{-11}
Child (10 years)	8.1×10^{-10}	3.8×10^{-9}	1.9×10^{-10}	2.6×10^{-9}	1.4×10^{-10}	1.4×10^{-10}	8.0×10^{-9}	1.6×10^{-10}
Infant	2.4×10^{-9}	1.1×10^{-8}	5.7×10^{-10}	7.7×10^{-10}	4.2×10^{-10}	4.2×10^{-10}	2.4×10^{-8}	4.9×10^{-10}

* Lungs, Liver, Intestines. **Red bone marrow.

Committed doses by ingestion of ^{99}Tc contaminated material are shown in Figure 2.4.2. The most important differences between the doses calculated for adults, ten year old children and one year old infants arise from the smaller body size of children and infants, as well as differences in feeding habits.

Studies have been made to assess the toxicity of ^{99}Tc and whether it is toxic to man. Most work has been made using rats as analogues, feeding them large amounts of ^{99}Tc in an iodine depleted diet (Gerber *et al.* 1989). High levels of ^{99}Tc caused a reduction in T4 levels, decreased iodine uptake and a reduction in fertility. The chemical toxicity to the thyroid is not observed as most damage is due to the radiological effects of ^{99}Tc. Given that the rats in the study had been fed 200–100 times more Tc than iodine in their diet it was concluded that Tc toxicity does not represent a stochastic risk to man.

2.5. Reference List.

Aarkrog A., Dahlgaard H., Hellstadius L., Hansen H .& Holm E. 1983. Radiocaesium from Sellafield effluents in Greenland water. Nature **304**. 49 – 51.

Aarkrog A., Boelskifte S., Dahlgaard H., Duniec S., Hallstadius L., Holm E. & Smith J.N 1987. Technetium-99 and Ceasium-134 as long distance tracers in Arctic waters. Estuarine, Coastal and Shelf Science. **24.** 637-647.

Aarkrog A. 1988. The radiological Impact of the Chernobyl Debris compared with that from Nuclear weapons fallout. J. Environ. Radioactivity **6** 151-162.

Allard B., Kigatsi H., Torstenfeld B. 1979. Technetium: reduction and sorption in granitic bedrock. Radiochem. Radioanal. Lett. **37.** 223 - 239.

Amersham 1976. The radiochemical centre, Amersham, medical products 1976.

Anders E. 1960. The radiochemistry of technetium. Office of Technical Studies. Washington DC.

Aoyama M. 1988. Evidence of stratosphere fallout of cesium isotopes from the Chernobyl accident. Geophys. Res Lett. **15.** 327 – 330.

Aoyama M., Hirose K. & Sugimara Y. 1991. The temporal variation of stratosphere fallout derived from the Chernobyl accident. J. Environ. Radioact. **13.** 103 – 115.

Aprosi G. & Masson M. 1981. Toxicité et action massique de l'isotope 99; transferts eau-sediments – annélides. Chateau. France: EDF.- CHATOU; Rapport EDF-DER-HE 31-81.16.

Aston S.R., Gasuad J., Oreioni B & Pasi P. 1984. Observations on the adsorption and geochemical association of technetium, neptunium, plutonium, americium, and californium with deep sea sediments. In: Cigna A. & Myttenaere C (eds) International symposium on the behaviour of long lived radionuclides In the marine environment. La Spezia. CEC. Report EUR-9214-EN. 179 – 187.

Attrep M., Enochs J.A. & Broz L.D. 1971. Atmospheric technetium-99. Environ. Sci. Tech. **5.** 344 - 355.

Bailey M.F., Dahl L.F. 1965. The crystal structure of ditechnetium dicarbonyl. Inorg. Chem. **4.** 1140 – 1145.

Baldas J. 1994. The coordination chemistry of technetium. In: Sykes A.G. (ed). Advances in inorganic chemistry. **41.** Academic Press inc. San Diego. 1-123.

Baldas J. 1996. In: Topics in current chemistry. 176: Technetium and Rhenium; Eds: Yoshihara K., Omori T. Springer. Berlin 1996 37-76.

Bass Becking L.G.M., Kaplan I.R., Moore D. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potential. J. Geology **68.** 243-84.

Beasley T.M., Palmer H.E. & Nelp W.B. 1966. Distribution of technetium in humans. Health Physics **12.** 1425 – 1435.

Beasley T.M., Lorz H.V. 1986. A review of the biological and geochemical behavior of technetium in the marine environment. In: Desmet G., Myttenaere C (eds). Technetium in nature. 197-218 Elsevier.

Beasley T.M., Dixon P.R., Mann L.J. 1998. ^{99}Tc, ^{236}U, and ^{237}Np in the snake river plain aquifer at the Idaho National Engineering and Environmental Laboritory Idaho Falls, Idaho. Environ. Sci. Tech. **32.** 3875-3881.

Bondetti E.A. & Garten.C.T. 1985. Speciation of ^{99}Tc and ^{60}Co: Correlation of laboratory and field observations. In: Bulman R.A. & Cooper J.R. Speciation of fission and activation products in the environment. Elsevier. London. 79 – 93.

Boyd G.E. 1959. Technetium and Promethium. J. Chem. Ed. **36.** 3-14.

Bramman J.L., Sharpe R.M., Thom D., Yates G. 1968. Metallic fission-product inclusions in irradiated oxide fuels. J. Nucl. Matt. **25.** 201 - 215.

Browne E. & Firestone R.B. 1986. Table of radioactive isotopes. John Wiley and sons. New York.

Carlsen L., Jensen B.S., Nilsson K. 1984. The migratory chemistry of technetium. Brussels CEC: C.E.C. report. EUR 9543 EN (mirage project).

Choppin G., Lilenzin J.O., & Rydberg J. 1996. Radiochemistry and Nuclear Chemistry. Butterworth-Heinemann Oxford, U.K.

Colodner D., Sachs J., Ravissa G., Turekian K., Edmond J., Boyle E. 1993. The geochemical cycle of rhenium: a reconnaissance. Earth Planet. Sci. Lett. **117.** 205 - 221.

Colton R. 1965. The chemistry of Rhenium and Technetium. Interscience, New York.

Cotton F.A., Davidson A., Day V.W., Gage L.D., Trop H.S. 1979. Inorg. Chem **18.** 3024.

Crusius J., Calvert S., Pedersen T., Sage D. 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxi, sub oxic and sulphidic conditions of deposition. Earth Planet. Sci. Lett. **145.** 65 - 78.

Dahlgaard H. 1993. Anthropogenic radioactivity in the Arctic Seas: Time trends and present levels. In Radioactivity and environmental Security in the oceans: New research policy priorities in the Arctic and North Atlantic. Woods Hole, Massachusetts. USA 49 – 63.

Davison A., Trop H.S., de Pamphilis B.V., Jones A.G. 1982. Tetrabutyl-ammonium tetrachorooxotechnetate(V). In: Fackler J.P. (ed.). Inorganic synthesis. **XXI.** Wiley Interscience. New York. 160 - 162.

Deutsh E., Lisbon K., Vanderheyden J-L., Ketring A.R., Maxon H.R. 1986. Nucl. Med. Biol. **13.** 465.

Dixon P., Curtis D.B., Musgrove J., Roensh F., Roach F., Rokop D. 1997. Analysis of naturally produced Technetium and Plutonium in Geologic materials. Anal. Chem. **69.** 1692 - 1699.

Edington D.N., Nelson D.M. 1986. The chemical behaviour of long lived radionuclides in the marine environment. In: Behaviour of long lived radionuclides associated with deep sea disposal of radioactive wastes: Report of a coordinated research program organized by the International Atomic Energy Agency, Tech report IAEA, Vienna 1986, 41.

Ferm R. 1993. World armaments and disarmament. Appendix 6A -SIPRI Year book 1993. Oxford Uni. Press, Oxford.

Fischer N. 1982. Bioaccumulation of technetium by marine plankton. Env. Sci. Technol. **16.** 579 - 581.

Fowler S.W., Benayoun G., Parsi P., Essa M.W.A., Schulte E.H. 1981. Experimental studies on the bioavialability of technetium in selected marine organisms. In: Impacts of radionuclide releases into the Marine Environment. Vienna IAEA 319-39.

Fowler S.W., Aston S.R., BenayonG. & Parsi P. 1983. Bioavailabilty of Technetium from artificially labeled Northeast Atlantic deep sea sediments. Mar. Environ. Res. **8.** 87 – 100.

Frolich P.N., Klinkhammer G.P., Bender M.L., Luedke N.A., Heath G.R., Cullen D., Dauphin P. 1979. Early oxidation of organic matter in pelagic sediments of the Eastern Equitorial Atlantic: Suboxic diagenesis. Geochimica et Cosmochimica Acta. **43.** 1075-1090.

Gerber G.B., Hegela M., Vankerkom J., Kirckman R., Maisin J.R. and Lambiet-Colloer M. 1989. Toxicity of 99Tc: Can it represent a risk to man? Health Physics **57.** 345-350.

Goromov G.G. 1976. Uptake of plutonium and other nuclear wastes by plankton. Mar. Sci. Comm. **2.** 227 - 247.

Gmelin. 1983. Gmelin hand book of inorganic Chemistry, 8th Ed. Tc supplement Vol 2. Springer Verlag. Berlin-Hindleberg-New York.

Gray J., Jones S.R., Smith A.D. 1995. Discharges to the environment from the Sellafield site 1951-1992. J. Radiol. Prot. **15.** 99-131.

Gueguenìat P., Solomon J.C., Wartel M., Cabioh L., Frazier A. 1993. Transfer pathways and transit time of dissolved matter in the Eastern English Channel, indicated by space time radiotracer measurement and hydrodynamic modeling. Estuarine, Coastal and Shelf Science **36.** 477 – 494.

Harper P.V., Lathrop K.A., McCardle R.J., Andros G. 1964. The use of technetium-99m as a clinical scanning agent for thyroid liver and brain. Medical Radioisotopes Scanning Vol.**2.** IAEA.

Henrot J., Garten C.T., Blaglock B.G. 1988. Behaviour of technetium in soil: Sorption-desorption processes. Oak ridge national laboratory, Oak ridge, TN, Environmental Sciences division; publication no 3072; ONRL-TM-10721.

Henrot J. 1989. Bioaccumulation and chemical modification of technetium by soil bacteria. Health Physics **57.** 238 – 245.

Hidaka H. Shinotuka K., Hollinger P.H. 1993. Geochemical behaviour of ^{99}Tc in the Okolo natural fission reactors. Radiochim. Acta **63.** 19-22.

Higuchi H., Katsu H., HashimotoT., Nonaka N., Yoshimuzu K., Omine M., TakanoN. & Abe T. 1988. Radioactivity in surface air and precipitation in Japan after the Chernobyl Accident. J.Environ. Radioact. **6.** 131 – 144.

Hileman J.C., Huggins D.K., Kaesz H.D. 1962. Derivatives of Tc carbonyl synthesis and properties of carbonyl halides and the penta carbonyl halide. Inorg. Chem. **1.** 933 - 938.

Holm E. Rioseco J. & Mattsson S. 1986. Technetium in the Baltic Sea. In: Desmet G., Mytteneare C. (eds) *Technetium in the environment*. London. Elsevier. 61 – 68.

Holm E. 1993. Radioanalytical studies of technetium in the environment: Progress and problems. Radiochim. Acta **63.** 57 – 62.

Holeman B.L., Sporn V., Jones A.G., Sia S.T.B. 1987. J. Nucl. Med. **28.** 13.

Huber A., Baumgartner F., Henkelmann R., Gauthier A. 1986. Spectroelectrochemical studies on the hexachlortechnetate(IV) and hexabromotechnetate complexes in aqueous media. Inorg. Chem. **26.** 3718 - 3722.

Klinkhammer G.P., Palmer M.R. 1991. Uranium in the oceans: Where it goes and why. Geochimica et Cosmochimica Acta **55.** 1799 - 1806.

Jaworowski Z., Kowonaka L. 1988. Troposphere and stratosphere distributions of radioactive iodine and cesium after the Chernobyl accident. J.Environ. Radioact. **6.** 145 – 150.

Jenkins I.L., Brown P.E. 1984. Characterisation of dissolution residues- fuel element cladding and fission product insolubles. Radiochim Acta **36.** 25 - 30.

Kendall G.M., Kennedy B.W., Greenhalgh J.R., Adams N., Fell T.P. 1987. Committed dose equivalent to selected organs and committed dose equivalent from ingestion of radionuclides. NRPB-GS7. HMSO.

Kenna B.T., Kuroda P.K. 1964. Technetium in nature. J. Inorg. Nucl. Chem. **26.** 493 - 499.

Kennish M.J. 1997. A practical handbook of estuarine and marine pollution. CRC Press. Boca Raton, Fla, USA.

Kershaw P.J., Baxter A. 1995. The transfer of reprocessing wastes from Northwest Europe to the Arctic. Deep Sea Res. **42.** 1413 – 1448.

Koyama M., Kanchika Y., Fujinaga T. Photochemical behaviour of the hexachlorotechnetate(IV)ion. 1968. Co-ord. Chem. Rev. **3.** 285 - 291.

Kuroda P.K. 1993. Technetium in nature and the age of the solar system. Radiochim. Acta **63.** 9-18.

Leonard K.S., McCubbin D., Brown J., Bonfield R.A., Brooks T. 1997. A summary report of the distributions of ^{99}Tc in UK coastal waters. Radioprotection Colloques **32.** 109 – 114.

Li Y.H., Gregory S. 1974. Diffusion of ions in seawater and deep sea sediments. Geochim. Cosmochim. Acta. **38.** 763-714.

Lieser K.H., Kruger A., Singh R.N. 1981. Extraktionsverhalten von Technetium im Purex-purzeB. Nucl. Entsorgund **1.** 247-261.

Lieser K.H., Bauscher C.H., Nakashima T. 1987. Dissolution of TcO_2 in aqueous solutions under various conditions. Radiochim. Acta **42.** 191-200.

Lieser K.H. 1993. Technetium in the nuclear fuel cycle, in medicine and in the environment. Radiochim. Acta **63.** 5-8.

Livingston H.D. 1995. Arctic radioactivity and transport processes: an introduction. Deep Sea Res. **42.** 1337 – 1339.

Masson M., Aprosi G., Lanicèce A., Gueguenіat P. & Belot Y. 1981. Approches experémetales de l' étude des transfers du technétium à des sédiments et à des espèces marine benthiques. In: Impacts of radionuclides releases into the marine environment. Proceedings of an International Atomic Energy Agency conference, Vienna. IAEA; IAEA-SM-248/124 341 – 359.

Masson M., Patti F., Colle C., Roucoux P., Grauby A. & Saas A. 1989. Synopsis of French experimental and in situ research on the terrestrial and marine behavior of technetium. Health Physics **57.** 269 – 279.

Masson M., Van Weers A.W., Groothius R.E.J., Dalhgaard H., Ibbett R.D., Leonard K.S. 1995. Time series for seawater and seaweed of ^{99}Tc and ^{125}Sb originating from releases at La Hague. J. Marine Systems **6.** 397 – 413.

McAfee J.G., Fuger C.F., Stern H.S., Wogern H.N., Migita T. 1964. ^{99m}Tc pertechnetate for brain scanning. J. Nuclear. Medicine. **5.** 811.

Mendeleev D.I. 1869. J. Russian. Chemistry. Society. **1.** 60.

Noddack I., Noddack W. 1925. Tacke, Oberg, Sitzber preuss. Akad. Wiss. Physikamath. Klasse. **19.** 400.

Omori T. 1996. In: Yoshihara K., Omori T. (eds). Topics in current chemistry. **176:** Technetium and Rhenium: Springer. Berlin 253-273.

Page H. 1980. United Kingdom experience of production of uranium fluorides. In: Production of yellowcake and uranium fluorides IAEA Vienna.

Pearson R.G. 1963. Hard and soft acids and bases. J. Am.Chem. Soc. **85.** 3533 - 3539.

Pentreath R.J., Jeffries D.F., Lovett M.B., Nelson D.M. 1984. The behaviour of transuranic and other long lived radionuclides in the Irish Sea and its relevance to the deep sea disposal of Radioactive waste. In: Proc. 3rd NEA Seminar on Radioecology (Tokyo) NEA OECD, Paris rue A. Pascal 203-220.

Perrier C., Segre E. 1937. Some chemical properties of element 43. J. Chem. Phys. **5.** 712 – 716.

Perrier C., Segre E. 1939. Some chemical properties of element 43 II. J. Chem. Phys. **7.** 155-156.

Rard J.A. 1983. Critical review of the chemistry and thermodynamics of technetium and some of its inorganic compounds and aqueous species, Lawrence Livermore Nat. Lab. Report no UCR1-53440.

Schreiner F., Fried S., Friedman A. 1981. Diffusion of the neptunyl (V) and pertechnetate ions in marine sediments. In: The scientific basis for nuclear waste Management Vienna, IAEA. 241-72.

Schwochau K., Pleyer U. 1993. Technetium complexes, the complexing agents, the preparation of complexing agents and the use of complexes. Radiochim. Acta. **63.** 103-110.

Scoppa P., Schulte E.H., Secondini. 1983. Application of ^{95m}Tc in experimental radioecology: Chemical form and behaviour in the marine environment. In: Deutsh E., Nicolini M. & Wagner H.N. Technetium chemistry and nuclear medicine. Cortina International. Erona. 219 – 226.

Segre E., Wu C.S. 1940. Fission products of U Phys. Rev. **57.** 552 - 557.

Sekine T., Watenabe A., Yoshihara K., Kim J.I. 1993. Complexation of Technetium with humic acid. Radiochim. Acta **63.** 87-90.

Sullivan R.P. 1951. In: National Nuclear Energy Series -10. **9.** 778. McGraw-Hill, New York.

Thomas C.W. 1978. The concentrations of ^{241}Am and ^{99}Tc in surface air at Richland, Washington. Report. BNWL-2000, Batelle, Pacific Northwest Laboratory Richland, Washington.

Till J.E., Hoffmann F.O., Dunning D.E. 1979. A new look at ^{99}Tc releases to the atmosphere. Health Physics **36.** 21.

Till J.E. 1986. Source terms for technetium-99 from nuclear fuel cycle facilities. In Desmet G., Myttenare C. (eds) Technetium in the environment. Elsevier. London. 1-20.

Torstenfeld B. 1981. Technetium in the geologic environment; a literature survey. PhD Thesis, University of Stockholm.

Vinogradov I.V., Zaitiseva L.L., Koranev M.I., Sheplekov S.V. 1974. Stability of alkali metals and ammonium hexachlorates and hexabromates. Russ. J. Inorg. Chem. (Engl. Trans.) **19.** 1488-1490.

Whicker F.W., Schultz V. 1982. Radioecology: Nuclear energy and the environment. **1.** CRC Press, Boca Raton, Fl.

Whitehead N.E., Ballstra S., Holm E., Walton A. 1988. Air radionuclide patterns observed at Monaco from the Chernobyl accident. J. Environ. Radioact. **7.** 249 – 264.

Wildung R.E., McFadden K.M., Garland T.R. Technetium sources and behaviour in the environment. J. Environ. Qual. **8.** 156 – 161.

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Review of methods for the determination of ^{99}Tc in environmental samples

Chapter 3. Review of Methods for the Determination of ^{99}Tc in Environmental Samples

3.1. Introduction

The determination of ^{99}Tc from environmental materials is of great importance in assessing the environmental impact of discharges of this nuclide. Much work on the separation of this radioisotope has been reported with acceptable recoveries and limits of detection. However, determination of ^{99}Tc in environmental samples is complicated by:

1. The lack of any gamma emission.
2. The low concentrations of ^{99}Tc usually present.
3. The volatility of pertechnetate.
4. The variable speciation of ^{99}Tc.
5. Radiometric and isobaric interferences potentially present in the sample.

In order to determine ^{99}Tc concentrations in environmental samples, it is necessary to both concentrate the ^{99}Tc and to remove any potential interferences. These take the form of: (1). Chemical interferences, which will affect the recovery of ^{99}Tc during the separation chemistry. (2). Other radionuclides produce energy overlaps that may cause interference during β determination. Radionuclides with potential interferences include ^{60}Co, ^{63}Ni, ^{103}Ru, ^{106}Ru, ^{110m}Ag as well as many other alpha and gamma emitting radioisotopes (Holm 1993). (3). Potential isobaric interferences for mass-spectrometric determination of ^{99}Tc, usually ^{99}Mo and ^{99}Ru (Ihsanullah and East 1993).

Previously published methods showed that the analytical separation scheme of ^{99}Tc can be divided into several distinct stages:

1. Choice of an appropriate yield monitor.
2. Sample preparation/ ashing.
3. Leaching/ dissolution of the ^{99}Tc from the sample matrix.
4. Isolation of ^{99}Tc from the bulk sample matrix and efficient separation of ^{99}Tc from potential interferences.
5. Measurement of ^{99}Tc.

3.2. Yield Monitor

A yield monitor is frequently used to correct for losses of Tc during the chemical separation procedures, as recovery is not 100% and varies from sample to sample depending on the composition of each. In some analytical procedures no yield monitor is employed and an assumption of chemical recovery is made from duplicate samples or standard addition procedures. Most methods for ^{99}Tc determination use one of the following:

3.2.1. Technetium-95m

^{95m}Tc ($t_{½}$ 60 days) has been used as a yield monitor for the determination of ^{99}Tc (Ihsanullah and East 1993, Silva *et al.* 1988). ^{95m}Tc is a gamma emitter so consequently the final Tc fraction must be counted using γ spectrometry in addition to the assay of ^{99}Tc using liquid scintillation counting or mass spectrometry. Whilst ^{95m}Tc will not interfere isobarically with the determination of ^{99}Tc by ICP-MS, there is considerable interference when determination is made by Liquid Scintillation Counting (LSC) (Goldchert and Sedlet 1969). The half life of the ^{95m}Tc isotope is too long for it to be allowed to decay before determination of the ^{99}Tc. ^{95m}Tc decays to ^{95}Mo avoiding contamination of the sample with isotopes of mass-99 and so methods using ^{95m}Tc will have a lower limit of detection than those using ^{99m}Tc (Hirano *et al.* 1989).

3.2.2. Technetium-97

^{97}Tc ($t_{½}$ 2.6 x 10^6 years) is another possible yield monitor for use with determination by ICP-MS or by LSC, but attempts to obtain a pure β-emitting source have been unsuccessful due to contamination from other isotopes of Tc (Long and Sparks 1988).

3.2.3. Technetium-97m

^{97m}Tc ($t_{½}$ 91 days) is also frequently used as a yield monitor and has the same advantages and dis-advantages as ^{95m}Tc (Kaye *et al.* 1982). ^{97m}Tc decays by γ-emission and β decay (Brown and Firestone 1986) so determination has been made either by γ spectrometry or by electroplating onto an iridium cathode, followed by counting using a proportional counter. Use of the proportional counter and an aluminium shield means that the yield and ^{99}Tc activity can be determined on the same instrument (Kaye *et al.* 1982).

3.2.4. Technetium-99m

^{99m}Tc ($t_{½}$ 6 hours) has been used as a yield monitor in a number of methods for the determination of ^{99}Tc (Chen *et al* 1994, Holm *et al* 1984). Separate detecting equipment is required as ^{99m}Tc is a γ-emitter. Spectra from the ^{99m}Tc yield monitor and the ^{99}Tc in the sample overlap during liquid scintillation counting so simultaneous detection cannot be made (Banavali *et al.* 1995). However, the ^{99m}Tc activity decays quickly so that any interference form the ^{99m}Tc monitor can be quickly minimised. A period of seven days (> 25 half lives) from the determination of the yield monitor has been found to be sufficient to allow the ^{99m}Tc monitor to decay away (Banavali *et* al. 1995). ^{99m}Tc decays to ^{99}Tc and will increase the limit of detection but is easily corrected for because the relative specific activities of ^{99}Tc and ^{99m}Tc are known.

3.2.5. Rhenium

Rhenium has an atomic mass suitably different from ^{99}Tc so that there are no isobaric interferences with determination by ICP-MS (Matsuoka *et al* 1990). Although ^{187}Re has one of the longest half lives of any primordial isotope, ^{187}Re decays with a low energy β-emission (Emax 2.5 keV), and any interference is overcome by windowing on a liquid scintillation counter. Rhenium is a scarce element (0.7 ppb Earth's crust) so is unlikely to be present in large quantities in environmental samples (CRC 1995). The chemistry of Re is similar to that of Tc as it is also in group VIIb of the periodic table. There are, however, significant differences between the chemistries of Re and Tc which will be especially obvious during anion exchange chromatography, where differing distribution coefficients will lead to different retention and elution characteristics, introducing errors into the determination (Goldchurt and Sedlet 1969). There will therefore inevitably be fractionation between rhenium and technetium during anion exchange and solvent extraction stages. Consequently, careful choice of separation procedures must be made to minimise these differences in order that an accurate chemical yield may be obtained (Anders 1960, Golchurt and Sedlet 1969).

3.3. Sample preparation

3.3.1. Solid samples

3.3.1.1. Ashing

Ashing of the sample is required to destroy organic matter and to aid leaching of Tc from the sample. Aids to the ashing procedure include calcination of the sample before heating (Garcia Leon 1990), or addition of oxalic acid (Nicholson *et al.* 1993). However Tc, as pertechnetate, is extremely volatile and at temperatures of 500°C losses of 55 % have been reported (Harvey *et al* 1991). Ramping the furnace from 250°C to 600°C with an increase of 50°C per hour has been shown to reduce losses of Tc, particularly when sample pre-treatment is also used (Harvey *et al.* 1991). Loss of Tc is unpredictable and where samples are dry ashed at 400°C, 450°C, and 500°C for up to 48 hours there was no correlation between loss of ^{99}Tc and seaweed species, temperature and time of ashing (Momoshima *et al.* 1991). The volatility of Tc can be reduced by the addition of an agent to prevent the formation of pertechnic acid in the sample. Addition of ammonia prior to ashing neutralises the free acidic sites on complex organic molecules, inhibiting the formation of $HTcO_4$ (Foti *et al.* 1972, Harvey *et al.* 1991). HCl can also be used to reduce to Tc to its Tc^{IV} state thus fixing it and preventing loss (Harvey *et al.* 1991). The most effective agent for the prevention of loss of Tc from samples during ashing was found to be ammonia solution, as long as the furnace was operated on a ramped program (Wigley *et al.* 1999).

3.3.1.2. Digestion

Extraction and solublisation of Tc from solid samples has been attempted using acid leaching, fusion and distillation. Several different acids have been used to leach Tc from sample matrices. These include: Concentrated HNO_3 (Chen *et al.* 1990, Chu 1984, Hirano *et al.* 1989), 8 M HNO_3 (Wigley *et al.* 1999), 4M HNO_3 (Riley and Siddiqui 1982), 6 M HCl + H_2O_2 (Harvey *et al.* 1991) and 3 M H_2SO_4 (Garcia Leon, 1990; Walker *et al.*, 1980; Holm *et al.*, 1984). All these leaching agents except 6 M HCl + H_2O_2 are oxidising and so solubilize the Tc by conversion of any Tc in the sample matrix to TcO_4^-.

A Na_2O_2 fusion at temperatures of 400°C to 500°C has also been used to extract Tc from soils and sediments (Foti *et al.* 1972, Dixon *et al.* 1997, Holenbach *et al.* 1994, Kaye *et al.* 1982). The fusion residue is then dissolved in water prior to isolation of Tc. Losses of ^{99}Tc from the fusion procedure are not reported.

Distillation of Tc from sample matrices has been used to isolate Tc (Tagami and Uchida 1993). The sample is first acidified to convert the Tc to TcO_4^- and is then heated to 950°C for 3 hours, volatilising any Tc in the sample matrix. The Tc in the distillate is trapped in 0.5 M K_2CO_3 solution for concentration and isolation.

3.3.2. Aqueous Samples

Aqueous samples tend to have very low ^{99}Tc activities so large sample sizes are required. Samples require filtering and some pre-concentration before Tc isolation (Garcia Leon 1990). This can be done by:

(1) Repeated co-precipitation as Tc^{IV} with $Fe(OH)_2$, through the addition of $K_2S_2O_5$ and NaOH (Momoshima *et al.* 1993).

(2) Co precipitation of Tc^{VII} with copper sulphide (Goldchurt and Sedlet 1969).

(3) Boiling to reduce the fluid volume. The addition of H_2O_2 during boiling aids the destruction of any organic material which may interfere in the decontamination chemistry later on (Davis *et al.* 1993).

(4) Extraction directly onto ion-exchange resin (Chen *et al.* 1990, Beals 1996, Davis *et al.* 1993, Ihsanullah and East 1994, Riley and Siddiqui 1982).

3.4. Decontamination

Potential interferences to the determination of ^{99}Tc are shown (Table 3.1).

Table 3.1. Potential interferences in the determination of ^{99}Tc (Holm 1993, Garcia Leon 1990, CRC 1995)

^{99}Tc measurement	Interference	Source
Radiometric	^{60}Co	Activation Product
Radiometric	^{63}Ni	Fission product
Mass Spectrometry	^{99}Mo	Fission product
Mass Spectrometry	^{99}Ru	Stable Ru (12.7%)
Radiometric	^{103}Ru	Fission product
Radiometric	^{106}Ru	Fission product
Radiometric	^{110m}Ag	Fission product

The decontamination process also acts as a useful concentrator for Tc. Most decontamination processes for Tc fall into one of four categories: precipitation, ion exchange, extraction chromatography, or solvent extraction.

3.4.1. Precipitation

An iron hydroxide scavenge to isolate Tc from other matrix elements has been reported (Garcia-Leon 1990). If Tc is present in solution as TcO_4^- it will not co-precipitate with the $Fe(OH)_3$ whilst many of the interfering radionuclides, principally actinides and many transition metals, will. In aqueous samples Tc may be reduced to Tc^{IV} with 0.7 g/l $FeSO_4.7H_2O$, then $FeCl_3.6H_2O$, and then neutralised with NH_4OH (Garcia-Leon 1990). The precipitate is then filtered off and dissolved with the Tc in 3M H_2SO_4. $Fe(OH)_2$ precipitation with $K_2S_2O_5$ has been used to concentrate and purify technetium from aqueous samples as Tc^{IV} (Momoshima *et al.* 1993). The precipitate is then oxidised and re-dissolved in HCl. The Fe^{3+} is then precipitated with NaOH and discarded. The process is repeated and the remaining solution is then taken to solvent extraction.

A copper sulphide precipitation has been used for decontamination, as copper sulphide will carry Tc^{VII} quantitatively as technetium heptasulphide in 0.2 to 3 N HCl (Golchert and Sedlet 1969). HCl is used as CuS would be decomposed by HNO_3. The precipitate is separated and then dissolved with 50% H_2O_2 in 1 N sulphuric acid and heated at 90°C for 15 minutes. 2 ml of xylene is also added to dissolve any elemental sulphur. Ru is subsequently removed by solubilisation of Ru with sodium hypochlorite to form Ru^{VII} and then reduction to insoluble Ru^{IV} oxide by addition of 10 ml of absolute alcohol (Golchert and Sedlet 1969).

Addition of a hold-back carrier, containing 1 mg/ml Co, Mn, Ce, and Fe, and precipitation of metal carbonates on addition of NaOH and Na_2CO_3 has been used to isolate many of the matrix elements from Tc which remain in solution (Banavaili *et al* 1995). After centrifugation the precipitate is discarded and the Tc retained in the supernatant.

3.4.2. Anion exchange and extraction chromatography

Both extraction chromatography and anion exchange procedures are used to isolate Tc and to concentrate Tc. Strong and weak base anion exchange resins, including Dowex 1x8 resin and AG 1x8 resin are selective for pertechnetate and perrhennate anions under alkaline and neutral conditions (Ihsanullah and East 1994, Harvey *et al.* 1991). The elution patterns for Re and Tc on most ion exchange columns are different, with the Re eluting before Tc and care must be taken to ensure complete elution of both elements if Re is being used as a yield monitor (Goldchurt and Sedlet 1969). If the sample has a significant Br concentration (*e.g.* seawater or acid digests of seaweeds) there may be a reduction in efficiency of the resin (Riley and Siddiqui 1982). Extraction onto a resin which is designed to cope with high halide concentrations is required (*e.g.* Duolite A101D anion exchange resin).

The extraction chromatography resin TEVA™ gives good separation of Tc from matrix elements (Davis *et al.* 1993, Butterworth *et al.* 1995). This is particularly the case for Ru which is not quantitatively separated from Tc by anion exchange. Sample solutions are loaded onto a column in a solution of 0.1 M hydrochloric acid. The resin is then rinsed with 25ml 0.1 M HCl, the raffinate discarded, and the Tc eluted with 10 ml 6M HNO_3 (Banavali *et al.* 1995).

Organic compounds will affect the efficiency of the separation chemistry (Davis *et al.* 1993) and must be separated from a sample solution. Amberlite-XAD-7 resin can be used to remove associated organics from solution and provides a useful decontamination stage (Davis *et al.* 1993).

3.4.3. Solvent extraction

Often a separate solvent extraction stage is used to remove Ru from solution as this is often not achieved quantitatively by ion exchange alone (Harvey *et al.* 1991, Dale *et al.* 1996).

The use of tri-isooctylamine (TiOA) for the isolation of ^{99}Tc from potential interferences has been reported to be effective (Golchert and Sedlet 1969). Most cations require a much lower pH for their extraction into TiOA in xylene than ^{99}Tc which is present as the TcO_4^- anion (Takeuechi *et al.* 1993). TnOA in xylene has also been used to isolate Tc from Ru in the sample solution (Dale *et al* 1996, Ihsanullah and East 1994). The xylene fraction can be added directly to the liquid scintillation cocktail, which improves the final counting efficiency (Wigley *et al.*1999). TnOA supported in a polypropylene microporous film has also been used to extract Tc from a sulphuric acid solution (Ashraf Chaudray and Ahmed 1996). This allows the osmotic stripping of ^{99}Tc from the feed solution, across the membrane into a stripping solution, usually NaOH.

^{99}Tc can be extracted from H_2SO_4 solutions in the presence of HF using tri-butyl phosphate (TBP) in xylene (Garcia Leon 1990, Mortia *et al.* 1993). At concentrations greater than 4 M HCl, Tc^{VII} is reduced to Tc^{IV} and so is less efficiently extracted into TBP (Watenabe and Hasimoto 1995).

The extraction of 57 elements as quaternary (propyl, butyl and hexyl) amine complexes into methylisobutylketone (MIBK), from five media (HF, HNO_3, H_2SO_4, HCl, and NaOH) was tested as a function of normality (Maeck *et al* 1961). Tc showed good extraction from all media except nitric acid at high normality, as the MIBK is oxidised by high nitric acid concentrations.

Tc has been extracted as a hexa-thiourea-Tc^{III} complex into 0.01 M dicarbollylcobaltate (III) in nitrobenzene from an acid solution (Kopunec *et al* 1994). The order of the rate of formation of hexathiourea-Tc^{III} was fastest in HCl, then $HClO_4$, HNO_3 and finally H_2SO_4. The concentration of the hexathiourea-technetium complex can then determined using spectrophotometric methods.

A comparison of the TOA, MIBK and TBP solvent extraction methods shows TOA has the highest extractability and back extractability of Tc, (Table 3.2) (Hirano *et al.* 1989).

Table 3.2 Extractabily of technetium by three different solvents, and back extractability into 5M NaOH (Hirano *et al.* 1989).

	Extractability %	Back extractability %
MIBK	50	74
TBP	82	20
TOA-Xylene	94	98.5

3.5. Determination of ^{99}Tc

There are a variety of methods available for the final determination of ^{99}Tc in environmental samples although measurements are commonly made using either Liquid Scintillation Counting (LSC) or Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Recent advances in the use of Accelerator Mass Spectrometry (AMS) have achieved significantly lower limits of detection (McAninich *et al.*1998).

3.5.1. Mass Spectrometry

Mass spectrometric methods are employed for ^{99}Tc determination with ICP-MS commonly used and Accelerator Mass Spectrometry (AMS) less commonly used despite its greater sensitivity. Methods using Thermal Ionisation Mass Spectrometry (TIMS) determination of ^{99}Tc have been developed but this technique is not used routinely due to the very high temperatures required for Tc ionisation (Kaye 1975).

3.5.1.1. Inductively Coupled Plasma – Mass Spectrometry

ICP-MS can be used to measure concentrations of ^{99}Tc and yield monitors simultaneously (Ihsanullah and East 1994, Momoshima *et al.* 1993). Interferences to the determination of ^{99}Tc by ICP-MS are isobaric and so easily identified and removed from solution (Gray and Date 1989). ^{99}Mo and ^{99}Ru are reported as being the principal isobaric interferences along with some molecular species of S (Ihsanullah and East 1994). Separation of ^{99}Tc from these must be achieved prior to determination. The sample solution should be 2% HNO_3 and have a salt concentration of less than 1% (Ihsanullah and East 1993) to avoid potential interferences from chloride species and damage to the Pt skimmer cones. These conditions may not exist following a standard separation procedure so a subsequent ion exchange phase may be required. Advances in the development of laser ablation, slurry nebulisation or electro-thermal vaporisation of solids make ^{99}Tc determination by ICP-MS much more attractive as it may simplify the sample preparation procedure (Fardy and Warner 1992). However sensitivity is significantly lower.

ICP-MS is a particularly sensitive technique with limits of detection ranging from 2 to 0.3 mBq/g for most solid sample matrices (Dixon *et al.* 1997, Ihsanullah and East 1994, Morita *et al.* 1993, Tagami *et al.* 1993). For a 1 litre aqueous sample the detection limits may be as low as 0.04 mBq/ml (Beals 1996).

3.5.1.2. Accelerator – Mass Spectrometry

Accelerator Mass Spectrometry (AMS) provides an ultra sensitive method of determination. In the most common AMS configuration negative technetium ions are generated in a Cs sputter source, passed through a magnetic sector and accelerated through a potential of several MV to a positive terminal. At the terminal, passage through a thin foil or low pressure gas generates positive ions of high charge, which then accelerate back to ground potential where they pass through further electrostatic and magnetic selection. For ^{99}Tc typically a terminal potential of 9 MV and a carbon stripping foil are used (McAninich *et al.*1998). Individual ions of the tracer isotope are counted by standard high-energy nuclear detection techniques and the ^{99}Tc is quantified by measurement of its ion beam current (King *et al.* 1997). Some isobaric interferences from ^{99}Ru and molecular sulphur species have been reported but are minimised by isolation of ^{99}Tc prior to determination (McAninich *et al.*1998). ^{99}Tc determination by AMS has a reported limit of detection of 0.5 – 0.6 pg to 10 fg per sample (Carling and Day 1998, McAninich *et al.* 1998). AMS is however expensive and access to instrumentation is limited.

3.5.2. Radiometric methods

3.5.2.1. Liquid Scintillation Counting

Separate analysis of yield monitors must be made when determination is by Liquid Scintillation Counting (LSC). Gamma emitting isotopes of technetium (^{99m}Tc, ^{97m}Tc and ^{95m}Tc) will require determination by γ-spectrometry and must be allowed to decay so that there is no interference with the ^{99}Tc spectrum (Banavali *et al* 1995). Potential interferences from the daughters must also be considered. If Re is used as a yield monitor it must also be determined prior to ^{99}Tc determination using spectrographic methods (ICP-AES) or gravimetricly using tetraphenyl asonium chloride (TPAC) (Harvey *et al.* 1991).

Quench is a problem during LSC determination in the form of either colour quench or impurity quenching as a result of undesired chemicals in the scintillation solution. These chemicals include chloroform, potassium dichromate, perchloric acid, sodium acetate and water, which is also a highly efficient quenching agent (Lawson *et al.* 1985, Pacer 1980). Ideally all potential quenching agents should be removed from the sample before the addition of scintillant. The addition of scintillant directly to the xylene fraction after solvent extraction or addition of TEVA™ resin prior to elution avoids the input of any aqueous quenching agents (Wigley *et al.* 1999). ^{99}Tc has a self-quenching effect with a 1 to 6 % decrease in efficiency per order of magnitude increase of ^{99}Tc concentration. Increasing the volume of the scintillation cocktail helps to lessen this effect and produces a rise in counting efficiency (Lawson *et al.* 1985). LSC techniques are cost effective and easily available. Ultra low level instruments incorporate both passive and active shielding and can have limits of detection comparable to those of ICP-MS.

3.5.2.2. Beta counting

Beta counting is achieved either using an anthracene screen counter, a gas flow proportional counter or a Geiger-Muller tube (Garcia-Leon 1990). Determination of yield monitors is performed either by separate determination or by screening ^{99}Tc β-emission from the detector using a Perspex or aluminium shield, while determination of a γ-emitting yield monitor is made (Kaye *et al.* 1982). Beta counting has the advantage of being cheap and readily available but is not as sensitive as LSC or ICP-MS.

3.5.2.3. Neutron Activation analysis

Thermal neutron activation is a very sensitive method for the determination of Tc owing to the relatively high neutron capture cross section (20 barns), for thermal neutrons (Long and Sparks 1988). Irradiation of ^{99}Tc with thermal neutrons produces ^{100}Tc (n,γ reaction) which has a half life of 15.8 s. Approximately 94% of the ^{100}Tc decays by 3.4 MeV β radiation followed by a sequence of two γ ray emissions. By this process it is possible to determine amounts of the order of 10^{-11} to 10^{-12} g (Foti *et al.* 1972). The main disadvantages of this method are the relatively short half-life of ^{100}Tc and the requirement for a nuclear reactor.

3.5.3. Other Methods

^{99}Tc can be determined gravimetrically by the precipitation of ^{99}Tc as a sulphide (Boyd and Larson 1960, Rulfs and Meinke 1952), as a nitron pertechnetate (Perrier and Segre 1939) or as tetra phenyl arsonium pertechnetate (TPAC) (Willard and Smith 1939). The TPAC method has proved to be the most effective method as there are fewer problems associated with the effects of contaminants during the precipitation procedure. The TPAC method is usable for Tc determination down to levels of approximately 5μg/ ml (3kBq/ml) in a pre-concentrated solution.

Instrumentation for typical trace element determination has also been used for the determination of Tc at relatively high levels in samples. These methods include X-ray fluorescence (XRF) spectrometry (Garner and Spies 1986), atomic absorption spectrometry (Kaye and Ballou 1978), spectroscopy and colourimetry (Long and Sparks 1988) and polarography (Magee *et al.* 1959). These methods are less sensitive and hence are not commonly used for determination of ^{99}Tc in environmental samples (Table 3.3).

Table 3.3. Detection limits for ^{99}Tc using various methods

Determination method	Limit of detection
Liquid scintillation Counting	10^{-12} g
ICP-MS	10^{-12} g
TIMS	10^{-12} g
AMS	10^{-15} g
Beta Counting	10^{-9} g
Gravimetry	10^{-6} g
Neutron Activation Analysis	10^{-12} g
XRF	10^{-6}g
Atomic absorption	10^{-8}g
Spectrophotometry	10^{-6} g
Polarography	10^{-8} g

3.6. Discussion

A selected summary of methods for ^{99}Tc determination in solid environmental samples and aqueous environmental samples is presented (Table 3.4, Table 3.5). Methods of sample preparation, decontamination and determination are presented along with typical recoveries and limits of detection, so that a comparison between methods designed to determine ^{99}Tc in similar samples can be made.

Table 3.4. A summary of methods for the determination of ^{99}Tc in solid environmental samples.

Sample Type	Typical Sample Size	Yield Monitor	Initial Treatment	Digestion	Purification and separation	Determination	Recovery	L.O.D.	Reference
Marine Biota	1g	Re		Microwave digestion in conc HNO_3	**EC** unspecified	AMS	90 – 100%	1 mBq/g	Carling and Day 1998
Seaweeds	10-20g	^{99m}Tc		Conc HNO_3	**SE** 5% TiOA in xylene	GM Gas flow Counting	70-75%	N/A	Chen *et al.* 1990
Vegetation	10g	^{95m}Tc	Wet ash with conc HNO_3	Conc HNO_3	$CaCO_3$ Scavenge **AE** Dowex 1 X-4 anion exchange resin	Beta Counting	60-78%	0.4 mBq / g (3000 mins)	Chu 1984
Geological materials	2.5 -15g	Isotope dilution technique	N/A	Na_2O_2 Fusion	**SE** TPAC in CCl_4 **SE** 8 M HNO_3 Further Na_2O_2 Fusion **AE** AGMP Resin **AE** Bio Rad column 1 X-8	ICP-MS	10-80%	0.7 mBq /g	Dixon *et al.* 1997
Vegetation	25g	^{95}Tc		Na_2O_2 fusion at 725°C	$FeOH_3$ Scavenge **AE** Dowex 1x8 resin **SE** Into Cyclohexanone + back to water Distillation into 10 ml water at 400°C	Neutron Activation Analysis	80%	6 mBq / g	Foti *et al.* 1972
Sediments Algae	N/A	^{99m}Tc	600°C for 1 hour + oxalic acid	3 M H_2SO_4	$FeOH_3$ Scavenge **SE** TBP (with HF)	Gas Flow Proportional Counting	50-70%	(Data suggests) 1.0 mBq/g	Garcia Leon 1990
Seawater, sediments, Biota	N/A	Re	450°C wet with NH_4OH	6 M HCl + H_2O_2	$FeOH_3$ Scavenge **AE** Anion exchange resin Sulphide precipitation Precipitation as TPAR	Beta Counting	85 - 99%	14 mBq /sample	Harvey *et al.*1991
Marine Algae	1 kg	^{95m}Tc in stds	Air dried	Conc HNO_3	**SE** 30% TnOA in xylene **SE** MEK	Beta Counting	70%	N/A	Hirano *et al.* 1989
Marine algae, Sea water	1 kg	^{95m}Tc	Air dried	Conc HNO_3	**AE** BIO-RAD AG 1xX8 **SE** 30% TnOA in xylene **SE** MIBK	Beta counting	70%	N/A	Hirano *et al.* 1993
Soils	0.25g	Re	470°C for 30 mins	Na_2O_2 Fusion dissolved in 50ml water	**EC** TEVA-Spec	Flow Injection ICP-MS	N/A	10 mBq / g	Hollenbach *et al.* 1994

Soils, Biota, Sediments	15-100g	^{99m}Tc	600°C for 30 mins wet with HCl or NH_4OH Oxalic acid aids ashing	3 M H_2SO_4 + K_2SO_4 + H_2O_2	Tc co-precipitation with $Fe(OH)_2$ **SE** TBP (with HF)	GM Gas Flow Counter	50-80%	9 mBq/g (1400 mins)	Holm *et al.* 1984
Algae, Soils, Sediments	1-30g	^{95m}Tc	600°C for 24 hrs Algae wet ashed with conc HNO_3	2 M H_2SO_4	**SE** 5% TiOA in xylene **AE** Dowex 1 X-8-Cl^-	ICP-MS	65-70%	0.3 mBq/g	Ihsanullah and East 1994
Vegetation, Soils, Sediments	15g	^{97m}Tc	Temperature not given	Na_2O_2 Fusion	**SE** AG1-X8 resin	GM Gas Flow Counting	50%	44 mBq/	Kaye *et al.* 1982
Soil	N/A	Standard Addition of ^{99}Tc	N/A	H_2O_2 leach	**EC** TEVA-Spec	AMS	60%	0.3mBq Sample	McAninich *et al.* 1998
Soil	N/A	^{95m}Tc	N/A	HNO_3	$FeOH_3$ Scavenge **SE** TBP in xylene **AE** Anion exchange resin SE **Cyclohexanone** SE **CCl_4**	ICP-MS	N/A	2 mBq/kg	Morita *et al.* 1993
Seaweed	1 g	None	Refluxed conc HNO_3	4 M HNO_3	**AE** Duolite A101D resin $FeOH_3$ Scavenge SE MIBK	Liquid Scintillation Counting	> 90%	4 mBq / g	Riley + Siddiqui 1982
Soil	150 - 250g	^{95m}Tc	950°C for 3 hours	Tc trapped in 0.5 M K_2CO_3	**SE** Cyclohexanone + 20 ml CCl_4	ICP-MS	52 - 64%	< 0.3 mBq/g	Tagami *et al.* 1993
Soils, Sediments, Vegetation	15 – 40 g	N/A	500°C for 30 mins	H_2SO_4 6 N + 10 g $K_2S_2O_8$	**SE** TBP	Liquid Scintillation Counting	N/A	37 mBq/g	Walker *et al.* 1980
Environmental samples	5-10g	^{99m}Tc	250°C-550°C ramped 50°C /hr	8M HNO_3 at 125°C	$FeOH_3$ Scavenge **AE** Anion exchange resin **SE** 5% TnOA in xylene	Liquid Scintillation Counting	75 – 95%	1.6 mBq/g	Wigley *et al.* 1999

Table 3.5. A summary of methods for the determination of ^{99}Tc in aqueous environmental samples.

Sample Type	Typical Sample Size	Yield Monitor	Digestion	Purification and separation	Determination	Recovery	L.O.D.	Reference
Sea water	200 Litres	^{99m}Tc	N/A	$FeOH_3$ Scavenge **SE** CCl_4 at pH4 **SE** Cyclohexanone +5% TiOA/xylene	Beta Counting	N/A	14 mBq/m^3	Aarkrog *et al. 1987*
Aqueous samples	1 litre	^{97}Tc	N/A	**EC** TEVA-Spec	ICP-MS	90%	40 mBq / l	Beals 1996
Seawater	200-400 l	^{99m}Tc	30% H_2O_2 + H_2SO_4 to pH1	**AE** AG1-X4 resin $FeOH_3$ Scavenge Evaporate Ru with 5% NaOCl solution **SE** 5%TiOA in xylene	GM Gas flow Counting	70-75%	N/A	Chen *et al.* 1990
Seawater	500 litres	^{99m}Tc	N/A	**AE** AG1-X4 resin $FeOH_3$ Scavenge Evaporate Ru with5% NaOCl solution **SE** 5%TiOA in xylene	GM Gas flow Counting	70-80%	3 mBq/m^3	Chen *et al.* 1994
Borehole waters	1 litre	Standard Addition	Acidified to 0.1 N HNO_3 + 10 ml 30% H_2O_2	Remove organic material with Amberlite XAD-7 **EC** TEVA Spec	Liquid Scintillation Counting (Instagel)	72 - 78%	37 mBq / l	Davis *et al.* 1993
Environmental water samples	1 litre	None Spiked stds	HNO_3 (5 ml/l)	Ru O_2 precipitation $FeOH_3$ Scavenge CuS precipitation **SE** 5%TiOA in xylene	Beta counting	80%	19 mBq / l (1000 mins)	Goldchurt and Sedlet 1969
Seawater,	N/A	Re	6 M HCl + H_2O_2	$FeOH_3$ Scavenge **AE** Anion exchange resin Sulphide precipitation Precipitation as TPAR	Beta Counting	85 - 99%	14 mBq/sample	Harvey *et al.*1991
Water	5-30 litres	^{95m}Tc	N/A	**AE** Dowex 1 X-8 **SE** 5% TiOA in xylene **AE** Dowex 1 X-8-Cl	ICP-MS	65-70%	0.25 mBq / l	Ihsanullah and East 1994
Water	1 litre	^{99m}Tc or ^{95m}Tc	H_2O_2	$FeOH_3$ Scavenge Carbonate Scavenge **AE** AG 1x8 resin	Liquid Scintillation Counting	N/A	N/A	Nevissi *et al.* 1994

Seawater	N/A	^{95m}Tc	N/A	Fe(OH)$_2$ precipitation FeOH$_3$ Scavenge **SE** MIBK **AE** Dowex 1 X-8 resin **SE** CCl$_4$	ICP-MS	54%	0.1 Bq / ml	Momoshima *et al.* 1993
Seawater	10 litres	None	+ Bromine Water	**AE** Duolite A101D resin FeOH$_3$ Scavenge SE MIBK	Liquid Scintillation Counting	> 90%	0.04 mBq / g	Riley + Siddiqui 1982
Water	200 litres	N/A	40 ml H$_2$SO$_4$ + KMnO$_4$	SE TBP	Liquid Scintillation Counting	N/A	0.6 mBq/l	Walker *et al.* 1980

Key for Tables 3.3 and 3.4.

AE Anion exchange chromatography

AGMP Ammonium molybdophosphate silica

EC Extraction chromatography

GM Geiger Muller

ICP-MS Inductively coupled plasma mass spectrometry

LDPE Low density Polythene

LOD Limit of detection

MEK Methyl ethyl ketone

MIBK Methyl iso-butyl ketone

SE Solvent Extraction

TBP Tri-butyl phosphate

TiOA Tri (iso) octylamine

TnOA Tri octylamine

TPAC Tetra phenyl arsonium chloride

TPAR Tetra phenyl arsonium perrhenate

N/A Information not available in this paper.

Beta Counting implies one of three methods. These are GM counting, anthracene screen counting, or gas flow proportional counting. The exact method was not mentioned in the original reference.

A variety of different yield monitors are routinely used during the determination of ^{99}Tc. Most of these are isotopes of Tc, although Re is still used despite doubts about the possible fractionation of Re from Tc during decontamination stages. Some methods use no yield monitor which would lead to significant errors during determination due to variability in the chemical recovery.

Digestion and solubilisation of Tc from the sample is carried out using a variety of methods. Many of these include Na_2O_2 fusions or hot strong oxidising acids where there is a risk of volatilisation. Care must be taken to ensure minimum loss of Tc through volatilisation, however use of reducing leaching agents (*e.g.* HCl at concentrations of greater than 4 M) may lead to incomplete solubilisation of Tc as much of the Tc will be precipitated as insoluble TcO_2. Decontamination primarily consists of exchange chromatography, occasionally coupled with a $Fe(OH)_3$ scavenge and a subsequent solvent extraction phase to separate Tc from Ru. Optimum recoveries are found in the methods using several decontamination steps back to back rather than relying solely on one purification step. There is an exception with the use of TEVA™ resin.

Final determination is most commonly made using radiometric methods or by ICP-MS, with ICP-MS and LSC giving low levels of detection with reasonable ease. AMS has proven to be the most sensitive method but has not been used on large sample sizes. Other methods prove to be too insensitive for use in the determination of environmental samples but may be useful for the determination of ^{99}Tc in nuclear waste. The lowest levels of detection are achieved by AMS and ICP-MS with some methods using LSC giving comparable limits of detection. ICP-MS and LSC methods do tend to have much larger typical sample sizes aiding the reduction of the limit of detection. Gas flow proportional counting is not as sensitive as ICP-MS or LSC but is the most commonly used due to its availability for routine analysis.

3.7. Reference List

Aarkrog A., Boelskifte S., Dahlgaard H., Duniec S., Hallstadius L., Holm E., Smith J.N. 1987. Technetium-99 and Caesium-134 as long distance tracers in Arctic waters. Estuarine, Coastal and Shelf Science **24.** 637-647.

Anders E. 1960. The radiochemistry of technetium. Office of Technical Studies. Washington DC.

Ashraf Chaudray M., Ahmad B. 1996. Technetium-99m extraction and transport across Tri-n-octylamine - xylene based supported liquid membranes. J. Radioanal. Nucl. Chem. **204** 379-400.

Banavali A.D., Raimondi J.M., Moreno E.M., McCurdy D.E. 1995. The determination of technetium-99 in low level radioactive waste. Radioactivity and Radiochemistry **6.** 26 – 35.

Beals D.M., Hayes D.W. 1996. Technetium-99, Iodine-129 and tritium in the wastes of the Savannah River Suite. Sci. Total. Environ. **173.** 101 – 115.

Browne E. & Firestone R.B. 1986. Table of radioactive isotopes. John Wiley and sons. New York.

Butterworth J.C., Livens F.R., Makinson P.R. 1995. Development of a method for the determination of low levels of technetium-99. Sci. Total. Environ. **173-174.** 293-300.

Carling R.S., Day J.P. 1998. The determination of technetium-99 by accelerator mass spectrometry with particular application to marine samples. Technetium 1998 abstracts. Meeting at SOC 7-7 April 1998.

Chen Q., Dahlguaard H., Nielsen S.P. 1984. Determination of ^{99}Tc in sea-water at ultra low levels. Anal. Chim. Acta **285.** 177 – 180.

Chen Q., Dahlgaard H., Hanson H.J.M., Aarkrog A. 1990. Determination of ^{99}Tc in environmental samples by anion exchange and liquid – liquid extraction at calculated valency. Anal. Chim. Acta **228.** 163 – 167.

Chu N.Y., Feldstien J. 1984. Radiochemical determination of technetium-99. Talanta **31.** 809 – 813.

CRC. 1996. A handbook of Chemistry and Physics. 76th Edition. Lide D.R. (Ed.) CRC Press. New York.

Dale C.J., Warwick P.E., Croudace I.W. 1996. An optimised method for technetium-99 determination in low level waste by extraction into tri-n-octylamine. Radioactivity and Radiochemistry **7.** 23 - 31.

Davis T.M., Nelson D.M. Thompson E.G. 1993. Monitoring of ^{99}Tc in borehole waters using an extraction chromatographic resin. J. Radioactivity & Radiochemistry **4.** 14 – 18.

Dixon P., Curtis D.B., Musgrove J., Roensh F., Roach F., Rokop D. 1997. Analysis of naturally produced technetium and plutonium in geologic materials. Anal. Chem. **69.** 1692 - 1699.

Fardy J.J., Warner I.M. 1992. Determination of ^{99}Tc in environmental materials by ICP-MS. Radioanal. Nucl. Chem. **157.** 239.

Foti S., Delucchi E., Akamian V. 1972. Determination of picogram amounts of technetium in environmental samples by Neutron Activation Analysis. Anal. Chim. Acta **60.** 269 - 276.

Garcìa Leòn M. 1990. Determination and levels of ^{99}Tc in environmental and biological samples. J. Radioanal. Nucl. Chem. **138**. 171 - 179.

Garner W., Spies H. 1986. Determination of technetium by x-ray fluorescence spectrometry. Anal. Chem. **58.** 1261-1263.

Goldchurt N.W., Sedlet J. 1969. Radiochemical determination of technetium-99 in environmental water samples. Anal. Chem. **41.** 669 – 672.

Gray A.L., Date A.R. 1989. Trace element determination by Inductively Couple Plasma Techniques. 1st ed. Blakie, Glasgow, UK.

Harvey B.R., Ibbett R.D., Williams K.J., Lovett M.B. 1991. The determination of technetium-99 in environmental materials. MAFF Directorate of Fisheries research: Aquatic Environmental Protection: Analytical methods **8.** 1 - 22.

Holenbach M., Grohs J., Manich S. 1984. Flow injection sample pretreatment for the determination of radionuclides in soils by ICP-MS. Anon. 21st annual conference of the Federation of Analytical Chemistry and Spectroscopy Societies. **257.** 110.

Holm E., Rioseco J., Garcìa Leòn M. 1984. Determination of ^{99}Tc in environmental samples. Nucl. Inst. Meth. Phys. Res. **233.** 204 - 207.

Holm E. 1993. Radio-analytical studies of technetium in the environment: Progress and problems. Radiochim. Acta **63.** 57 – 62.

Holm E., Rioseco J., Garcìa Leòn M. 1984. Determination of ^{99}Tc in environmental samples. Nuclear Instruments and Methods in Physics research **233.** 204 - 207.

Hirano S., Matsuba M., Kamada H. 1989. The determination of ^{99}Tc in marine algae. Radioisotopes **38.** 186 – 189.

Hirano S., Matsuba M. 1993. Concentrations of technetium-99 in marine algae and sea water. Radiochim. Acta **63.** 79 – 82.

Ihsanullah, East B.W. 1993. Chemical recoveries of Technetium-99 for various procedures using inductively coupled Plasma - Mass Spectrometry. Radioactivity and Radiochemistry **4.** 14-18.

Ihsanullah, East B.W. 1994. Method for the determination of technetium-99 in environmental samples using ICP-MS. Radioactivity and Radiochemistry **5.** 20 – 26.

Kaye J.H., Ballou N.E. 1978. Determination of technetium by atomic absorption spectrometry. Anal. Chem. **44.** 2076-2078.

Kaye J.H., Merrill J.A., Kinnson R.R., Rapis M.S., Bailou N.E. 1982. Radiochemical determination of technetium-99. Anal. Chem. **54.** 1154 - 1163.

King S.J., Oldham C., Popplewell J.F., Carling R.S., Day J.P., Fifield L.K., Creswell R.G., Liu K., diTada M.L. 1997. Determination of Aluminium-26 in biological materials by accelerator mass spectrometry. Analyst **122.** 1049-1055.

Kopunec R., Blazek M. 1994. Comparative study of pertechnetate reduction by thiourea using spectroscopic solvent extraction and ion exchange methods. J. Radionanal. Nucl. Chem. **183.** 171-180.

Lawson B.L., Powell C.R., Pinkerton T.C. 1985. Quantification of ^{99}Tc by LSC: An evaluation of chemical quenching by liquid chromatographic eluents. J. Radioanal. Nucl. Chem. **94.** 71-86.

Long S.E. and Sparks S.T. 1988. A literature survey of techniques for the analytical determination of technetium-99. UK AEA unpublished report.

McAninich J.E., Marchetti A.A., Berquist B.A., Stoyer N.J., Nimz G.J., Cafee M.W., Finkel R.C., Moody K.J., Sideras-Hadded E., Buchholz B.A., Esser B.K., Porctor I.D. 1998. Detection of technetium-99 by accelerator mass spectrometry: preliminary investigations. J. Radioanal. Nucl. Chem. **234.** 125-129.

Maeck W.J., Booman G.L., Kussy M.E., Rein J.E. 1961. Extraction of the elements as Quaternary Propyl, Butyl and Hexyl amine complexes. Anal. Chem. **33.** 1775 - 1750.

Magee R.J., Scott J.A.P., Wilson C.L. 1959. Manganese, technetium and rhenium in standard electrode potentials in aqueous solutions. Talanta **2.** 376.

Matsuoka N., Umatat T., Okamura M., Momoshima N., Takashima Y. 1990. Determination of ^{99}Tc from the aspect of environmental radioactivity. J. Radioanal. Nucl. Chem. **140.** 73 – 78.

Momoshima N., Sayd M., Takashama Y. 1995. Determination of technetium-99 in coastal seawater collected in Fukuoka Japan. J. Radioanl. Nucl. Chem. **197.** 245-251.

Morita S., Tobita K., Kurabayshi M. 1993. Determination of technetium-99 in environmental samples by ICP-MS. Radochim. Acta **63.** 63 – 67.

Nevissi A.E., Siverson M., Strebin R.S., Kaye J.H. 1994. Radiochemical determination of technetuim-99. J. Radioanl. Nucl. Chem. **177.** 91 – 99.

Nicholson S., Howarth J.M., Sanders T.W., Blaine L.M. 1993. Determination of low levels of technetium-99 in environmental samples by ICP-MS. Sci. Total. Environ. **130-131.** 113-117.

Pacer R.A. 1990. Evaluation of counting efficiency, possible container sorption and quenching characteristics in the liquid scintillation counting of ^{99}Tc. Int. J. Appl. Rad. Isot. **31.** 731-736.

Perrier C., Segre E. 1939. Some chemical properties of element 43 II. J. Chem. Phys. **7.** 155-156.

Riley J.P., Siddiqui J.A. 1982. The determination of Technetium-99 in seawater and marine algae. Anal. Chim. Acta. **139.** 167 – 176.

Riley J.P., Siddiqui S.A. 1986. The occurrence of technetium in the Irish Sea. Mar. Poll. Bull. **17.** 229-229.

Rulfs C.L., Meinke W.W. 1952. Observations on some chemical and physical properties of technetium and its compounds. J. Am. Chem. Soc. **74.** 235.

Tagami K., Uchida S. 1993. Separation procedure for the determination of technetium-99 in soil by ICP-MS. Radiochim. Acta **63.** 69 - 72.

Takeuchi M., Tawaka S., Yamawaki M. 1993. Solvent extraction of Tc VII and Re VII from nitric acid solution with the mixture of CM.P6 and TBP. Radiochim. Acta **63.** 79-100.

Walker C.R., Short B.W. Spring H.S. 1980. The determination of technetium-99 by liquid scintillation counting. In: Lyon W.S. (ed). Radioelement Analysis. Ann Abor. Michigan 101 – 110.

Watanabe S., Hashimoto K. 1995. Solvent extraction of technetium in urine with TBP. J. Radioanal. Nucl. Chem. **201.** 361 - 370.

Wigley F., Warwick P.E., Croudace I.W., Caborn J., Sanchez A.L. 1999. Optimised method for the routine determination of technetium-99 in environmental samples by liquid scintillation counting. Anal. Chim. Acta **380.** 73-82.

Willard H.H., Smith G.M. 1939. Tetraphenylarsonium chloride as an analytical reagent for the determination of rhenium. J. Indust. Eng. **11.** 305-306.

Chapter 4

Optimised method for the determination of technetium-99 in environmental samples by liquid scintillation counting

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Optimised method for the routine determination of Technetium-99 in Environmental Samples by Liquid Scintillation Counting

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4.1. Abstract

A method has been developed for the routine determination of ^{99}Tc in a range of environmental matrices using ^{99m}Tc ($t_{½}$ = 6.06 hours) as an internal yield monitor. Samples are ignited stepwise to 550°C and the ^{99}Tc is extracted from the ignited residue with 8M nitric acid. Many contaminants are co-precipitated with Fe $(OH)_3$ and the Tc in the supernatant is pre-concentrated and further purified using anion exchange chromatography. Final separation of Tc from Ru is achieved by extraction of Tc into 5% tri-n-octylamine in xylene from 2M sulphuric acid. The xylene fraction is then mixed directly with a commercial liquid scintillant cocktail. The chemical yield is determined through the measurement of ^{99m}Tc by gamma spectrometry and the ^{99}Tc activity is measured using liquid scintillation counting after a further two weeks to allow decay of the ^{99m}Tc activity. Typical recoveries for this method are in the order of 70 -95%. The method has a detection limit of 1.7 Bq kg^{-1} based on a two-hour count time and a 10g sample size. The chemical separation for twenty-four samples of sediment or marine biota can be completed by one analyst in a working week. A further week is required to allow the samples to decay before determination.

Technetium/analysis/liquid scintillation analysis/environmental samples

4.2. Introduction

Technetium-99 ($t_{½}$ = 2.2 x10^5 years) is a fission product of ^{235}U with approximately a 6% yield. Tc only exists naturally in minute quantities at 0.25 – 0.31 parts per trillion in pitchblende arising from spontaneous fission (Kenna and Kuroda 1964). Most ^{99}Tc in the environment is derived from the discharge of fission waste products from nuclear fuel reprocessing plants and from weapons' fallout. The total input of ^{99}Tc to the environment from weapons' fallout is estimated at 140 TBq Aarkrog *et al.* 1986), while discharges to the marine environment from Sellafield reprocessing plant have been estimated at 1220 TBq from 1954 to 1996 (BNFL Reports 1983-1997; Gray *et al.* 1995). There have been significant increases in inputs of ^{99}Tc into the Irish Sea since the commissioning of the Enhanced Actinide Removal Plant (EARP) in 1994 (Leonard *et al.* 1997) and subsequent treating of stockpiled Medium Active Concentrate (MAC) waste. Discharges from EARP in 1995 were 180 TBq with a reduction to 150 TBq in 1996 (BNFL Reports 1983-1997).

The aim of this study was to develop an effective and robust method for ^{99}Tc determination particularly suited to measurement of the isotope in sediments and marine biota. The low concentrations in many environmental samples, the volatility of Tc, Tc speciation and spectral interferences from yield monitors all cause potential difficulties.

4.3. Methodology

4.3.1 Instrumentation

Determination of ^{99}Tc was made using a using a Wallac 1220 Quantulus™ Ultra Low Level Liquid Scintillation Counter. Liquid Scintillation Counting (LSC) was chosen in preference to Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The benefits of LSC for routine determination of ^{99}Tc include cost effectiveness and limits of detection which are to comparable with ICP-MS. Gas flow proportional counting and anthracene screen counting were not considered to be sensitive enough.

Technetium-99m was measured using a Canberra well-type high purity germanium (HPGe) gamma ray spectrometer. The spectral deconvolution program Fitzpeaks (JF Computing, Stanton in the Vale, UK.) was used to analyse gamma spectra.

4.3.2 Reagents

Analytical reagents and deionised water were used throughout this study. Tri-n-octylamine and mixed xylenes were supplied by Aldrich Chemicals. Instagel™ and Ultima Gold AB™ liquid scintillation cocktails were supplied by Packard UK Ltd, Pangborne, U.K. GoldStar and Ecosafe liquid scintillation cocktails were supplied by Meridian, Epsom, U.K. All other reagents were supplied by Fisher Scientific Ltd, Loughbrough, U.K. Technetium-99 was supplied as sodium pertechnetate by the National Physical Laboratory (NPL), and ^{99m}Tc as Na pertechnetate was generously supplied by Southampton General Hospital.

4.3.3 Method Summary

A schematic summary of the method used for the determination of ^{99}Tc in environmental samples is shown in Figure 4.1. The method can be divided into sample preparation, acid leaching, decontamination and determination stages.

4.3.4 Yield Determination

The ^{99m}Tc yield monitor was counted using a well-type (HPGe) γ ray spectrometer using the 140 keV emission line. As ^{99m}Tc decays to ^{99}Tc, the decay of the yield monitor will contribute to the activity of ^{99}Tc in the sample. The contributed activity is small with a 100 kBq ^{99m}Tc spike decaying to 0.3 mBq of ^{99}Tc daughter. The concentration of ^{99}Tc produced by the decay of ^{99m}Tc in each sample is calculated after correction for the background count.

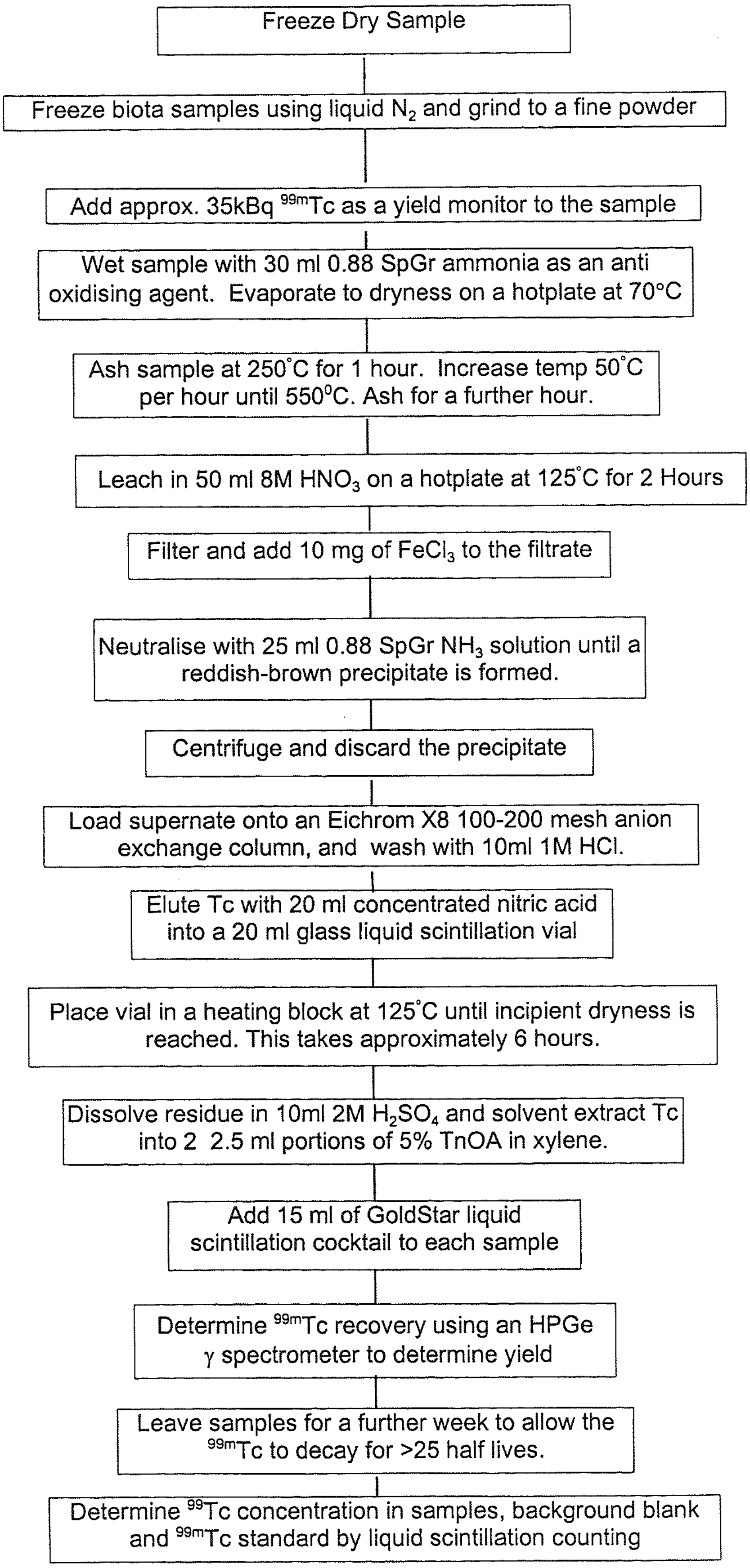

Figure 4.1.Schematic method for the determination of ^{99}Tc in environmental samples.

4.4. Discussion

The different stages in the analytical procedure were investigated in order to determine the optimum conditions for the separation, purification and measurement of ^{99}Tc (*i.e.* where losses of Tc are minimised and contaminants are effectively separated from ^{99}Tc). The loss of Tc at each of the following stages was determined using a ^{99m}Tc spike: (1) sample preparation and ashing; (2) leaching; (3) separation chemistry. Optimisation of ^{99}Tc recovery was tested by using homogenised seaweed, lobster and sediment samples in the ashing and leaching stages. Testing of the reproducibility of the method was made using an in-house reference material. Determination was made on each sub-sample to assess the effectiveness of extraction of ^{99}Tc from the sample matrix. This is because the yield monitor cannot be relied on to act as a faithful comparison until all matrix-bound Tc is in solution.

4.4.1 Choice of Yield Monitor

A number of different isotopes of Tc, and stable Re, have been used as yield monitors for Tc analysis (Table 4.1). As Re could not be relied upon to faithfully follow the Tc separation chemistry, a Tc isotope other than ^{99}Tc was required. Technetium-99m was chosen due to its availability and its readily measurable gamma emission. The short half life of ^{99m}Tc (6.06 hours) also means that the isotope may be allowed to decay prior to the measurement of the ^{99}Tc.

Table 4.1. Potential tracer elements for determination of recovery of ^{99}Tc.

Tracer	Half Life	Determination method	Disadvantages	Reference
^{95m}Tc	60 days	γ spectrometry	Spectral interference / separate determination method required / availability	Goldchurt and Sedlet 1969; Kaye *et al.* 1982
^{97}Tc	2.6×10^6years	ICP-MS	availability / high cost	Beals and Hayes 1996
^{97m}Tc	91 days	γ spectrometry	Spectral interference / separate determination method required / availability	Kaye *et al.* 1982
^{99m}Tc	6.06 hours	γ spectrometry	Spectral interference / separate determination method required / short half life	Chen *et al.* 1994; Holm *et al.* 1984; Martin and Hylko 1987
Re	Stable	ICP-MS, ICP-AES Gravimetric analysis	Spectral interference / separate determination method required / differing chemistry	Harvey *et al.* 1987; Matsuoka *et al.* 1990

4.4.2 Sample preparation

Biota and sediment samples are first freeze-dried and then ground to a fine powder. It was found that the distribution of ^{99}Tc in samples, particularly seaweeds, was heterogeneous. Many seaweeds proved difficult to grind when simply dried. A fine powdered sample was readily obtained however; by first freezing the samples in liquid nitrogen, prior to grinding. Samples with a more delicate tissue structure, such as lobster (*Hommarus gammarus*) and are easily ground without prior freezing.

4.4.2.1 Ashing Conditions

Some previous methods have suggested that loss of Tc may occur on ashing due to the volatilisation of technetium anhydride (Tc_2O_7); the product of dehydrating pertechnic acid ($HTcO_4$) on heating (Harvey *et al.* 1991). Pertechnic acid is formed by the oxidation of Tc in the presence of organic acids. The addition of ammonia to the sample prior to ashing neutralises the free acidic sites on complex organic molecules to inhibit the formation of $HTcO_4$ (Harvey *et al.* 1991; Foti *et al.* 1972). Hydrochloric acid has also been used to prevent the volatilisation of Tc by reducing Tc to its less volatile +4 oxidation state (Harvey *et al.* 1991).

Some controversy exists over the optimum ashing temperature for Tc determination. Losses of more than 50% have been observed at temperatures greater than 500°C (Harvey *et al.* 1991) while ashing temperatures of to up 600°C (Garcia Leon 1990) and 750°C (Holm *et al.* 1984; Tagami and Uchida 1993) have been used with no apparent losses of ^{99}Tc.

a) Effect of temperature and wetting agents on Tc loss during ashing

Ammonia and HCl were tested for their efficiency at reducing the loss of Tc, in samples of marine biota and sediments. In addition 2% $SnCl_2$ was investigated as the compound is widely used as a reducing agent. Approximately 10g of sample was taken and spiked with ^{99m}Tc. Samples were then wetted with either concentrated hydrochloric acid, 2% tin (II) chloride in hydrochloric acid, or 0.88 Specific Gravity (Sp.Gr.) ammonia. A control sample spiked with ^{99m}Tc and which had no other pre-treatment was also ignited. The samples were dried on a hotplate at 125°C and the initial ^{99m}Tc activity determined using an HPGe γ spectrometer. The samples were then heated in a furnace ramped at 50°C per hour to temperatures between 450°C and 900°C. Samples were heated to temperatures between 450°C and 550°C in a furnace with an internal capacity of 80 litres. Samples ignited to 750°C and 900°C were heated in a tube furnace. The ^{99m}Tc activity was again determined and any loss of ^{99m}Tc due to volatilisation was calculated (Figure 4.2a).

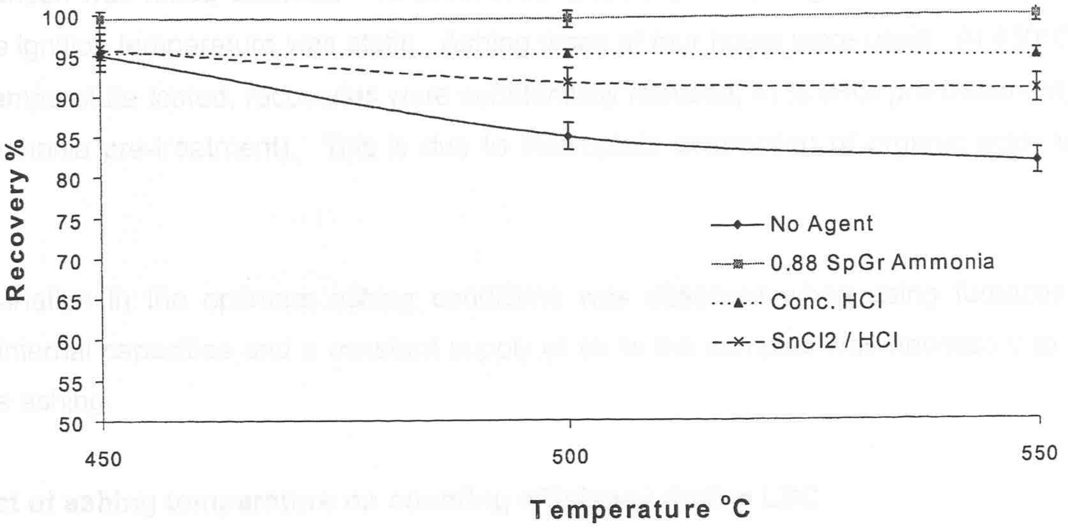

Figure 4.2a. Loss of ^{99m}Tc during ashing. Results are on triplicate measurements of sediment and marine biota samples spiked with ^{99m}Tc. All samples were ignited in a ramped furnace from 250°C with an increase of 50°C per hour. Error bars at 2σ.

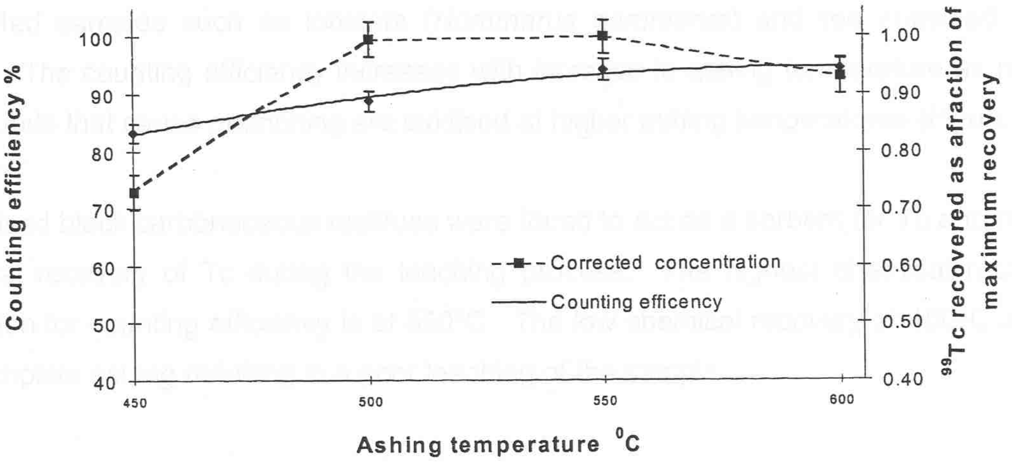

Figure 4.2b. Counting efficiency and loss of ^{99}Tc through separation chemistry as a function of ashing temperature. Homogeneous lobster samples were ashed to 450°C, 500°C, 550°C and 600°C. The remainder of the determination was made using identical conditions, the samples measured by liquid scintillation counting and the final concentrations shown as a percentage of the maximum recovery at 550°C. Measurement was also made of the counting efficiency. Error bars at 2σ.

For sediments, seaweed and lobster samples there was no appreciable loss of Tc at temperatures up to 550°C when ammonia was added prior to ignition. Samples pre-treated with $SnCl_2$ or HCl showed losses of over 5%, while the greatest losses were observed from samples which had no pre-treatment (Figure 4.2a).

A comparison was made between ^{99}Tc recoveries when the sample ignition was ramped and when the ignition temperature was static. Ashing times of four hours were used. At 450°C, the lowest temperature tested, recoveries were substantially reduced, 47% (HCl pre-treatment) and 39% (ammonia pre-treatment). This is due to incomplete destruction of organic acids in the sample.

Some variation in the optimum ashing conditions was observed when using furnaces with smaller internal capacities and a constant supply of air to the samples was necessary to allow complete ashing.

b) Effect of ashing temperature on counting efficiency during LSC

The counting efficiency and apparent ^{99}Tc concentration were determined for a range of ashing temperatures (Figure 4.2b).

It was found that ashing at less than 500°C resulted in incomplete oxidation and subsequent high quenching in the final sample during liquid scintillation analysis. This was especially true in pigmented samples such as lobsters (*Hommarus gammarus*) and red seaweed (*Chrondus cripus).* The counting efficiency increases with increase in ashing temperature as more of the compounds that cause quenching are oxidised at higher ashing temperatures (Figure 4.2b)

Unoxidised black carbonaceous residues were found to act as a sorbent for Tc and reduced the chemical recovery of Tc during the leaching process. The highest chemical recovery after correction for counting efficiency is at 550°C. The low chemical recovery at 450°C is the result of incomplete ashing resulting in a poor leaching of the sample.

4.4.2.2 Leaching

a) Acid type

The effectiveness of several different leaching agents was tested on seaweed, lobster and sediment samples and the comparative recoveries determined (Figure 4.3a). Nitric acid (8 M) showed the highest recovery of ^{99}Tc from 'in-house' seaweed, sediment and lobster reference samples. HCl was less efficient at leaching Tc than HNO_3. This can be explained by the partial reduction of Tc(VII) to Tc(IV) in HCl at concentrations greater than 4 M (Pruett 1981; Watenabe and Hashimoto 1995). Recovery of ^{99}Tc when leaching with diluted *aqua regia* or 8M HCl + 3% H_2O_2 is also lower than that recovered with 8M HNO_3. The reasons for this are unclear but may also be due to loss of Tc through reduction.

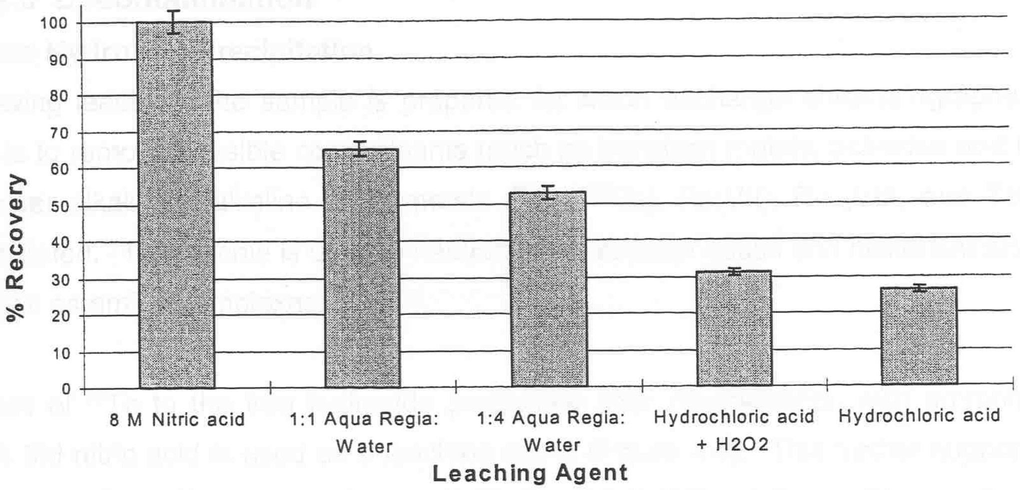

Figure 4.3a. Total ^{99}Tc leached from the sample matrix, using different leaching agents, as a percentage of the total recovered with nitric acid. All samples were heated at 125°C for 2 hours. Error bars at 2σ.

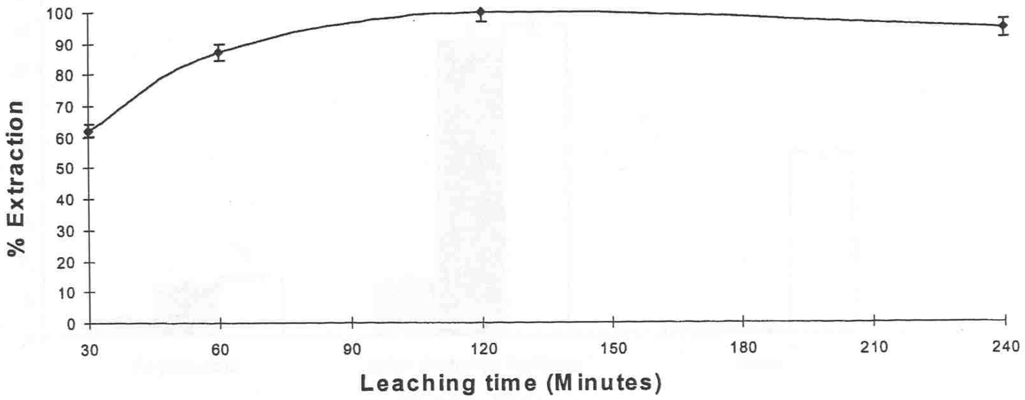

Figure 4.3b. Effect of leaching time on recovery of ^{99}Tc from sample matrices. Homogenous samples were leached for 30 minutes, 60 minutes, 120 minutes and 240 minutes on a hotplate at 125°C in 8 M nitric acid. The remainder of the determination was carried out under identical conditions. Error bars at 2σ.

b) Leaching Time

The effect of leaching time using 8M nitric acid on a hotplate at a temperature of 125°C was tested (Figure 4.3b). The maximum recovery was observed in samples leached for 120 minutes. Samples leached for shorter periods were not thoroughly attacked by the acid resulting in lower recoveries.

4.4.2.3 Decontamination

a) Iron Hydroxide Precipitation

Following leaching, the sample is prepared for anion exchange chromatography. The initial step is to remove possible contaminants (such as transition metals, actinides and lanthanides). However alkali and alkaline earth metals (^{90}Sr, ^{137}Cs), Re(VII), Ru (VIII) and Tc(VII) are not precipitated. If ammonia is used to neutralise the solution cobalt and nickel are also retained in solution as amine complexes.

Losses of ^{99}Tc to the iron hydroxide precipitate after neutralisation with ammonia are lower when 8M nitric acid is used as a leaching agent (Figure 4.4). This further supports the notion that some of the Tc is reduced to insoluble Tc (IV) in HCl solutions. The small quantity of Tc lost to the iron hydroxide precipitate from nitrate solutions is most likely to be occluded Tc (VII).

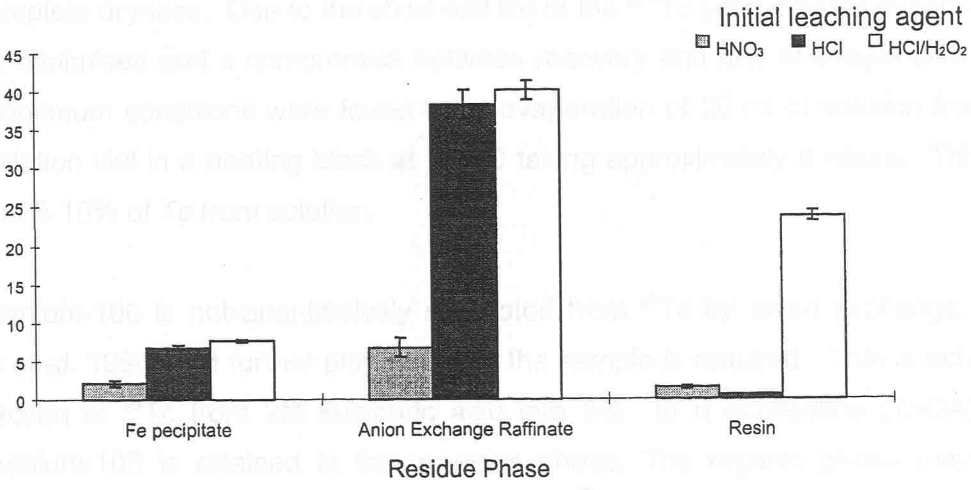

Figure 4.4 Loss of ^{99m}Tc yield monitor to residue phases with different leaching agents. Error bars at 2σ.

b) Anion Exchange Chromatography

Analytical grade anion exchange resin 1X8 (100-200) mesh (Eichrom) was used both for decontamination and concentration of the sample. Technetium is retained on the anion exchange column from alkaline solution. Alkali and alkaline earth metals and divalent transition metals pass through the column into the raffinate separating most of the main contaminants including ^{60}Co, ^{63}Ni, ^{90}Sr and ^{137}Cs from Tc. The anion exchange column also separates Tc from Ca, which would interfere with the solvent extraction separation.

The solutions containing ammonium nitrate, formed by the neutralisation of nitric acid with ammonia, were found to give substantially lower losses of Tc to the raffinate than from ammonia solutions containing ammonium chloride (Figure 4.4). This is expected, as the K_D for Tc in alkaline nitrate media on anion exchange resin is higher than in the corresponding chloride media (Korkish 1989). When solutions are loaded in chloride media with H_2O_2 present from the leaching process, retention of ^{99}Tc on the resin after elution of Tc are higher than if H_2O_2 is not used (Figure 4.4)

c) Solvent extraction

The Tc is eluted from the anion exchange resin column with concentrated nitric acid, evaporated and dissolved in 2 M sulphuric acid for solvent extraction. Some workers noted that potential losses of Tc could occur during this evaporation step. The loss of Tc is increased by the presence of chloride (Dixon *et al.* 1997), and the smallest loss is achieved by evaporation at temperatures less than 80°C.

This study found that the geometry of the container had a significant effect on Tc losses. Losses were higher from beakers than from glass scintillation vials. The vials were narrower and had a restriction at the top, which enhanced refluxing of the solution thereby reducing the amount of Tc lost during evaporation. Loss of Tc occurred if the sample in the vial was heated to complete dryness. Due to the short half life of the ^{99m}Tc yield monitor evaporation times need to be minimised and a compromise between recovery and rate of evaporation must be struck. The optimum conditions were found to be evaporation of 20 ml of solution from a 20 ml liquid scintillation vial in a heating block at 125°C taking approximately 6 hours. This resulted in the loss of 5-10% of Tc from solution.

Ruthenium-106 is not quantitatively separated from ^{99}Tc by anion exchange chromatography Dale *et al.* 1996) and further purification of the sample is required. This is achieved by solvent extraction of ^{99}Tc from 2M sulphuric acid into 5% tri n octylamine (TnOA) in xylene [21]. Ruthenium-106 is retained in the aqueous phase. The organic phase may then be mixed directly with commercial scintillation cocktails As no aqueous phase is then present to contribute to quench, counting efficiencies are higher than if an aqueous solution is mixed directly with the scintillant.

Table 4.2a. Extraction of contaminants into tertiary amines in xylene from 2M sulphuric acid (After Maeck *et al.* 1961).

Element	Extraction into tertiary amines
Tc, Re, Au, Ta.	Quantitative extraction
Mo, W, Ag, Cd.	Partial extraction
Ru, Mn, Fe, Cr, Ni, Co, U, Np, Pu, Am, Be, Na.	No extraction

Table 4.2b. Activities of abundant radioisotopes before and after decontamination.

Sample Type	Potential interferent	Bq in original Sample	Bq after decontamination	Decontamination factor
Seaweed	^{137}Cs	16	<0.016	> 1000
	^{241}Am	11	<0.015	> 730
	$^{106}Ru/^{106}Rh$	5.6	<2	> 3
Sediment	^{137}Cs	12540	<0.017	> 740000
	^{241}Am	24673	<0.014	> 1760000
	$^{106}Ru/^{106}Rh$	8.4	<2	>5

d) Decontamination factors

The effectiveness of the method for decontamination of radionuclides in marine biota and sediment samples was determined for some abundant radionuclides by measuring their activities before and after decontamination chemistry (Table 4.2b). ^{137}Cs, ^{241}Am and ^{106}Ru were chosen as all are usually present in environmental samples and may produce an interference when determination is made by liquid scintillation counting.

The absence of ^{137}Cs, ^{241}Am and ^{106}Ru in the γ spectra of the final liquid scintillation source coupled with the absence of any high energy β emitting isotopes in the liquid scintillation spectra, indicates effective removal of any potential interferants.

The distribution coefficients for Ru between 5% tri-iso octylamine (TiOA) in xylene and 0.5 M H_2SO_4 are as low as 1.7×10^{-3} (Chen *et al.* 1990).

e) Chemical recovery

Table 4.3. Typical recoveries of ^{99m}Tc after separation chemistry

Sample	**Mean Recovery**	**Recovery Range %**	**n**
Method blank	93%	88 - 97	9
Ravenglass sediments	81%	74 - 92	60
Ascophylum nodosum	74%	70 - 79	36
Chrondus crispus	79%	72 - 85	24
Lobster	75%	72 - 78	16
All types	85%	70 - 95	170

Typical chemical recoveries for the method vary between 70% to 95% with a mean of 85% (Table 4.3). Variation depends mainly on the differing sample matrix, with better recoveries generally observed for samples with lower organic carbon content.

4.4.2.4 Liquid Scintillation Counting

Liquid scintillation counting was used to measure the activity of ^{99}Tc in the samples, with di-isopropyl-naphthalene based scintillation cocktails giving the best limits of detection. However it was found that ^{99m}Tc produced a significant interference if it had not decayed (Figure 4.5).

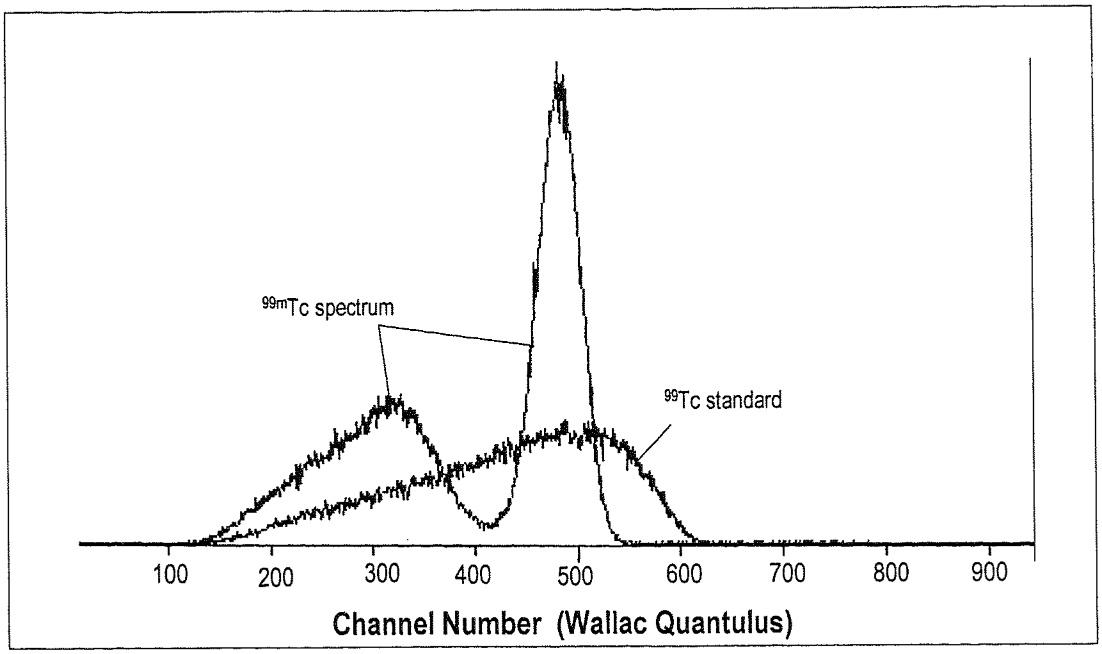

Figure 4.5. Interference of ^{99m}Tc on a ^{99}Tc spectrum.

A ^{99m}Tc standard counted immediately after the determination of the yield monitor has an activity of 5800 dpm and gives a count of 1100cpm, whilst the activity from a typical ^{99}Tc sample is 700 cpm. An interference at such a high level would mean that a reliable determination of low level environmental samples would not be possible, if the ^{99m}Tc yield monitor is not allowed to decay first. A period of seven days (> 25 half-lives) from the determination of the yield monitor was found to be sufficient. This means that the minimum length of time required for the determination of ^{99}Tc is two weeks.

4.4.2.5 Method statistics and reference materials

Method blanks were run though the separation procedure to determine the detection limit (L_D) (Currie *et al.* 1968). For a count time of 120 minutes, a counting efficiency of 90%, a sample weight of 10g and a chemical recovery of 85%, the method has a detection limit of 1.7 Bq kg^{-1}. Reductions could also be made in L_D with an increase in the sample size or a longer count time.

4.4.2.6 Accuracy and precision of the method

As no international environmental reference materials exist for Tc, it was necessary to test the method using a material prepared as a preliminary reference samples at the Scottish Universities Research and Reactor Centre (SURRC). All activities of these samples determined using this method fall within preliminary working ranges established at "Technetium 1998" (8-9 April 1998, at a conference held at Southampton Oceanography centre) (McCartney 1998) (Table 4.4).

Table 4.4. Measured activities of preliminary reference materials.

Sample	Sample activity Bq kg^{-1} Measured	1σ	Working Range Bq kg^{-1} Reported *
A	5.3	2	1.8 – 5.3
B	36.7	2	37 – 88
C	4233	70	3000 – 4700
D	16441	1050	13000 – 23000
E	142383	6200	102000 - 172000

*Preliminary working values presented at Technetium 1998 (McCartney 1998)

4.5. Conclusions

1. A method has been developed to determine ^{99}Tc in a variety of environmental matrices including seaweed, lobster and sediments, using ^{99m}Tc as the yield monitor. Tc-99m was found to be the most suitable yield monitor.
2. 0.88 SG ammonia was found to effectively reduce the loss of ^{99}Tc through volatilisation during ashing.
3. The optimum ashing condition was to gradually increase the temperature from 250°C to 550°C at 50°C increments per hour as it minimises losses of Tc.
4. Optimum leaching was found to be with 8M nitric acid heated for two hours on a hotplate at125°C.
5. Initial concentration and decontamination of ^{99}Tc was using an iron hydroxide precipitation, anion exchange using Eichrom X8 (100–200) mesh anion exchange resin, and removal of ruthenium by solvent extraction of Tc into 5% TnOA in xylene.
6. The yield monitor is determined using a HPGe γ-ray spectrometer. Recoveries are typically in the range of 75% -95%.
7. Determination of ^{99}Tc is made after a further week following the ^{99m}Tc decay. The method has a limit of detection of 1.7 Bq kg^{-1} assuming a 10g sample size and a 2 hour count time.

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4.6. Reference List

Aarkrog A., Dahlgaard H., Hallstadius L., Holm E., Mattsson S., Rioseco J. In Desmet G., Myttenaere C. (Eds). "*Technetium in nature*". Elsevier. Science, London, UK. 69-78.

Beals D.M., Hayes D.W. 1996. Technetium-99, iodine-129 and tritium in the wastes of the Savannah River Suite. Sci. Total. Environ. **173.** 101 – 115.

BNFL. 1983-1987. Annual report on the radioactive discharges and monitoring of the environment. Directorate of Health, Safety & Environmental Protection. BNFL. Warrington.

Chen Q., Dahlgaard H., Hanson H.J.M., Aarkrog A. 1990. Determination of ^{99}Tc in environmental samples by anion exchange and liquid – liquid extraction at calculated valency. Anal. Chim. Acta **228.** 163 – 167.

Currie L.A. 1968. Limits for qualitative detection and quantitative determination: Application to radiochemistry. Anal. Chem. **40.** 586 - 593.

Dale C.J., Warwick P.E., Croudace I.W. 1996. An optimised method for technetium-99 determination in low level waste by extraction into tri-n-octylamine. Radioactivity and Radiochemistry **7.** 23 - 31.

Dixon P., Curtis D.B., Musgrove J.,Roensh F., Roach F., Rokop D. 1997. Analysis of naturally produced technetium and plutonium in geologic materials. Anal. Chem. **69.** 1692 - 1699.

Foti S., Delucchi E., Akamian V. 1972. Determination of picogram amounts of technetium in environmental samples by neutron activation analysis. Anal. Chim. Acta **60.** 269 - 276.

Garcìa Leòn M. 1990. Determination and levels of ^{99}Tc in environmental and biological samples. J. Radioanal. Nucl. Chem. **138.** 171 - 179.

Gray J., Jones S.R., Smith A.D. 1995. Discharges to the environment from the Sellafield site 1951-1992. J. Radiol. Prot. **15.** 99-131.

Goldchurt N.W., Sedlet J. 1969. Radiochemical determination of technetium-99 in environmental water samples. Anal. Chem. **41.** 669 - 673.

Harvey B.R., Ibbett R.D., Williams K.J., Lovett M.B. 1991. The determination of technetium-99 in environmetal materials. MAFF Directorate of Fisheries research: Aquatic Environmental Protection: Analytical methods **8.** 1 - 22.

Holm E., Rioseco J., Garcìa Leòn M. 1984. Determination of ^{99}Tc in environmental samples. Nuclear Instruments and Methods in Physics research **233.** 204 - 207.

Kaye J.H., Merrill J.A., Kinnson R.R., Rapis M.S., Bailou N.E. 1991. Radiochemical determination of technetium-99. Anal. Chem. **54.** 1154 - 1163.

B.T. Kenna, P.K. Kuroda. 1964. Technetium in nature. J. Inorg. Nucl. Chem. **26.** 493 - 499.

Korkish J. 1989. Handbook of ion exchange resins: Their application to inorganic analytical chemistry. CRC Press. Boca Raton, Fla, USA.

Leonard K.S., McCubbin D., Brown J., Bonfield R.A., Brooks T. 1997. A summary report of the distributions of ^{99}Tc in UK coastal waters. Radioprotection Colloques **32.** 109 – 114.

Maeck W.J., Booman G.L., Kussy M.E., Rein J.E. 1961. Extraction of the elements as quaternary propyl, butyl and hexyl amine complexes. Anal. Chem. **33.** 1775 - 1750.

Martin J.E., Hylko J.M. 1987. Measurement of ^{99}Tc in low level radioactive waste from reactors, using ^{99m}Tc as a tracer. J. Appl. Radiat. Isot. **38.** 447 - 450.

Matsuoka N., Umatat T., Okamura M., Monoshima N., Takashima Y. 1990. Determination of ^{99}Tc from the aspect of environmental radioactivity. J. Radioanal. Nucl. Chem. **140.** 73 – 78.

McCartney M. 1997. Personal communication. Paper presented at Tc 1998, a conference held at the Southampton Oceanography Centre.

Pruett D.J. 1981. The solvent extraction behaviour of technetium: Part II the hydrochloric acid- tri-n-butyl phosphate system. Radiochim. Acta, **29.** 107

Tagami K., Uchida S. 1993. Separation procedure for the determination of Technetium-99 in soil by ICP-MS. Radiochim. Acta **63.** 69 - 72.

Watanabe S., Hashimoto K. 1995. Solvent extraction of technetium in urine with TBP. J. Radioanal. Nucl. Chem. **201.** 361 - 370.

Chapter 5

Optimised method for the sequential extraction of ^{99}Tc from sediments

Chapter 5. Optimised method for sequential extraction of ^{99}Tc from sediments

5.1. Abstract

A method has been developed for the sequential extraction of ^{99}Tc from sediments. The extraction procedure uses an operationally defined method to extract exchangeable Tc, reducible Tc and oxidisable Tc. An initial water wash has been added to extract any occluded Tc, and a final leach in 8 M HNO_3 is used to dissolve any residual Tc. Isolation of ^{99}Tc uses extraction onto TEVA resin for extracts 1-4 and the isolation procedure defined by Wigley *et al.* (1999) to purify extract 5. ^{99m}Tc is used as a yield monitor, and determination is by liquid scintillation counting. Limits of detection are dependent on the amount of ^{99m}Tc tracer added but were found to be as low as 5.5 Bq/kg for a sample of a mass of 2 g. Samples determined by sequential extraction showed ^{99}Tc in each of the extractable fractions but with differing ^{99}Tc activities in either exchangeable or oxidisable fractions in separate samples.

5.2. Introduction

This chapter describes the results of an operationally defined extraction system for ^{99}Tc in sediments. This is due to the low concentrations of Tc in most sediments, the volatility of Tc, Tc speciation during decontamination chemistry as well as possible interferences from yield monitors. After the extraction procedure the method is designed to quantitatively separate ^{99}Tc from potential interferences, concentrating the sample enough so that determination can be made.

Several methods have been developed for the sequential extraction of metals from sediments. Most are based on the Tessier procedure which attempts to extract particular compounds or oxidation states of an element (Tessier *et al.* 1979). Results obtained using slightly different extraction procedures and experimental conditions can vary widely (Robinson 1985, Tipping *et al.* 1985, Rauret *et al.* 1989). Although much useful information has been gained from such studies careless use of these techniques without an understanding of their flaws and limitations leads to the generation of erroneous or misleading data (Pickering 1981).

Chemical speciation can be defined as: "The process of identifying and quantifying the different species, forms or phases present in a material, or the description of these" (Davidson *et al.* 1994). The species can be defined (a) functionally, (b) operationally, according to the reagents or procedures used in their isolation, or most specifically (c) as particular compounds or oxidation states of an element (Ure 1990). Most samples collected for radiometric determination are significantly disturbed by the sample collection procedure and subsequent exposure to an oxidizing environment particularly during freeze-drying and dissagregation of sediment. Sequential extraction does however, provide a physio-chemical association gradient between metals and associated solid particles (Martin *et al.* 1987). This is best expressed by an operationally defined procedure, which will not attribute ^{99}Tc activities to chemical forms or oxidation state which are likely to have been altered.

Accumulation of Tc has been observed in both aerobic and anaerobic sediments in laboratory experiments (Fowler *et al.* 1983, Henrot 1989). Sediments can therefore be assumed to act as a sink for Tc, although due to the conservative behavior of the TcO_4^- oxy-anion, the possibility of Tc re-mobilization as a result of Eh or pH changes in the sediment profile can be significant. The bulk determination of ^{99}Tc activity in sediment does not give a reliable estimate of the likely environmental impact, or possible dose from transfer from the saltmarsh sediments into the food chain. Transfer to the food chain may be the through direct transfer from sediment to food through nutrient uptake, grazing or if sediments are dredged and used as landfill (Fostner *et al.* 1990). Sequential extraction enables determination of the potential availability or remobilization of ^{99}Tc species within the sediment. A method for the sequential extraction and determination of ^{99}Tc would therefore allow an assessment of the potential environmental impact of ^{99}Tc discharges.

In aerobic sediments Tc is thought to be present as TcO_4^- which is belived to act conservatively (Fowler *et al.* 1983). The method should therefore try to distinguish between Tc that has simply dried in the sediment and Tc that has been adsorbed to particulate material. It is also possible that Tc may have been co-precipitated within diagenetic minerals or accumulated by organic material or organisms within the sediment, and the method should aim to distinguish between these.

5.3. Methodology

5.3.1. Instrumentation

Determination of ^{99}Tc was made using a using a Wallac 1220 Quantulus Ultra Low Level Liquid Scintillation Counter. ^{99m}Tc was measured using a Canberra well-type high purity germanium (HPGe) gamma ray spectrometer. The spectral deconvolution programme Fitzpeaks (JF Computing, Stanton in the Vale, UK) was used to analyse gamma spectra.

5.3.2. Reagents

Analytical reagents and deionised water were used throughout this study. TEVA resin was supplied by Hichrom Ltd, Cupar, Fife, U.K. Gold Star liquid scintillation cocktail was supplied by Meridian, Epsom, U.K. All other reagents were supplied by Fisher Scientific Ltd, Loughbrough, U.K. ^{99}Tc was supplied as sodium pertechnetate by the National Physical Laboratory (NPL), and ^{99m}Tc as ammonium pertechnetate was obtained from Southampton General Hospital.

5.3.3. Method Summaries

This method was developed using saltmarsh sediments from the Thornflatt saltmarsh, Esk Estuary as no standard reference materials exist for ^{99}Tc in sediments. Sediment was taken from the Waarde saltmarsh on the Westerschelde Estuary, southwest Netherlands to act as a method blank as sediment from the top few centimeters was not found to have bulk ^{99}Tc activities above limits of detection. Bulk determination of total ^{99}Tc activity in each sample was made using a standard procedure for bulk ^{99}Tc analysis (Wigley *et al.* 1999). TEVA resin was used to isolate ^{99}Tc as this readily extracts Tc from most sample solutions except where there is a high nitrate concentration (Hichrom 1996). As the final extraction is made using nitric acid, isolation of Tc was by the method described in Chapter 4. This procedure was not found to work effectively for all extracts due to the variations in the chemistry of the extract solutions. A schematic summary of the method used for the sequential extraction and determination of ^{99}Tc in sediments is shown (Figure 5.1).

5.3.4. Yield Determination

The ^{99m}Tc yield monitor was counted using a well-type (HPGe) γ ray spectrometer using the 140 keV emission line. As ^{99m}Tc decays to ^{99}Tc, the decay of the yield monitor will contribute to the activity of ^{99}Tc in the sample. The contributed activity is small with a 100 kBq ^{99m}Tc spike decaying to 0.3 mBq of ^{99}Tc daughter. The concentration of ^{99}Tc produced by the decay of ^{99m}Tc in each sample is calculated after correction for the background count.

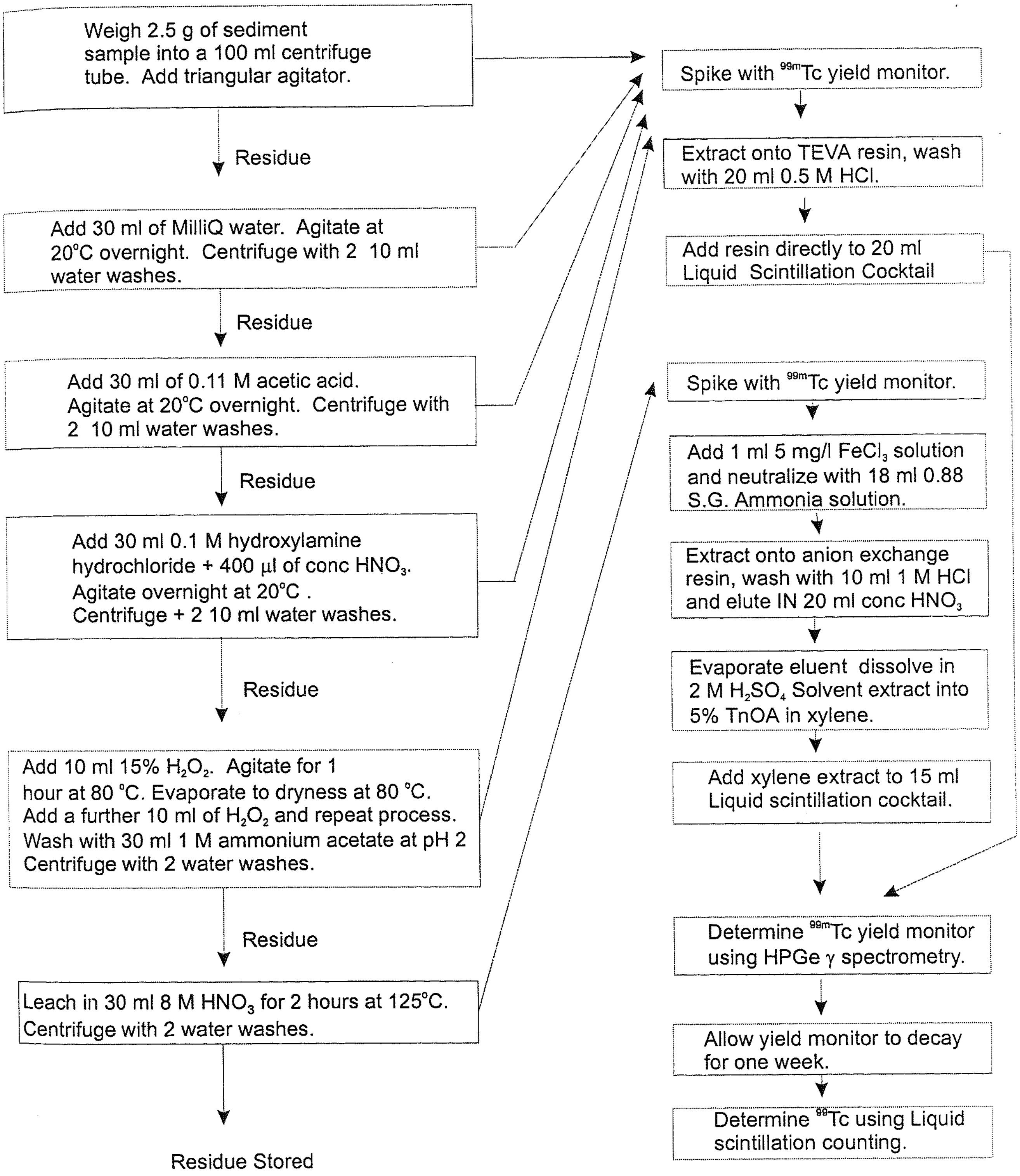

Figure 5.1. Schematic method for the sequential extraction, decontamination and determination of ^{99}Tc in sediments.

5.4. Discussion

The different stages in the extraction and analytical procedures were investigated in order to determine optimum conditions for the extraction, purification and measurement of ^{99}Tc (*i.e.* where losses of Tc are minimized and the contaminants effectively separated from ^{99}Tc). Losses and recovery of Tc were determined using ^{99m}Tc spikes during both the extraction and decontamination procedures.

5.4.1. Extraction method

Sequential extracts were chosen to represent water soluble Tc, adsorbed Tc, reducible Tc, oxidisable Tc, and residual Tc. A method exists for the sequential extraction and speciation of heavy metals in sediments, which extracts an adsorbed fraction, a reducible fraction and an oxidisable fraction (Davidson *et al.* 1994). Sequential leaching was carried out in a 100 ml centrifuge tube agitated by a triangular stirring bar and that allows efficient leaching of the sample. This proved to be more effective than an end-over-end shaker particularly where leaching at an elevated temperature was required. Centrifugation is carried out at 1500G (Howe 1998. Pers. Com.). The washings were found to contain residual Tc, which was quantitatively removed by a further two washes with Milli-Q water (Figure 5.2).

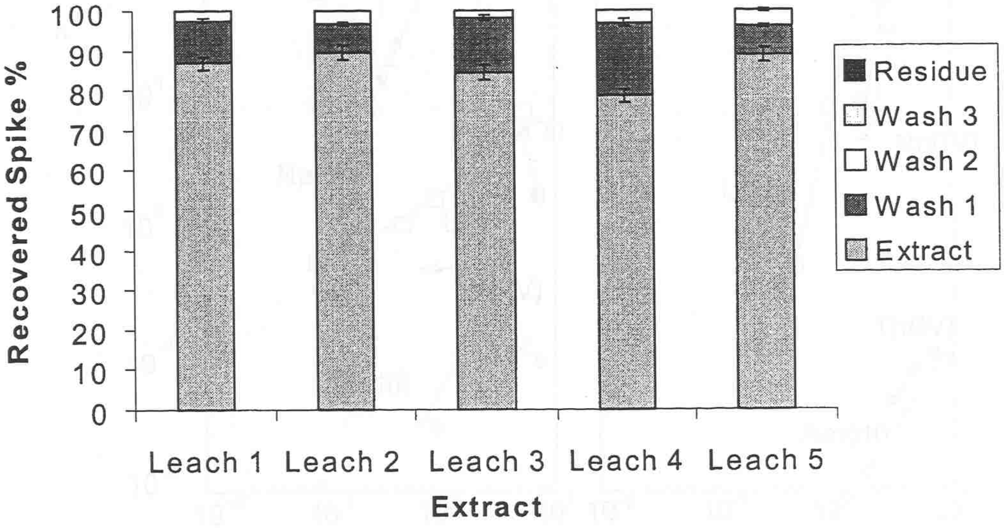

Figure 5.2. ^{99m}Tc spike recovered from sequential extracts and washings of residue to the determinant solution after centrifugation. This experiment was carried out using 'Blank' sediment spiked with ^{99m}Tc. Leach 1 is a water wash. Leach 2 is with 0.1 M acetic acid. Leach 3 is with 0.1 M hydroxylamine hydrochloride. Leach 4 is with 2 x 10 ml 15% hydrogen peroxide. Leach 5 is with 8 M nitric acid.

5.4.2. Decontamination

TEVA resin was used for decontamination of ^{99}Tc from potentially interfering radionuclides (including ^{60}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am) from extracts 1-4. It was found that as little as 0.5g (dry weight) of TEVA resin was required for complete extraction of Tc from approximately 50 ml of extract solution. The resin was then washed with 20 ml 0.5 M HCl to remove any actinides that may be present (Figure 5.3). The resin is then added directly to the scintillant. The main interferences when using liquid scintillation counting are ^{60}Co, ^{63}Ni, ^{106}Ru and ^{110m}Ag as well as possible interferences from γ-emitting radioisotopes like ^{137}Cs and ^{241}Am (Holm 1993, Garcia Leon 1990). These are all quantitatively separated from ^{99}Tc during the extraction process (Table 5.1).

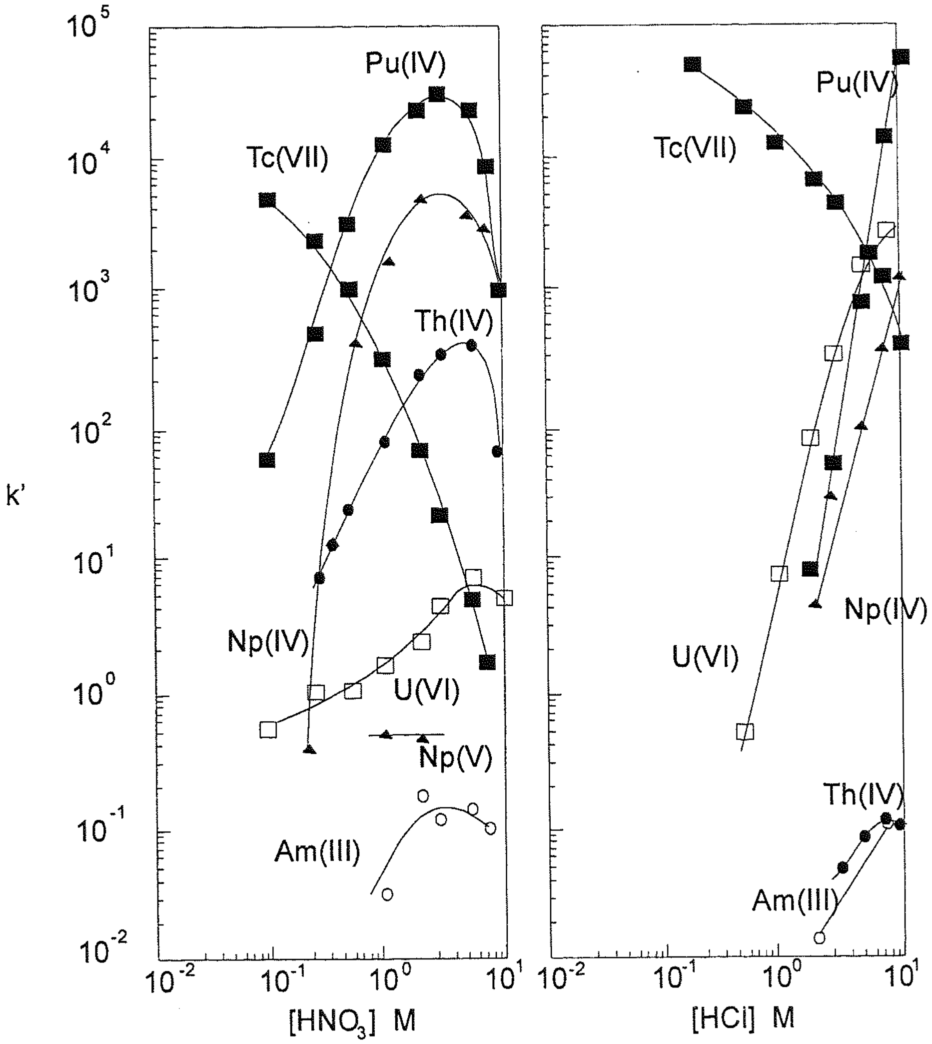

Figure 5.3. Acid dependency of k' for various ions at 23°C (Hichrom 1996).

Potential interferences present in Extract 5 are separated from ^{99}Tc using an iron hydroxide precipitation, anion exchange chromatography and a final extraction into 5% TnOA in xylene (Wigley *et al.* 1999). This procedure was chosen for ^{99}Tc isolation as the high nitrate concentration makes adsorption of Tc to the TEVA resin inefficient (Figure 5.3) and does not allow quantitative removal of either ^{241}Am or ^{137}Cs from the sample (Table 5.1). This decontamination procedure was found to give poorer recoveries for extracts 1-4 than using TEVA resin due to the varied nature of the sample solutions.

Table 5.1. Activities of abundant radioisotopes before and after decontamination for a sediment taken from the Thornflatt Saltmarsh, Cumbria.

Extract Fraction	**Potential interference**	**Bq in original extract**	**Bq after decontamination**
1	^{137}Cs	<0.2	<0.2
	^{241}Am	<0.04	<0.04
2	^{137}Cs	0.7	<0.2
	^{241}Am	3.1	<0.04
3	^{137}Cs	0.6	<0.2
	^{241}Am	31	<0.04
4	^{137}Cs	5.0	<0.2
	^{241}Am	22	<0.04
5 (TEVA)	^{137}Cs	18	2.8
	^{241}Am	19	6.2
5	^{137}Cs	18	<0.2
	^{241}Am	19	<0.04
Residue	^{137}Cs	17	N/A
	^{241}Am	2.3	N/A

In the original samples ^{60}Co and ^{106}Ru activities were approximately at their limits of detection. After decontamination neither of these radioisotopes was observed interfering with ^{99}Tc during liquid scintillation counting.

5.4.3. Reproducibility

Sediments samples were taken from the Thornflatt saltmarsh on the Esk Estuary and their ^{99}Tc activity determined. These samples were sub-divided into three aliquots and each was determined using the sequential extraction method.

Table 5.2. Reproducibility of the sequential extraction procedure.

Extraction Step	Sample Rc7-2 Mean (n=3) Bq/kg	RSD (%)	Sample Rc7-13 Mean (n=3) Bq/kg	RSD (%)	Sample Rc7-19 Mean (n=3) Bq/kg	RSD (%)
1	9	5	< 6.2		44	7
2	8	9	< 5.6		34	2
3	23	9	116	4	13	5
4	106	5	22	9	15	3
5	23	6	19	3	12	8
Sum	170		65		120	
Total*	180	3	69	4	115	4

* Total activities were determined on a separate sample subset using a bulk determination method (Wigley *et al.* 1999).

Where ^{99}Tc activities were above detection limits, there is a variation of less than 10% relative standard deviation in the reproducibility of results (Table 5.2). The error may be propagated through the determination and so a sum total should not be relied on. Several factors may contribute to the lack of precision, including variability of sampling and the efficiency and selectivity of the extraction procedure as well as errors arising from the decontamination process, although the yield monitor should correct for these.

5.4.4. Chemical recovery and limits of detection

Table 5.3. Typical recoveries of ^{99m}Tc after separation chemistry.

Extract Fraction	Mean Recovery	Recovery range %	n
Extract A	95%	83 – 100	36
Extract B	99%	97 – 100	36
Extract C	96%	91 – 100	36
Extract D	95%	89 – 100	36
Extract E (TEVA)	3.5%	1.25 – 9	36
Extract E ($Fe(OH)_3$, anion exchange, extraction into TnOA)	81%	74 -92	36
All extracts	93%	84 - 100	180

Typical recoveries for the sediments determined vary slightly for the first four fractions but are over 90%, showing good extraction of the Tc to the TEVA resin (Table 5.3). As fraction 5 has a high concentration of nitrate the extraction of Tc from solution is also not efficient with approximately 3.5% of Tc extracted from solution. A decontamination procedure using iron hydroxide precipitation, anion exchange chromatography, and extraction into TnOA in xylene

(Wigley *et al.* 1999), gives a better recovery although not as high as extraction of the first four fractions with TEVA resin (Table 5.3).

Table 5.4. Limits of detection for sequential extracts (Currie 1968). Based on a count time of 480, minutes a sample weight of 1g and typical chemical recoveries (Table 5.3).

Extract Fraction	L_D (Bq / kg)
1	6.3
2	5.5
3	7.0
4	6.4
5	7.1

Limits of detection (L_D) were calculated (Table 5.4) using the typical recoveries. Variations in the limits of detection are mainly due to differing levels of ^{99}Tc, which has decayed from the ^{99}Tc yield monitor.

5.5. Environmental implications of sequential extraction data

Sediment samples were collected from the Thornflatt Saltmarsh, River Esk, Cumbria, in July 1996. Sub-samples were analyzed for ^{99}Tc and the samples with peak activities determined using the sequential extraction method (Figure 5.3).

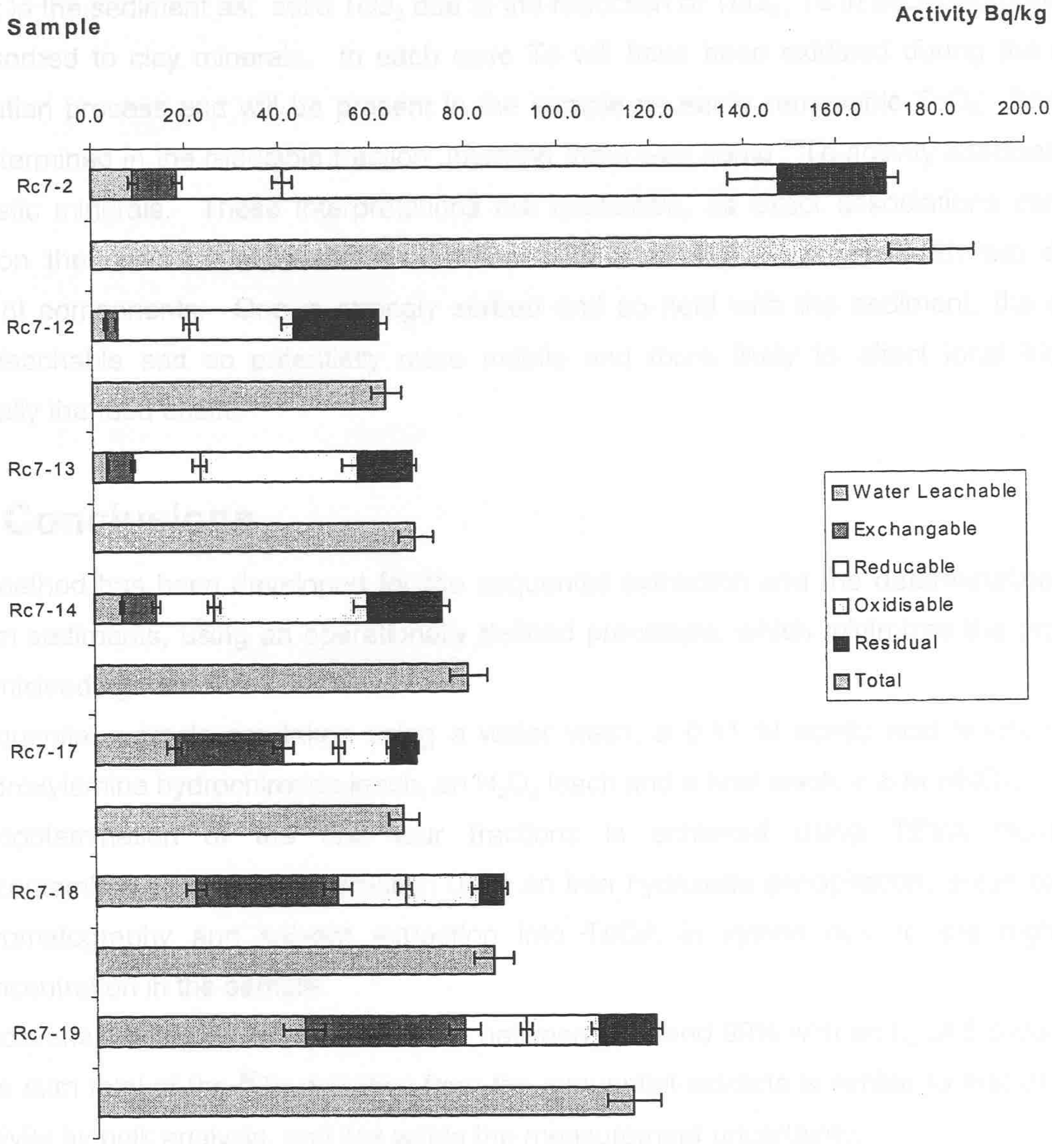

Figure 5.3. Comparison of operationally defined partitioning of ^{99}Tc in a sediment core compared to bulk analysis for each sample. Error bars for the sequential extracts are at 10% based on triplicate determinations, and at 5% for the bulk analyses.

^{99}Tc is measurable in all fractions of the sediment samples (Figure 5.3) with different samples containing different proportions of ^{99}Tc in each extract. The total ^{99}Tc activity from all sequential extracts differs slightly from that of the bulk analysis for each sample but is always within the measurement uncertainty. This difference is likely to be due to a propagation of errors during the sequential extraction process. There is also no trend of bulk analyses being higher or lower than that of the sum of the extraction method.

In samples where the ^{99}Tc activities are highest in the oxidisable fractions (samples 2, 12, 13, 14,), accumulation is likely to be in association with organic material or strong associations with a minerogenic fraction in the sediment. In samples where ^{99}Tc activity is dominantly associated with the water soluble and the exchangeable fractions, ^{99}Tc in these samples is likely to be present in the sediment as: solid TcO_2 due to the reduction of TcO_4^-, Tc in occluded pore water, or Tc sorbed to clay minerals. In each case Tc will have been oxidized during the sample preparation process and will be present in the sample as easily removable TcO_4^-. Some ^{99}Tc was determined in the reducible fraction, implying there was some ^{99}Tc activity associated with diagenetic minerals. These interpretations are qualitative, as exact associations cannot be made on the basis of sequential extractions. Tc is clearly associated with two different sediment components. One is strongly sorbed and so held with the sediment, the other is easily leachable and so potentially more mobile and more likely to affect local biota and eventually the food chain.

5.6. Conclusions

1. A method has been developed for the sequential extraction and the determination of ^{99}Tc from sediments, using an operationally defined procedure, which minimizes the production of misleading data.
2. Sequential extracts are taken using a water wash, a 0.11 M acetic acid leach, a 0.1 M hydroxylamine hydrochlroride leach, an H_2O_2 leach and a final leach in 8 M HNO_3.
3. Decontamination of the first four fractions is achieved using TEVA resin whilst decontamination of the final fraction uses an iron hydroxide precipitation, anion exchange chromatography and solvent extraction into TnOA in xylene due to the high nitrate concentration in the sample.
4. Recoveries during decontamination are between 81% and 99% with an L_D of 5.5 Bq/kg.
5. The sum total of the ^{99}Tc activities from the sequential extracts is similar to that of the ^{99}Tc activity by bulk analysis, and lies within the measurement uncertainty.
6. Samples collected from the Esk Estuary contain measurable ^{99}Tc activity in each of the fractions. Some fractions have most ^{99}Tc easily leached from the sample and for others the ^{99}Tc is only leached from the sample using a strong oxidizing agents. This implies that ^{99}Tc is associated with more than one sediment component.

5.7. References

Aarkrog A., Dahlgaard H., Hallstadius L., Holm E., Mattsson S.. Rioseco J. 1986. In Desmet G., Myttenaere C. (eds). "*Technetium in nature*" Elsevier. 69 – 78.

Currie L.A 1968. Limits for qualitative detection and quantitative determination: Application to radiochemistry. Anal. Chem. **40.** 586 - 593.

Davidson C.M., Thomas R.P., McVey S.E., Perala R., Littlejohn D. and Ure A. 1994. Evaluation of a sequential extraction procedure for the speciation of heavy metals in sediments. Anal. Chim. Acta **291.** 277-286.

Forstner U., Ahlf W., Calmano W., Kersten M., Schoer J. 1990. NATO. ASI. Series G. **23.** 1.

Fowler S.W., Aston S.R., Benayon G., Parsi P. 1983. Bioavailabilty of technetium from artificially labelled North East Atlantic deep sea sediments. Mar. Environ. Res. **8.** 87 – 100.

Garcìa Leòn M. 1990. Determination and levels of ^{99}Tc in environmental and biological samples. J. Radioanal. Nucl. Chem. **138.** 171 - 179.

Gray J., Jones S.R., Smith A.D. 1995. Discharges to the environment from the Sellafield site 1951-1992. J. Radiol. Prot. **15.** 99-131.

Henrot J. 1989. Bioaccumulation and chemical modification of technetium by soil bacteria. Health Physics **57.** 238 – 245.

Hichrom 1996. Personal communication.

Holm E. 1993. Radioanalytical studies of technetium in the environment: Progress and problems. Radiochim. Acta **63.** 57 – 62.

Kennedy V.H., Sanchez A.L., Oughten D.H., Rowland A.P. 1997. Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake. Analyst **122.** 89-100.

Kenna B.T., Kuroda P.K. 1964. Technetium in nature. J. Inorg. Nucl. Chem. **26.** 493 - 499.

Leonard K.S., McCubbin D., Brown J., Bonfield R.A., Brooks T. 1997. A summary report of the distributions of ^{99}Tc in UK coastal waters. Radioprotection Colloques **32.** 109 – 114.

Martin J.M., Nirel P., Thomas A.J. 1987. Sequential extraction techniques: Promises and problems. Mar. Chem. **22.** 313 - 314.

Pickering W.F. 1981. Selective chemical extraction of soil components and bound metal species. Crit. Rev. Anal. Chem. **2.** 233-266.

Rauret G., Rubio R., Lopez-Sanchez J.F. 1989. Int. J. Environ. Anal. Chem. **36.** 69 - 78.

Robinson G.D. 1984. Sequential chemical extractions and metal partitioning in hydrous Mn-Fe oxide coatings: Reagent choice and substrate composition affect results. Chem. Geol. **47.** 97-112.

Tessier A., Campell P.G.C. and Bisson M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. **51.** 844-85.

Tipping E., Heaterington N.B., Hilton J., Thompson D.W., Bowles E. and Hamilton-Taylor J.H. 1985. Artifacts in the use of selective chemical extraction to determine distributions of metals between oxides of manganese and iron. Anal .Chem. **57.** 1944-1946.

Ure A.M. 1990. In Alloway (Ed.), Soils. Blakie and Son, Glasgow.

Wigley F., Warwick P.E., Croudace I.W., Caborn J., Sanchez A.L.. 1999. Optimized method for the routine determination of technetium-99 in environmental samples by liquid scintillation counting. Analytica Chimica Acta **380.** 73-82.

Chapter 6

The behaviour of ^{99}Tc in a saltmarsh environment

Chapter 6. Behaviour of ^{99}Tc in saltmarsh sediments.

6.1. Abstract

This chapter is a study of the chemical behaviour of Tc in saltmarsh sediments. Radionuclide activity depth profiles of sediment cores taken from the Thornflatt saltmarsh, Carlaverock saltmarsh and Ribble Estuary were determined along with stable elements. Variations in the ^{99}Tc activity profiles are studied by comparison with discharge from Sellafield and the diagenetic processes, shown by stable element trends, occurring in the sediment cores. The elevated post-EARP discharges are manifested at the top of most of the sediment cores, while the high ^{99}Tc discharges from Sellafield in 1979 are not seen to directly correlate with ^{99}Tc maxima in the sediment cores. ^{99}Tc accumulations occur where fluctuations in the redox potential in the sediments, indicated by fluctuations in stable element trends, are observed. A further attempt is made to clarify the Tc-sediment associations using a sequential extraction procedure. ^{99}Tc in sediment samples from the maxima seen to correlate with Sellafield discharges is only removed by strong oxidizing agents while ^{99}Tc associated with maxima which correlate with fluctuations in redox potential is removed in a water wash and exchangeable fraction. This can be interpreted as initial accumulation of Tc as strongly bound species, followed by subsequent oxidation and remobilization of Tc. This is followed by secondary accumulation where redox conditions are favorable.

6.2. Introduction

The inability of the Enhanced Actinide Removal Plant (EARP) to separate ^{99}Tc from the waste stream as well as the processing of previously stockpiled wastes brought about a 20 fold increase of ^{99}Tc discharges to the environment (BNFL Reports 1983-1997). Other inputs of ^{99}Tc to the Irish Sea also occur from BNFL Springfields, BNFL Capenhurst and from weapons fallout (Chapter 2). Accumulation of ^{99}Tc in marine organisms has been thoroughly studied (Bonnotto *et al.* 1985, Masson *et al.* 1989, Busby *et al.* 1997). However, to date only laboratory based studies have been made on the geochemical behaviour of ^{99}Tc in sediments (Fowler 1983, Masson *et al.* 1989, Henrot 1989).

Thermodynamic data suggests that Tc will be present in oxygenated seawater as TcO_4^- which will behave conservatively (Till 1986). Approximately 10% of discharged ^{137}Cs associates with the particle phase (Jeffries *et al.* 1973) whilst nearly all the ^{241}Am is particle associated (Day and Cross 1981). According to published K_D data ^{99}Tc will show 30 times less association with particulate than ^{137}Cs (IAEA 1985). Tc is therefore believed to behave conservatively in well oxygenated seawater (Aarkrog *et al.* 1986). Laboratory based experiments suggest possible mechanisms for the accumulation of Tc in sediments including: sorption to inorganic particulate, precipitation as TcO_2, or bio-accumulation into sediments (Fowler *et al.* 1981, 1983, Masson *et al.* 1989). These experiments showed that there was significant accumulation of Tc in anoxic, carbon-rich sediments, but aerobic sediments showed no determinable accumulation. Laboratory experiments have also emphasised the role of bacterial fixing as an agent for Tc accumulation in both soils and sediments (Henrot 1989).

Saltmarsh sediments are known to act as a sink for contaminants released into estuarine and coastal waters (Clifton 1991). Depending on their chemical behaviour contaminants released into coastal waters will often sorb to suspended particulate and colloid material (IAEA 1985, Hamilton 1989), or micro organisms suspended in the water column (Masson 1989). This material will eventually deposit and the contaminants will become incorporated in the sediment column. These sediments may be deposited either offshore or in coastal areas.

The study of contaminated sediments deposited in coastal, particularly estuarine systems, is interesting as it is in these systems that contaminated sediments have greatest potential of reaching the food chain (Clifton 1991). Saltmarsh sediments in particular can act as a reservoir for radionuclides or as a source of these radionuclides to the local environment. Uptake of Tc from contaminated sediments may be directly by ingestion of the sediments themselves, from seawater into which ^{99}Tc has been re-dissolved, or from ingestion of other organisms which have become contaminated with ^{99}Tc from the sediment.

Saltmarsh sediments also represent a suitable environment for the study of the behaviour of radionuclides with sediments. This is due to the fine grained nature of most saltmarsh sediments and the high sedimentation rates in the saltmarshes studied. Modifications on the geochemical system should be a result of diagenetic processes rather than reworking of the sediments, consequently a saltmarsh will show a clearer sedimentation history than would be observed, for example, in a tidal mudflat or an offshore mudbank.

6.3. Sample Sites

The study of the accumulation and migration of ^{99}Tc in saltmarsh sediments was made using saltmarshes found bordering the Irish Sea. Due to their proximity to the point of discharge, saltmarshes in the vicinity of the Sellafield site are most likely to contain sediments labelled with higher levels of ^{99}Tc. Elevated levels of ^{99}Tc in seawater close to the point of discharge have also been reported (Leonard *et al.* 1997). Three sites were chosen for this study, exhibiting different sedimentary characteristics and mineralogy (Figure 6.1). The accretionary and geochemical nature of each site, as well as the input of radionuclides to each site, have been reported (Hamilton and Clarke 1984, Horrill 1984, Kershaw *et al.* 1990, Sanchez *et al.* 1997, Stanners and Aston 1981).. This aids the study of the accumulation and migration of Tc within each marsh

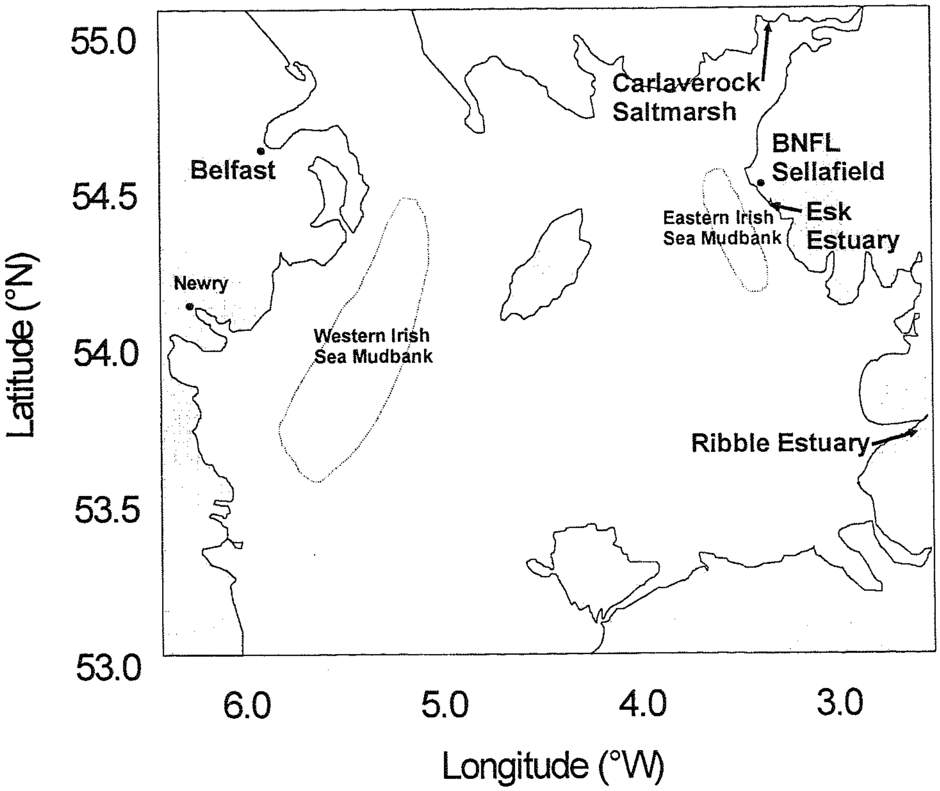

Figure 6.1. Location of the three sample sites. Location of mudbanks after Jackson *et al.* 1995.

All three sites (Carlaverock, Thornflatt (Esk Estuary) and Ribble marshes) receive an input of sediment derived from the Eastern Irish Sea Mudbank (Figure 6.1) (Jackson *et al.* 1995). Further input of sediment from local rivers is negligible in the case of the Carlaverock Saltmarsh. However, the sediment input to the Thornflatt marsh is dominated by sand derived from the dunes to the South West (Hamilton and Clarke 1984) with a component of the sediments reaching the marsh derived from the volcanic province of the Lake District. The regional geology and upland nature of the drainage basin will also lower the pH of the incoming river waters. The Ribble has a drainage basin with a large exposure of Carboniferous Limestones. This will consequently provide a greater supply of carbonate to the river system and will result in a higher pH in the river waters.

Each of the different sites has a different grainsize dominating the sediments. The Thornflatt marsh is composed of muddy silts, the sediments of the Carlaverock marsh are slightly coarser and the Ribble sediments are fine muds. The variations in grainsize will result in differences in the permeability of each of the sediments and so the likelihood of the development of reducing conditions within the sediment. In addition, in coarser sediments the clay to quartz and feldspar ratio is reduced, which may also affect the accumulation of Tc within the sediment. Prevailing bottom currents move sediments from the Eastern Irish Sea Mudbank predominantly in a southerly direction towards the Esk and Ribble estuaries (Figure 6.2). Sediment from the northern end of the mudbank will be transported northward toward the Solway Firth and Carlaverock.

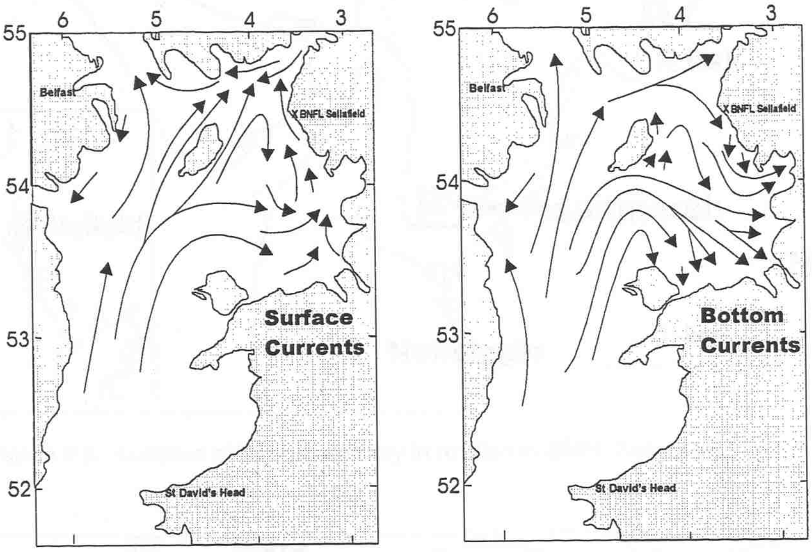

Figure 6.2. Surface and bottom current patterns for the Irish Sea (after Hill *et.al.* 1997).

6.3.1. Esk Estuary

The Thornflatt saltmarsh is a small marsh located on the northern side of the Esk Estuary approximately 10 km south of the Sellafield site (UK national Grid SD089947) (Figure 6.3). The total area of the Thornflatt saltmarsh is approximately 5.5 ha at high tide.The saltmarsh is sheltered by dunes located to the southwest minimizing storm events, is not easily accessible, is ungrazed and is hence not disturbed by the general public or by livestock.

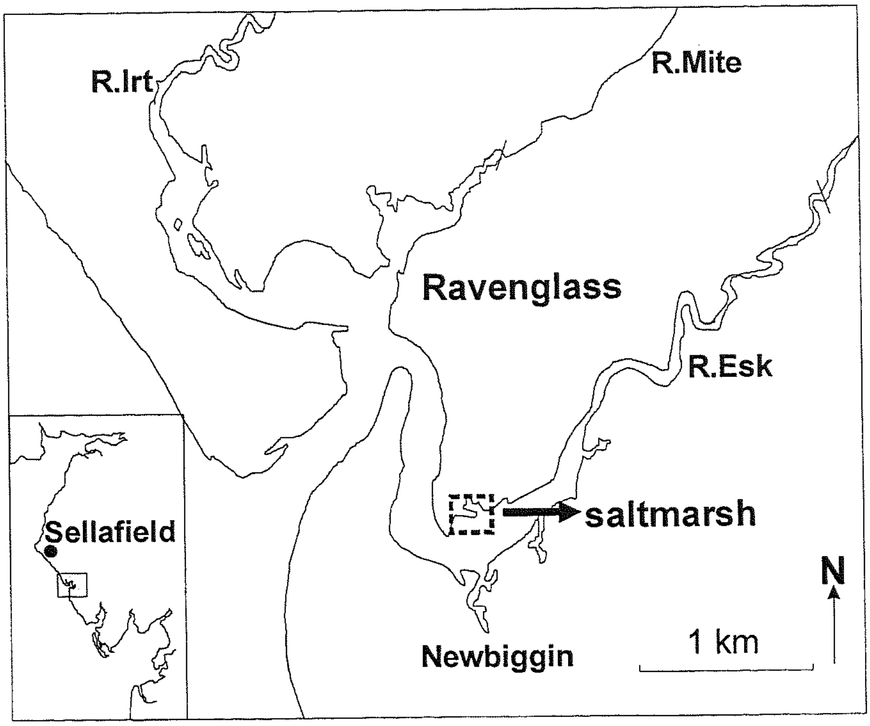

Figure 6.3. Location of the Esk estuary in relation to BNFL Sellafield.

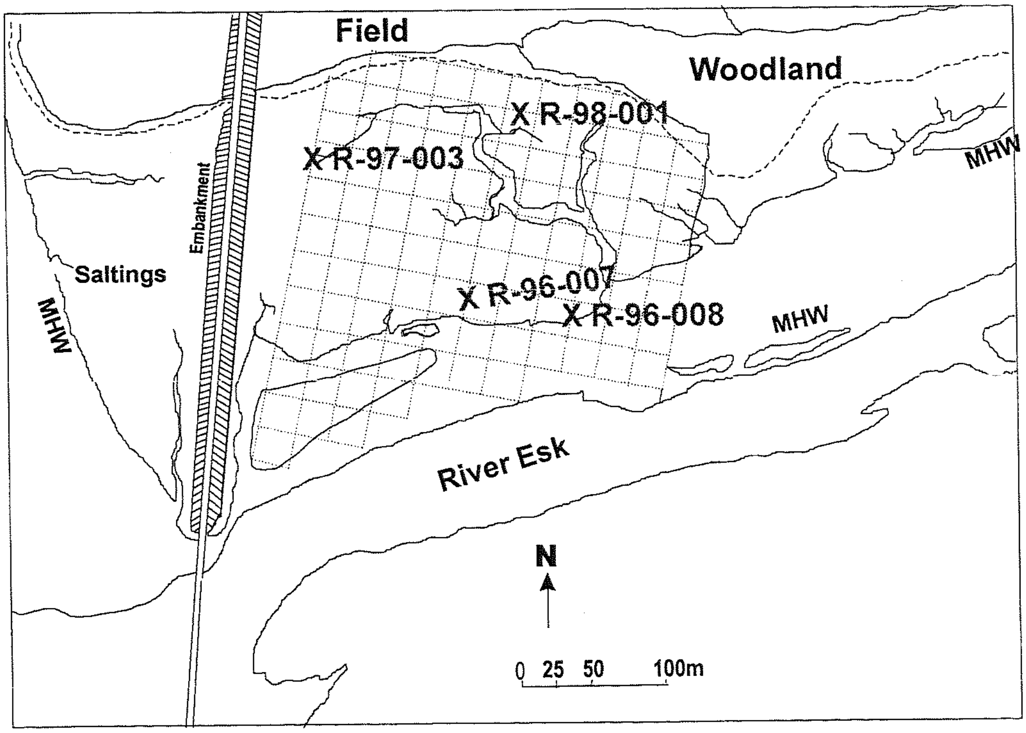

Figure 6.4. Map of the Thornflatt saltmarsh showing the sampling positions for the four cores taken. (Grid after Horrill 1984)

Four cores were collected from the Thornflatt marsh over a period of 3 years. The cores were collected from a number of locations over the site to permit any spatial variability in ^{99}Tc accumulation to be assessed (Figure 6.4) (Table 6.1). Cores were collected away from grid intersections to minimise any effects resulting from previous sampling.

Table 6.1. Summary of core samples collected from the Thornflatt Marsh

Core sample	Collection Date	Location (Grid positions after Horrill 1984)	Core length (cm)
R-98-001	November 98	C 1.5	60
R-97-003	June 97	A 3.5	60
R-96-007	June 96	W 6.5	60
R-96-008	June 96	E 6.5	80

6.3.2. Carlaverock Saltmarsh

The Carlaverock Saltmarsh is located near to Meldrum, Dumfrieshire, on the Solway coast. The marsh lies just off the Blackshaw Bank with the centre of the sampling hexagon at NY 02756480 (Figure 6.5).

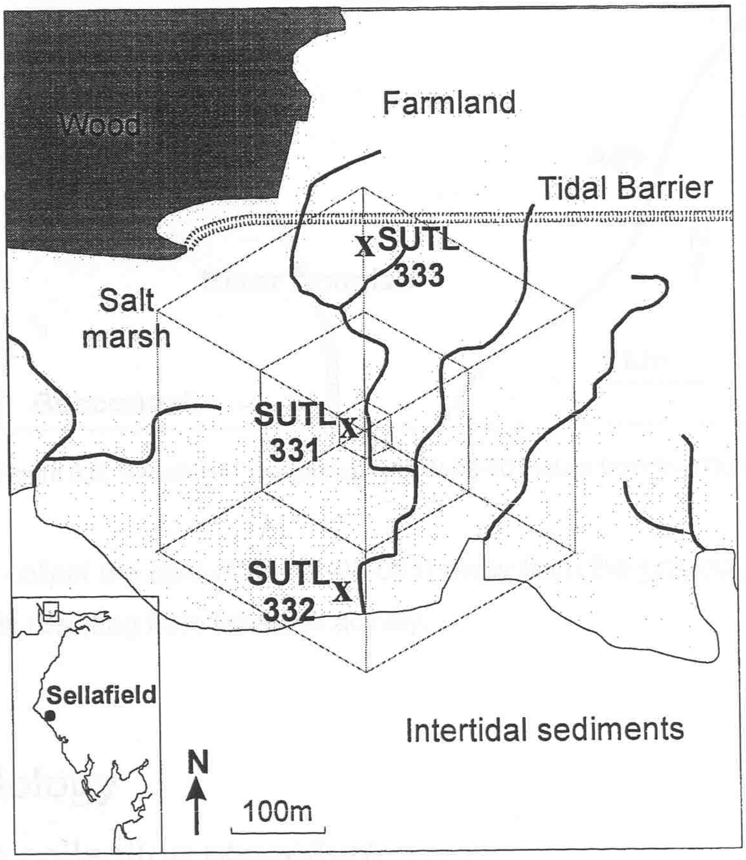

Figure 6.5. Location of the core samples collected from the Carlaverock Saltmarsh.

Three cores were collected from the Carlaverock saltmarsh by Dr David Sanderson (SURRC) in December 1996. Cores were collected in a transect from the front to the rear of the marsh, again avoiding intersections on an established sampling grid. Positions at which the core samples were collected are indicated (Figure 6.5.).

6.3.3. Ribble estuary

A core was collected from the marsh on the bank of the River Douglas, a tributary to the River Ribble at grid reference SD 44302635 (Figure 6.6). The sample site was chosen as it is approximately 1 km from the discharge point of BNFL Springfields. The site had also been reported to have elevated levels of ^{137}Cs in surface scrapes (Sanchez *et al.* 1997).

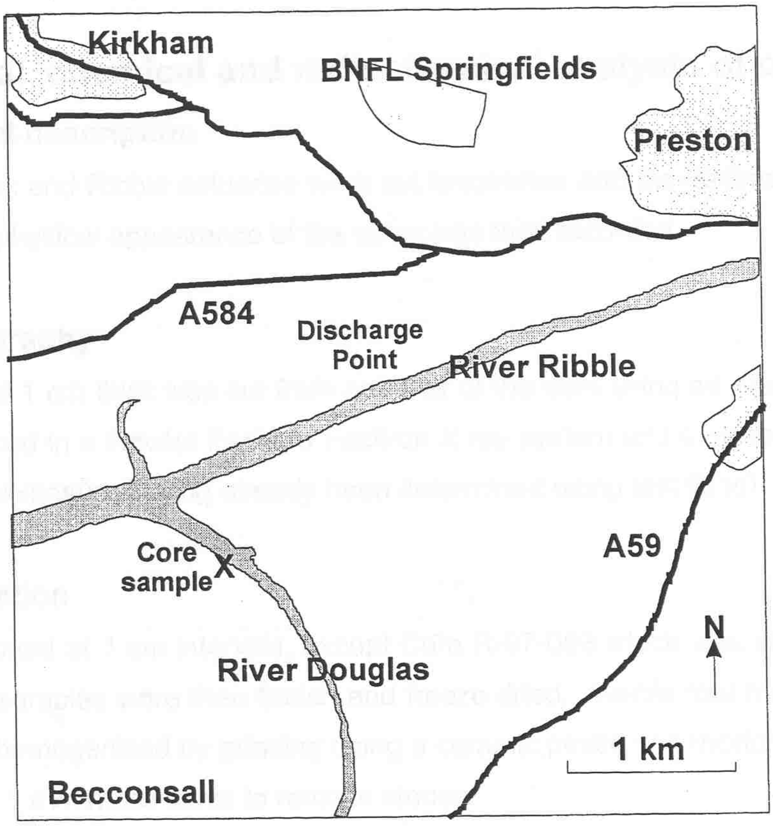

Figure 6.6. Location of the core sample W-98-001 taken from the Ribble Estuary.

Care was taken to collect the core (Core W-98-001) away from the grazed pasture to avoid the disturbed sediments resulting from livestock activity.

6.4. Methodology

6.4.1. Sample collection procedure

Care was taken to collect the cores away from the intersections of any existing sampling grids as there have been surface scrape samples taken at these points prior to this study. As a result any core samples taken from these points may show an incomplete or disturbed sediment record.

Cores taken from the Esk and Ribble Estuaries and from the Carlaverok saltmarsh were collected by insertion of a 100mm diameter PVC tube, chamfered at one end, into the sediment.

The compression of the collected sediment core was calculated by measuring the difference of the height of the sediment in the tube relative to the surface of the marsh. The cores were then extracted. This was aided by excavation around the core tube to allow lateral movement to break the bottom of the sediment core. The extracted cores tubes were then sealed at the ends by wrapping in polythene and stored at approximately 4°C prior to preparation.

6.4.2. Physical, chemical and radiochemical analysis of core samples

6.4.2.1. Physical description

Cores from the Esk and Ribble estuaries were cut lengthwise and the sediment halved using a cheesewire. The physical appearance of the cores was then recorded.

6.4.2.2. X-radiography

A slab of sediment 1 cm thick was cut from one half of the core using an electro-osmotic knife. The slab was placed in a Hewlet Packard Faxitron X-ray system and exposed for 2 mins at 56 kV (The optimum exposure having already been determined using test films).

6.4.2.3. Preparation

Cores were sectioned at 1 cm intervals, except Core R-97-003 which was sectioned at 0.5 cm intervals. These samples were then frozen and freeze dried. Visible root matter was removed and the samples homogenised by grinding using a ceramic pestle and mortar. The sample was passed through a 1 mm mesh sieve to remove stones.

6.4.2.4. Major and Trace element analysis

An aliquot of the dried sample was ignited at 900°C for a minimum of 2 hours to decompose any organic matter present. 0.800g of the ignited material was intimately mixed with 4.000g of a eutectic (4:1) mixture of lithium metaborate and lithium tetraborate in a grain stabilised Pt-Au crucible. The mixture was heated to 1200°C in a muffle furnace to melt the flux and dissolve the sediment sample. The melt was then cast into a Pt-Au mould and cooled to produce a bead suitable for XRF determination of major elements. 10g of ground sample was pressed into a pellet for trace element determination using a pressure of 12 tonnes per square inch. Determination for both Trace and Major elements was made using a Philips 1400 sequential X-ray fluorescence spectrometer. Precision for XRF analyses was generally in the range of 1-5% and the accuracy of determinations was checked using certified reference materials.

6.4.2.5. Carbon and Carbonate Analysis

Total carbon analysis was performed on a Carlo Erba CHNO-S elemental analyser. The sample was ignited by flash pyrolysis and the combustion gases separated by gas chromatography. Final detection of the gases was achieved using a flame ionisation detector. Calcium carbonate was determined by coulometric analysis via the CO_2 evolved on H_3PO_4 acid hydrolysis. Standards of known elemental composition were measured to permit quantification.

6.4.2.6. Gamma spectrometric analysis

Approximately 20g of sample was transferred to a 22ml polythene liquid scintillation vial and the exact mass of the sample recorded. The sample was then counted on a well-type high purity germanium (HPGe) detector. The resulting energy spectrum was deconvoluted and the activity of each identified radionuclide calculated using the Fitzpeaks software package (JF Computing, Stanton in the Vale, U.K.). The gamma spectrometer was previously calibrated for both energy and efficiency against an Amersham QCY-48 mixed radionuclide standard adsorbed onto a sediment matrix (Croudace, 1991). Method accuracy was regularly assessed by counting IAEA 135 Irish Sea sediment.

6.4.2.7. Bulk ^{99}Tc analysis

^{99}Tc was determined by liquid scintillation counting after chemical separation (Wigley *et al.* 1999). A sample size of approximately 5 g was taken and duplicate analyses were performed on several samples within the core, particularly at ^{99}Tc activity peaks.

6.4.2.8. Sequential ^{99}Tc analysis

Sequential ^{99}Tc analysis was made on Core R-98-001 using the method described in Chapter 5. A sample size of 2-3 g was used and final determination was made by liquid scintillation counting with ^{99m}Tc used as internal yield. Triplicate analyses were made on separate sub-samples to evaluate reproducibility.

6.5. Results and Discussion

The discharge of radionuclides from Sellafield is documented (Gray *et al.* 1995, BNFL Reports 1990-1998) and discharge data for ^{99}Tc, ^{137}Cs and ^{241}Am are presented (Figure 6.7). All three radionuclides show peaks in discharges in the mid to late 1970s, and recent high ^{99}Tc activities related to EARP discharges.

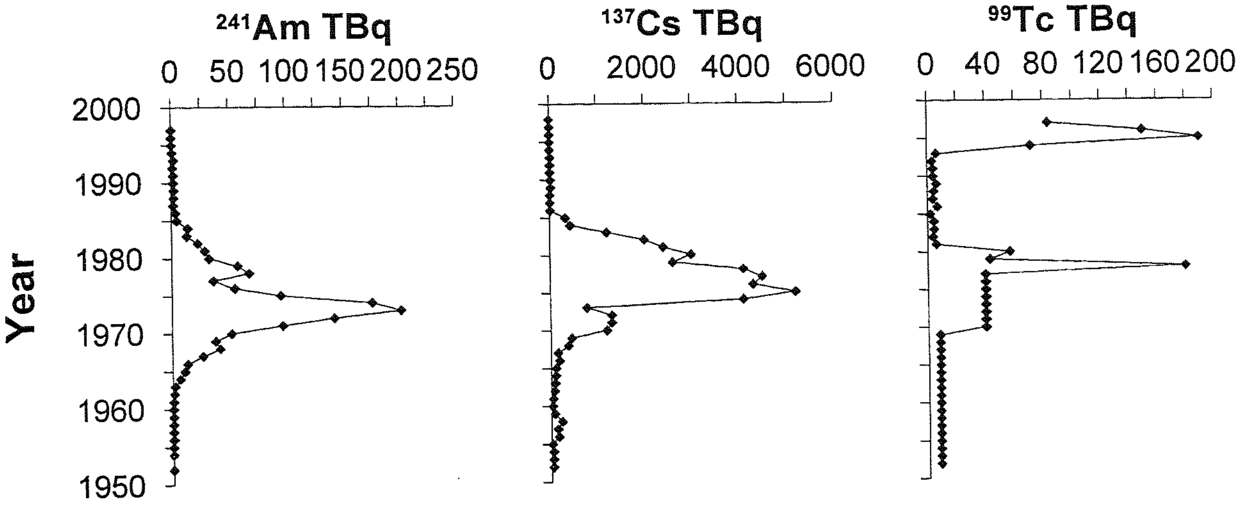

Figure 6.7. Discharge profiles for ^{99}Tc and ^{137}Cs from Sellafield. ^{241}Am data are derived from both ^{241}Am discharged from Sellafield and ^{241}Am ingrowth from the decay of ^{241}Pu (decay corrected to 2000). Data from Gray *et al.* 1995 and BNFL Reports 1990-1998.. ^{99}Tc data prior to 1978 is derived from environmental studies of ^{99}Tc in fucoid seaweeds on the Scandinavian and Greenland coasts as discharge data prior to this are not known (Aarkrog *et al.* 1986).

Sellafield is the dominant source of radionuclides to the Irish Sea (Leonard *et al.* 1997). Consequently the radionuclide activity profiles determined in each core will be affected by the discharges from Sellafield. Therefore temporal fluctuations in discharge levels of each radionuclide potentially reflected in activity profiles within each core are due to accretion of contaminated material on each marsh. The exact nature of the activity profiles will be a function of a number of variables including:

- The distance from the point of discharge.
- The composition of the deposited sediments
- Early diagenetic processes within the sediment column.

When continual accretion of sediments occurs particle reactive radionuclides such as ^{137}Cs and ^{241}Am will be expected to reflect the discharge profile. More conservative radionuclides like ^{99}Tc will not be expected to reflect the discharge profile as faithfully and significant accumulations may be as a result of other mechanisms.

6.5.1. Comparison of ^{99}Tc activities in separate sample areas

6.5.1.1. Radionuclide Profiles on the Thornflatt Saltmarsh

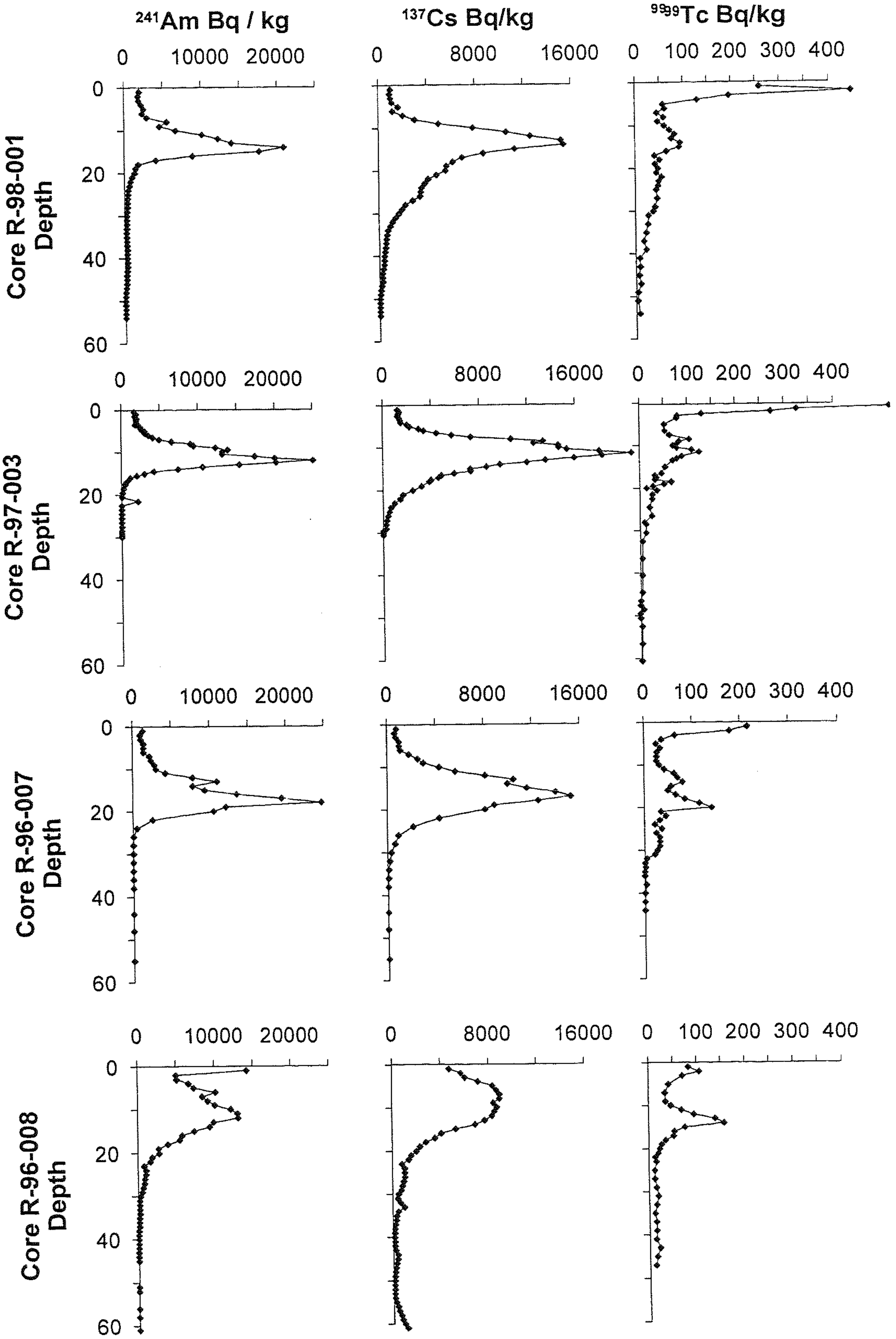

Figure 6.8. Radionuclide activities in the four cores collected from the Thornflatt Saltmarsh. Core collection dates were R-98-001: November 1998, R-97-003: July 1997, R-96-007 and R-96-008: July 1996.

Cores R-98-001, R-97-003 and R-96-007 show profiles for ^{241}Am and ^{137}Cs (Figure 6.8) which reflect the discharges of these two isotopes from BNFL Sellafield (Figure 6.7). The peaks produced in the sediment profile are sharp and in each case show a small difference in depth between the peak ^{137}Cs and ^{241}Am activities which reflects the one year difference in their peak maxima discharges. Core R-96-008 has peaks for ^{137}Cs and ^{241}Am that appear to be more attenuated. This is likely to be as the result of some post depositional mixing, which reworks some of the contaminated sediment and has the effect of attenuating the peaks for more particle reactive elements. Core R-96-008 was taken from the front of the marsh near to the main creek which drains the marsh. Water flow related to inundation and draining of the marsh is likely to be higher in this area so that reworking of the sediment can take place. A difference in the vegetation type overlying the sediment may also contribute to a localised reworking effect.

A peak in ^{99}Tc activity was also observed at the top of each core, reflecting the recent discharge from the EARP plant at Sellafield. Further down each core other ^{99}Tc activity peaks are observed at similar depths to the peaks activities of ^{137}Cs and ^{241}Am. As these observed peaks in ^{137}Cs and ^{241}Am activity are related to the peak discharges of ^{137}Cs and ^{241}Am in the 1970s it is probable that the observed ^{99}Tc activity peaks are associated with the peak discharge of ^{99}Tc in 1979.

6.5.1.2. Radionuclide profiles on the Carlaverock Saltmarsh

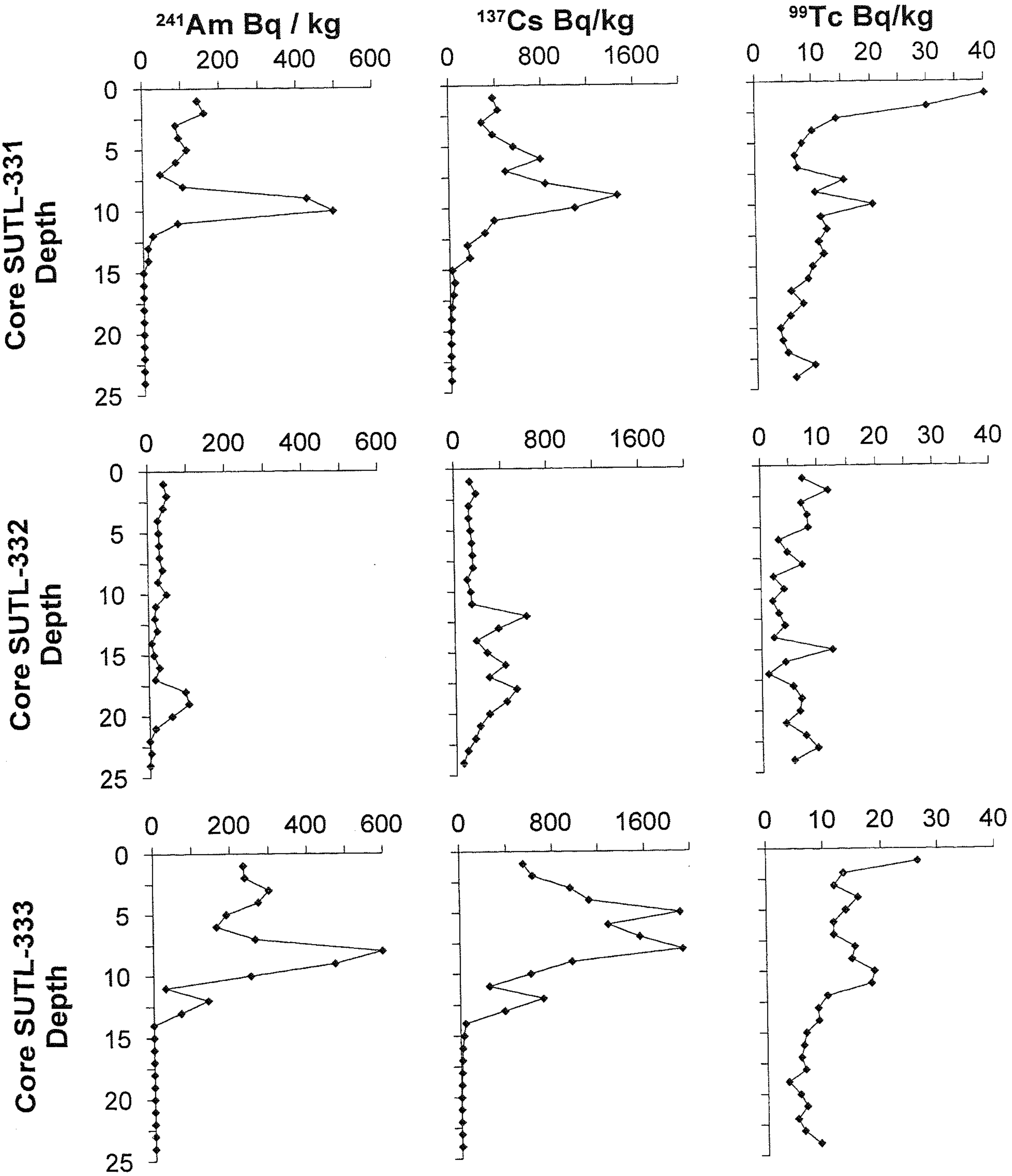

Figure 6.9. radionuclide profiles for cores from the Carlaverock Saltmarsh. All cores collected December 1996.

^{241}Am and ^{137}Cs profiles for Cores SUTL-331 and SUTL-333, collected from the middle and rear of the marsh, have well defined peaks (Figure 6.9), a product of the Sellafield discharge history. Unlike the profiles from the Thornflatt Marsh, which show a marked decrease in activity in both ^{137}Cs and ^{241}Am toward the top of the cores, the profiles from the Carlaverock marsh do not. This broadening of ^{137}Cs and ^{241}Am profiles is likely to be the result of sediment mixing. Core

SUTL-331, which was collected at the front of the marsh, shows much lower ^{241}Am and ^{137}Cs activities than the other cores, with peaks at a greater depth indicating a greater accumulation rate.

^{99}Tc activities in each of the cores are close to detection limits in core SUTL-332 (Figure 6.9). Peaks in activity are observed at the top of cores SUTL-331 and SUTL-333 which are a reflection of the recent EARP discharges. ^{99}Tc activity peaks are also observed at depths similar to those of ^{241}Am and ^{137}Cs. It may therefore be inferred that they may be the result of peak discharge in 1979. The ^{99}Tc profile for core SUTL-332 shows no obvious peaks and even the recent EARP discharges are not reflected in this core.

6.5.1.3. Radionuclide profiles from the Ribble estuary

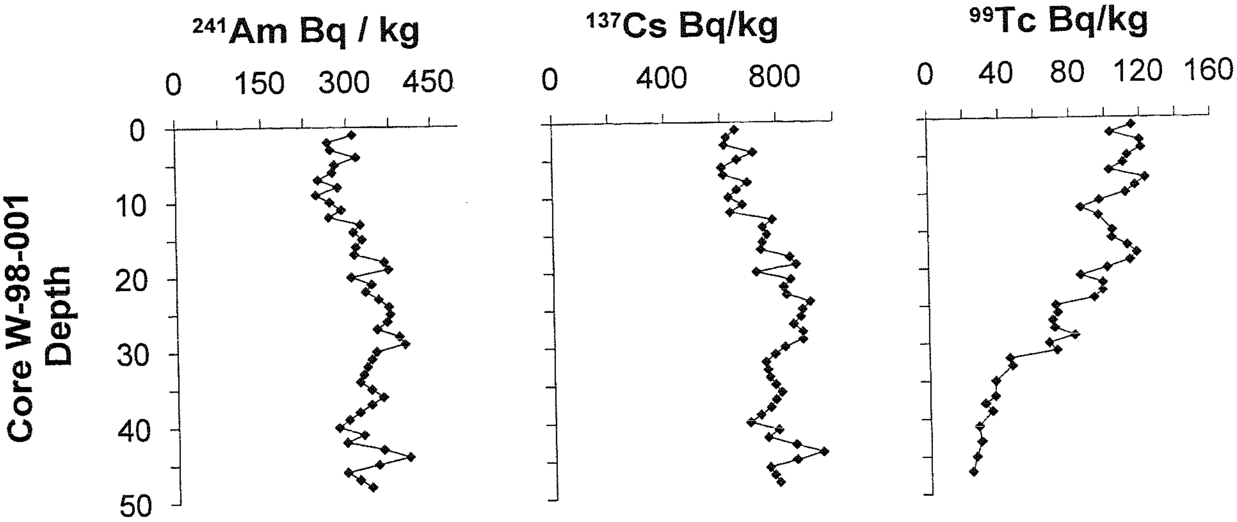

Figure 6.10. Radionuclide profiles from Core W-98-001, collected from the Ribble Estuary.

^{241}Am and ^{137}Cs profiles in core W-98-001 (Figure 6.10) show no obvious maxima related to the discharges from Sellafield (Figure 6.7). ^{241}Am and ^{137}Cs activity profiles show some small-scale variation but generally remain constant down the core. The lack of peaks associated with Sellafield discharges indicates that post depositional mixing of the sediments has occurred.

6.5.1.4. Comparison of ^{99}Tc activity with discharge.

A direct comparison between the activities for each nuclide in individual 1 cm sub-samples would give a misleading representation of the relative accumulation of radionuclides in each core. This is due to the temporal variation in the peak discharge for anthropogenic radionuclides from Sellafield and the different transit times for radionuclides to sample sites. This will lead to a vertical separation between the activity maxima for different radionuclides. In order to gain a comparison peak activity values from profiles within each core, known to represent peak discharges from Sellafield, should be compared rather than radionuclide activities within each 1 cm sub-sample as a study of the entire core will remove problems with temporal effects. It is important that each peak taken for comparison is known to correlate with discharge from Sellafield. This means that the lower ^{99}Tc activity peaks cannot be used as it is not certain that the Tc accumulations have not undergone some post depositional migration. Data from the Ribble core W-98-001 is also not usable as there are no clear radionuclide profiles which may indicate mixing has occurred.

The maximum activity values for ^{241}Am and ^{137}Cs determined in each core, regardless of depth were ratioed to the maximum ^{99}Tc activity corresponding to the recent EARP discharges (Table 6.2). ^{99}Tc activities at the top of the sediment cores, corresponding to the recent discharges, were taken as the recent input was less likely to have undergone any post depositional change. The same was done for peak ^{241}Am, ^{137}Cs and post EARP ^{99}Tc discharges from Sellafield (Table 6.2). Ingrowth of ^{241}Am form ^{241}Pu was accounted for.

Table 6.2. ^{241}Am :^{99}Tc, ^{137}Cs:^{99}Tc and ^{241}Am:^{137}Cs ratios for Sellafield discharges and cores collected from the Thornflatt Marsh and Carlaverock Merse. Observed data represents mean values of maxima observed in cores collected at both sites. All Carlaverock cores collected December 1996. . Core collection dates were R-98-001: November 1998, R-97-003: July 1997, R-96-007 and R-96-008: July 1996.

	^{241}Am/^{99}Tc	^{137}Cs/^{99}Tc	^{241}Am/^{137}Cs
Thornflatt*	89 ± 18	61 ± 17	1.4 ± 0.2
Carlaverock*	14.5 ± 3	54 ± 18	0.3 ± 0.1
Sellafield discharge**	1.22	27	0.02

*Values are means taken for all cores on the marsh.
**Data from Gray *et al.* 1995, BNFL Reports 1993-1997.

The ratio of the peaks in discharge for ^{241}Am and ^{99}Tc compared to the ratios of ^{241}Am and ^{99}Tc in the cores taken from the Thornflatt saltmarsh show that Am is much more particle reactive than Tc. The lower ^{241}Am:^{99}Tc ratio in the Carlaverock sediments is a result of lower amounts of Am reaching the marsh due to its greater distance from Sellafield. The ^{137}Cs:^{99}Tc ratios in the Thornflatt and Carlaverock saltmarshes show a much smaller decrease with distance than is seen with the ^{241}Am:^{99}Tc ratios. This would be expected due to the more mobile nature of Cs and Tc compared to Am.

Table 6.3. Mean measured peak activity: peak discharge ratios (x10^{-12}).

	^{99}Tc	^{137}Cs	^{241}Am
Thornflatt*	1.7	2.9	101
Carlaverock*	0.14	0.25	1.96

Relative distribution coefficients can be obtained from the ratio of the measured peaks compared to discharge (Table 6.3). In the sediment cores from the Thornflatt marsh 59 times as much of the ^{241}Am discharged from Sellafield is found in the ^{241}Am maxima compared to ^{99}Tc in the upper peaks. Comparatively there is only twice as much of the ^{137}Cs discharged found in the maxima of the measured profile than of ^{99}Tc. In the Carlaverock cores only 14 times as much of the ^{241}Am discharge is seen compared to that of ^{99}Tc, probably due to the increasing distance from Sellafield, however there is still twice the amount of the ^{137}Cs discharge seen in the sediments compared to that of ^{99}Tc. Tc has been assumed to have a k_D of 100 and Cs a k_D of 3000 (IAEA 1985), if there is such little change in the ratios with distance this suggests that the two elements have k_Ds in this environment which are closer than previously reported.

6.5.2. Reliability of sediments as indicators for historical ^{99}Tc discharge

Saltmarsh sediments have been used as indicators for the historical discharge of radionuclides which are particle reactive. For example ^{241}Am has a k_D of 10^6 from seawater to Esk Estuary saltmarsh sediment (Stanners and Aston 1979, Day and Cross 1981). In many of the cores in which ^{241}Am was determined the shape of the ^{241}Am measured profile closely matches that of the discharge profile for ^{241}Am from the Sellafield site. The ^{99}Tc profiles in many of the cores are similar to that of discharge from Sellafield (Figures 6.8, 6.9, 6.10. and 6.7).

To determine whether the ^{99}Tc profiles observed in the cores are a reflection of historical discharge, or whether other processes affect ^{99}Tc accumulation, a direct comparison between the discharge profile and the observed profiles must be made. In order to do this the lag time for sediments to reach the sample sites and the rate of accretion of the sediments must be determined. These can be calculated from the radionuclide activity data, the core lamination data and knowledge of the discharge levels of radionuclides from Sellafield. It must also be assumed that:

- All radionuclides are sourced from Sellafield discharge.
- Compression of the core has been consistent during sampling.
- ^{137}Cs and ^{241} Am are particle reactive in these sediments.
- Compaction of the sediments has been consistent.
- There have been no intermittent periods of erosion.

6.5.2.1. Determination of Lag time

The discharge of radionuclides from Sellafield to the local marine environment will swamp the input of radionuclides from other sources. It is possible to check for erosion and inconsistencies in the core profiles by using the laminations seen in the X-radiographs.

The lag time taken for radionuclides to reach the sample site is also important when using radionuclides as a dating method. The lag time taken for sediments reaching a saltmarsh from the point of discharge has been calculated (Stanners and Aston 1979). This process uses two isotopes, which have significantly different half-lives. ^{134}Cs and ^{137}Cs are most commonly used. ^{134} Cs has a half life of 2.06 years whilst the half-life for ^{137}Cs is 30 years. ^{134}Cs:^{137}Cs ratios in sediment samples taken from the marsh are measured and compared with known values for discharge. The difference in ratio results from the decay of ^{134}Cs in transit. This can be used to calculate the transit time and a number of lag times along the Cumbrian Coast have been reported. A period of two years is required for the transport of sediments from Sellafield to the North of Maryport Harbour (Kershaw *et al.* 1990). A lag time of 1.5 years has been calculated for the transit of sediments to Maryport and Workington Harbours as well as the Duddon estuary (Stanners and Aston 1981). A value of approximately one year for the transit of sediment bound radionuclides to the Esk Estuary has been calculated (Hamilton and Clarke 1984). The transport of these sediments to the Solway Firth and the Carlaverok saltmarsh takes approximately 3.9 years (McDonald *et al.* 1990).

No ^{134}Cs activities above the limit of detection were measured in the cores collected from the saltmarsh. This is due to the low ratio of ^{134}Cs:^{137}Cs in the discharge with a range between 0.04 and 0.05. Interference from other gamma emitting radionuclides makes it impossible to detect ^{134}Cs in the saltmarsh under routine analysis. It is more likely that the lack of observed ^{134}Cs in the marsh sediments is due to these analytical limitations rather than the complete decay of ^{134}Cs in transit. Consequently, a lag time of 1 year for sediment transport to the Thornflatt Saltmarsh and a transit time of 3.9 years for transport to Carlaverock, as suggested by previous workers has been used for accretion rate calculations. Conservative radionuclides including ^{99}Tc show little adsorption to particulate matter and so tend to disperse more quickly than nuclides such as ^{241}Am and ^{137}Cs (Fowler 1983). Transit times for conservative radionuclides from Sellafield to the Clyde Sea area have been estimated at less than 8 months (Baxter *et al.* 1979) and a ^{99}Tc discharge pulse has been measured in the North Channel two months after discharge (Leonard *et al.* 1997). Consequently the lag time for ^{99}Tc discharges to reach the Thornflatt marsh, the Carlaverock marsh or the Ribble estuary is less than that for non-conservative elements.

6.5.2.2. Calculation of accretion rate

Laminations

X-radiography of the cores identified alternating light and dark bands at regular intervals throughout the core. These are likely to be due to the compositional variations of sediment input associated with seasonal variations. This stratification down the core permits the calculation of sedimentation rate as one lamination pair, comprising one dark and one light band, represents the deposition during one year. Therefore, by counting the annual cycles over a set depth the deposition rate can be calculated. To avoid the effects of differing sedimentation rates or an uneven compaction of the core the accumulation rate was determined over the entire length of the core.

Anthropogenic Radionuclides

The ^{137}Cs and ^{241}Am profiles can be used to determine the sedimentation rates of cores collected from close to the discharge point for Sellafield, as the discharge history is well known (Ramsay and Raw 1987). ^{241}Am and ^{137}Cs are particularly suitable tracers for this purpose as both have a high K_D from seawater to sediments (IAEA 1985) and Cs is readily incorporated into the crystal lattice of both smectite and illite clays and a proportion remains immobile during diagenetic processes (Deer *et al.* 1992). Both radionuclides are γ-emitting and so easily determined.

In order to calculate the accretion rate using this method it is assumed that the maxima in the core corresponds to the maxima in the discharge history and that there has been no significant post-depositional migration. The lag time must also be taken into account to correct for the time taken for the discharge signal to reach the marsh. The calculation is shown in equation [6.1].

$$A = \frac{M + (M / 100 \times C)}{(S - D) - L}$$

A = accretion rate

M= measured depth

C = Compression of Core

S = Year of sampling

L = Lag Time

D= Year of discharge

[6.1]

6.5.2.3. Estimation of Accumulation rate on the Thornflatt Saltmarsh.

A similar value for the accretion rate was obtained by using the ^{241}Am, ^{137}Cs and lamination methods (Table 6.4). The accretion rates for different cores show some variation from 0.6 cm/year to 0.9 cm/year. As the sediment cores were collected from different locations on the marsh different rates of sedimentation are expected. Core R-96-007 which was collected from the front of the marsh (Figure 6.4) shows a higher accretion rate than Core R-97-003 and Core R-98-001 which were collected towards the rear of the marsh. Core R-96-008 was also collected toward the front of the marsh but shows a comparatively low accretion rate. This may be explained as the result of a higher energy environment closer to the main creek which drains the marsh. This would mean that less sediment is deposited in this area.

Table 6.4. Accretion rates for the different dating methods used. Values are in cm/year. ^{99}Tc values are calculated for lag time of 0 to 1 year.

Dating method	R-98-001	R-97-003	R-96-007	R-96-008
^{241}Am	0.64	0.68	0.88	0.57
^{137}Cs	0.67	0.65	0.88	0.55
Laminae	0.6	0.7	0.9	0.6
Mean	**0.6**	**0.7**	**0.9**	**0.6**
^{99}Tc	0.79 – 0.83	0.72 – 0.76	(0.80 – 0.85)* 1.14 – 1.21	0.78 – 0.82

*Upper of two ^{99}Tc peaks possibly associated with 1979 discharge.

The accretion rate values calculated for each of the cores if ^{99}Tc is used consistently show higher values than those for more particle reactive radionuclides (Table 6.4) except for the small peak at 14 cm in Core R-96-007. This suggests that the peaks in ^{99}Tc may not be a reflection of historical discharge patterns but may be the result of other processes. In order to understand more about the comparison between measured and discharged ^{99}Tc it is necessary to normalise each of the cores so that a comparison can be made between observed activity peaks and periods of peak discharge of radionuclides from Sellafield.

6.5.2.4. Estimation of Accumulation rate on the Carlaverock Saltmarsh.

Lower accumulation rates were observed in the rear of the Carlaverock marsh than the front (Table 6.5). Within each core the ^{241}Am and ^{137}Cs methods give good agreement to the rate of accumulation. The accumulation rate calculated using ^{99}Tc data shows some variation. In Cores SUTL-331 and SUTL-333 the ^{99}Tc calculated rate is greater than those of both ^{137}Cs and ^{241}Am. In Core SUTL-332 the accumulation rate was similar, but the lack of clearly defined peaks in the profiles for ^{137}Cs and ^{241}Am increases the error in the calculated accumulation rate for this core.

Table 6.5. Accretion rate data for cores on the Carlaverock Saltmarsh. Values are in cm/year. ^{99}Tc values are calculated for a lag time between 0 to 3.9 years.

Dating method	SUTL-332*	SUTL-331	SUTL-333
^{241}Am	1.10	0.58	0.46
^{137}Cs	1.11	0.55	0.49
Mean	**1.11**	**0.57**	**0.48**
^{99}Tc	0.88-1.12	0.50 – 0.60 0.59 – 0.75	0.58 – 0.82

*Core SUTL-332 does not show clear peaks so the accretion rates are tenuous

6.5.2.5. Estimation of Accumulation rate in the Ribble estuary

The accumulation rate of Core W-98-001, taken from the Ribble Estuary has not been calculated due to the lack of radionuclide peaks observed within the core.

6.5.2.6. Comparison with BNFL Sellafield discharge

A chronological record for all cores is established using ^{241}Am since this radionuclide is assumed to be irreversibly sorbed in the sediment. The accretion rate is assumed to be consistent down the core and this is supported by the lamination record. The normalisation of core sediment sub-samples to correlate with the releases from Sellafield enables a comparison of the ^{99}Tc discharge history and the ^{99}Tc activity, Equation [6.2]. This correction factor must be used to normalise each of the core profiles so that a direct inter-comparison can be made (Figure 6.11).

$$N = S-(d \times A_{(Am)}) + L_{(e)}$$

N = Normalisation factor
S = Year of sampling
d = depth of sub-sample
$A_{(Am)}$ = Accretion rate using ^{241}Am
$L_{(e))}$ = Lag time for a specific element
[6.2]

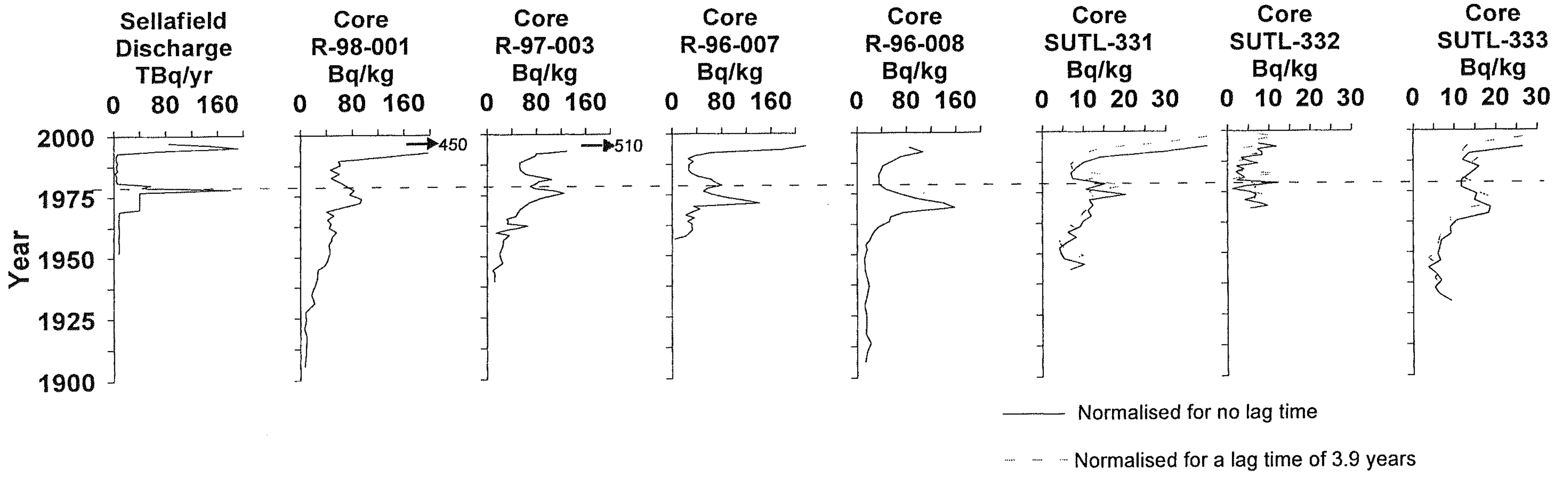

Figure 6.11. ^{99}Tc activity profiles normalised for depth to year of Sellafield discharge.

The recent high discharges from BNFL Sellafield are mirrored in the top of each of the collected cores. A peak in the ^{99}Tc activity related to peak discharge observed in 1979 can be seen in each of the cores although only in Core R-96-007 is there a measured peak in ^{99}Tc activity at this point. In each of the other cores the peak in ^{99}Tc activity occurs at a lower depth than would be expected for the 1979 peak. In Core R-96-007 there is also a second peak observed at a depth of 20 cm which has no correlation with the Sellafield discharge. In core SUTL-331 the ^{99}Tc activity peak correlates well with peak discharge. Core SUTL-333 shows a distinct movement of ^{99}Tc down the core profile. An input of contaminated sediment from the Eastern Irish Sea mudbank, which will have a lag of 3.9 years, correlates better than the direct input from seawater (Figure 6.11). In the Thornflatt marsh the lag time is too short to observe the different inputs as the lag time would only give 1 year's separation. The comparative movement of ^{99}Tc within the core profiles could be achieved by either sediment mixing or post depositional processes such as oxidation and remobilization of Tc before secondary deposition under favourable redox conditions.

Post depositional mixing can result in broadening of radionuclide activity profiles up or down a core profile. Mixing would alter the profiles for all the radionuclides used for the calculation of accretion rates and as good profiles are observed for both ^{137}Cs and ^{241}Am in most of the core profiles it is unlikely that there has been any post depositional mixing. This is confirmed by the differences in accretion rates when calculated using ^{99}Tc data compared to ^{137}Cs, ^{241}Am or lamination data. Remobilization of ^{99}Tc in core profiles by dissolution and re-precipitation of Tc as a result of post depositional diagenetic processes would be supported by geochemical trends.

6.5.3. Correlation of ^{99}Tc and Core geochemistry

6.5.3.1. Thornflatt Sediments

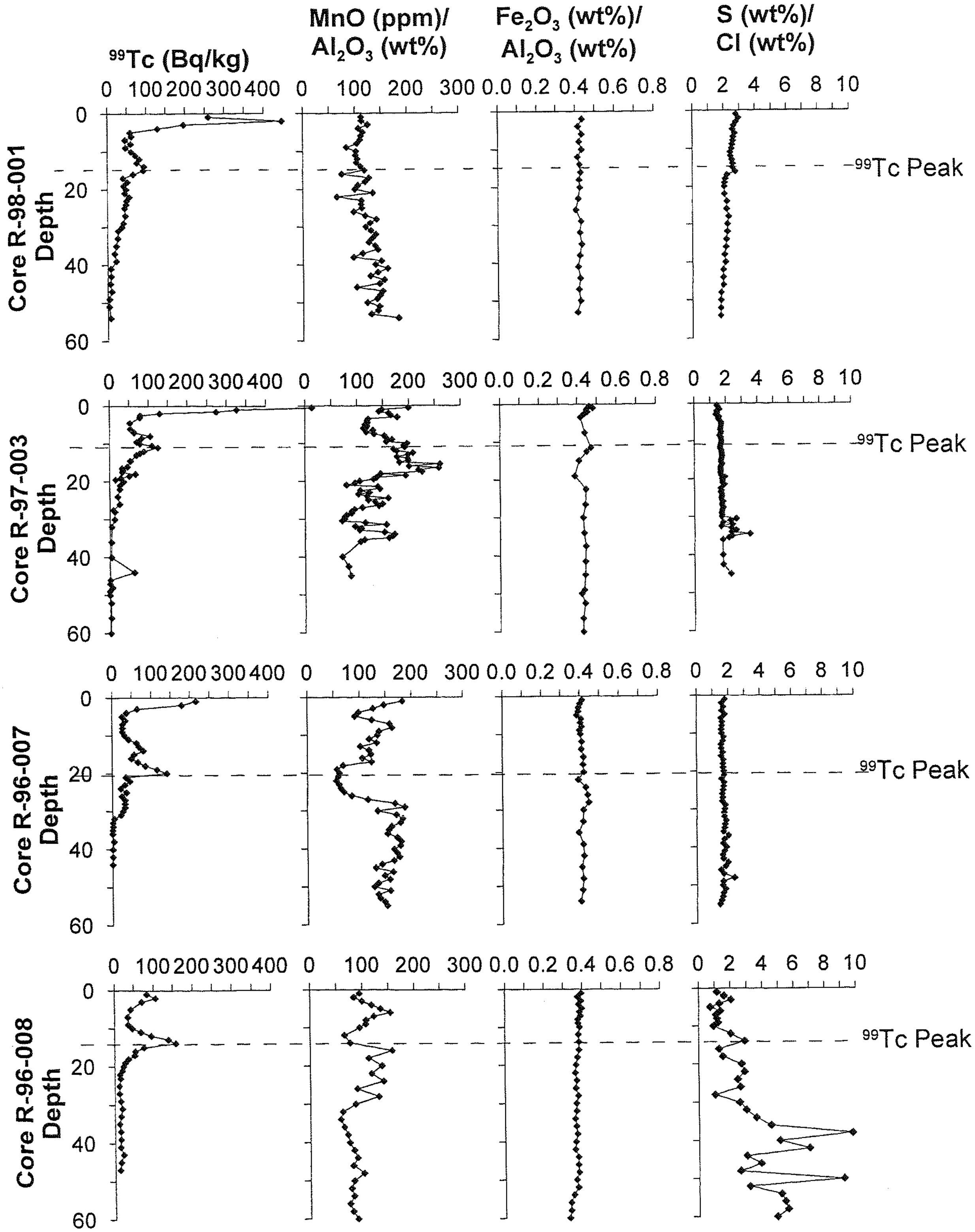

Figure 6.12. A comparison of Tc with redox sensitive element trends.

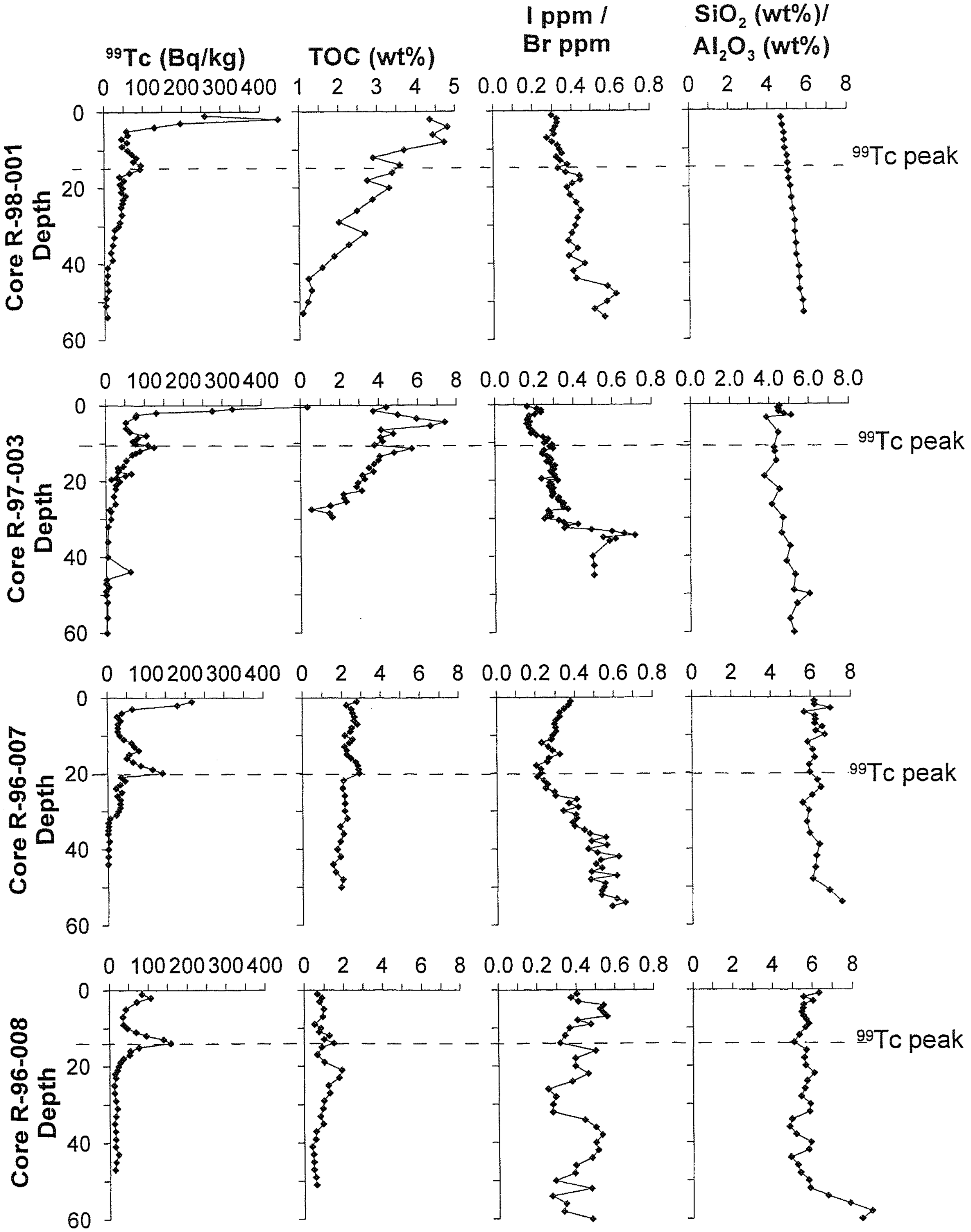

Figure 6.13. Comparison of ^{99}Tc with core components

The cores collected from the front of the marsh (R-96-007 and R-96-008) show more distinct peaks in their ^{99}Tc activity profiles than those collected towards the back of the marsh (R-98-001 and R-97-003). These have much more attenuated ^{99}Tc peaks suggesting that much of the ^{99}Tc has migrated down the core with no secondary accumulation occurring. In core R-96-008 and at 20 cm in Core R-96-007 there is a good correlation between the ^{99}Tc peak and a low in the MnO:Al$_2$O$_3$ and

I:Br ratios, indicating a drop in the redox potential (Figures 6.12 and 6.13) (Berner 1981). These correlations are however, not observed in Cores R-98-001 and R-97-003, when ^{99}Tc activity peaks correlate with discharge.

The Fe_2O_3:Al_2O_3 ratio in all cores remains constant down each core, indicating that none of the sediments have a reduction potential low enough for the reduction of Fe^{III} to Fe^{II}. Correlations between ^{99}Tc peaks and peaks in the S:Cl ratio can be observed at 16 cm in Core R-98-001 and at 14 cm in Core R-96-008 (Figure 6.12).

In each of the cores peaks in the TOC concentration coincide with peaks in ^{99}Tc activity peaks (Figure 6.13). Good associations are seen in Core R-96-007 at 20 cm and Core R-96-008 at 14 cm and it is possible that the increase in TOC requires increased amounts of oxygen for decay. This localised depletion in oxygen from the sediment is likely to be responsible for the reduction of ^{99}Tc from Tc^{VII} to Tc^{IV} as well as Mn^{IV} to Mn^{II}. The consistent mineralogical content of the cores reflected by the Si:Al profiles suggests that the ^{99}Tc peaks are unlikely to be the result of sorption resulting from localised changes in the sediment mineralogy.

There are no clear associations seen between the high ^{99}Tc activities at the top of the core and the sediment geochemistry. It is therefore likely that the high activities here are the result of the higher concentrations in the local environment. It would appear that after deposition ^{99}Tc is remobilised and migration of Tc is seen within the core profile with secondary accumulation occurring only when the redox conditions are favourable.

6.5.3.2. Carlaverok Sediments

^{99}Tc activity profiles are clearer in the cores collected away from the front of the marsh, but still do not show good accumulation of ^{99}Tc in the core profile. There is no correlation of ^{99}Tc with changes in the profiles of MnO:Al_2O_3 Fe_2O_3:Al_2O_3 or I:Br ratios (Figure 6.14), which was observed in the cores take from the Esk estuary (Figures 6.12, 6.13). The cores do not show strong evidence of the development of redox zonation within their profiles, the MnO:Al_2O_3 profile for Core SUTL-333 indicates that the core at depths greater than 6cm may be approaching a sub-oxic environment. This is not supported by evidence from Fe_2O_3:Al_2O_3 or I:Br ratios. The S:Cl ratio profile tends to be flat with a slight increase towards the top but there does not seem to be any correlation with ^{99}Tc activities.

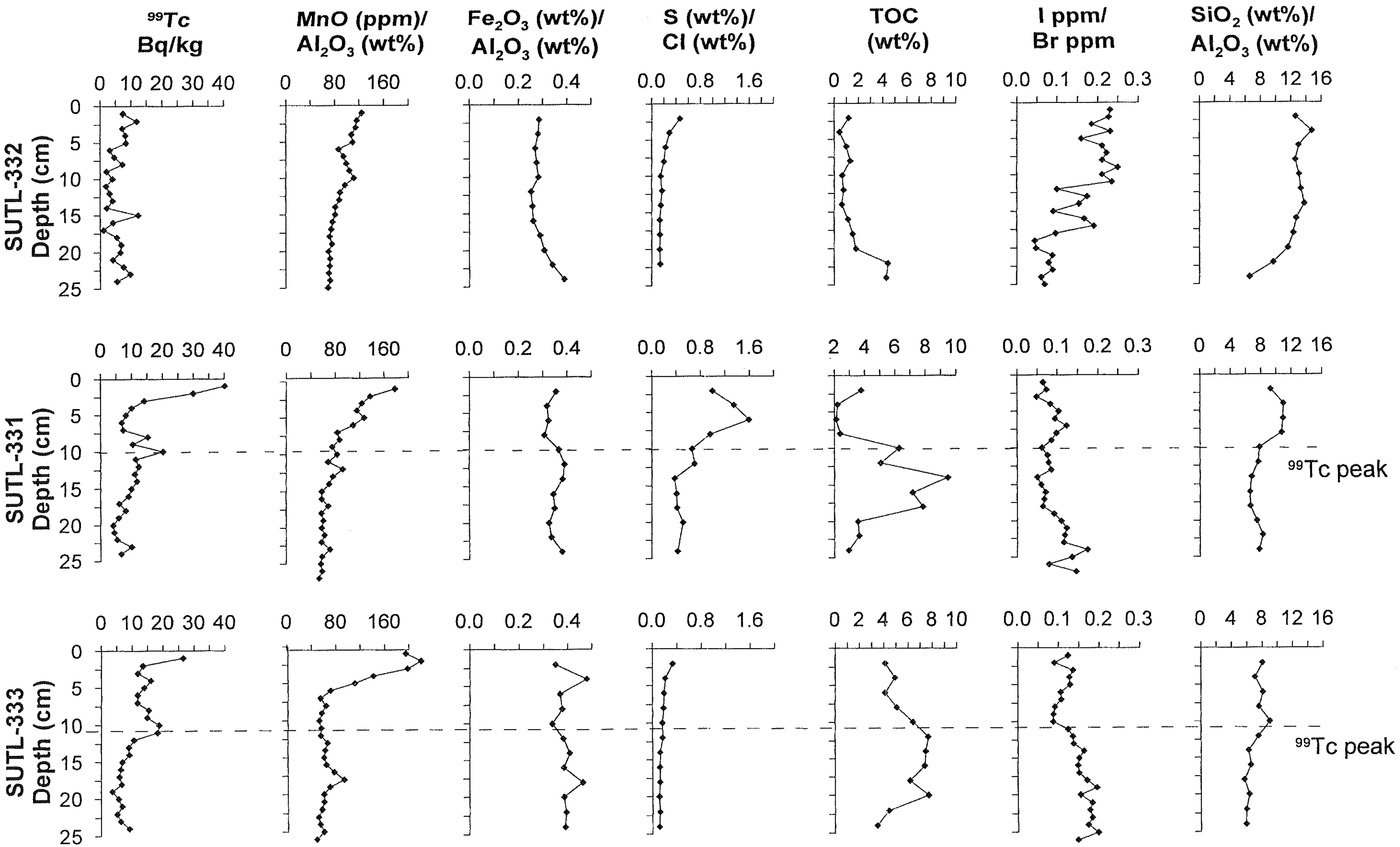

Figure 6.14. A comparison of ^{99}Tc activities with the geochemical nature of the Carlaverok Cores.

The strongest correlations with the ^{99}Tc peak activity maxima are with elevated TOC values and Si:Al ratios below a value of 10. These correlations exist for the ^{99}Tc peak at 10cm in Core SUTL-331, and with the ^{99}Tc activity peak at 12cm in core SUTL-333. The Si:Al ratio in each of the cores is high compared to the Thornflatt sediments which exhibit an average ratio of 5. The Carlaverock sediments have ratios ranging from 7 to 15. This is an indication of the greater amount of quartz and the coarser grained nature of the cores compared to those of the Thornflatt marsh. Lows in the Si:Al ratio indicate an increase in the amount of clay in the sediment to which the ^{99}Tc may be sorbed. The correlation with the TOC may indicate that much of the ^{99}Tc in these sediments may be associated with organic material.

Post-EARP discharges of ^{99}Tc are manifested at the top of the cores, and are a result of the recent elevation in concentrations rather than any geochemical conditions. However, in the very sandy conditions of Core SUTL-332 even these are not seen. The ^{99}Tc maxima occur at greater depths in Cores SUTL-331 and SUTL-333 and are slightly broader but correlate well with the expected discharges (Figure 6.11). The attenuation of the ^{99}Tc activity peaks is likely to be due to remobilisation of Tc and subsequent movement of Tc in the sediment profile. As the cores do not show the development of any obvious redox zones secondary enrichment of Tc is not occurring.

6.5.3.3. Ribble sediments

A lack of definitive Tc discharge data from the Springfields site, as well as evidence from flat ^{137}Cs and ^{241}Am profiles, (Figure 6.10) indicate that the core is well mixed. This means that it is difficult to directly relate ^{99}Tc sediment profiles to any discharge history. There are however, correlations between ^{99}Tc activity peaks and variations in the redox conditions in the core (Figure 6.15).

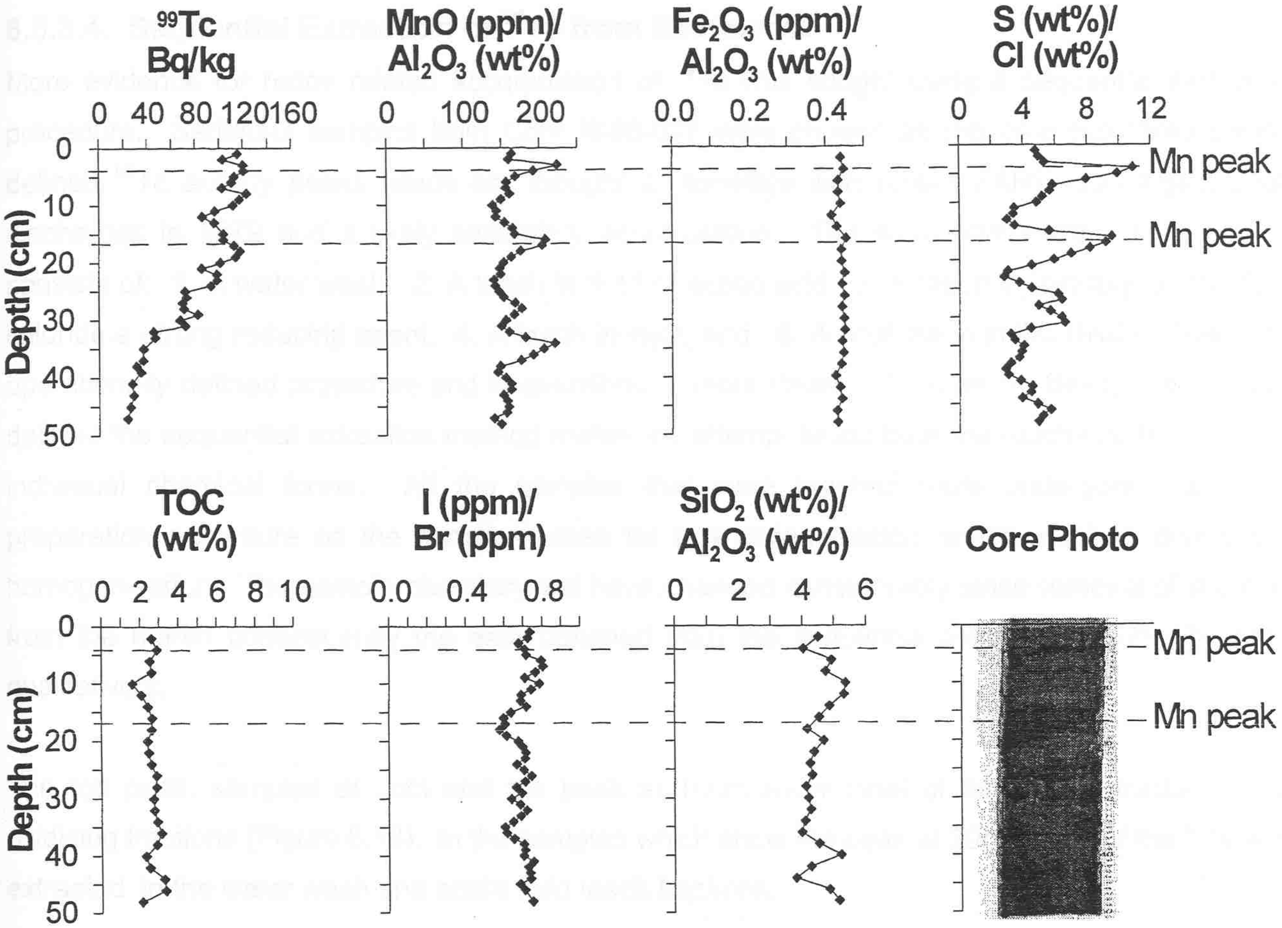

Figure 6.15. A comparison of ^{99}Tc activities with the geochemical nature of the Ribble core W-98-001.

Unlike the cores collected from the other saltmarshes Core W-98-001 shows clear development of sulphidic zones. This is observed as dark bands in the core and as peaks in the S:Cl ratio. Both ^{99}Tc activities and the $MnO:Al_2O_3$ ratio increase in the dark sulphur rich bands. There are no corresponding changes in the $Fe_2O_3:Al_2O_3$ or Si:IAl ratios or the TOC concentration. A slight decrease in the I:Br ratio can also be observed at these points.

These trends indicate immobilisation of both Tc and Mn as stable forms. These are most likely to be as insoluble oxides, carbonates or sulphides(Coleman 1985). Immobilisation as oxide species is unlikely as Mn^{II} is soluble and unlikely to precipitate as $MnOH_2$. Maxima are observed for Mn at the same depths as those for S which implies that the reduction potential is low enough to permit immobilisation of Mn species as carbonates or sulphides.

Previous work has suggested that the bacterial reduction of iron and sulphate may also include other metals, principally Mn (Coleman 1985). Consequently the relative rates of reduction of Fe^{III} and sulphate not only control the formation of iron sulphide and associated carbonate but also may be responsible for the metabolism of TcO_4^- and MnO_2 and their reduction to stable forms.

6.5.3.4. Sequential Extraction of ^{99}Tc from Sediments

More evidence for redox related accumulation of ^{99}Tc was sought using a sequential extraction procedure. Sediment samples from Core R-96-007 were chosen as the core has three clearly defined ^{99}Tc activity peaks which are thought to correlate with recent EARP discharges, peak discharges in 1979 and a likely secondary accumulation. The sequential extraction procedure consists of: 1. A water wash, 2. A leach in 0.11 M acetic acid, 3. A leach in hydroxyl ammonium chloride a strong reducing agent, 4. A leach in H_2O_2 and, 5. A final leach in 8M HNO_3. This is an operationally defined procedure and is described in more detail in Chapter 5. Being operationally defined the sequential extraction method makes no attempt to attribute the leachable fractions to individual chemical forms. All the samples that were leached have undergone the same preparation procedure as the samples taken for bulk determination, which involves drying and homogenisation. The sample chemistry will have changed considerably since removal of the core from the marsh consequently the data obtained from the sequential extracts can only be used qualitatively.

The top peak, sampled at 2cm and the peak at 14cm show most of the ^{99}Tc extracted in the oxidising fractions (Figure 6.16). In the samples which show the peak at 20cm most of the ^{99}Tc was extracted in the water wash and acetic acid leach fractions.

The peaks at 2cm and 14 cm correlate well with the discharge profile of ^{99}Tc from Sellafield (Figure 6.11). The fact that Tc is extracted in the oxidisable fractions suggests that it is strongly associated with a component of the sediment matrix. This could be the organic material or a strong Tc-clay mineral association.

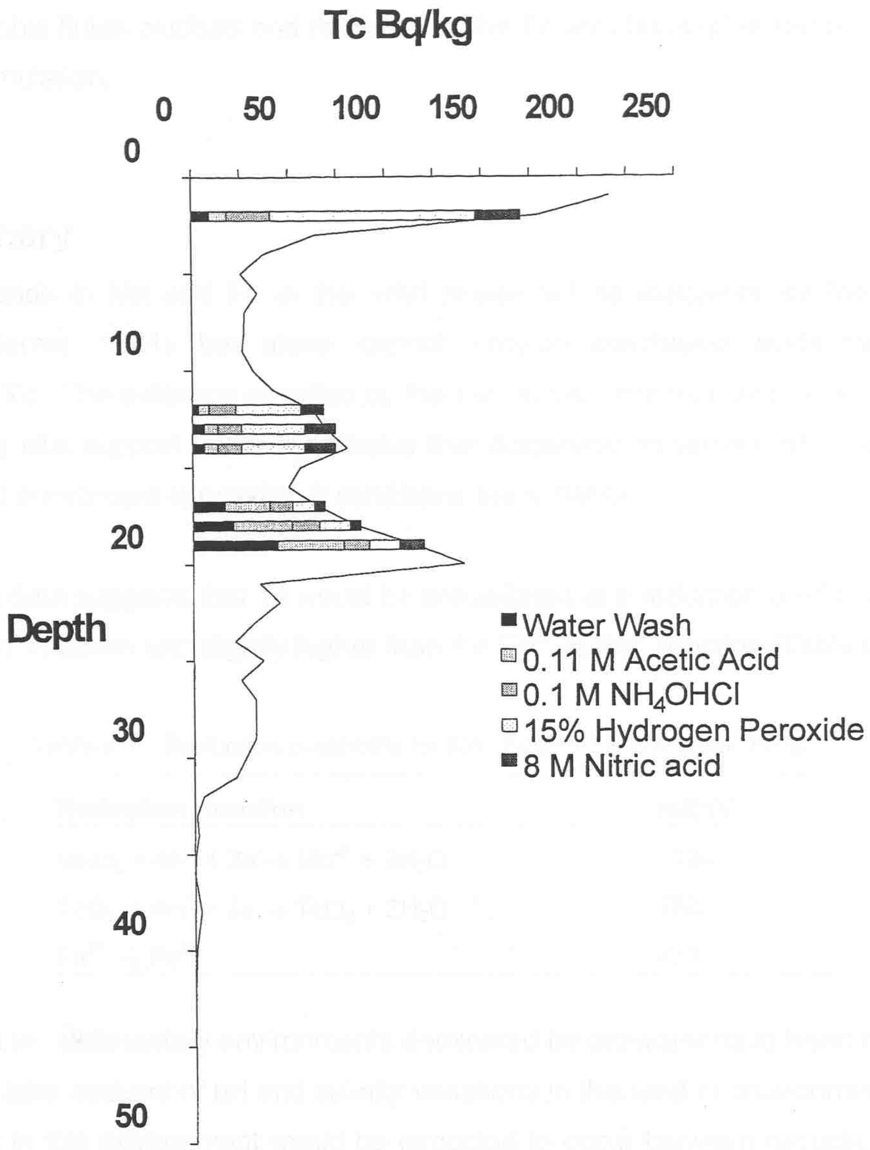

Figure 6.16. Sequential extraction data from Core R-96-007.

The MnO: Al_2O_3 and I/Br profiles of Core R-96-007 imply a localised reduction spot at a depth of 20cm (Figure 6.13). Sequential extraction data from ^{99}Tc in the samples taken from the peak at a depth of 20cm in Core R-96-007 indicate that most Tc present as an easily soluble form. These data help substantiate the hypothesis that this peak has formed by the secondary accumulation of Tc by diagenetic processes. It is likely that the Tc has either been reduced from TcO_4^- to TcO_2 or the pertechnetate has been reduced to a form which is more favourably adsorbed to the clay fraction. In either case the Tc in the sample will have been re-oxidised to TcO_4^- during the sample preparation procedure and so easily dissolved and removed in the first two fractions. This is not like the more strongly bound Tc seen in the ^{99}Tc maxima at 2 cm and 14 cm which is not readily dissolved.

The sequential extraction data infer that the ^{99}Tc is initially accumulated in the sediments as strongly bound species, probably to the organic fraction or sorbed to minerals. Subsequent exposure to aerobic fluids oxidises and remobilises the Tc until favourable redox conditions permit secondary accumulation.

6.5.4. Summary

Geochemical trends in Mn and Fe in the solid phase act as indicators for the potential redox environment (Berner 1981) but alone cannot provide conclusive evidence of secondary accumulation of Tc. The evidence provided by the sequential extraction experiments, although only qualitative, gives vital support to the hypothesis that diagenetic movement of Tc in a sedimentary environment and enrichment is possible if conditions are suitable.

Thermodynamic data suggests that Tc would be precipitated at a reduction potential lower than that of the Mn^{IV} to Mn^{II} reaction and slightly higher than the Fe^{3+} to Fe^{2+} reaction (Table 6.7).

Table 6.7. Reduction potentials for Mn, Tc and Fe (Vanysek 1996)

Reduction Reaction	**mE°/V**
$MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O$	1224
$TcO_4^- + 4H^+ + 3e \rightarrow TcO_2 + 2H_2O$	782
$Fe^{3+} \rightarrow Fe^{2+}$	771

Redox reactions in sedimentary environments dominated by seawater have been modelled (Turner *et al.* 1981) and take account of pH and salinity variations in this kind of environment (Figure 6.17). Reduction of Tc in this environment would be expected to occur between reduction of Mn and Fe, close to the post oxic redox boundary. In cores R-96-007 and R-96-008 concentrations of ^{99}Tc which do not correlate with discharge peaks are observed, they do however correlate with drops in the $MnO:Al_2O_3$ ratio indicating a reduction of Mn^{IV} to Mn^{II}. No significant reduction of Fe is observed in any of the core profiles collected from any of the three sample sites. In all other cores there is no reduction observed in the Mn profiles, but there are also no peaks in ^{99}Tc activity unrelated to discharge. Core data imply that the reduction of TcO_4^- to TcO_2 takes place between the reduction potentials of Mn^{IV}/Mn^{II} and Fe^{III}/Fe^{II} (Figure 6.17). This region is where reduction would be expected based on published thermodynamic data (Table 6.7).

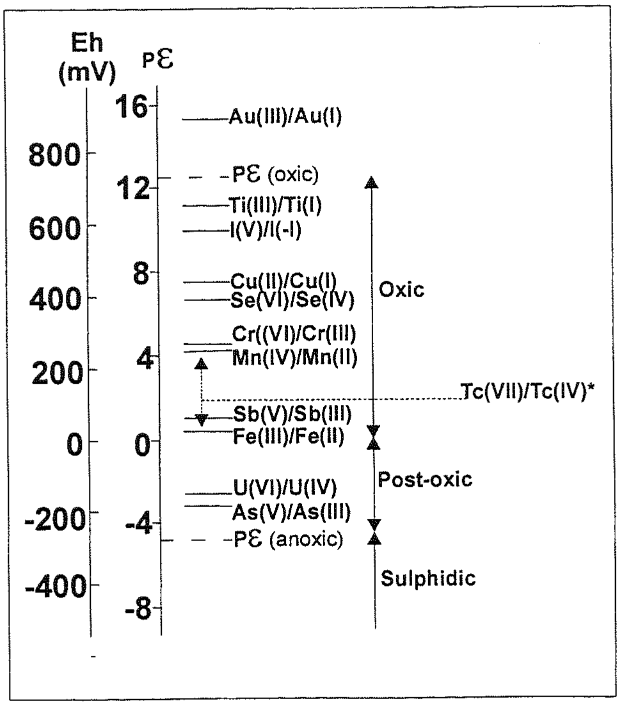

Figure 6.17. Equilibrium electron activity diagram for elements in model seawater (after Turner *et al.* 1981), together with inferred geochemical environment classifications (Berner 1981). The Eh/pE correlation is for 298°K (pE = EhF/2.3RT, and the pE values of the axic and anoxic boundaries are for O_2/H_2O and the onset of both sulphate reduction and methanogenesis, respectively (Turner 1981). *The spread for Tc(VII)/Tc(IV) is based on observations from collected cores.

In the more reducing environment of Core W-98-001, accumulation of Tc is seen to occur at similar points to Mn. It is therefore possible that the same mechanisms responsible for Mn accumulation (*e.g.* formation of goethite, siderite and alabandite) are also responsible for Tc accumulation.

Enrichment of Tc occurs higher in the core than would be expected from the study of Re as a geochemical analogue of Tc. Re has been reported to become enriched at redox potentials lower than those for both Mn^{IV} Mn^{II} and Fe^{III} Fe^{II} half equations (Crusius *et al.* 1996). As Tc enrichment is observed in cores where there is no depletion of Fe associated with the reduction of Fe^{III} to Fe^{II} it must be assumed that Tc enrichment occurs at a higher redox potential than that of Re.

In both the Carlaverock and the Thornflatt saltmarshes the ^{99}Tc profile remains similar to the discharge profile towards the rear of the marsh. Slight attenuation of the peaks is observed but in neither marsh is there any significant secondary enrichment in these cores. The cores taken from closer to the front of the marsh show greater attenuation of their ^{99}Tc profiles. In Core SUTL-332 on the Carlaverock marsh very little ^{99}Tc is seen in the collected core and it is possible that the Tc has migrated to a depth below the bottom of the core, or laterally through advection (Carr and Blackley 1986). In Cores R-96-007 and R-96-008 some migration of the ^{99}Tc has been observed before secondary accumulation. As these cores are also the only ones studied which have developed redox related $MnO:Al_2O_3$ profiles it appears that only the front edge of the marsh had developed the redox conditions necessary for secondary accumulation of Tc.

6.6. Conclusions

1. Recent EARP related discharges are manifested at the top of the cores collected from the Thornflatt saltmarsh and the Carlaverock saltmarsh.

2. ^{99}Tc:^{137}Cs ratio peaks compare to that of Sellafield discharge and are similar in both the Thornflatt and the Carlaverock cores indicating that the proportion of ^{99}Tc reaching the saltmarsh remains half that of ^{137}Cs despite the increase in distance.

3. Sediments cannot be used to reflect discharge levels of ^{99}Tc due to possible diagenetic migration of ^{99}Tc within the core profile. ^{99}Tc maxima do not correlate well with ^{99}Tc discharge data in cores which exhibit clear measured ^{137}Cs and ^{241}Am activity profiles which correlate well with ^{137}Cs and ^{241}Am discharge profiles from Sellafield.

4. Initial accumulation is as strongly bound species, possibly derived from both contaminated sediments and as an input of ^{99}Tc contaminated water to the marshes through vegetation.

5. Subsequent oxidation remobilises Tc and secondary accumulation occurs where redox conditions are favourable. These require a reduction potential between those for Mn^{IV}/Mn^{II} and Fe^{III}/Fe^{II} as suggested by published thermodynamic data.

6. In reducing sediments accumulation of Tc corresponds with that of Mn. It is likely that the same accumulation mechanisms (*e.g.* formation of goethite, siderite and alabandite) are therefore responsible.

6.7. Reference List

Aarkrog A., Dahlgaard H., Hellstadius L., Hansen H ., Holm E. 1983. Radio-caesium from Sellafield effluents in Greenland waters. Nature **304.** 49 – 51.

Aarkrog A., Dahlgaard H., Hallstadius L., Holm E., Mattsson S., Rioseco J. 1986. In Desmet G., Myttenaere C. (eds.) "*Technetium in nature*" 69 – 78. Elsevier.

Baxter M.S., McKinley I.G., MacKenzie A.B., Jack W. 1979. Windscale Radio-caesium in the Clyde Sea area. Mar. Poll.Bull **10.** 116- 120.

Beasley T.M., Lorz H.V. 1986.
A review of the biological and geochemical behavior of technetium in the marine environment. In Desmet G., Myttenaere C. (eds.) "*Technetium in nature*" 197-218 Elsevier.

Berner R.A. 1981. A new geochemical classification of sedimentary environments. J. Sed. Pet. **51.** 359-365.

BNFL. 1983-1997. Annual report on the radioactive discharges and monitoring of the environment. Directorate of Health, Safety & Environmental Protection. BNFL. Warrington.

Bonnotto S., Kirkmann R., Van Baelen J., Hurtgon C., Cogneau M., Van Der Ben D., Verthe C., Bouquegneau J.M. 1985. Behaviour of technetium in marine algae. In: Bulman R.A. & Cooper J.R. (eds.) *Speciation of fission and activation products in the environment.* Elsevier, London. 382 – 390.

Busby R., McCartney M., McDonald P. 1997. Technetium-99 concentration factors in Cumbrian seafoods. Radioprotection Colloques **32.** C2 311-316.

Carr A.P., Blackley M.W.L. Implications of sedimentological and hydrological processes on the distribution of radionuclides: The exampleof a saltmarsh near Ravenglass, Cumbria. Estuarine, Coastal and Shelf Science. **22.** 529-543.

Clifton R.J. 1991. The use of radionuclides (unsupported ^{210}Pb, ^{7}Beand ^{137}Cs) in describing the mixing characteristics of estuarine sediments. In : Radionuclides in the study of marine processes, Elsevier Applied Science 255-264.

Coleman M.L. 1985. Geochemistry of diagenetic non-silicate minerals: kinetic considerations. Phil. Trans. R. Soc. Lond. A. **315.** 39-56.

Croudace I.W. 1991. A reliable and accurate procedure for preparing low activity efficiency calibration standards for germanium gamma-ray spectrometers. J. Radioanal. Nucl. Chem. Lett. **153(2).** 151-162.

Cundy A.B., Croudace I.W. 1995. Physical and chemical associations of radionuclides and trace metals in estuarine sediments: an example from Poole Harbour, Southern England. J. Environ. Radioact. **29.** 191-211.

Crusius J., Calvert S., Pedersen T., Sage D. 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxi, sub oxic and sulphidic conditions of deposition. Earth Planet. Sci. Lett. **145.** 65 - 78.

Day J.P., CrossJ.E. 1981. ^{241}Am from the decay of ^{241}Pu in the Irish Sea. Nature **292.** 43-45.

Deer W.A. Howie R.A., Zussman J. 1992. An introduction to the rock forming minerals. Longman Scientific Press. Harlow.

Fowler S.W., Benayoun G., Parsi P., Essa M.W.A., Schulte E.H. 1981. Experimental studies on the bio-availability of technetium in selected marine organisms. In: Impacts of radionuclide releases into the Marine Environment. Vienna IAEA 319-39.

Fowler S.W., Aston S.R., BenayonG., Parsi P. 1983. Bio-availability of Technetium from artificially labeled North East Atlantic deep sea sediments. Mar. Environ. Res. **8.** 87 – 100.

Gray J., Jones S.R., Smith A.D. 1995. Discharges to the environment from the Sellafield site 1951-1992. J. Radiol. Prot. **15.** 99-131.

Henrot J. 1989. Bio-accumulation and chemical modification of technetium by soil bacteria. Health Physics **57.** 238 – 245.

Hamilton E.I., Clarke K.R. 1984. The recent sedimentation history of the Esk Estuary, Cumbria, UK: The application of radiochronology. Sci. Total. Environ. **35.** 325-386.

Hamilton E.I. 1985. Radionuclides and large particles in estuarine sediments. Mar. Poll. Bull. **20.** 603-607.

Hill A.E., Brown J., Fernand L. 1997. The summer gyre in the western Irish Sea: Shelf sea paadigms and management implications. Esturaine, Coastal and Shelf Science **44.** (A) 83-95.

Horrill A.D. Concentrations and spatial distribution of radioactivity in an ungrazed saltmarsh. In Coughtrey P.J. (ed.). British Ecological Society, Special publication No 3, Blackwell, Oxford 199-215.

IAEA Technical Report. 1985. Sediment k_D's and concentration factors for radionuclides in the marine environment. IAEA Vienna.

Jeffries D.F., Preston A., Steele A.K. 1973. Distribution of caesium-137 in British coastal waters. Mar. Poll. Bull. **4.** 118 - 122.

Kenna B.T., Kuroda P.K. 1964. Technetium in nature. J. Inorg. Nucl. Chem. **26.** 493 - 499.

Kershaw P.J., Woodhead D.S., Malcom S.J., Allington D.J., Lovett M.B. 1990. A sediment history of the Sellafield discharges. J. Environ. Radioact. **12.** 201-241.

Leonard K.S., McCubbin D., Brown J., Bonfield R.A., Brooks T. 1997. A summary report of the distributions of ^{99}Tc in UK coastal waters. Radioprotection Colloques **32.** 109 – 114.

Masson M., Patti F., Colle C., Roucoux P., Grauby A., Saas A. 1989. Synopsis of French experimental and in situ research on the terrestrial and marine behaviour of technetium. Health Physics **57.** 269 – 279.

McDonald P., Cook G.T., Baxter M.S., Thomson J.C. 1990. Radionuclide transfer from Sellafield to South West Scotland. J. Environ.Rad. **12.** 285-298.

Ramsay J.D.F., Raw G. 1987. Physical characteristics of colloids and particulates in coastal sediments and seawater. DOE Report No: DOE/RW/87.066. HMSO. London.

Sanchez A.L., Horrill A.D., Howard B.J., Singleton D., Mondon K. 1997. Radionuclides in tide washed pastures bordering the Irish sea coast of England and Wales. Water Air and Soil Pollution **106.** 403-424.

Stanners D.A., Aston S.R. 1979. The determination of estuarine sedimentation rates by 134/137 Cs and other artificial Radionuclide profiles. Estuarine, Coastal and Shelf Science **9**. 529-541.

Stanners D.A., Aston S.R, 1981. An improved method of determining sedimentation rates by the use of artificial radionuclides. Estuarine, Coastal and Shelf Science **13**. 101–106.

Till J.E., Hoffmann F.O. and Dunning D.E. 1979. A new look at ^{99}Tc releases to the atmosphere. Health Physics **36.** 21-.

Turner D.R., Whitfield M., Dickson A.G. 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25C and 1 atm pressure. Geochim. Cosmochim. Acta **45.** 855 - 881.

Vanysek P. 1996. Electrochemical series. In: Lide D.R. (ed). *Handbook of chemistry and physics.* CRC Press. London. 8.21-8.31.

Wigley F., Warwick P.E., Croudace I.W., Caborn J., Sanchez A.L. 1999. Optimised method for the routine determination of technetium-99 in environmental samples by liquid scintillation counting. Anal. Chim. Acta **380.** 73-82.

Chapter 7

Spatial accumulation and Inventory of ^{99}Tc in the Thornflatt saltmarsh, Esk Estuary: Implications for saltmarsh sediments as sinks for ^{99}Tc

Chapter 7. Spatial accumulation and inventory of ^{99}Tc in the Thornflatt Salt Marsh, Esk Estuary: Implications for saltmarsh sediments as sinks for ^{99}Tc.

7.1. Abstract

^{99}Tc discharges to the environment increased tenfold after the commissioning of the EARP Plant in 1994 and subsequent reprocessing of previously stockpiled wastes. As a result of this, studies of ^{99}Tc activities in marine organisms indicated a dramatic rise in the activities of ^{99}Tc in shellfish and *Fucoid* seaweeds. However, due to the conservative nature of the pertechnetate oxyanion, aerobic sediments had not been considered as potential sinks for ^{99}Tc. A preliminary study of sediment cores taken from the Thornflatt Saltmarsh, Esk Estuary, Cumbria, indicated that all ^{99}Tc along with ^{137}Cs and ^{241}Am in the sediment column was found in the top 50 cm. A spatial study of ^{99}Tc activities in the Thornflatt saltmarsh was made to assess potential input mechanisms for ^{99}Tc to the sediment column. Cores were taken to a depth of 50 cm, homogenised and the total ^{99}Tc inventory (accumulated deposition: Bq/m^2) was determined. A spatial distribution could then be mapped independent of variability in ^{99}Tc with depth. Spatial data for ^{99}Tc activities indicate greater accumulation of Tc along the front of the marsh and in the marsh centre in close proximity to the major drainage creeks. Further analyses for ^{137}Cs, ^{241}Am, trace and major elements as well as variation in sediment accumulation rate were undertaken. Correlation of ^{99}Tc with other sediment components suggests that Tc input mechanisms are different from those radionuclides which are more readily sorbed to inorganic particulates (*e.g.* ^{241}Am). A good correlation with Ca indicates that the highest Tc accumulation is in areas which also have a high proportion of shell fragments; implyung areas which are frequently inundated. The total inventory over the marsh was estimated using ordinary kriging and was found to be 1.64 GBq of ^{99}Tc which represents 1.3 x10^{-6} of the total ^{99}Tc discharge from Sellafield. This is a higher proportion of the discharge than would be expected when compared to the published k_D of Tc in sediments, although these are only first approximations. Saltmarsh sediments may therefore be a more important sink for conservative radionuclides than previously thought, though a higher proportion of more particle reactive radioisotopes discharged accumulate in saltmarsh sediments. Potential routes of the transfer of ^{99}Tc to the food chain have been highlighted though further study of transfer factors, but quantification of these must be made before a dose estimate for ^{99}Tc held within saltmarsh sediments can be made.

7.2. Introduction

This study has shown that Tc accumulates in sediments, both in aerobic and anaerobic environments (Chapter 6). Tc was also found to be mobile in the sediment column, with a downward migration of the ^{99}Tc activity peaks observed in most cores. In two cores collected from the Thornflatt saltmarsh (Core R-96-007 and Core R-96-008) remobilization and secondary accumulation of ^{99}Tc was observed, at depths where a localised drop in reduction potential could be inferred from tends in the MnO/Al_2O_3 ratio. Although the input of ^{99}Tc into the saltmarsh is still only partially understood, radionuclide activity data presented in Chapter 6 imply that Tc is transported to the saltmarshes studied in a similar manner to ^{137}Cs.

In order to study the input and spatial variation of ^{99}Tc to the marsh surface scrape samples will not be truly representative, as they only reflect the recent input of Tc to the marsh, and will consequently be temporally restricted. The activity of radionuclides present in surface scrape samples may be altered by surface silt loading on a day to day basis due to a variety of conditions including rainfall, tidal height, and weather conditions. Surface scrape samples also make no representation of the higher activities of radionuclides which may be held at greater depth within the sediment profile. The entire contaminated sediment column should be considered when an assessment of the inventory of radionuclides is made, as a large proportion of the sediment column may be remobilised during storm events or dredging. Vegetation on the marsh will also be drawing nutrients from depth within the sediment which may include the entire contaminated sediment column. A study of the entire sediment column is therefore important when a consideration is made of the potential dose from a contaminated saltmarsh. The low distribution coefficient of Tc (10^2; IAEA 1985) indicates that Tc is conservative in nature and so may readily diffuse into the sediment, although this depends on the sediment permeability. To circumvent these problems cores need to be taken to a sufficient depth below where the radionuclides may have migrated. This depth must be investigated by sectioning cores and the determination of ^{99}Tc to depths below the activity profile prior to the collection of the inventory cores. The spatial distribution of integrated Tc within homogenised cores may be then determined irrespective of temporal variation and post depositional vertical migration.

Due to its conservative nature Tc accumulation in aerobic sediments, and their role as a potential sink, has not previously been considered. Tc accumulation both due to primary input and secondary accumulation as a result of post depositional processes means that sediments must be considered as sinks for Tc as well as other possible contaminants. Subsequent erosion or dredging of Tc contaminated sediments would lead to the rapid redissolution of Tc as pertechnetate and remobilization into the environment. Previous work has studied the distribution of other radionuclides derived from BNFL Sellafield to saltmarshes in the Irish Sea

(Day and Cross 1981, Stanners and Aston 1981, Horrill 1984, Hamilton and Clarke 1984, Howard and Livens 1991, Fridlington *et al.* 1997, Poole *et al.* 1997, Sanchez *et al.* 1997), although most of this work has used 1 cm surface scrapes for analysis.

The primary potential dose from ^{99}Tc held in the sediments is through direct ingestion or inhalation of contaminated sediment (MacKenzie and Scott 1993). A less significant doe to individuals inhabiting the marsh is either through external dose through occupancy of the sites or internal dose derived from the transfer of radionuclides to food products. This may either be through the ingestion of contaminated material by grazing livestock (Sanchez *et al.* 1997) or bio-accumulation of ^{99}Tc to marine organisms, particularly shellfish (Busby *et al.* 1997) following remobilization after a storm event.

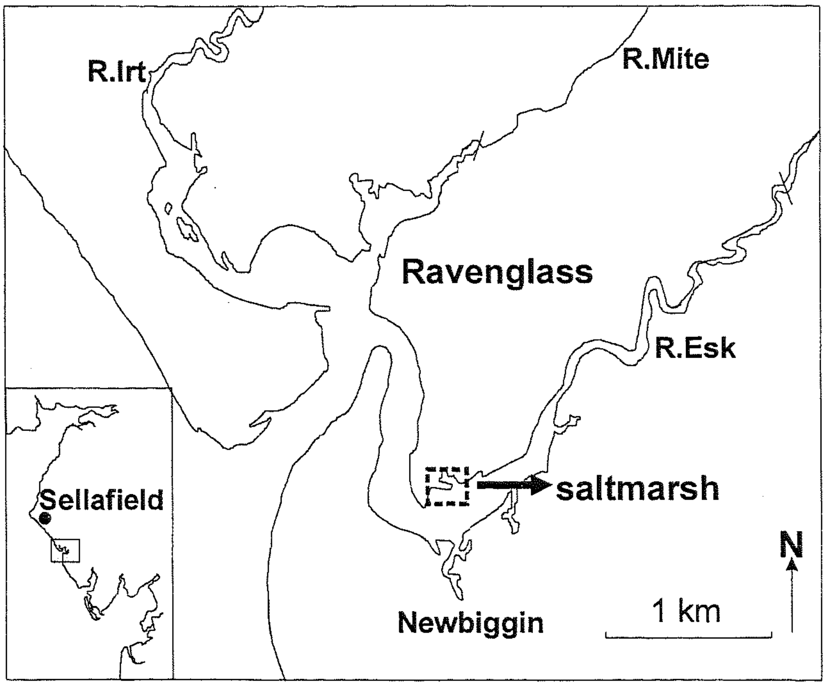

Figure 7.1. Location of the Esk estuary in relation to BNFL Sellafield.

The Thornflatt saltmarsh was chosen as a study site as the marsh is known to contain sediments contaminated with measurable activities of ^{99}Tc (Chapter 6). The marsh is located on the northern side of the Esk Estuary, approximately 10 km south of the Sellafield site (UK national Grid SD089947, Figure 7.1). The marsh receives a component of the Sellafield discharge and is relatively sheltered from storms. The saltmarsh is relatively undisturbed since it is ungrazed and not visited by the general public.

7.3. Methodology

7.3.1. Sampling

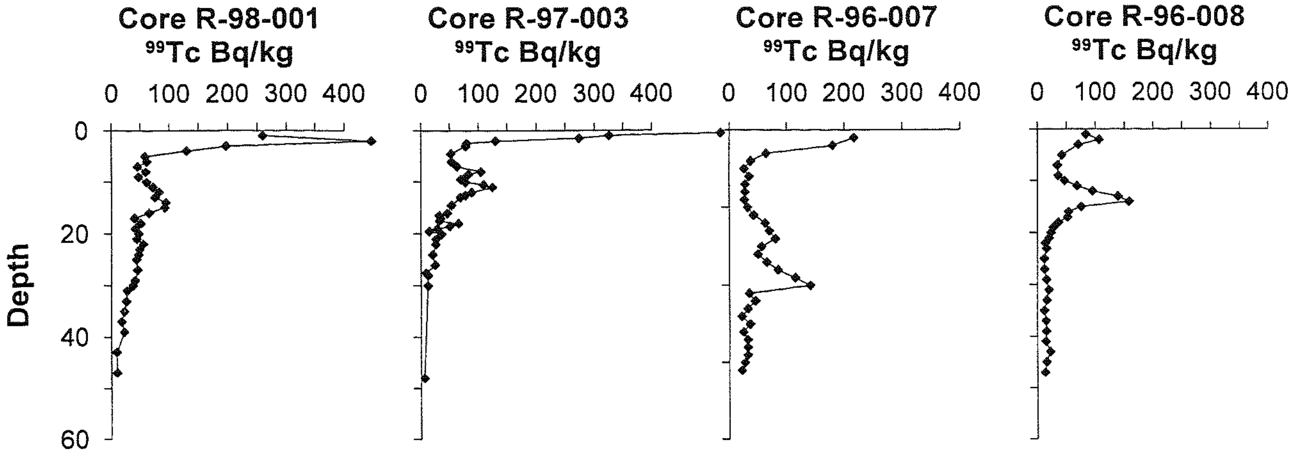

Figure 7.2. ^{99}Tc profiles in cores taken from the Thornflatt Saltmarsh (see Chapter 6).

^{99}Tc and other anthropogenic radionuclides derived from Sellafield were seen to reach their limits of detection by a depth of 50 cm in the cores collected from the Thornflatt marsh (Figure 7.2) for the study of the behaviour of ^{99}Tc in sediments (Chapter 6). Cores were therefore taken to a depth of 50 cm to determine their inventories for this study. After homogenisation these cores will contain all the radionuclides which have been deposited at that site whether there has been some downward diagenetic movement or not. Consequently the total activity of ^{99}Tc input to a particular area of the marsh can be determined. Lateral migration of ^{99}Tc in sediments cannot be accounted for using this technique. This study therefore gives an indication of time integrated spatial distribution that does not purely represent variation in Tc deposition rates but also takes account of post depositional-processes which may be responsible for migration of Tc.

15 cores were collected from the saltmarsh in November 1998 using a pre-established sampling grid (Horrill 1984) for reference (Figure 7.3). A further 12 cores were collected in March 1999 to increase the sampling resolution.

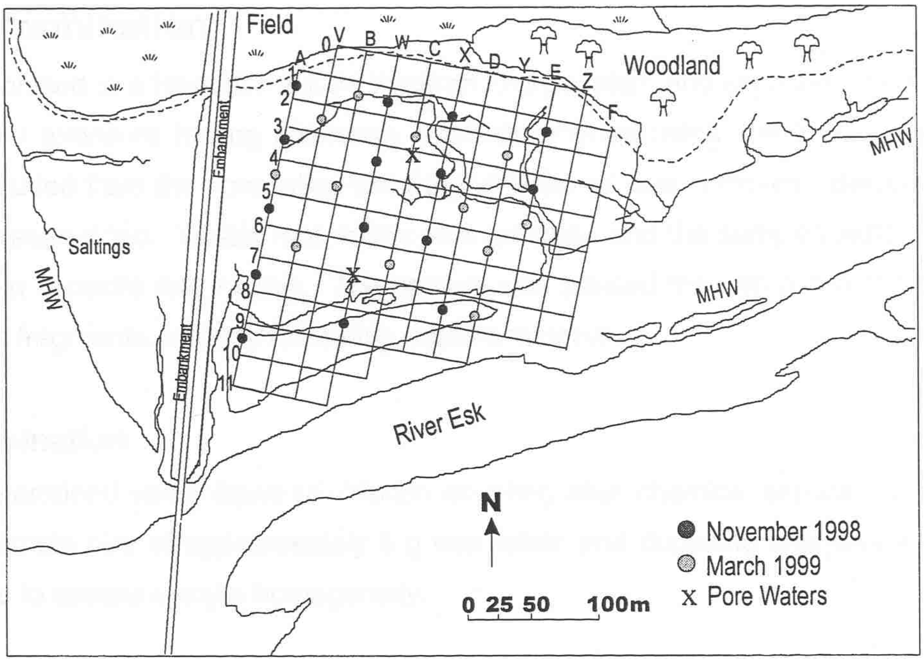

Figure 7.3. Location of core samples collected from the Thornflatt saltmarsh

Samples were taken by insertion of a 36 mm (internal diameter) PVC tube to a depth of 50 cm. The compression was determined by measuring the depth from the top of the core tube to the sediment core compared to the external sediment surface. The core tube was then twisted to break the sediment at the bottom before being extracted. The depth of the hole left by the sediment cores was measured to ensure that a depth of exactly 50 cm was reached. Care was taken to collect cores away from the intersection points on the grid as these sites have been previously disturbed by sampling and so may not be representative.

Vegetation samples were collected in November 1998. Plants were carefully uprooted and excess sediment removed by washing in seawater. Samples were then bagged and transported to Southampton. All samples were stored at 4°C and rewashed in fresh water prior to analysis.

Pore-water samples were supplied by Dr Francis Livens of the Department of Chemistry, University of Manchester. Pore-water samples were collected in porous pots inserted into the saltmarsh sediments. Eh and pH were determined immediately after extraction and the samples acidified with 5 ml concentrated nitric acid prior to transportation to Southampton.

7.3.2. Determination

Cores were placed in a Hewlett Packard Faxitron X-ray system and exposed for 6 mins at 56 kV (The optimum exposure having previously been determined using test films). Sediment was carefully extruded from the core tubes ensuring all material was removed. Samples were then frozen and freeze-dried. Visible root matter was removed and the samples were homogenised by grinding in a pestle and mortar. The sample was passed through a 1 mm mesh sieve to remove lithic fragments and any remaining organic material.

^{99}Tc determination

^{99}Tc was determined using liquid scintillation counting after chemical separation (Wigley *et al.* 1999). A sample size of approximately 5 g was taken and duplicate analyses were made on each sample to ensure sample homogeneity.

γ spectrometry

Approximately 20g of sample was transferred to a 22ml polythene liquid scintillation vial and the exact mass of the sample recorded. The sample was then counted on a well-type high purity germanium (HPGe) detector. The resulting energy spectrum was deconvoluted and the activity of each identified radionuclide calculated using Fitzpeaks software. The gamma spectrometer was previously calibrated for both energy and efficiency against an Amersham QCY-48 mixed radioisotope standard adsorbed onto a sediment matrix (Croudace 1991). Perodic checking was also made by counting IAEA 135 (marine mud).

X-ray fluorescence analysis

An aliquot of the dried sample was ignited at 900°C for a minimum of 2 hours to decompose any organic matter present and to remove other volatiles. 0.800g of the ignited material was intimately mixed with 4.00g of a eutectic (4:1) mixture of lithium metaborate and lithium tetra borate in a grain stabilised Pt-Au crucible. The mixture was then heated to 1200°C in a muffle furnace to melt the flux and the sediment sample. The melt was then cast into a Pt-Au mould and cooled to produce a bead suitable for XRF determination of major elements.

10g of ground sample was pressed into a pellet for trace element determination. Determination for both trace and major elements was made using a Philips PW1400 sequential X-ray fluorescence spectrometer. Precision for XRF analyses was generally in the range of 1-5% and the accuracy of determinations was checked using certified reference materials (*e.g.* USGS-MAG-1).

CHNO-S determination

Total carbon analysis was performed on a Carlo Erba CHNO-S elemental analyser. The sample was ignited by flash pyrolysis and the combustion gases separated by gas chromatography. Final detection of the gases was achieved using a flame ionisation detector. Calcium carbonate was determined by coulometric analysis via the CO_2 evolved on H_3PO_4 acid hydrolysis. Standards of known elemental composition were measured to permit quantification.

7.4. Results and discussion

7.4.1. Spatial distribution of ^{99}Tc on the Thornflatt marsh

^{99}Tc activities in each of the cores were plotted on a grid corresponding to the sampling grid of Horrill (1984). The data were then contoured using the UNIX based Generic Mapping Tool (GMT) by block meaning data at a frequency of 0.2 of each grid square, corresponding to 5 m^2 plots on the marsh. This produced a smooth contour plot for the data available (Figure 7.4).

The area with the maximum accumulation of ^{99}Tc is at the front of the marsh on the low marsh cliff. There is a definite trend of high ^{99}Tc activities toward the front of the marsh with a general decline in activities toward the north west corner (Figure 7.4). An area of elevated ^{99}Tc activities exists in the mid rear of the marsh, close to the end of the major creek that drains most of the marsh.

These localised areas of increased ^{99}Tc activity suggest that there must be some regional factors responsible for the heterogeneous accumulation of ^{99}Tc across the marsh. A variety of factors could be responsible including: variations in the vegetation cover across the marsh, variations in the organic input to the sediment, localised differences in the mineralogy, differences in the pore water content, variations in the stability of redox conditions within the marsh, or the frequency of inundation. Other radionuclides and stable elements have been well studied and so a correlation of ^{99}Tc activities with these elements can be used to evaluate the nature of Tc accumulation over the marsh.

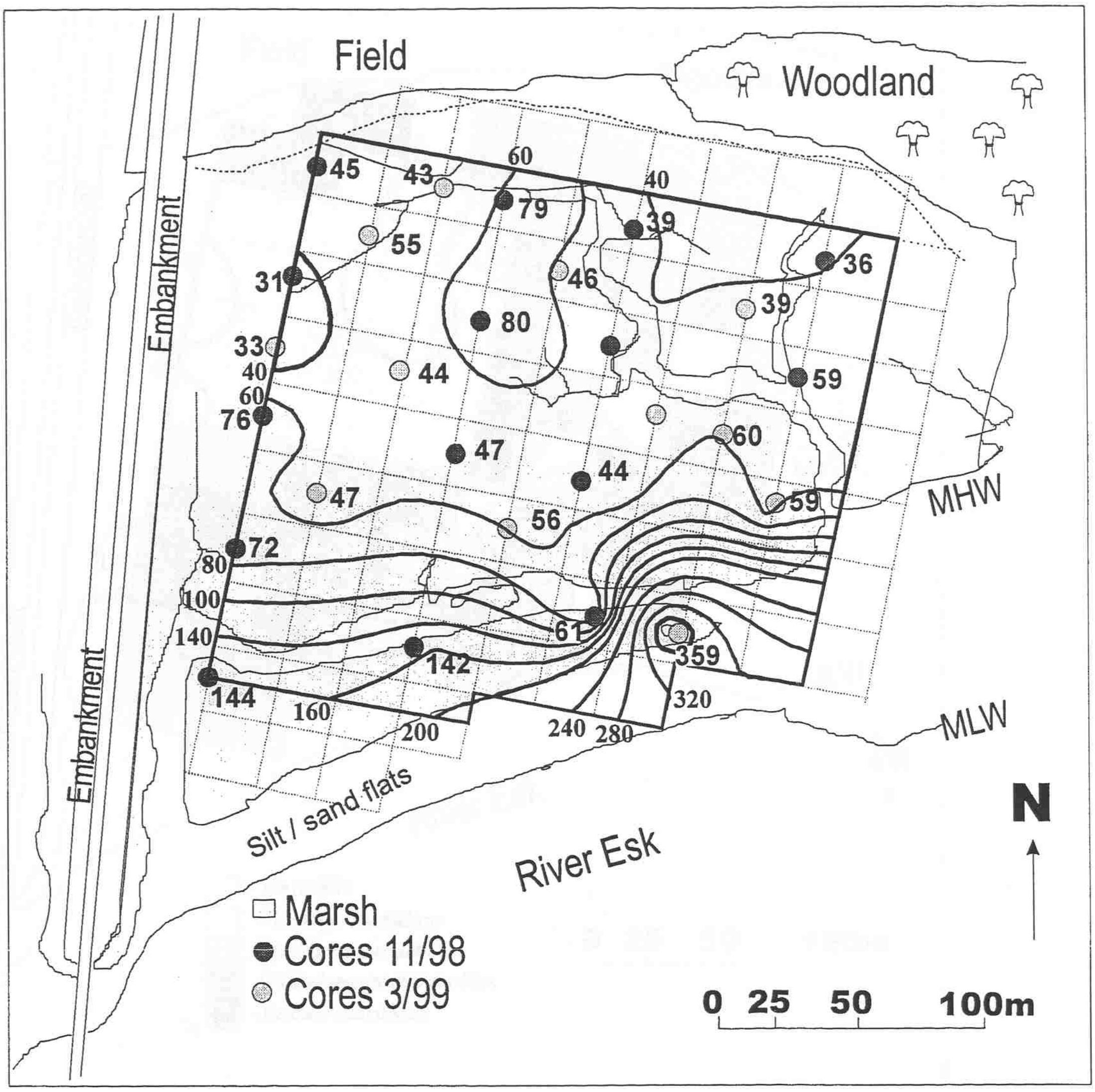

Figure 7.4. ^{99}Tc activity concentrations on the Thornflatt Saltmarsh. Activities are in Bq/kg.

7.4.2. ^{99}Tc correlation with vegetation type

A previous study of the role of vegetation in the accumulation of radionuclides (not ^{99}Tc) to the Thornflatt saltmarsh attributed physical processes, particularly tidal mechanisms to be the most important factors influencing accumulation (Horrill 1984), although the form of the vegetation was found to be important in determining deposition rates. A comparison between ^{99}Tc activities in the sediment cores and the defined vegetation zones on the marsh indicate no clear link between vegetation type and the spatial distribution of ^{99}Tc (Figure 7.5).

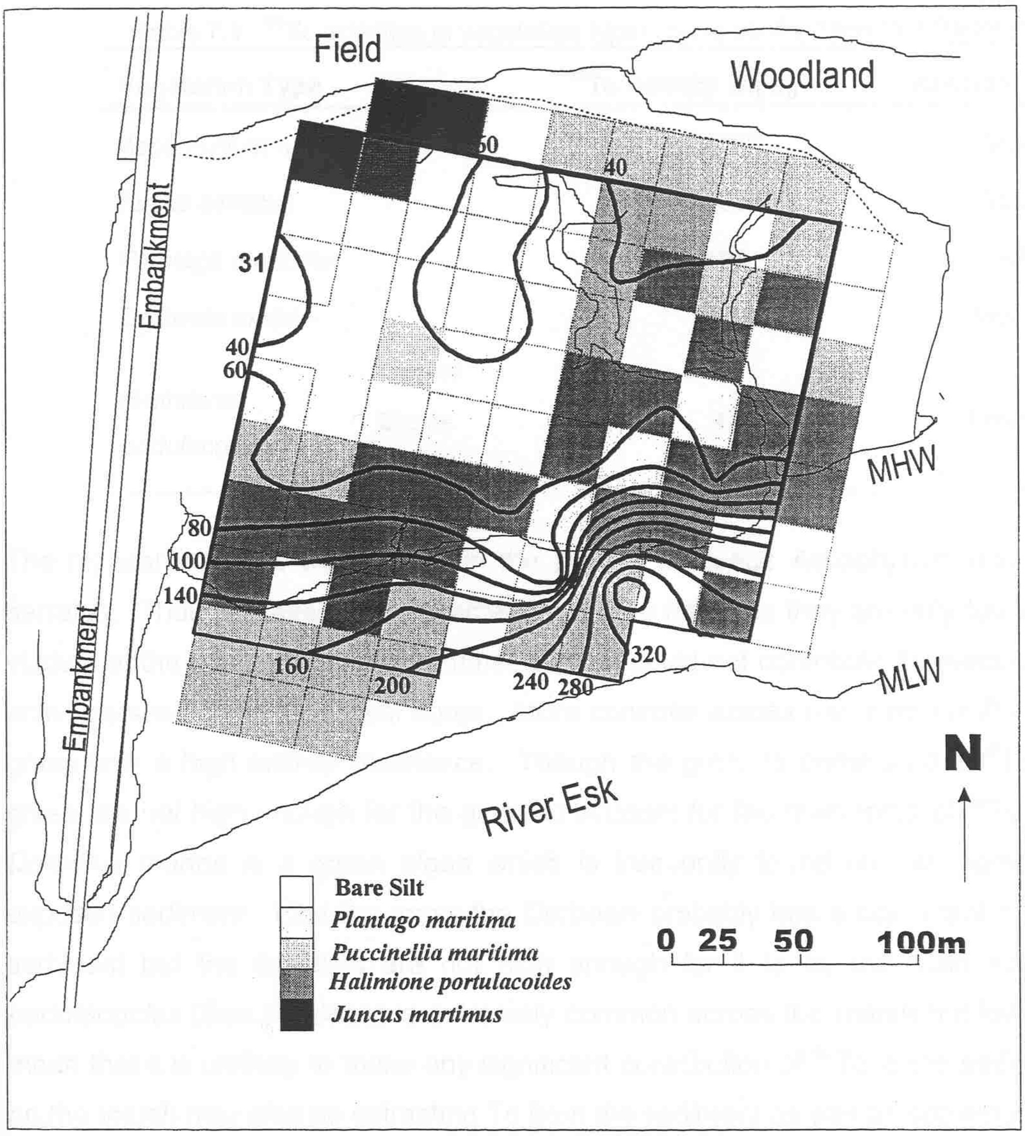

Figure 7.5. Distribution of dominant vegetation species on Thornflatt saltmarsh, compared to variations in ^{99}Tc activity (Bq/kg) (after Horrill 1984).

The determination of ^{99}Tc in individual biota was made (Table 7.1) as the dominant species plotted (Figure 7.5) may not be the species responsible for Tc input to the sediment. High ^{99}Tc activities in any one species which was extensive across the marsh would indicate a potential source for input of ^{99}Tc to the sediment once the host plant had died and become incorporated into the sediment.

Table 7.1. ^{99}Tc activities in vegetation types found on the Thornflatt Saltmarsh.

Vegetation Type		**^{99}Tc Activity Bq/kg**	**Abundance**
Ascophyllum nodosum		76000	Scarce
Fucus serratus		20000	Scarce
Plantago maritima		104	Medium
Derbesia marina		320	Medium
Halimione portulacoides	Leaves	15	Frequent
	Stems	47	
	Roots	64	

The highest activities were found in the brown seaweeds *Ascophyllum nodosum* and *Fucus serratus.* Though these have extremely high ^{99}Tc activities they are only found growing on the viaduct at the western end of the marsh and so could not contribute the necessary input for the activities seen in the sediment cores. More common across the marsh is *Plantago maritima* a grass with a high salinity resistance. Though the grass is common the ^{99}Tc activities in the grass are not high enough for the grass to account for the main input of ^{99}Tc to the sediment. *Derbesia marina* is a green algae which is frequently found on the marsh where there is exposed sediment. Like the grass the *Derbesia* probably has a significant input of ^{99}Tc to the sediment but the activities are not high enough for it to be the main source. *Halimione portulacoides* (Sea purslane) is extremely common across the marsh but low activities of ^{99}Tc mean that it is unlikely to make any significant contribution of ^{99}Tc to the sediment. Vegetation on the marsh may also be extracting Tc from the sediment as well as seawater. A clearer study of potential Tc input would come from correlation of ^{99}Tc activities with core components.

7.4.3. ^{99}Tc correlation with core components

Activity data for ^{99}Tc, ^{137}Cs, ^{210}Pb and ^{241}Am as well as major and trace element data, water content, total organic carbon and carbonate, and accretion rates were correlated using Pearson's product-moment coefficient of correlation (r). The results were then plotted on a Cluster Tree (Figure 7.6).

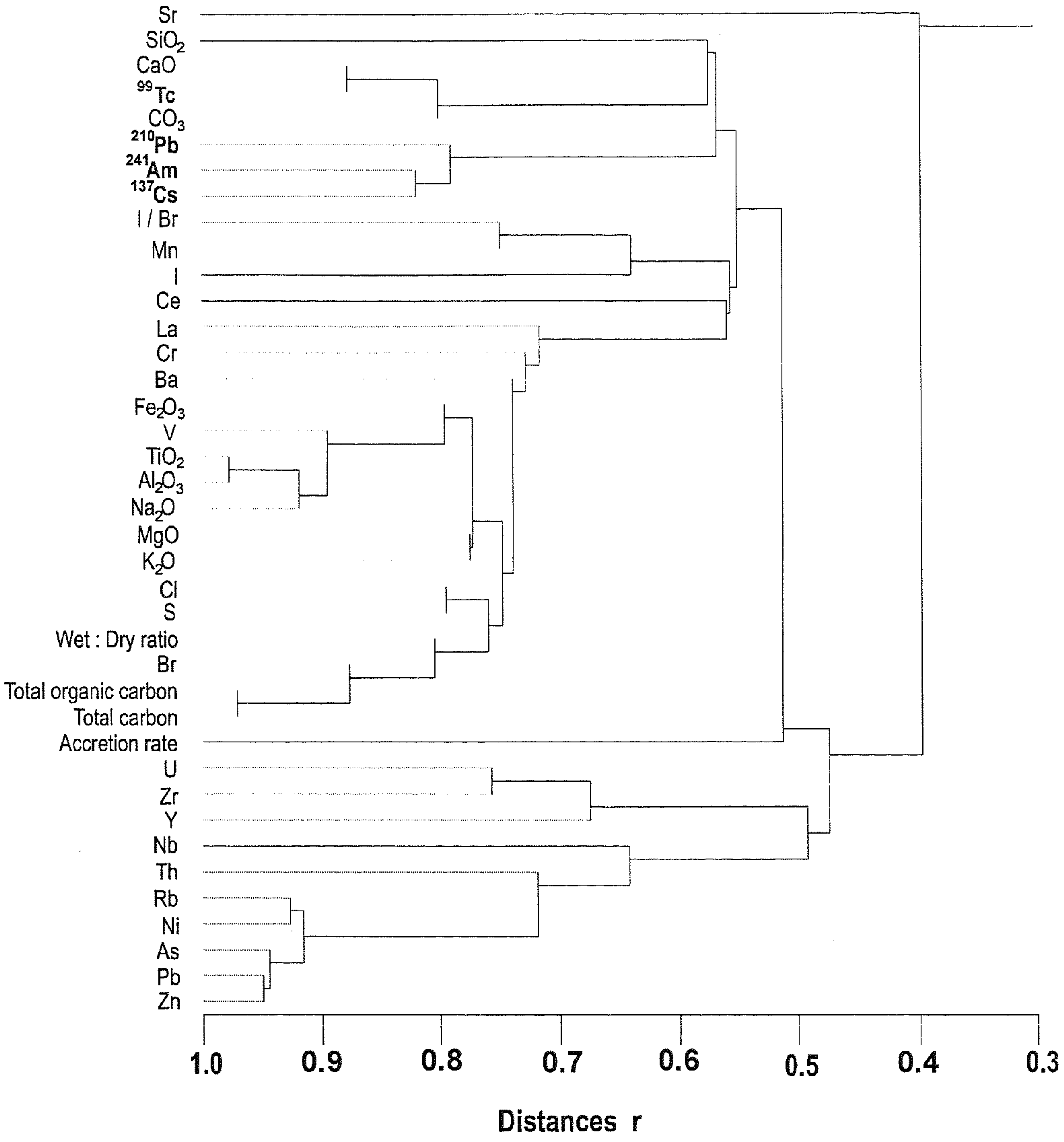

Figure 7.6. Cluster Tree for Pearson's correlation of Core components

7.4.3.1. Justification of the correlation method

Al and Ti are often used as analogues for clay minerals (Cundy and Croudace 1994) and have good correlations with Na, V, and Fe which are also dominantly found in the clay component, though this depends on the clay. Mg and K are also associated with the clay component.

Total carbon and total organic carbon (TOC) have a good correlation indicating that most of the carbon present in the sediments is organically derived. These correlate well with Br which is known to associate with organic material as well as sea water. Sulphur and chlorine, which are most abundant in seawater, imply that pore water is most commonly associated with organic material. Organic material is absorbent and would have higher wet: dry ratio hence high correlation with pore-water.

Heavy metals (*e.g.* Pb, Ni, As) show good correlation with each other but not with the clay mineral group, indicating that they are either present as the result of a pollution event or the presence of heavy minerals in the sediment.

7.4.3.2. ^{99}Tc correlation

^{99}Tc correlates only weakly (r= 0.05 and 0.2) with ^{241}Am and ^{137}Cs. This weakness of correlation is interpreted as being due to different input mechanisms for ^{99}Tc compared with other anthropogenic radionuclides. All the other radionuclides determined are strongly sorbed to inorganic particulate and tend to be input into the marsh by the accretion of inorganic sediment. As Tc does not correlate well with these radionuclides it is assumed that Tc is not accumulated into marsh sediment associated with inorganic material.

^{99}Tc has a correlation of r=0.88 with CaO, and also correlates well with carbonate (Figures 7.6). The strong correlation between ^{99}Tc and CaO does not mean that there is a distinct link between the behaviour of Ca and Tc in the environment. It is more likely that Ca and CO_3 indicate areas which are likely to have a high input of shell fragments which then correlate with high ^{99}Tc activities indicating a mechanistic similarity in their accumulation, rather than a direct association.

Elevated levels of both the Ca and CO_3 components in some of the cores are the result of either an increase in the input of detrital $CaCO_3$ or the growth of carbonate concretions. There is no evidence for secondary carbonate nodules in any of the cores taken (Chapter 6) although the quantity of shell fragments does vary between and within cores. The main source of these shell fragments to the marsh is the mussel beds which stretch from the viaduct by the marsh to the mouth of the Esk (Figure7.1). The concentration factor for ^{99}Tc from seawater by mussels (*Mytylus edulis*) is 2 (Masson *et al.* 1989). The mussels themselves are not likely to be responsible for the elevated ^{99}Tc input.

Increased concentrations of shell fragments represented by an increase in the Ca and CO_3 concentrations at the front of the marsh may be an indicator of more frequent inundation compared to other areas. In an area with a higher inundation frequency the sediments will have a greater exposure to contaminated water or water containing contaminated particulate, leading to elevated ^{99}Tc activities in these sediments.

An increase in inundation frequency does not necessarily correspond to an increase in accretion rate. If this was the case a good correlation between ^{99}Tc activities and the accretion rate would be expected and this is not observed. The poor correlation between ^{99}Tc activities and the pore water component represented by the wet : dry ratio (Figure 7.6) implies that Tc within the sediment column is sorbed to the sediment component and does not remain in the pore water solution. This is confirmed by activities of ^{99}Tc below the limits of detection for two samples (Table 7.2).

Table 7.2. ^{99}Tc activity in pore water samples.

Sample Location (Horrill Grid (Figure 7.3))	**Eh(mV)**	**pH**	**^{99}Tc activity mBq/l**
W7	285	6.2	<5
C3	20	7.5	<4

The transfer of Re, a geochemical analogue of Tc, from seawater to sediment also occurs within the top few centimetres of the sediment (Colander *et al.* 1993). It therefore appears that both Tc and Re are behaving in a similar manner although the exact mechanisms for sorption of Re to minerogenic surfaces are still unclear. A greater understanding of the differences in adsorption between Re and other oxyanions will aid the understanding of the scavenging mechanisms of Tc.

7.4.4. Sediments as sinks for ^{99}Tc: Relative inventories

The inventory for each of the cores was calculated for up to 50cm depth and for a 1 m^2 area using equation [7.1.].

$$I = \frac{A \times M}{\mathrm{a}} \times 1$$

I = inventory (Bq/m^2)
A = Activity (Bq/g) (dry)
M = Total dry mass of sediments in each core (g)
a = Area of the core surface (m^2)

[7.1]

Estimation of the whole marsh inventory for different radionuclides from the limited number of cores taken requires that spatial prediction of the inventories over the entire marsh be made. The appropriate method for prediction of these data is ordinary kriging. Kriging makes inferences on unobserved values of the random process (in this case the determined inventories in the cores) from data observed at known spatial locations (Cressie 1993). Ordinary kriging refers to spatial prediction under the condition that the coefficients of the linear predictor sum to 1 (Matheron 1971, Journel and Huijbreghts 1978) which therefore guarantees uniform unbiasedness.

The data were subject to ordinary kriging using the following grid parameters:

Number of X (East-West) grid points: 10
Number of Y (North-South) grid points: 10
Minimum X value at center of grid: 1.00
Minimum Y value at center of grid: 1.50
Maximum X value at center of grid: 9.00
Maximum Y value at center of grid: 9.50

The structural model was run using the following variogram parameters:

Nugget (c0): 0.00
First rotation angle (azimuth, or degrees clockwise from North): 0.00
Second rotation angle (dip, or degrees down from azimuthal): 0.00
First anisotropy index (anis1=ahmin/ahmax): 1.00
Sill (c): 1.00
Range (a): 1.00

During the kriging process a mean value for each of the radionuclides was determined from the contour plots produced (Figure 7.8). The mean values are based on the inventories beneath the kriged area (Table 7.3a) and were then taken to estimate the radionuclide inventories within the study area.

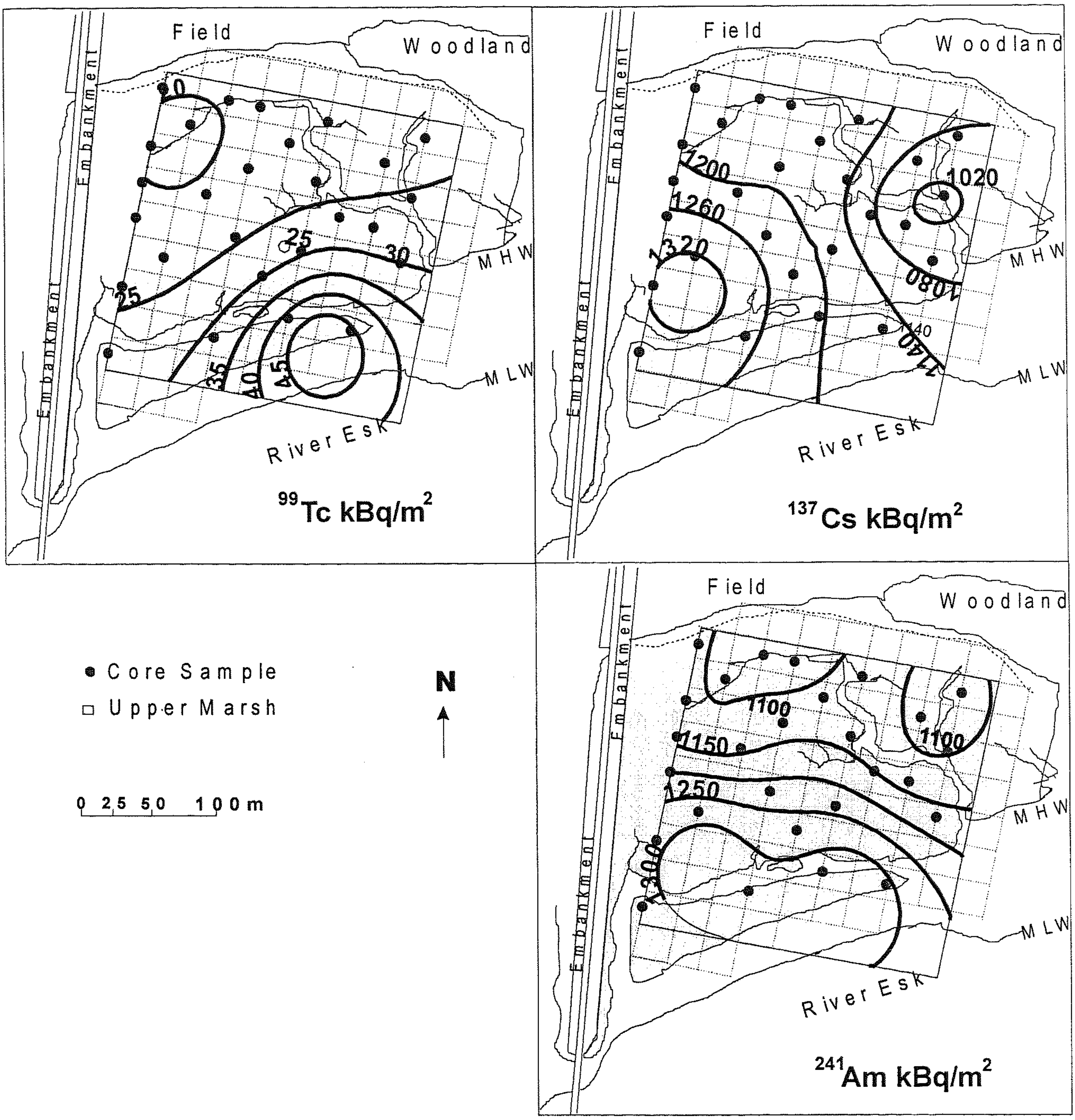

Figure 7.8. Contour plots for radionuclide data after ordinary kriging.

Table 7.3a. Mean inventory values across the kriged area in the Thornflatt marsh.

Radionuclide	Mean inventory kBq/m^2
^{99}Tc	26.3
^{137}Cs	1180
^{241}Am	1180

Table 7.3b. Proportion of Total Sellafield discharge held in sediments within the marsh area sample for kriging (Discharge data from: Gray *et al.* 1995. BNFL Reports 1992-1997).

Radionuclide	Study area sediments
^{99}Tc	1.3 x10^{-6}
^{137}Cs	1.8 x10^{-6}
^{241}Am	1.4 x10^{-4}

The inventory data were ratioed to Sellafield discharges to determine the proportion of the discharge of each radionuclide that is present in the marsh (Table 7.1b). From this the relative retention of each of the radionuclides was inferred. Cs has a retention factor of 1.4 times that of Tc and Am a retention factor 107 times that of Tc. A direct comparison between ^{99}Tc and ^{241}Am must however be regarded with caution due to the substantial ingrowth of ^{241}Am from the decay of ^{241}Pu. Until ^{241}Pu data is available for the inventory cores comparison between discharge and inventory cannot be made, though a comparison between the inventory and published distribution coefficient data indicates the relative mobilities of each element.

A much higher proportion of ^{99}Tc discharged from Sellafield is being transferred and incorporated into the marsh sediments than would be suggested by standard distribution coefficient data (Table 7.4). This is due to the more-conservative nature of Tc compared to that of either Am or Cs.

Table 7.4. Recommended k_D values for anthropogenic elements. (IAEA 1985, NEA/OECD 1982).

Element	Minimum k_D	Maximum k_D	Recommended k_D
Tc	1 x10^{1}	1 x10^{4}	1 x10^{2}
Cs	1 x 10^{2}	2 x10^{4}	3 x10^{3}
Am	2 x10^{5}	2 x 10^{7}	2 x10^{6}

The ratio for measured ^{99}Tc: ^{241}Am is 9.7 x10^{-3}:1 compared to the ratio for recommended k_Ds for Tc :Am which is 5 x 10^{-5}:1. This gives a 9.1 x10^{-3} difference between the two indicating that there is a considerable amount more ^{99}Tc held within the marsh than could have been inferred from a determination of ^{241}Am and a calculation based on distribution coefficient data. The ratio for measured ^{99}Tc:^{137}Cs is 0.69: 1 compared to the ratio for recommended k_Ds for Tc: Cs which is 3.33 x10^{-2}:1. This again gives a large difference between observed and expected values. A difference is also observed between the measured and expected ^{137}Cs and ^{241}Am ratios. At the saltmarsh a ratio of 1:1 for the ratio between measured ^{137}Cs: ^{241}Am ratio exists which agrees with determinations of the ^{137}Cs: ^{241}Am ratio in recent surface scrape samples (Sanchez *et al.* 1997). In this previous work ^{137}Cs: ^{241}Am ratios were seen to increase away from the Sellafield discharge point to 2:1 and 5:1 for the estuaries further south to as high as 10:1 by the North Wales coast. The total proportion of discharges of ^{99}Tc from Sellafield accumulated in the

Thornflatt saltmarsh are not as high as the proportions of ^{137}Cs or ^{241}Am but are higher than would be inferred from a comparison of the published k_D values (Table 7.5). As both ^{99}Tc and ^{137}Cs both show greater than expected accumulation compared to that of ^{241}Am, given relative k_Ds, sediments are therefore acting as more important sinks for conservative radionuclides, particularly ^{99}Tc, than previously thought. Although aerobic saltmarsh sediments are still not such important sinks for ^{99}Tc as for the more particle reactive elements (*e.g.* Am or Pu) the potential dose to the public from accumulated ^{99}Tc in sediments is potentially higher than would have been estimated previously.

Inventory data were only collected from the Thornflatt marsh, however a number of cores were collected from Carlaverock Merse, their radionuclide activities determined and a comparison of ratios of determined maxima compared to discharge maxima made in Chapter 6.5.1. (Table 7.5).

Table 7.5. Radionuclide ratios for inventory cores and activity profile maxima in sub-sampled cores.

Sample set	**^{241}Am: ^{99}Tc**	**^{137}Cs: ^{99}Tc**	**^{241}Am: ^{137}Cs**
Thornflatt Inventory Cores	44: 1	44: 1	1:1
Thornflatt Sub-sampled Cores	89: 1	61: 1	1.4 :1
Carlaverock Sub-sampled Cores	15: 1	54: 1	0.3: 1

There is a variation between the ratios in the sub-sampled cores taken from the Thornflatt marsh and the inventory ratios as the spatial accumulation of all three radionuclides differs (Figure 7.5). The ratios do provide an interesting guide and show that while the ^{241}Am: ^{99}Tc and ^{241}Am: ^{137}Cs ratios show a marked decrease of 83% with increasing distance from the point of discharge the ^{137}Cs: ^{99}Tc ratio shows only a smaller decrease of 11%. Previous work has reported that 10% of ^{137}Cs discharged from BNFL Sellafield is transported to the Esk estuary saltmarshes sorbed to particulate (Jeffries *et al.* 1973) whilst all ^{241}Am arrives sorbed to inorganic material (Day and Cross 1981). The similar ^{137}Cs: ^{99}Tc ratio implies that the distribution of ^{99}Tc is similar to that of ^{137}Cs and a drop in the ^{137}Cs: ^{99}Tc ratio is evidence that in excess of 90% of the ^{99}Tc reaching the marshes is in solution.

Determination of ^{99}Tc inventories using more easily determinable radionuclides (usually γ-emitters) as analogues is not possible as the mechanisms for the accumulation of ^{99}Tc to a saltmarsh sediments are different from those of other radionuclides (Chapter 7). Tc is also readily remobilised within the sediment column (Chapter 6), consequently ^{99}Tc accumulations cannot be quantitatively represented using other radioisotopes as analogues. A semi-quantitative estimate of the extent of ^{99}Tc contamination of saltmarshes, either from Sellafield discharges or from a large scale release of fission products to the environment, could be made using ^{137}Cs as a proxy. This can be done because the ^{137}Cs:^{99}Tc ratio declines slowly with distance and the Thornflatt inventory: total discharge ratio is known (Table 7.1b).

7.4.5. Implications for dose estimates

^{99}Tc is a weak beta emitter and so negligible dose will arise from direct external exposure to the saltmarsh sediments. More significant dose will arise from the intake of contaminated material, either the sediments themselves or foodstuffs grown on the marsh (Figure 7.9). Another potential input is possible as a result of remobilization of sediments and contamination of seafood with ^{99}Tc.

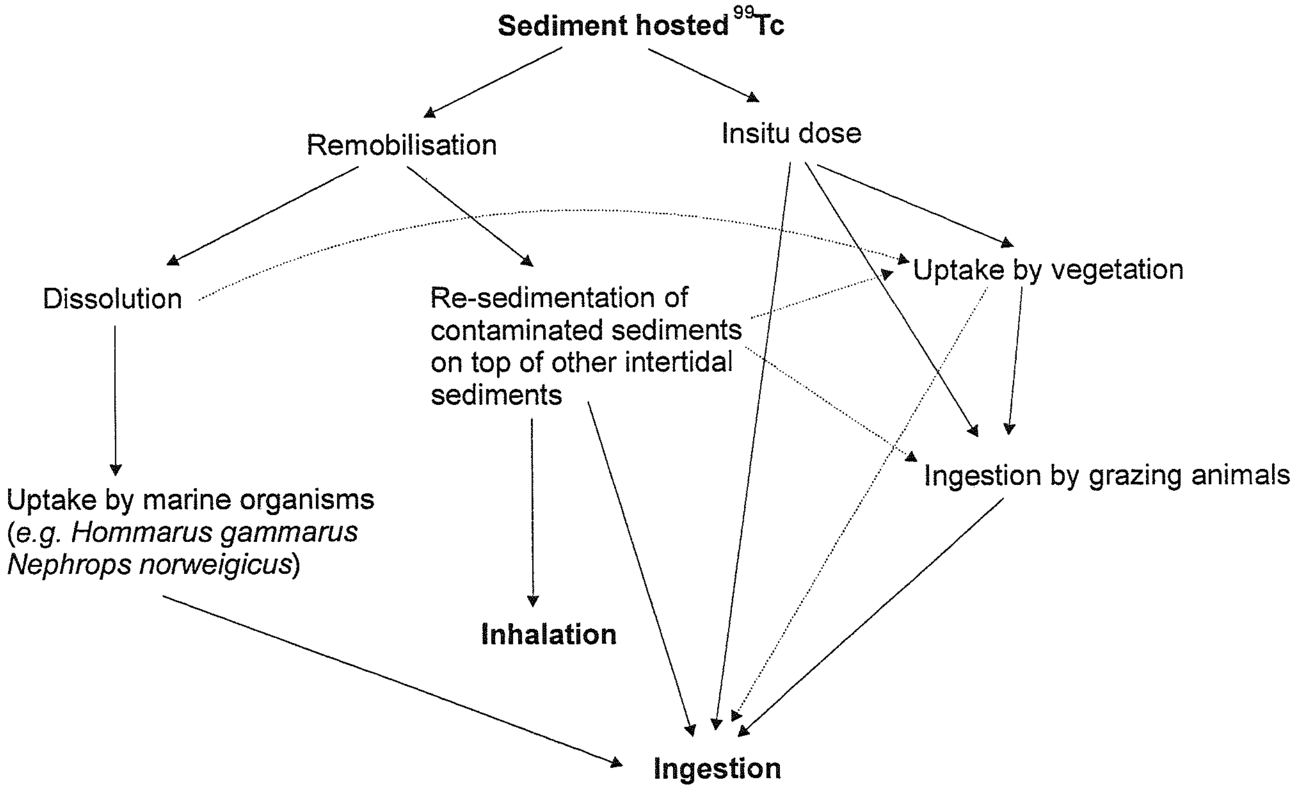

Figure 7.9. Potential pathways for the transfer of ^{99}Tc from a sediment sink to the human food-chain.

Transfer of ^{99}Tc from soils to vegetation has been studied, with transfer factors ranging from 0.0006 for the transfer of Tc from soil to rice to 79.4 for the transfer of ^{99}Tc to lettuce (Muramatsu *et.al.* 1995, Yanagisawa and Muramatsu 1996). An attempt was made to determine the transfer factors of Tc from sediments to saltmarsh plants (IAEA 1985), however transfer factors determined in these reports are believed to be too high (Yanagisawa and Muramatsu 1993) and should be regarded with caution. Subsequent transfer of ^{99}Tc from vegetation to grazing animals has also been studied (Table 7.5).

Table 7.6. Transfer factors for the Transfer of ^{99}Tc from vegetation to grazing animals (Jones 1983, Ennis *et al.* 1988).

Livestock	Milk	Meat
Cow	1.2×10^{-4}	7.3×10^{-7}
Goat	$7.4 \times 10^{-4} - 1.6 \times 10^{-3}$	3.0×10^{-5}
Chicken	!	3.3×10^{-2}

Work published on the specific activity effect in the metabolism of Tc has resulted in the validity of tracer experiments for the uptake of Tc to animals to be questioned (Ennis *et al.*1988). Another potential pathway for ^{99}Tc transfer to animals is from ingestion of sediment adhered to vegetation. As yet there has been no study made of the transfer of Tc from sediment to grazing animals, although 90% of ^{137}Cs ingested is through this route (Ennis *et al.* 1988). This transfer is therefore potentially an important mechanism for the transfer of ^{99}Tc to livestock. Whilst the transfer of Tc from saltmarsh sediments is extremely likely, further study into quantification of transfer mechanisms must be made before an assessment of the potential dose derived from the total inventory of ^{99}Tc within the Thornflatt saltmarsh is possible.

7.5. Conclusions

1. ^{99}Tc inventories are greatest toward the front of the marsh and also higher in the marsh centre, when in proximity to the drainage channels.
2. Variations in vegetation cove have no apparent effect on the distribution pattern of accumulated ^{99}Tc. This is based on the vegetation patterns determined by Horrill (1984), though little change in vegetation patterns was observed on visiting the marsh.
3. ^{99}Tc activities determined in different vegetation types imply that Tc is not accumulated by transfer through marsh flora.
4. A strong correlation between Tc and Ca also implies that the highest ^{99}Tc accumulation occurs in areas which are frequently inundated.
5. Absence of ^{99}Tc in pore waters and poor correlation between ^{99}Tc and the wet: dry ratio infer that ^{99}Tc is sorbed to a sediment component rather than remaining in solution.
6. The study area has been calculated to hold 1.64 GBq of ^{99}Tc in the sediments exposed above low water. This represents 1.3×10^{-6} of the total ^{99}Tc discharge from Sellafield.
7. Saltmarsh sediments are a more important sink for conservative radioisotopes like ^{99}Tc than can be inferred from published distribution coefficient data, though the relative proportion of discharge held within the marsh is still considerably less than for more particle reactive radioisotopes.
8. Many potential routes for the transfer of ^{99}Tc to the food chain exist. Further study is required for quantification of these pathways in order that dose estimates can be calculated.

7.6. Reference List

Aarkrog A., Dahlgaard H., Hallstadius L., Holm E., Mattsson S., Rioseco J. 1986. In: Desmet G., Myttenaere C. (eds.) "*Technetium in nature*". 69 - 78 Elsevier.

Aarkrog A., Carlson I., Chen Q.J., Dahlgaard H., Holm E., Huynh-Ngol L., Jensen L.H., Neilson S.P., Nlies H. 1988. Origin of ^{99}Tc and its use as a marine tracer. Nature **335.** 338-340.

BNFL. 1983-1997. Annual report on the radioactive discharges and monitoring of the environment. Directorate of Health, Safety & Environmental Protection. BNFL. Warrington.

Busby R., McCartney M., and McDonald P. 1997. Technetium-99 concentration factors in Cumbrian seafoods. Radioprotection Colloques **32.** C2 311-316.

Colodner D., Sachs J., Ravissa G., Turekian K., Edmond J., Boyle E. 1993. The geochemical cycle of rhenium: a reconnaissance. Earth Planet. Sci. Let. **117.** 205 - 221.

Cressie N.A.C. 1993. Statistics for spatial data. John Wiley and Sons, New York. 105-211.

Croudace I.W. 1991. A reliable and accurate procedure for preparing low activity efficiency calibration standards for germanium gamma-ray spectrometers. J. Radioanal. Nucl. Chem. Letters, **153(2).** 151-162.

Cundy A.B., Croudace I.W. 1995. Physical and chemical associations of radionuclides and trace metals in estuarine sediments: an example from Poole Harbour, Southern England. J. Environ. Radioactivity. **29.** 191-211.

Day J.P., Cross J.E. 1981. ^{241}Am from the decay of ^{241}Pu in the Irish Sea. Nature **292.** 43-45.

Ennis M.E., Johnson J.E., Ward G.M., Voigt G.M. 1988. A specific activity affecting the metabolism of Tc. Health Physics **54.** 157-160.

Fridlington M.A., Allen J.R.L., McDonald P., Rae J.E. 1997. Radionuclide depositional history in the Solway Firth, UK. Radioprotection-Colloques **32.** 293-298.

Fowler S.W., Aston S.R., BenayonG., Parsi P. 1983. Bioavailabilty of technetium from artificially labeled North East Atlantic deep sea sediments. Mar. Environ. Res. **8.** 87 – 100.

Gray J., Jones S.R. and Smith A.D. 1995. Discharges to the environment from the Sellafield site 1951-1992. J. Radiol. Prot. **15.** 99-131.

Hamilton E.I., Clarke K.R. 1984. The recent sedimentation history of the Esk Estuary, Cumbria, UK: The application of radiochronology. Sci. Total. Environ. **35.** 325-386.

Horrill A.D. 1984. Concentrations and spatial distribution of radioactivity in an ungrazed saltmarsh. In Coughtrey P.J. (ed.). British Ecological Society, Special publication No 3, Blackwell, Oxford 199-215.

Howard B.J., Livens F.R. 1991. Radioactive contamination of tide-washed pastures. MAFF contract report No. 2069. ITE Merlewood Research station, Grange-Over-Sands, UK.

IAEA Technical Report. 1985. Sediment k_Ds and concentration factors for radionuclides in the marine environment. Int. Atomic Energy. Agency. Vienna.

Jeffries D.F., Preston A., Steele A.K. 1973. Distribution of ceasium-137 in British coastal waters. Mar. Poll. Bull. **4.** 118 - 122.

Jones B. 1983. Metabolism of technetium in goats. J. App. Rad. Isot. **34.** 837-839.

Journel A.G., Huijbregts C.J. 1978. Mining Geostatistics. Academic press, London.

Kenna B.T., Kuroda P.K. 1964. Technetium in nature. J. Inorg. Nucl. Chem. **26.** 493 - 499.

Kenna B.T., Kuroda P.K. 1964. Technetium in nature. J. Inorg. Nucl. Chem. **26.** 493 - 499.

Leonard K.S., McCubbin D., Brown J., Bonfield R.A., Brooks T. 1997. A summary report of the distributions of ^{99}Tc in UK coastal waters. Radioprotection Colloques **32.** 109 – 114.

Mackenzie A.B., Scott R.D. 1993. Sellafield waste radionuclides in the Irish Sea intertidal and saltmarsh sediments. Environmental Geochemistry and Health. **15.** 45-57.

Masson M., Patti F., Colle C., Roucoux P., Grauby A., Saas A.. 1989. Synopsis of French experimental and in situ research on the terrestrial and marine behavior of technetium. Health Physics **57.** 269 – 279.

Matheron G. 1971 The theory of regionalised variables and it's applications. Cahier du Centre Morphologie Mathimatique. **5.** 439-468.

Muramatsu Y., Yoshida S., Ban-nai T. 1995. Tracer experiments on the behaviour of radio-iodine in the soil-plant-atmosphere system. J. Radioanal. Nucl. Chem. Articles. **194.** 303-310.

Poole A.J., Denoon D.C., Woodhead D.S. 1997. The distribution and inventory of ^{137}Cs in sub-tidal sediments of the Irish Sea. Radioprotection-Colloques **32.** 263-270.

Stanners D.A., Aston S.R, 1981. An improved method of determining sedimentation rates by the use of artificial radionuclides. Estuarine, Coastal and Shelf Science **13.** 101 – 106.

Sanchez A.L., Horrill A.D., Howard B.J., Singleton D., Mondon K. 1997. Radionuclides in tide washed pastures bordering the Irish sea coast of England and Wales. Water Air and Soil Pollution **106.** 403-424.

Till J.E. 1986. Source terms for technetium-99 from nuclear fuel cycle facilities. In Desmet G., Myttenare C. (eds) Technetium in the environment. Elsevier. London. 1-20.

Wigley F., Warwick P.E., Croudace I.W., Caborn J., Sanchez A.L. 1999. Optimised method for the routine determination of technetium-99 in environmental samples by liquid scintillation counting. Anal. Chim. Acta **380.** 73-82.

Yanagisawa K., Muramatsu Y. 1993. Transfer of technetium from soil to vegetables. Radiochim. Acta. **63.** 83-86.

Yanagisawa K., Muramatsu Y. 1996. Transfer of technetium from soil to plant. Proceedings of the Russian-Japanese seminar on technetium, Moscow 1996.

Chapter 8

Summary and Conclusions

Chapter 8. Summary and Conclusions

8.1.1. Accumulation of ^{99}Tc in saltmarsh sediments

^{99}Tc is present in sediments collected from the Thornflatt saltmarsh, Carlaverock saltmarsh and Ribble Estuary. The highest ^{99}Tc activities have been determined in the Thornflatt saltmarsh sediments with a decrease in activity away from the point of discharge. ^{99}Tc activities in the Carlaverock marsh are only just above detection limits. Distinct peaks in ^{99}Tc activity are observed in core profiles, and are considered to result from fluctuations in the amount of ^{99}Tc discharged from Sellafield and from variations in the redox potential within the sediment.

8.1.2. Geochemical constraints on accumulation.

Trends in Mn and Fe profiles in the sediment act as indicators for fluctuations in redox environment and show good correlation with some the ^{99}Tc activity profiles in cores R-96-007 and R-96-008 in the Thornflatt marsh and Core W-98-001 from the Ribble estuary. Sequential extraction experiments, despite the qualitative nature, give support to the hypothesis of diagenetic movement of Tc in a sedimentary environment and enrichment if conditions are suitable. Where a secondary enrichment of ^{99}Tc is observed in sediment cores, it correlates with a reduction in the MnO/Al_2O_3 ratio which is an indicator of the reduction of Mn^{IV} to Mn^{II}. There is no correlation with fluctuations in the $Fe_2O_3/A/_2O_3$ ratio indicating that secondary accumulation of Tc occurs before the redox potential in the sediments drops low enough to allow the Fe^{III} to Fe^{II} half reaction to proceed. This is expected behaviour given the reduction potential of the Tc^{VII} to Tc^{IV} reaction compared to standard geochemical models (Frolich *et al.* 1979). However Tc, accumulation occurs at higher redox potentials than its analogue Re which has been reported to become enriched at redox potentials lower than those of the Fe^{III} to Fe^{II} half reaction (Colodner *et al.* 1993).

Where the sediments show sulphidic reduction zones (Core W-98-001) Tc is seen to accumulate at similar points to highs in the MnO/Al_2O_3 ratio. Mn has been reported to accumulate in sediments through metabolism by sulphate-reducing bacteria more commonly associated with the reduction of Fe^{III} and strong evidence has been reported for the metabolism of Tc by sulphate-reducing bacteria under favourable laboratory conditions (Coleman *et al.* 1993). It is therefore possible that the same mechanisms responsible for Mn accumulation (*e.g.* formation of goethite, siderite and alabandite) are also responsible for Tc accumulation in a reducing environment.

8.1.3. Input mechanisms

Spatial variations across the Thornflatt marsh and the ^{99}Tc activities of several biota inhabiting the marsh were studied to discover the possible nature of the inputs of ^{99}Tc to a saltmarsh environment. Whilst some of the marine biota, especially *fucoid,* seaweeds have extremely high ^{99}Tc activities, these were not abundant enough on the marsh. More common vegetation like *Puccinellia maritima, Derbsia marina* and Sea Purslain, had much lower ^{99}Tc activities and would not account for the total input of ^{99}Tc to the sediment column.

Correlations between ^{99}Tc and various core components in inventory cores were made as these allow correlation between each of the core components and ^{99}Tc activities removing inconsistencies related to temporal variations in^{99}Tc discharge. A good correlation was observed for ^{99}Tc activities with both CaO and CO_3 concentrations. Increased Ca and CO_3 probably result from an increase in the proportion of shell fragments in the sediment. The ^{99}Tc input is more likely to be related to the higher frequency of inundation which these fragments represent rather than the fragments themselves given the low concentration factors of Tc in molluscs. ^{99}Tc activities below limits of detection in pore waters as well as poor correlation between ^{99}Tc activities and the wet : dry ratio indicate that the ^{99}Tc within the sediment profile is sorbed to some component of the sediment and not merely present in the pore water. Sequential extraction experiments from samples towards the top of the sediment column imply that as the ^{99}Tc requires oxidising reagents to dissolve it Tc is accumulated with some form of strong inorganic or organic association rather than being immobilised as a reduced form.

A poor correlation between the activities of ^{99}Tc and other radionuclides discharged from the EARP plant indicates that different input mechanisms are responsible. Radionuclides like ^{241}Am are strongly sorbed to sediment and so their input is directly related to the input of minerogenic material to the marsh. As Tc does not correlate well with these radionuclides it can be assumed that Tc is not introduced to the marsh sorbed to inorganic material. Collected data imply that the transfer of Tc is from seawater to the sediment and is analogous to that of Re. The transfer of Re to the sediment has been reported to occur below the sediment/water interface (Colodner *et al.* 1993), though the scavenging mechanisms for Re are still unclear. The same is true of Tc.

8.1.4. Relevance of aerobic sediments as sinks

A greater proportion of the ^{241}Am and ^{137}Cs discharges are held in the Thornflatt saltmarsh than is found for of the ^{99}Tc. However, a greater proportion of ^{99}Tc is being transferred from Sellafield discharges and incorporated into the marsh sediments than would be suggested by previously published standard distribution coefficient data. Differences in the accumulation mechanisms between Tc and other radionuclides means that a quantitative assessment of the ^{99}Tc inventory cannot be made as the ^{99}Tc inventory will be greater than would be expected if an inventory was made using ^{137}Cs or ^{241}Am as an indicator. Saltmarsh sediments are therefore more important sinks for Tc than would be expected from assessments made using other radionuclides as tracers.

^{99}Tc is a weak β-emitter so negligible dose will arise from direct external exposure to the sediments. More significant doses are likely to arise from ingestion of contaminated material. This requires transfer of ^{99}Tc to food through grazing animals or the inhalation of contaminated dust. Further study is required before quantification of the transfer of ^{99}Tc to humans through these routes can be made.

8.1.5. Reference list

Coleman M.L. 1985. Geochemistry of diagenetic non-silicate minerals: kinetic considerations. Phil. Trans. R. Soc. Lond. A. **315.** 39-56.

Colodner D., Sachs J., Ravissa G., Turekian K., Edmond J., Boyle E. 1993. The geochemical cycle of rhenium: a reconnaissance. Earth Planet. Sci. Lett. **117.** 205 - 221.

Frolich P.N., Klinkhammer G.P., Bender M.L., Luedke N.A., Heath G.R., Cullen D., Dauphin P. 1979. Early oxidation of organic matter in pelagic sediments of the Eastern Equitorial Atlantic: Suboxic diagenesis. Geochimica et Cosmochimica Acta. **43.** 1075-1090.

8.2. Conclusions

- A method was developed for the routine determination of ^{99}Tc in environmental samples. The emphasis was placed on producing a method which was user friendly and cost effective. The procedure developed had high tolerances during the separation chemistry and chemical recoveries were in the order of 70% for most sample matrices. Limits of detection were as low as 1.7 Bq/kg using a Quantulus ultra low level liquid scintillation counter. These detection limits were found to be comparable to detection limits using ICP-MS which used to be regarded as a more sensitive technique. The method performed well in a recent inter-laboratory comparison exercise and has since been adopted by four other laboratories for routine determination of ^{99}Tc on environmental samples.

- Sequential extraction of ^{99}Tc from sediments has been achieved for the first time, using an operationally define extraction procedure. As the extraction is operationally defined it does not attempt to provide misleading data by directly attributing extracted ^{99}Tc to specific sediment fractions or oxidation states. High chemical recoveries were achieved using TEVA resin for the isolation of ^{99}Tc from potential interferences which lead to a limit of detection of 5.5 Bq/kg. Interpretation of data from sediments collected from the Thornflatt saltmarsh, Esk Estuary indicate that ^{99}Tc is both easily extracted from the sediments and strongly sorbed to a sediment component. The proportion of ^{99}Tc in each extract varied from sample to sample indicating that Tc was associated with different sediment components in different samples.

- ^{99}Tc was found in saltmarsh sediment in both oxidised and reduced zones and ^{99}Tc profiles were observed for the first time. ^{99}Tc activity profiles in sediment cores taken from the Thornflatt and Carlaverock saltmarshes indicated some evidence of discharge history, though ^{99}Tc maxima in sediment cores did not coincide with expected maxima from Sellafield discharges after correction for lag time and accumulation rate.

- Secondary accumulation of Tc was discovered in both aerobic and anaerobic sediments. Comparison of ^{99}Tc with fluctuations in the concentration profiles of MnO and Fe_2O_3 confirmed that the redox behaviour of Tc in environmental sediments correlates with published thermodynamic data based on laboratory experiments. This was the first time that the correlation between the laboratory derived data and the behaviour of Tc in the environment was established.

- A study of the spatial variations has been made to assess the input mechanisms of ^{99}Tc to saltmarsh sediments was made using a novel sampling technique. A strong correlation between ^{99}Tc and CaO implied a mechanistic association between the two. Elevated CaO was considered to be the result of greater quantities of shell fragments, therefore ^{99}Tc accumulation occurred in the most frequently inundated areas. The same correlation technique indicated that the accumulation of Tc is different to that of other radionuclides, and that Tc accumulation was not dependent on clay mineral quantity, organic material or pore water. The exact component to which the sediment is sorbed was unclear, but the accumulation mechanisms appeared to be similar to those reported for Re.

- The inventory of ^{99}Tc held within the Thornflatt saltmarsh was also calculated. It was found that proportionally less of the ^{99}Tc discharge from Sellafield was held in the marsh than that of ^{137}Cs and ^{241}Am. However, it was discovered that a higher proportion of ^{99}Tc is transferred from Sellafield and incorporated into saltmarsh sediments than has been implied from published standard distribution coefficient data. This study concluded that saltmarsh sediments are therefore a more important sink for ^{99}Tc than assumptions made from inventories of other radionuclides would suggest, and therefore the potential risk of ^{99}Tc is also greater than previously believed.

Appendix 1

Analytical methods and quality assurance

Appendix 1. Analytical Methods and Quality Assurance

A1.1. Introduction

This appendix comprises a description of the analytical instrumentation and the theory behind its operation. Also included is reference material and standard data to verify the stability of instruments and allow quantitative interpretation of the results presented in Appendix 2.

A1.2. Sampling

Three sample types were collected for determination. These were: 100mm diameter cores of depths of up to 1 m depth collected for geochemical profiling, 36mm diameter cores of 0.5m depth collected for spatial analysis and inventory determination, and samples of estuarine organisms.

100mm Cores were collected by insertion of a 1.5m PVC tube, chamfered at one end, into the marsh surface to a depth of approximately 1m. The compression of the core was determined by measuring the difference of the height of the sediment in the tube relative to the surface of the marsh. The area around the core was excavated to allow lateral movement to brake the bottom of the core in order to aid core retrieval. Extracted core tubes were then sealed at the ends by wrapping in polythene prior to transportation.

36mm Cores were collected by insertion of a 1m tube exactly 0.5m into the sediment. Compression was measured in the same way as for the larger cores. The cores were twisted to break the sediment at the base and extracted. The depth of the hole left by the core tube was measures to ensure the extracted core was exactly 50cm. The ends of the extracted core tubes were again sealed with polythene prior to transportation.

Biota samples were collected from sample localities, washed in local seawater to remove any sediment and sealed in polythene sample bags for transportation the laboratories in Southampton.

A1.3. Sample preparation

Sediment cores were stored at 4°C prior to preparation. Cores were sectioned vertically, photographed, X-rayed and visually logged prior to any further sample.

X-radiography was carried out using a Hewlett-Packard Faxitron X-ray machine. Core sections were placed in a sand filled box to reduce the "edge" effects. Exposure times varied from 6 to 24 minutes at 56 KeV depending on the thickness of the core and the sediment matrix.

10cm diameter cores were then sectioned at intervals of 0.5cm – 1cm. Individual samples were then weighed wet, freeze dried and then weighed again to determine the water content. Samples were then ground to a powder first using a mortar and pestle and then in tungsten carbide pots using a TEMA® gyratory swing mill.

36mm cores were carefully extruded from the core tubes ensuring all sediment had been removed. Samples were the weighed before and after freeze-drying to establish water content and were then homogenised by grinding with a mortar and pestle. Sediment required for XRF analysis was ground further in tungsten carbide pots using a TEMA® gyratory swing mill.

Organic material collected from the Thornflatt Saltmarsh was stored at 4°C before preparation. All material was weighed before and after freeze-drying. Samples were then further homogenised using a Magimix™ food processor and where necessary by freezing in liquid nitrogen and further grinding with a pestle and mortar.

A1.4. X-ray fluorescence analysis

A1.4.1. Introduction

Determination of major and trace elements in the sediments was made using X-ray fluorescence analysis (XRF). This was done using a Philips® PW1400 automatic sequential wavelength dispersive X-ray spectrometer.

X-ray spectra for fluorescence determination are produced by the excitation of inner electrons of sample atoms by excitation of the sample with using a
high voltage source (Figure A1.1). This process is used both to produce primary X-rays and the fluorescence x-rays.

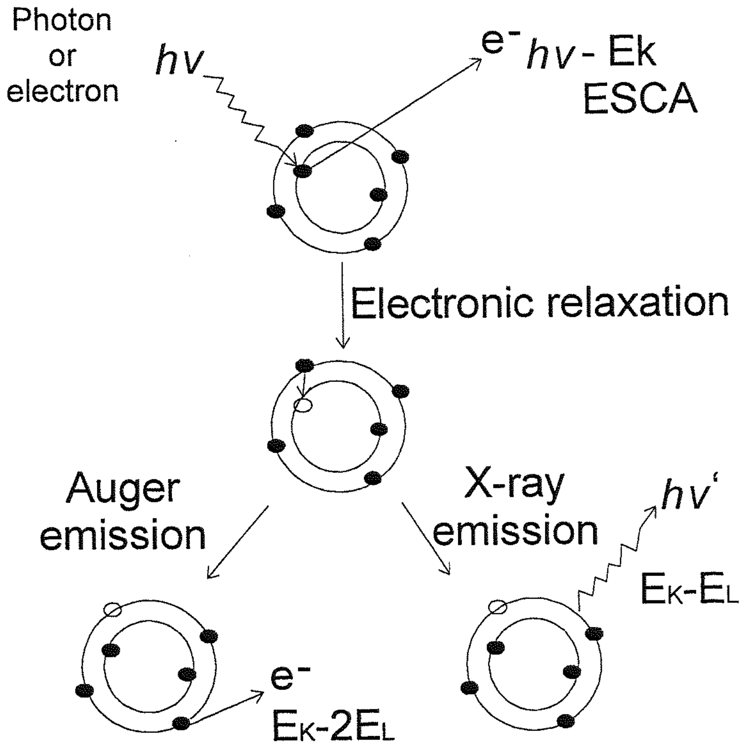

Figure A1.1. Interactions between high energy electrons or photons and inner shell electrons in atoms leading to X-ray generation.

The X-ray fluorescence spectrometer consists of a source, a dispersing device and a detector (Figure A1.2). The Philips® PW1400 automatic sequential wavelength dispersive x-ray spectrometer uses a rhodium x-ray tube and gas flow and or NaI scintillation detectors for routine determination. The dispersion device is usually a crystal though the type and orientation varies depending on the determinations being made.

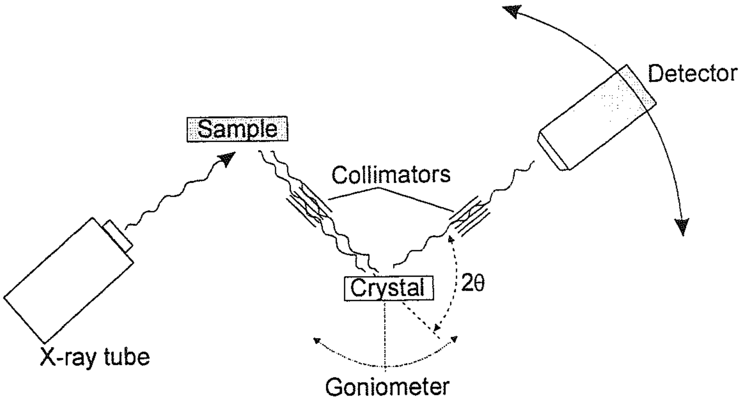

Figure A1.2. Schematic diagram for elemental determination by XRF Analysis.

X-rays produced by fluorescence of the samples are guided into a parallel beam by the use of a collimator (a pack of parallel metal plates). The mixture of X-rays produced by different elements is separated by diffraction through a crystal of known d-spacing and different diffraction crystals are used to provide the optimum resolution between peaks. LiF crystals are the most commonly used, orientated to either their 220 or 200 faces. LiF crystals also have the advantage that as both lithium and fluorine have low atomic numbers they are not 'seen' by the detector. Germanium crystals are also used orientated to the 111 face. The best resolution is obtained by synthetic diffractors, pentaerythritol (PE) is such a diffractor. PX1 is a multilayer diffractor consisting of alternating layers of silicon and tungsten. This gives good resolution between X-ray peaks particularly at low angles of 2θ.

Finally the intensity of the X-rays of each element is measured to determine the concentration of that element in the sample. In the PW-1400 the determination of peak intensity is made using either a gas-flow proportional counter (GFPC) or a NaI scintillation counter (Scint).

There are potential spectral interferences related to the production of both K an L type X-rays from each element. The L-lines are of lower energy and are at a longer wavelength than K-lines. This means that L-lines of heavy atoms have a similar wavelength to K-lines of lighter atoms and so may cause a spectral interference. There is also a potential interference from the x-ray tube. Potential interference is also possible from Bramstrlung radiation produced as a result of electron collision and also from the x-ray tube. X-ray photons are also absorbed by atoms within the sample if the energy is slightly greater than that of a transition, with long wavelengths more strongly absorbed than those of shorter wavelengths. Inter-element effects are however easily corrected for using DeJongh alpha coefficients.

A1.4.2. Preparation

Major Elements

Loss on ignition was also determined from the weighing of samples before and after ignition to 900°C. An aliquot of the dried sample was ignited at 900°C for a minimum of 2 hours to decompose any organic matter present. 0.800g of the ignited material was intimately mixed with 4.00g of a eutectic (4:1) mixture of lithium metaborate and lithium tetra borate in a grain stabilised Pt-Au crucible. The mixture was then heated to 1200°C in a muffle furnace to melt the flux and the sediment sample. The melt was then cast into a Pt-Au mould and cooled to produce a bead suitable for XRF determination of major elements.

Trace elements

10g of non-ignited ground sediment sample was pressed using a force of 12 tonnes per inch, into a pellet for trace element determination. Pellets were either 40mm or 30mm in diameter depending on the amount of sample material available. Standard reference materials were determined along with samples to assess accuracy for each element.

A1.4.3. Operating parameters

Absorption and enhancement matrix effects were corrected for using the influence coefficients supplied by Philips. Standard reference materials MAG1 and BEN were run with each batch of samples undergoing trace element determination. BRR was run with samples being determined for major elements. A reference monitor was also checked to ensure that there was no instrument drift. From the reference materials it is possible to ascertain the precision of XRF determination for each element. The parameters used for major element determination (Table A1.1) mean that all elements are well above their limit of detection the precision is typically less than 1% relative standard deviation (rsd). Using the standard Pw-1400 parameters for trace elements, the precision of the determinations is typically about 5% rsd and the limit of detection varies, though for the elements determined is in the range of 1-5 ppm (Table A1.2).

Table A1.1 Parameters for XRF major element analysis.

Element	X-Ray	Dispersion angle °2θ	Crystal	Kv	mA	Collimator	Detector
Si	Kα	109.295	PE	45	55	Coarse	GFPC
Al	Kα	18.100	PX1	45	55	Coarse	GFPC
Ti	Kα	86.295	LiF 200	50	50	Fine	GFPC
Na	Kα	25.850	PX1	45	55	Coarse	GFPC
Mg	Kα	21.265	PX1	45	55	Coarse	GFPC
Ca	Kα	113.280	LiF 200	50	50	Fine	GFPC
Fe	Kα	57.620	LiF 200	50	50	Fine	GFPC
P	Kα	141.165	Ge 111	45	55	Coarse	GFPC

Table A2.2 Parameters for determination of trace elements by XRF

Element	X-Ray	Dispersion angle °2θ	Crystal	Kv	mA	Collimator	Detector
Cr	Kα	69.430	LiF 200	50	50	Fine	GFPC
Cl	Kα	92.760	LiF 200	40	60	Coarse	GFPC
Mn	Kα	63.055	LiF 200	50	50	Fine	GFPC
S	Kα	110.870	Ge 111	50	50	Coarse	GFPC
As	Kα	34.040	LiF 200	60	40	Fine	GFPC/Scint
Pb	Lβ	79.365	LiF 200	95	25	Fine	Scint
Zn	Kα	41.855	LiF 200	60	40	Fine	GFPC/Scint
Ni	Kα	48.725	LiF 200	60	40	Fine	GFPC/Scint
Cu	Kα	45.060	LiF 200	60	40	Fine	GFPC/Scint
Br	Kα	29.970	LiF 220	95	25	Fine	GFPC/Scint
I	Kα	12.400	LiF 200	95	25	Coarse	Scint

A1.5. TOC and Carbonate analysis

A1.5.1. Total Carbon Analysis

Total Carbon analysis was performed on a Carbo Erba CHNO-S elemental analyser. All samples were oven dried before determination and stored in a dessicator prior to determination. Samples were weighed into tin capsules and sealed by crimping. The sample was ignited by flash pyrolysis at 1000°C and the combustion gases separated by gas chromatography. Final detection of the gases was achieved using a flame ionisation detector. Acetanalide (carbon content 71.09%) was run as a standard throughout the determination procedure at intervals of every 10 samples to ensure the accuracy of measurements was constant throughout (Figure

A1.3). Duplicate determinations were also made to determine the precision of the method and to ensure that no spurious results occurred due to sample heterogeneity.

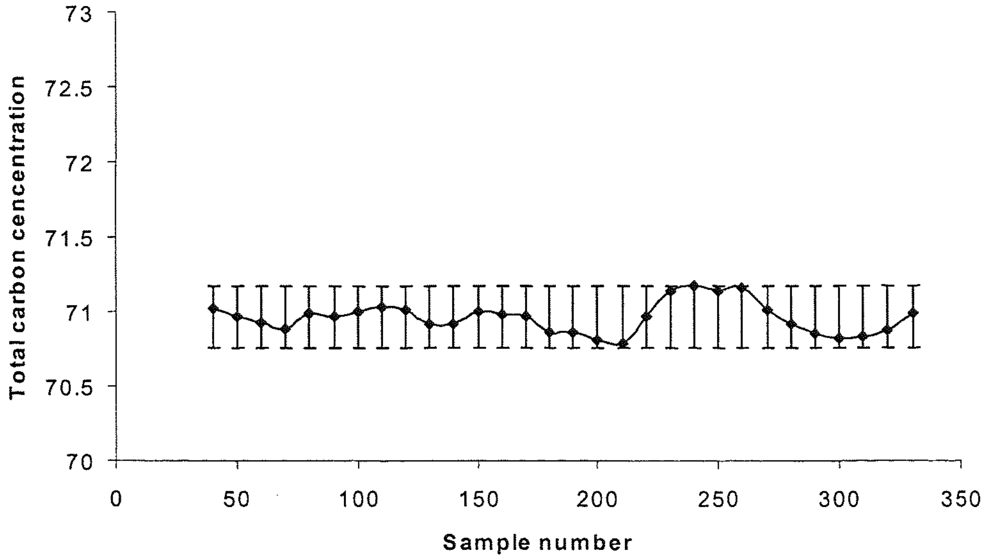

Figure A1.3. Running mean plot for Total Carbon standard data determinations made on the Carbo Ebra Elemental analyser. The standard contains 71.09 wt% carbon. The operating range is at 2σ.

A1.5.2. Carbonate Analysis

Samples were again oven dried and stored in a dessacator prior to analysis and then weighed in to aluminium foil caps. Calcium carbonate was determined on a UIC^{inc} Coulometrics System by coulometric analysis via the CO_2 evolved on H_3PO_4 acid hydrolysis. Standards of known elemental composition were measured to permit quantification. These were run every 15 samples and again show stability within two standard deviations throughout determination of all samples.

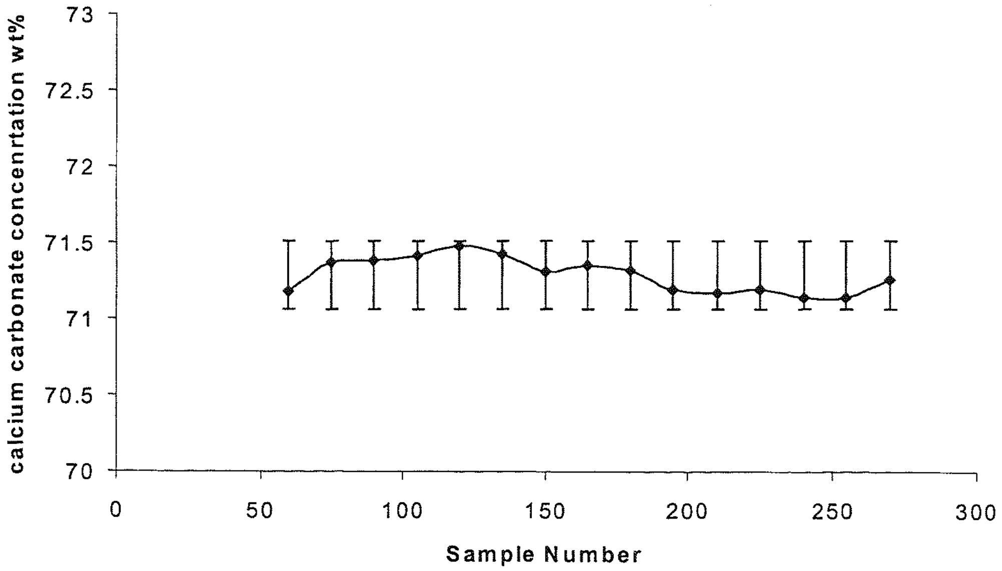

Figure A1.4. Running mean plot for Carbonate reference material data (Reference material 10549) by coulometric analysis. The standard contains 71.23 wt% Calcium carbonate and operating range is at 2σ.

A1.6. Radionuclide Determination

A1.6.1. γ-spectral analysis

A1.6.1.1. Introduction

Canberra High purity Germanium (HPGe) solid state semiconductors were the instrumentation used for the determination of γ-emitting radioisotopes throughout the PhD. Ionising radiation produces electron-hole pairs in semiconductor detectors, the number of these being proportional to the energy of the photon. The energy needed from the ionising radiation is therefore small and large numbers of e-h pairs are produced so good energy resolution is obtained.

Gamma-ray and x-ray spectroscopy is then possible as pulses can be sorted by height (current) and displayed as a distribution of total counts *vs.* energy. The HPGe detector has a very small intrinsic electrical conductivity, especially at low temperatures (-196°C in liquid nitrogen) so allows very small electrical pulses due to low energy gamma or X-ray photons to be detected.

A1.6.1.2. Operating parameters

^{137}Cs and ^{241}Am were determined in homogenised sediment samples using a Canberra 30% N-Type HPGe gamma ray spectrometer. Approximately 20g sediment powder was placed in the lead shielded well detector and counted until 10000 counts for the determinant peak were collected or until counting time exceeded 30000 seconds. Collecting 10000 counts minimises the counting error to 1%, where samples were less active a concession to instrument time was made and determinations with counting errors of less than 5% were accepted. The detector was routinely calibrated using matrix matched mixed radionuclide sources and all spectra were analysed by FITZPEAKS gamma deconvolution and analysis software. Effects of counting geometry were minimised by completely filling each vial.

The accuracy of ^{137}Cs and ^{241}Am activity measurements was verified through analysis of a standard Irish Sea sediment (IAEA 135).

^{137}Cs was determined using the 661 keV gamma line and ^{241}Am at 59 keV. The limit of detection of ^{137}Cs is 1.5 Bq/kg and ^{241}Am has a limit of detection of 2Bq for a count time of 30,000 seconds using this method. Standards were run on all detectors at a weekly interval and used to maintain accuracy, ensuring that there was no instrument drift and recalibrating where necessary.

Where ^{99m}Tc was measured to determine the recovery of ^{99}Tc in analytical separation methods, samples were counted against a known standard using the same geometry. Samples were determined until 10000 counts on the 140keV line had been obtained, and all samples were decay corrected back to midnight of the date of analysis to allow correlation between samples and standards and then calculation of yield.

A1.6.2. ^{99}Tc determination

The background and development of a method for the determination of ^{99}Tc is discussed in Chapters 3, 4, and 5. This includes the various method used for the chemical separation of ^{99}Tc from its potential interferants. A number of possible methods for the final determination of ^{99}Tc are discussed. This is however only with regard to their suitability for ^{99}Tc determination. A more detailed overview of liquid scintillation counting and optimisation of the liquid scintillation counter for ^{99}Tc determination is presented here.

A1.6.2.1. Liquid Scintillation Counting.

Low energy β particles are difficult to detect in gas ionisation chamber due to absorption of the β-particle by the membrane surrounding the chamber. It is possible to mix the sample with the gas in the chamber but there are practical difficulties in doing this. Liquid scintillation works by dissolving the sample in a solution containing a scintillator or phosphor. The ionising radiation from the sample leads to electronic excitation of solvent molecules. This excitation energy is transferred to the scintillator, this is followed by a period of relaxation and then a light flash. The light flash is then detected by a photocathode.

Scintillator solutions contain a solvent, a primary solute and sometimes a secondary solute. The purpose of the solvent is to keep the primary (and secondary) solute in solution and to absorb the initial radiation energy and so provide the electronic excitation necessary for scintillation to occur. The primary solute accepts the absorbed energy from the solvent producing a light flash (300-500 nm). Poly-aromatic hydrocarbons such as anthracene, naphthalene, p-tephenyl, 2.5-diphenyloxazol (PPO) are the most commonly used primary solutes. Efficiency drops off after an optimum scintillator concentration due to self absorption (quenching). Typically a concentration of $5g.l^{-1}$ PPO would be used in a liquid scintillant.
Secondary solutes are used for higher counting efficiencies. These absorb light produced by the primary solute and emit it at longer wavelengths. This gives better transmission through counter windows and less molecular absorption. For example dimethyl POPOP emits in the region 400-500nm and would typically be used at a concentration between 50-200 $mg.l^{-1}$.

β-radiation from a given nuclide presents a range of energies having a defined E_{max}. By using appropriate apparatus it is possible to express the activity of a nuclide in terms of its β-spectrum. The liquid scintillation spectrum is produced by radiation of different energies which are emitted by the sample, which will travel different distances within the scintillation cocktail producing light pulses of differing intensities. The number of light pulses at different intensities can then be recorded to produce a spectrum. Windowing of this spectrum can be used to remove potential interferants or simply to reduce the background. Quantitative counting must recognise counting efficiencies which are influenced by quenching. There are four types of quenching which may affect the counting efficiency:

Impurity quenching is the result of the impact of impurities on the ability of the solute to scintillate.
Colour quenching is the result of molecular absorption within the sample solution.
Dilution quenching is due to insufficient solute in the scintillation solution. Too much solute in the solution will lead to self absorption and so will also lead to reduction in counting efficiency.
Absorption quenching occurs if β-radiation is absorbed before interaction with the solvent. This is usually the result of poor dispersion of either the solute or the sample within the solution

The detection limit is determined by the signal to background ratio, or more specifically, by the error in the background determination. Therefore in order to reduce the limit of detection to as low as possible, the background must be minimised and the instrument must remain stable during the long counting times needed for low level samples. Both passive and active shielding are used by the 1220 Quantulus liquid scintillation counter to reduce noise from background radiation counts. In addition two programmable multi-channel analysers (MCA) can be set to register only when a signal is simultaneously received by both to remove background from electronic interference.

The passive shield consists of a massive asymmetrical lead shield (630 kg) which is lined internally with copper. The lead is thickest above the sample chamber (20cm) as the intensity of cosmic radiation is greatest from above. The surrounding lead shield is thick enough (7-12 cm) for attenuation of γ-radiation. The lead x-rays induced by cosmic radiation on the lead shield are absorbed by the copper wall of the liquid scintillation container.

The active guard is a mineral oil based scintillator and forms a cylinder around the counting chamber and the two photomulipier tubes. The photomultiplier tubes are also covered so that background attributed to Cerenkov radiation in the glass of the PM tubes, a result of the action of cosmic rays, can be detected. The active shield can be used to give anticoincidence signals to the analogue-to-digital converter, or to give a multichannel analyser "split" signal. The spilt signal guides the converted pulse to the second half of the dual multichannel analyser.

The Quantulus incorporates two dual multichannel analysers which are programmable so that logic signals from the coincidence unit, pulse analyser electronics, active shield or guard pulses can be selected to trigger or to inhibit analogue to digital conversion or to select the MCA memory half. An automatic spectrum stabilisation system continuously monitors the photomultipliers for any drift. This is done using an LED which flashes 60 times per second. The output from the photomultiplier is compared with a pre-set reference level and the voltage input to the photomultiplier tube adjusted if any drift has occurred.

A1.6.2.2. Optimisation for ^{99}Tc

A number of different liquid scintillants were trialed to find the most suitable for ^{99}Tc determination. Each scintillant was run as a blank and also as spiked ^{99}Tc standards. The optimum window for each of the ^{99}Tc spectra was determined for each scintillant and the counting efficiency of each determined by a comparison of the number of recorded counts per minutes and the activity of the sample. The background activity was determined by the number of counts per minute in the blank scintillant within the optimised counting window for that scintillant (Table A1.3).

Table A1.3. Optimised parameters for ^{99}Tc determination.

Scintillant	L_D (Bq/kg)	Counting efficiency	Optimised window	Background activity cpm
Goldstar	0.87	90.4	125-647	2.15
Hisafe 3	1.12	90.4	123-606	3.56
Ultima Gold AB	0.93	91.8	140-656	2.52
Ecosafe	0.91	88.8	123-609	2.25
InstaGel	0.90	64.2	118-421	1.19

Goldstar liquid scintillation cocktail was found to be the most efficient scintillation cocktail for ^{99}Tc determination, and so was used throughout this study.

A1.6.2.3. Instrument Stability

The stability of the Quantulus was continually measured by determination of blanks and standards over a period of two years. The determination of blanks indicates the background radiation levels affecting the instrument. In general the blank values all fall within 2 standard deviations with the exception of a period during August 1998 (Figure A1.5). This reflects a period of warm weather and some problems with the air conditioning in the building. Normally a three month cycle would be expected reflecting sunspot activity and therefore fluctuations in cosmic radiation. The fact that this is not seen in the background determinations made on the Quantulus shows that the shielding is attenuating most of the cosmic radiation. Increases in the background are therefore likely to be due to interference from instrument electronics.

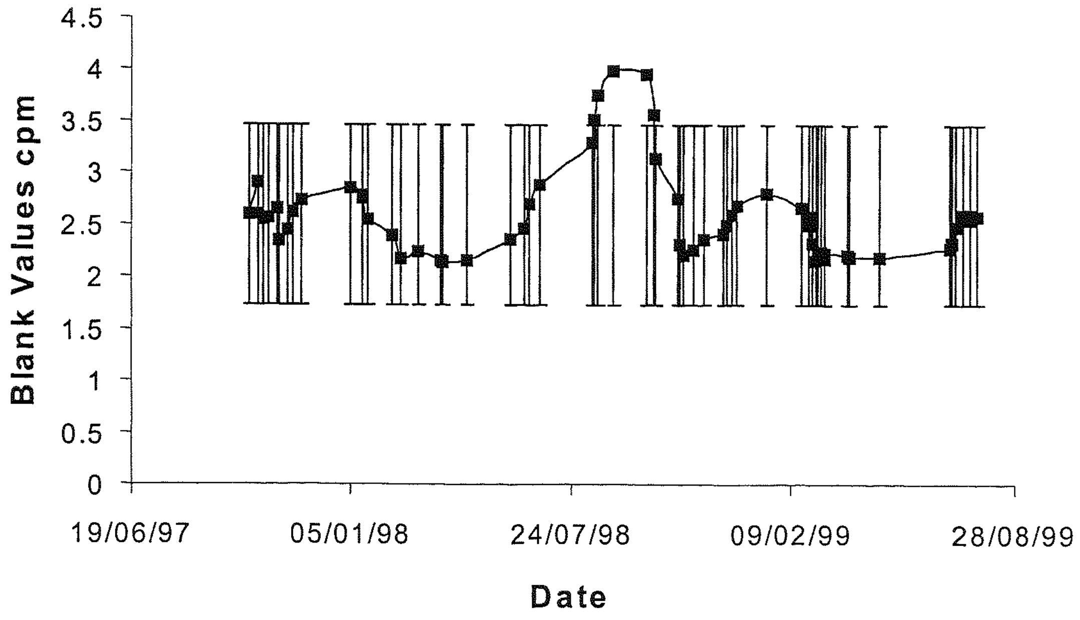

Figure A1.5. Running mean plot for blank determinations on the ^{99}Tc determination programme for the Quantulus. The operating range indicated is at 2σ.

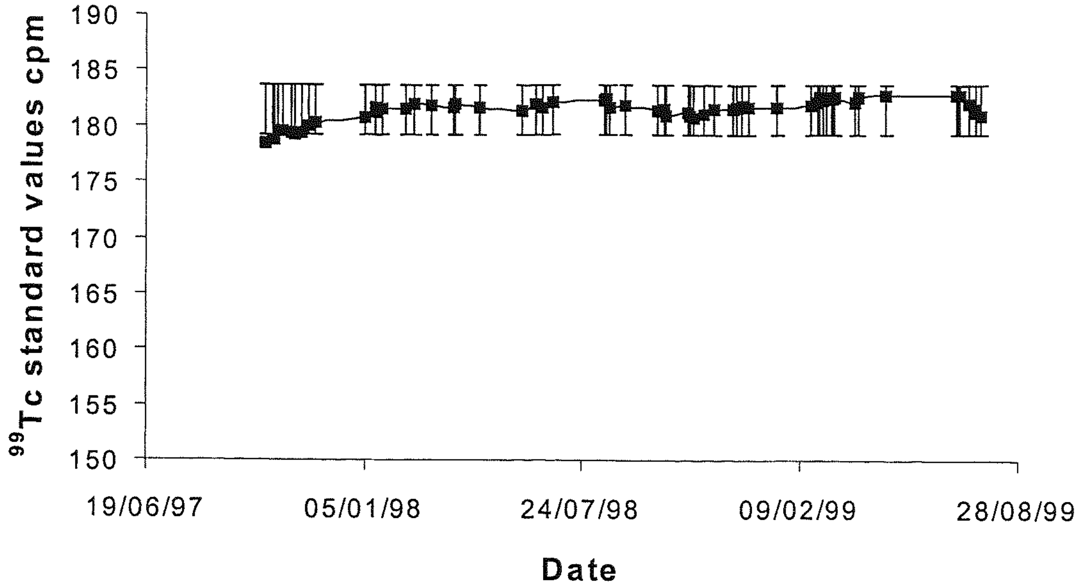

Figure A1.6. Running mean plot for ^{99}Tc standard determination. The standard has an activity of 196 Bq/sample. Operating range at 2σ.

A ^{99}Tc standard was counted with every batch of samples determined, so that samples could be corrected for counting efficiency (Figure A1.6). There appears to be a slight increase in counting efficiency with time but this remains within 2 standard deviations and still fluctuates.

A1.7. Normalisation of data

Normalisation of certain data to the aluminium content throughout cores and other sediment samples is effective in revealing whether differences in bulk concentration are due to variations in the abundance of the detrital mineral phase. Likewise normalisation of some data to the chlorine concentration throughout the sediment cores is an effective method for revealing whether difference is in bulk concentration are due to variations in the amount of sea-water originally present in these samples. Aluminium is often used as a proxy for mineralogical variation (Loring 1991) and has been shown to be representative of the clay mineral content of estuarine sediments (Cundy 1994). Chlorine has also been shown to be a proxy for trace elements dissolved in seawater (Zwalsmann *et al.* 1993). The normalising of data must be undertaken carefully since the results obtained may incorporate artefacts of the normalisation process.

A sample containing only organic detritus and clay mineral grains may have within the mineral lattice some elements which are absent from the surface of the organic materials. This means that their abundance will be controlled by the proportion of clay minerals within the sediment.

This will also be true for elements only found within the organic detritus. Peaks in the element concentration may me attributable to increased abundances of the carrier phase. Normalisation of the data to this carrier phase will therefore effectively remove variations in element concentration which are caused by the variable sediment composition.

If there is no reason for assuming that the element concentration is solely controlled by the abundance of a carrier phase then such normalisation may produce misleading results. For example if a sediment sample incorporating a third phase (and a second carrier phase) such as carbonate which also contributes some of the which is used for normalisation to the sediment subsequent normalisation may give erroneous results. This is as variations in the concentration of the desired element may not be proportional to the normalising parameter. This is known as the closed sum problem and needs to be considered prior to normalisation so that misleading results are not generated.

A1.8. Reference List

Cundy A.B. 1994. *Radionuclide and geochemical studies of recent sediments from the Solent estuarine system.* PhD thesis Southampton University.

Loring D.H. 1991. *Normalization of heavy metal data from estuarine and coastal sediments.* J. Marine Systems. **48.** 101-15.

Zwolsman J.J.G., Berger G.W., Van Eck G.T.M. 1993. *Sediment accumulation rates, historical input, post depositional mobility and retention of major elements and trace metals in saltmarsh sediments of the Scheldt estuary, S.W. Netherlands.* Marine Chemistry **44.** 73-94.

Appendix 2

Experimental data

Appendix 2. Experimental data.

A2.1. Introduction

This appendix comprises the analytical data collected for the determination of radionuclides and stable elements in the sediment and other samples collected for the completion of this thesis.

Where multiple determinations have been made mean values are displayed. The errors for the determination of different elements and radionuclides depend on the element in question and the means of determination. The precision of each determination is reflected by the number of significant figures quoted. The accuracy of determinations for each element or radionuclide is discussed in Appendix A with reference to certified reference materials. The accuracy of ^{99}Tc determinations is discussed in Chapter 4, and also in the recent inter-laboratory comparison exercise organised by Dr Martin McCartney of SURRC.

A2.2. Thornflatt Saltmarsh

A2.2.1. Core R-98-001

Stable and Radionuclide data

Depth	cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Wet ; Dry Ratio		1.78	1.74	1.71	1.75	1.74	1.66	1.67	1.69	1.60	1.60	1.59	1.56	1.53	1.53	1.55	1.55	1.58	1.56	1.60	1.64	1.60	1.56
Total Majors	wt%	na	98.69	na	100.94	na	99.47	na	99.30	na	99.27	na	100.79	na	98.96	na	97.65	na	100.01	na	99.43	na	na
SiO_2	wt%	na	56.38	na	58.58	na	59.27	na	59.61	na	60.35	na	61.64	na	60.99	na	60.51	na	62.69	na	61.95	na	na
TiO_2	wt%	na	0.72	na	0.74	na	0.75	na	0.73	na	0.76	na	0.81	na	0.77	na	0.74	na	0.78	na	0.76	na	na
Al_2O_3	wt%	na	12.01	na	12.12	na	12.18	na	11.83	na	12.45	na	13.01	na	12.23	na	11.74	na	12.50	na	12.22	na	na
Fe_2O_3	wt%	na	5.26	na	5.27	na	5.30	na	5.07	na	5.25	na	5.41	na	5.06	na	4.98	na	5.29	na	5.15	na	na
MnO	ppm	1673	1951	2210	1823	1853	1802	1757	1839	1573	1762	1872	1810	1299	1505	1571	1686	1725	1736	1773	1756	na	1532
MgO	wt%	na	2.56	na	2.58	na	2.51	na	2.31	na	2.35	na	2.44	na	2.35	na	2.19	na	2.16	na	2.01	na	na
CaO	wt%	na	2.03	na	1.51	na	1.37	na	1.23	na	1.16	na	1.23	na	1.24	na	1.11	na	0.91	na	0.81	na	na
Na_2O	wt%	na	1.92	na	2.46	na	1.72	na	1.71	na	1.76	na	1.75	na	1.79	na	1.88	na	1.80	na	1.82	na	na
P_2O_5	wt%	na	0.23	na	0.22	na	0.22	na	0.21	na	0.21	na	0.23	na	0.21	na	0.19	na	0.19	na	0.19	na	na
LOI	wt%	na	14.78	na	14.59	na	13.32	na	13.81	na	12.21	na	11.44	na	11.58	na	11.53	na	10.82	na	11.72	na	na
S	wt%	na	0.24	na	0.22	na	0.21	na	0.22	na	0.19	na	0.18	na	0.18	na	0.17	na	0.16	na	0.18	na	na
Cl	wt%	na	1.55	na	1.63	na	1.50	na	1.66	na	1.51	na	1.46	na	1.39	na	1.24	na	1.50	na	1.76	na	na
C org	wt%	na	4.36	na	4.82	na	4.43	na	4.73	na	3.69	na	2.90	na	3.58	na	3.39	na	2.75	na	3.30	na	na
CO_3	wt%	na	0.45	na	0.19	na	0.19	na	0.15	na	0.14	na	0.29	na	0.46	na	0.29	na	0.32	na	0.26	na	na
Rb	ppm	98	101	102	98	98	101	100	97	97	100	102	102	101	99	97	97	100	101	**98**	99	na	97
Sr	ppm	129	111	108	102	104	103	103	103	101	102	102	101	100	102	102	102	101	102	101	100	na	100
Ba	ppm	316	343	349	333	325	336	332	329	331	330	332	341	341	347	343	335	338	346	338	342	na	341
Br	ppm	194	205	215	225	237	214	238	237	195	204	196	168	158	163	179	167	159	**149**	180	196	na	161
I	ppm	91	105	111	112	114	105	103	112	101	109	109	85	85	97	93	97	111	105	114	116	na	99
As	ppm	19	20	21	19	23	37	23	20	19	21	22	22	20	21	20	21	20	21	22	23	na	21
Pb	ppm	68	67	70	76	79	426	105	71	67	71	72	73	73	75	77	77	83	88	84	82	na	75
Ni	ppm	34	34	35	33	35	35	34	34	34	36	36	36	35	35	35	35	37	35	34	33	na	33
Cr	ppm	103	108	177	107	116	119	123	108	111	107	117	116	120	121	134	128	120	108	111	107	na	97
Zn	ppm	159	159	166	166	158	161	163	158	155	148	157	161	155	164	163	163	166	162	160	157	na	147
V	ppm	108	115	112	108	112	113	111	106	106	113	113	115	108	112	109	108	115	114	111	113	na	106
Y	ppm	27	28	29	30	34	35	34	34	36	38	39	40	41	42	45	39	36	32	30	28	na	27
Zr	ppm	209	218	224	226	230	236	235	245	247	242	237	242	247	257	262	266	256	259	260	258	na	260
Nb	ppm	16	16	17	16	17	18	17	17	17	17	18	18	17	17	17	18	18	18	17	17	na	18
La	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Ce	ppm	61	61	56	53	60	58	60	55	53	59	64	60	64	55	56	50	62	47	53	49	na	54
^{99}Tc	Bq/kg	260	447	197	130	59	62	46	60	47	61	72	83	76	94	92	66	40	51	42	48	44	55
^{137}Cs	Bq/kg	1023	964	1032	1139	1652	1190	2035	3033	4970	7840	10610	12630	15160	15370	11320	8700	6930	6150	5610	5520	4780	4110
^{241}Am	Bq/kg	1983	1840	1908	2237	2542	2361	2964	5566	4630	6720	10150	12240	13990	20860	17630	8900	4140	1809	1469	1339	1019	803

Depth	cm	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Wet ; Dry Ratio		1.55	1.54	1.54	1.53	1.51	1.47	1.48	1.48	1.47	1.47	1.45	1.44	1.46	1.46	1.45	1.44	1.42	1.42
Total Majors	wt%	99.91	na	na	101.25	na	na	99.42	na	na	100.01	na	na	101.17	na	na	100.18	na	na
SiO_2	wt%	64.44	na	na	64.92	na	na	66.79	na	na	65.16	na	na	66.25	na	na	66.41	na	na
TiO_2	wt%	0.75	na	na	0.75	na	na	0.74	na	na	0.76	na	na	0.78	na	na	0.78	na	na
Al_2O_3	wt%	12.01	na	na	11.98	na	na	11.60	na	na	12.15	na	na	12.19	na	na	11.84	na	na
Fe_2O_3	wt%	5.10	na	na	5.18	na	na	4.96	na	na	5.23	na	na	5.17	na	na	4.96	na	na
MnO	ppm	na	1560	na	1520	na	1362	na	1319	na	1372	na	1220	na	1412	na	1223	na	1235
MgO	wt%	1.96	na	na	1.95	na	na	1.93	na	na	2.08	na	na	2.11	na	na	2.04	na	na
CaO	wt%	0.70	na	na	0.66	na	na	0.74	na	na	0.75	na	na	0.87	na	na	0.94	na	na
Na_2O	wt%	2.13	na	na	3.11	na	na	1.76	na	na	1.80	na	na	2.01	na	na	1.93	na	na
P_2O_5	wt%	0.16	na	na	0.16	na	na	0.15	na	na	0.16	na	na	0.17	na	na	0.17	na	na
LOI	wt%	9.85	na	na	9.68	na	na	8.09	na	na	9.03	na	na	8.74	na	na	8.33	na	na
S	wt%	0.15	na	na	0.15	na	na	0.13	na	na	0.14	na	na	0.13	na	na	0.12	na	na
Cl	wt%	1.29	na	na	1.30	na	na	1.15	na	na	1.18	na	na	1.17	na	na	1.17	na	na
C org	wt%	2.88	na	na	2.47	na	na	2.01	na	na	2.68	na	na	2.27	na	na	1.89	na	na
CO_3	wt%	0.17	na	na	0.20	na	na	0.19	na	na	0.15	na	na	0.18	na	na	0.30	na	na
Rb	ppm	na	98	na	100	na	96	na	98	na	103	na	96	na	98	na	95	na	96
Sr	ppm	na	100	na	99	na	99	na	98	na	100	na	97	na	98	na	98	na	97
Ba	ppm	na	349	na	347	na	344	na	344	na	355	na	347	na	363	na	357	na	360
Br	ppm	na	140	na	143	na	126	na	130	na	138	na	126	na	117	na	119	na	93
I	ppm	na	93	na	101	na	85	na	85	na	87	na	76	na	79	na	72	na	68
As	ppm	na	22	na	22	na	21	na	21	na	24	na	20	na	23	na	21	na	20
Pb	ppm	na	78	na	78	na	70	na	68	na	76	na	89	na	79	na	73	na	66
Ni	ppm	na	35	na	34	na	32	na	33	na	34	na	32	na	3	na	31	na	31
Cr	ppm	na	104	na	104	na	95	na	96	na	105	na	97	na	101	na	96	na	96
Zn	ppm	na	147	na	150	na	139	na	135	na	150	na	136	na	145	na	136	na	136
V	ppm	na	109	na	108	na	101	na	104	na	111	na	101	na	108	na	101	na	99
Y	ppm	na	27	na	26	na	26	na	26	na	26	na	27	na	28	na	26	na	27
Zr	ppm	na	275	na	271	na	277	na	279	na	266	na	264	na	269	na	272	na	266
Nb	ppm	na	17	na	17	na	18	na	18	na	17	na	18	na	17	na	18	na	17
La	ppm	na	30	na	31	na	30	na	33	na	35	na	30	na	31	na	27	na	29
Ce	ppm	na	59	na	63	na	56	na	55	na	63	na	64	na	44	na	50	na	49
^{99}Tc	Bq/kg	49	48	44	na	46	na	41	37	27	na	26	na	22	na	17	na	22	na
^{137}Cs	Bq/kg	na	3550	na	3410	na	2195	na	1643	na	1124	na	746	na	612	na	539	na	429
^{241}Am	Bq/kg	na	516	na	416	na	397	na	259	na	266	na	241	na	267	na	311	na	299

Depth	cm	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Wet ; Dry Ratio		1.41	1.38	1.40	1.39	1.39	1.40	1.40	1.38	1.37	1.38	1.36	1.32	1.34	1.33
Total Majors	wt%	99.14	na	na	98.86	na	na	97.70	na	na	100.65	na	na	99.25	na
SiO_2	wt%	65.15	na	na	65.93	na	na	63.39	na	na	66.57	na	na	67.16	na
TiO_2	wt%	0.76	na	na	0.77	na	na	0.75	na	na	0.80	na	na	0.74	na
Al_2O_3	wt%	11.65	na	na	11.84	na	na	12.19	na	na	12.63	na	na	11.59	na
Fe_2O_3	wt%	4.96	na	na	4.91	na	na	5.07	na	na	5.10	na	na	4.76	na
MnO	ppm	na	789	na	1024	na	1426	na	1368	na	1241	na	1174	na	1159
MgO	wt%	2.13	na	na	2.14	na	na	2.26	na	na	2.29	na	na	2.20	na
CaO	wt%	1.00	na	na	1.03	na	na	1.01	na	na	1.10	na	na	1.13	na
Na_2O	wt%	1.77	na	na	1.72	na	na	2.24	na	na	1.71	na	na	1.80	na
P_2O_5	wt%	0.15	na	na	0.17	na	na	0.15	na	na	0.17	na	na	0.15	na
LOI	wt%	8.89	na	na	7.60	na	na	7.82	na	na	7.41	na	na	7.00	na
S	wt%	0.10	na	na	0.10	na	na	0.08	na	na	0.09	na	na	0.08	na
Cl	wt%	0.96	na	na	0.99	na	na	0.91	na	na	0.94	na	na	0.85	na
C org	wt%	1.58	na	na	1.23	na	na	1.30	na	na	1.21	na	na	1.08	na
CO_3	wt%	0.27	na	na	0.41	na	na	0.33	na	na	0.22	na	na	0.48	na
Rb	ppm	na	95	na	97	na	102	na	99	na	102	na	93	na	98
Sr	ppm	na	98	na	97	na	98	na	96	na	97	na	97	na	96
Ba	ppm	na	332	na	345	na	348	na	331	na	349	na	340	na	360
Br	ppm	na	85	na	88	na	89	na	73	na	77	na	69	na	72
I	ppm	na	54	na	58	na	81	na	72	na	70	na	56	na	64
As	ppm	na	20	na	21	na	22	na	19	na	22	na	19	na	19
Pb	ppm	na	65	na	63	na	63	na	56	na	57	na	49	na	48
Ni	ppm	na	31	na	32	na	34	na	32	na	33	na	30	na	31
Cr	ppm	na	100	na	99	na	99	na	93	na	99	na	102	na	105
Zn	ppm	na	121	na	123	na	126	na	111	na	109	na	92	na	93
V	ppm	na	100	na	109	na	107	na	103	na	105	na	95	na	99
Y	ppm	na	27	na	26	na	25	na	26	na	27	na	26	na	25
Zr	ppm	na	284	na	272	na	261	na	279	na	275	na	292	na	284
Nb	ppm	na	18	na	18	na	18	na	17	na	18	na	17	na	17
La	ppm	na	30	na	26	na	34	na	29	na	25	na	25	na	28
Ce	ppm	na	61	na	57	na	66	na	67	na	45	na	49	na	46
^{99}Tc	Bq/kg	8	na	8	na	6	na	10	na	4	na	3	na	na	7
^{137}Cs	Bq/kg	na	404	na	248	na	263	na	102	na	16	na	7	na	10
^{241}Am	Bq/kg	na	336	na	219	na	222	na	61	na	7	na	32	na	41

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Stable and Radionuclide data

Depth	cm	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7	7.5
Total Majors	wt%	99.99	99.71	100.00	99.99	99.97	99.99	100.00	na	na	na	na	na	na	na	100.00
SiO_2	wt%	55.54	55.24	56.94	56.04	56.38	58.13	53.69	na	na	na	na	na	na	na	57.58
TiO_2	wt%	0.75	0.51	0.76	0.75	0.73	0.71	0.81	na	na	na	na	na	na	na	0.81
Al_2O_3	wt%	12.25	12.40	12.64	12.48	11.89	11.37	13.84	na	na	na	na	na	na	na	12.88
Fe_2O_3	wt%	5.67	5.97	5.65	5.67	5.23	4.86	5.79	na	na	na	na	na	na	na	5.66
MnO	ppm	2447	1840	1804	2005	1968	2023	1683	1640	1648	1564	1604	1484	1717	1532	1718
MgO	wt%	2.09	2.16	2.08	2.12	2.02	1.96	2.72	na	na	na	na	na	na	na	2.22
CaO	wt%	0.66	0.68	0.66	0.64	0.64	0.68	1.34	na	na	na	na	na	na	na	0.71
Na_2O	wt%	1.76	1.84	1.77	1.85	1.66	1.61	2.70	na	na	na	na	na	na	na	2.76
P_2O_5	wt%	0.17	0.17	0.18	0.17	0.15	0.16	0.29	na	na	na	na	na	na	na	0.25
LOI	wt%	18.35	17.96	16.57	17.50	18.58	17.92	16.02	na	na	na	na	na	na	na	14.22
S	wt%	0.44	0.35	0.34	0.41	0.44	0.47	0.46	na	na	na	na	na	na	na	0.43
Cl	wt%	5.93	4.52	4.14	5.61	5.93	6.55	5.65	na	na	na	na	na	na	na	4.90
C org	wt%	4.38	na	3.72	na	4.98	na	5.94	na	7.40	na	6.66	na	4.13	na	4.74
CO_3	wt%	3.22	na	2.94	na	2.13	na	1.18	na	0.75	na	0.42	na	0.62	na	0.76
Rb	ppm	94	104	108	103	99	98	98	97	101	99	103	101	100	104	106
Sr	ppm	140	111	108	106	106	108	107	106	105	107	106	105	103	103	107
Ba	ppm	312	318	324	324	308	301	307	298	297	286	311	296	301	308	319
Br	ppm	401	344	319	359	386	409	410	370	370	409	389	395	354	325	340
I	ppm	105	116	118	133	123	113	111	96	104	106	107	109	103	99	99
As	ppm	22	21	24	19	25	29	30	24	26	25	25	29	22	22	27
Pb	ppm	99	78	82	79	76	77	74	75	77	73	77	75	77	78	80
Ni	ppm	36	37	39	38	37	36	36	36	37	36	38	37	38	38	40
Cr	ppm	94	97	106	97	98	99	107	105	107	103	108	103	102	102	107
Zn	ppm	177	178	180	178	170	171	160	163	168	165	162	161	162	160	168
V	ppm	110	115	121	116	110	105	111	111	110	106	112	116	112	116	114
Y	ppm	26	29	30	29	30	32	34	35	34	33	34	36	38	38	40
Zr	ppm	171	185	194	188	185	188	199	199	193	187	205	205	213	221	217
Nb	ppm	14	15	16	15	15	15	16	15	15	15	16	15	15	16	17
La	ppm	31	33	35	36	36	34	36	32	33	33	37	36	37	37	38
Ce	ppm	47	57	63	49	60	55	56	60	57	58	56	51	54	66	57
^{99}Tc	Bq/kg	518	326	274	130	80	78			53			53		63	
^{137}Cs	Bq/kg	1262	1385	1315	1268	1386	1474	1512	2020	2240	3000	3400	4460	5720	7310	10670
^{241}Am	Bq/kg	1728	1952	1819	2019	1973	2023	1862	2470	2610	3040	3110	3570	4100	4950	6550

Depth	cm	8	8.5	9	9.5	10	10.5	11	11.5	12	12.5	13	13.5	14	14.5	15
Total Majors	wt%	na	na	na	na	na	na	na	100.00	na	99.16	na	na	na	na	na
SiO_2	wt%	na	na	na	na	na	na	na	56.11	na	58.22	na	na	na	na	59.28
TiO_2	wt%	na	na	na	na	na	na	na	0.81	na	0.08	na	na	na	na	0.84
Al_2O_3	wt%	na	na	na	na	na	na	na	13.18	na	13.54	na	na	na	na	13.60
Fe_2O_3	wt%	na	na	na	na	na	na	na	6.22	na	6.09	na	na	na	na	5.57
MnO	ppm	1971	2025	2176	2040	2577	2495	2520	2247	2361	2815	2699	2423	2713	2716	2476
MgO	wt%	na	na	na	na	na	na	na	2.22	na	2.38	na	na	na	na	2.36
CaO	wt%	na	na	na	na	na	na	na	0.64	na	0.75	na	na	na	na	0.79
Na_2O	wt%	na	na	na	na	na	na	na	2.23	na	2.21	na	na	na	na	2.41
P_2O_5	wt%	na	na	na	na	na	na	na	0.22	na	0.22	na	na	na	na	0.21
LOI	wt%	na	na	na	na	na	na	na	15.23	na	12.69	na	na	na	na	12.07
S	wt%	na	na	na	na	na	na	na	0.32	na	0.40	na	na	na	na	0.35
Cl	wt%	na	na	na	na	na	na	na	3.74	na	4.53	na	na	na	na	3.96
C org	wt%	na	4.09	na	4.19	na	3.79	na	5.68	na	4.77	na	4.05	na	3.99	na
CO_3	wt%	na	0.80	na	0.79	na	0.80	na	0.45	na	0.45	na	0.76	na	0.32	na
Rb	ppm	108	108	110	110	107	97	110	111	109	104	106	109	110	109	111
Sr	ppm	106	105	105	105	105	95	106	105	105	107	106	106	105	107	105
Ba	ppm	367	326	323	322	322	294	327	336	331	318	326	333	328	328	334
Br	ppm	325	297	289	274	273	231	254	267	308	361	306	266	255	243	257
I	ppm	109	115	123	114	108	106	112	124	122	139	116	111	112	110	107
As	ppm	18	27	25	23	20	15	17	22	27	32	22	24	17	21	25
Pb	ppm	81	81	83	84	85	67	88	92	93	96	95	96	95	90	97
Ni	ppm	41	39	41	41	41	33	41	39	41	42	42	41	41	42	43
Cr	ppm	112	107	114	114	113	105	120	123	126	125	137	127	122	120	119
Zn	ppm	190	176	177	176	179	157	187	187	186	192	190	191	193	189	192
V	ppm	118	118	121	123	114	110	121	122	122	123	122	124	122	115	124
Y	ppm	41	41	42	42	42	40	44	43	44	47	46	43	40	38	36
Zr	ppm	216	211	214	217	227	207	228	225	229	220	219	234	228	234	229
Nb	ppm	17	16	16	16	17	16	17	17	16	16	17	16	17	16	17
La	ppm	40	42	40	43	42	38	42	40	41	42	39	39	42	39	39
Ce	ppm	58	58	63	65	55	51	61	62	63	64	57	56	58	63	61
^{99}Tc	Bq/kg	105	83	78	70	78	109	125	na	89	78	69	na	na	54	na
^{137}Cs	Bq/kg	13340	12570	14590	14630	15300	18020	20670	18250	15910	13540	11990	9750	8600	7260	7300
^{241}Am	Bq/kg	9010	9410	12290	13860	13180	13150	17410	20050	25080	20220	15400	10620	7390	4230	2980

Depth	cm	15.5	16	16.5	17	17.5	18	18.5	19	19.5	20	20.5	21	21.5	22	22.5
Total Majors	wt%	na	na	na	na	na	na	na	100.01	na	na	na	na	na	na	99.54
SiO_2	wt%	na	na	na	na	na	na	na	58.09	na	na	na	na	na	na	61.45
TiO_2	wt%	na	na	na	na	na	na	na	0.78	na	na	na	na	na	na	0.86
Al_2O_3	wt%	na	na	na	na	na	na	na	15.43	na	na	na	na	na	na	13.57
Fe_2O_3	wt%	na	na	na	na	na	na	na	5.97	na	na	na	na	na	na	6.04
MnO	ppm	3594	2810	3662	3177	3343	2185	2951	2123	2007	1575	1416	1128	1961	1981	1441
MgO	wt%	na	na	na	na	na	na	na	2.21	na	na	na	na	na	na	2.36
CaO	wt%	na	na	na	na	na	na	na	0.24	na	na	na	na	na	na	0.84
Na_2O	wt%	na	na	na	na	na	na	na	1.96	na	na	na	na	na	na	1.91
P_2O_5	wt%	na	na	na	na	na	na	na	0.19	na	na	na	na	na	na	0.19
LOI	wt%	na	na	na	na	na	na	na	11.84	na	na	na	na	na	na	9.98
S	wt%	na	na	na	na	na	na	na	0.30	na	na	na	na	na	na	0.28
Cl	wt%	na	na	na	na	na	na	na	3.42	na	na	na	na	na	na	3.24
C org	wt%	3.75	na	3.49	na	3.73	na	3.16	na	3.27	na	2.93	na	2.85	na	3.12
CO_3	wt%	0.42	na	0.41	na	0.51	na	0.57	na	0.58	na	0.59	na	0.68	na	0.86
Rb	ppm	111	112	111	112	110	110	107	110	110	111	110	107	113	113	109
Sr	ppm	105	105	104	106	106	103	104	103	104	103	102	99	104	104	103
Ba	ppm	325	336	342	340	338	351	340	361	356	356	353	346	343	348	341
Br	ppm	278	264	250	272	306	265	276	265	262	241	243	220	245	256	239
I	ppm	124	127	116	129	137	121	132	127	98	122	107	100	106	120	110
As	ppm	24	19	15	15	30	26	16	28	23	28	22	19	17	25	20
Pb	ppm	99	94	102	98	96	99	97	103	99	100	90	85	88	87	96
Ni	ppm	43	42	44	42	42	40	41	40	42	39	39	38	40	42	41
Cr	ppm	115	116	114	114	113	105	104	104	103	110	103	106	110	106	109
Zn	ppm	205	192	204	197	198	187	191	195	193	183	182	168	185	188	178
V	ppm	123	126	125	123	114	123	115	121	122	118	119	123	124	122	120
Y	ppm	36	33	32	31	30	31	30	29	30	28	27	25	27	28	27
Zr	ppm	221	226	225	224	229	229	228	232	227	225	230	229	225	227	229
Nb	ppm	16	16	17	17	17	17	17	17	17	17	17	16	17	16	17
La	ppm	41	35	36	35	35	32	35	37	33	34	33	33	34	35	32
Ce	ppm	66	61	64	57	59	56	55	56	60	60	57	58	66	61	63
^{99}Tc	Bq/kg		46	32	35	32	66	51	29	15	36	na	27	na	26	na
^{137}Cs	Bq/kg	5920	4830	4600	4010	3850	na	3211	na	2476	na	1676	na	1443	na	968
^{241}Am	Bq/kg	1999	1148	925	640	496	na	260	na	152	na	65	na	2141	na	40

Depth	cm	23	23.5	24	24.5	25	25.5	26	26.5	27	27.5	28	28.5	29	29.5	30
Total Majors	wt%	na	na	na	na	na	na	na	100.00	na	na	na	na	na	na	100.02
SiO_2	wt%	na	na	na	na	na	na	na	61.55	na	na	na	na	na	na	64.02
TiO_2	wt%	na	na	na	na	na	na	na	0.91	na	na	na	na	na	na	0.84
Al_2O_3	wt%	na	na	na	na	na	na	na	14.86	na	na	na	na	na	na	13.62
Fe_2O_3	wt%	na	na	na	na	na	na	na	6.57	na	na	na	na	na	na	5.87
MnO	ppm	1695	1416	1666	2269	1758	1967	2192	2113	1621	1381	1286	1245	1106	1050	1038
MgO	wt%	na	na	na	na	na	na	na	2.51	na	na	na	na	na	na	2.36
CaO	wt%	na	na	na	na	na	na	na	0.82	na	na	na	na	na	na	0.79
Na_2O	wt%	na	na	na	na	na	na	na	2.22	na	na	na	na	na	na	2.16
P_2O_5	wt%	na	na	na	na	na	na	na	0.24	na	na	na	na	na	na	0.19
LOI	wt%	na	na	na	na	na	na	na	7.36	na	na	na	na	na	na	7.29
S	wt%	na	na	na	na	na	na	na	0.25	na	na	na	na	na	na	0.24
Cl	wt%	na	na	na	na	na	na	na	2.80	na	na	na	na	na	na	2.67
C org	wt%	na	2.19	na	2.22	na	2.32	na	1.50	na	0.54	na	1.46	na	1.60	na
CO_3	wt%	na	0.91	na	1.09	na	1.22	na	1.32	na	1.48	na	1.58	na	1.59	na
Rb	ppm	110	108	109	108	105	110	114	110	108	105	104	105	105	103	105
Sr	ppm	102	102	103	105	103	103	104	103	100	97	97	96	97	102	102
Ba	ppm	351	354	362	372	369	369	387	373	354	353	343	355	349	349	341
Br	ppm	249	240	212	212	210	209	207	199	187	183	200	188	205	213	227
I	ppm	115	112	97	108	106	110	114	109	103	107	86	82	87	96	90
As	ppm	25	18	18	25	24	18	18	18	16	22	19	21	21	25	25
Pb	ppm	88	84	85	94	89	98	98	96	81	78	75	74	79	79	79
Ni	ppm	41	38	41	40	39	42	42	42	40	35	36	36	37	38	38
Cr	ppm	104	100	102	107	108	102	106	108	103	95	102	99	97	101	100
Zn	ppm	180	171	173	175	167	175	185	179	170	153	153	150	151	155	158
V	ppm	121	120	120	121	118	125	121	125	117	113	111	113	114	106	114
Y	ppm	28	27	28	28	27	28	29	28	26	25	25	25	26	27	27
Zr	ppm	229	237	237	249	245	240	235	237	253	241	241	244	238	258	247
Nb	ppm	17	17	17	17	16	18	17	17	16	16	16	16	15	17	17
La	ppm	33	32	32	31	36	33	35	36	34	32	32	36	33	31	31
Ce	ppm	58	57	60	66	57	61	61	62	69	62	58	53	55	55	61
^{99}Tc	Bq/kg	na	na	21	na	na	na	25	na	na	9	13	na	na	na	12
^{137}Cs	Bq/kg	na	677	na	529	na	417	na	322	na	254	na	259	na	na	na
^{241}Am	Bq/kg	na	21	na	23	na	21	na	8	na	9	na	6	na	na	na

Depth	cm	30.5	31	31.5	32	32.5	33	33.5	34	34.5	35	35.5	36	37.5	40	41.5	42.5
Total Majors	wt%	na	na	na	na	na	na	na	100.01	na	na	na	na	100.06	na	99.99	na
SiO_2	wt%	na	na	na	na	na	na	na	63.41	na	na	na	na	65.34	na	64.95	na
TiO_2	wt%	na	na	na	na	na	na	na	0.84	na	na	na	na	0.80	na	0.83	na
Al_2O_3	wt%	na	na	na	na	na	na	na	13.69	na	na	na	na	12.95	na	13.33	na
Fe_2O_3	wt%	na	na	na	na	na	na	na	5.96	na	na	na	na	5.76	na	5.90	na
MnO	ppm	972	1577	2133	1310	1478	1421	2089	2354	2241	2082	1490	1398	na	950	na	1075
MgO	wt%	na	na	na	na	na	na	na	2.42	na	na	na	na	2.34	na	2.34	na
CaO	wt%	na	na	na	na	na	na	na	0.85	na	na	na	na	0.97	na	0.90	na
Na_2O	wt%	na	na	na	na	na	na	na	1.97	na	na	na	na	1.84	na	1.84	na
P_2O_5	wt%	na	na	na	na	na	na	na	0.18	na	na	na	na	0.18	na	0.19	na
LOI	wt%	na	na	na	na	na	na	na	7.92	na	na	na	na	7.32	na	6.92	na
S	wt%	na	na	na	na	na	na	na	0.13	na	na	na	na	0.20	na	0.13	na
Cl	wt%	na	na	na	na	na	na	na	1.07	na	na	na	na	1.07	na	1.08	na
C org	wt%	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
CO_3	wt%	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Rb	ppm	102	105	105	105	93	101	100	107	106	105	107	100	96	na	na	100
Sr	ppm	99	101	101	99	100	99	98	100	99	99	100	98	97	na	na	98
Ba	ppm	359	352	351	340	341	351	356	342	352	357	349	356	354	na	na	345
Br	ppm	159	148	140	142	111	103	93	99	83	89	84	0.6	na	78	na	67
I	ppm	81	81	93	81	62	79	87	103	93	78	81	0.4	na	72	na	52
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	68	75	76	81	75	73	66	68	67	57	51	51	na	43	na	44
Ni	ppm	36	38	39	37	34	36	36	39	38	37	36	35	na	31	na	33
Cr	ppm	101	104	98	101	94	98	99	97	99	98	99	95	na	88	na	90
Zn	ppm	146	155	158	155	140	138	134	140	131	118	111	101	na	90	na	91
V	ppm	112	118	108	111	106	111	108	116	115	110	109	106	98	na	na	97.4
Y	ppm	27	27	26	27	27	27	26	27	26	27	26	25	25	na	na	25
Zr	ppm	263	251	253	250	274	258	250	246	250	272	258	266	283	na	na	275
Nb	ppm	16	17	16	16	17	16	16	17	17	17	17	16	16	na	na	16
La	ppm	34	36	32	31	32	30	32	34	31	28	34	32	31	na	na	31
Ce	ppm	60	65	58	57	57	66	56	59	71	51	49	52	41	na	na	44
^{99}Tc	Bq/kg	na	na	na	5	na	na	na	na	na	na	na	4	na	4	na	na
^{137}Cs	Bq/kg	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
^{241}Am	Bq/kg	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na

Depth	cm	44	45	45	46	47	48	49	50	52	56	60
Total Majors	wt%	na	99.98	100.01	na	na	na	99.99	99.98	100.01	100.02	95.56
SiO_2	wt%	na	67.08	0.81	na	na	na	66.31	69.12	68.24	67.44	68.19
TiO_2	wt%	na	0.81	12.63	na	na	na	0.82	0.80	0.82	0.85	0.81
Al_2O_3	wt%	na	12.63	5.58	na	na	na	12.67	11.47	12.63	13.38	13.02
Fe_2O_3	wt%	na	5.58	0.06	na	na	na	5.51	4.84	5.56	5.74	5.59
MnO	ppm	na	1107	1107	na	na	na	na	na	na	na	na
MgO	wt%	na	2.23	0.93	na	na	na	2.24	2.07	2.20	2.36	2.16
CaO	wt%	na	0.93	1.84	na	na	na	0.94	1.02	0.89	0.91	0.73
Na_2O	wt%	na	1.84	2.62	na	na	na	1.81	1.77	1.84	1.87	1.82
P_2O_5	wt%	na	0.17	93.94	na	na	na	0.17	0.15	0.17	0.17	0.17
LOI	wt%	na	6.07	0.00	na	na	na	6.86	6.35	4.83	4.59	4.45
S	wt%	na	0.12	0.11	na	na	na	0.09	0.11	0.11	0.11	0.11
Cl	wt%	na	1.21	0.93	na	na	na	1.22	0.97	0.97	0.95	0.96
C org	wt%	na	na	na	na	na	na	na	na	na	na	na
CO_3	wt%	na	na	na	na	na	na	na	na	na	na	na
Rb	ppm	na	102	na	na	na	na	na	na	na	na	na
Sr	ppm	na	97	na	na	na	na	na	na	na	na	na
Ba	ppm	na	345	na	na	na	na	na	na	na	na	na
Br	ppm	na	78	80	na	na	na	na	na	na	na	na
I	ppm	na	62	64	na	na	na	na	na	na	na	na
As	ppm	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	na	43	43	na	na	na	na	na	na	na	na
Ni	ppm	na	33	33	na	na	na	na	na	na	na	na
Cr	ppm	na	91	91	na	na	na	na	na	na	na	na
Zn	ppm	na	90	90	na	na	na	na	na	na	na	na
V	ppm	na	108	na	na	na	na	na	na	na	na	na
Y	ppm	na	25.6	na	na	na	na	na	na	na	na	na
Zr	ppm	na	274	na	na	na	na	na	na	na	na	na
Nb	ppm	na	16.4	na	na	na	na	na	na	na	na	na
La	ppm	na	32.9	na	na	na	na	na	na	na	na	na
Ce	ppm	na	47.7	na	na	na	na	na	na	na	na	na
^{99}Tc	Bq/kg	63	na	na	0	0	6	0	0	2	2	1
^{137}Cs	Bq/kg	na	na	na	na	na	na	na	na	na	na	na
^{241}Am	Bq/kg	na	na	na	na	na	na	na	na	na	na	na

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Stable and Radionuclide data

Depth	cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Wet ; Dry Ratio		1.63	1.56	1.57	1.64	1.56	1.48	1.63	1.62	1.58	1.55	1.55	1.57	1.54	1.52	1.55
Total Majors	wt%	100.01	100.01	99.99	100.00	100.00	100.00	100.00	99.99	100.00	100.00	na	100.01	na	99.99	na
SiO_2	wt%	62.75	64.83	67.65	64.25	67.08	67.23	66.32	67.89	67.14	68.99	na	65.68	na	67.26	na
TiO_2	wt%	0.64	0.67	0.63	0.70	0.68	0.67	0.68	0.67	0.69	0.69	na	0.73	na	0.70	na
Al_2O_3	wt%	10.14	10.46	9.69	11.31	10.76	10.77	10.66	10.32	10.71	10.29	na	11.24	na	11.02	na
Fe_2O_3	wt%	4.19	4.22	3.84	4.47	4.16	4.40	4.32	4.25	4.30	4.17	na	4.62	na	4.51	na
MnO	ppm	1855	1543	1226	1115	983	1335	1685	1679	1477	1389	1279	1501	1136	1304	1331
MgO	wt%	2.16	2.11	1.95	2.20	2.04	2.05	2.07	1.93	2.02	1.93	na	2.08	na	2.08	na
CaO	wt%	3.82	3.03	1.89	1.59	1.38	1.26	1.28	1.22	1.24	1.26	na	1.24	na	1.29	na
Na_2O	wt%	2.02	1.92	1.93	2.03	2.05	2.04	2.03	1.95	1.89	1.86	na	1.97	na	1.94	na
P_2O_5	wt%	0.20	0.19	0.18	0.18	0.18	0.18	0.18	0.17	0.17	0.17	na	0.18	na	0.18	na
LOI	wt%	11.70	10.10	9.90	10.70	9.10	8.80	9.90	9.10	9.30	8.30	na	9.70	na	8.50	na
S	wt%	0.23	0.17	0.19	0.19	0.19	0.18	0.20	0.19	0.18	0.16	na	0.18	na	0.16	na
Cl	wt%	1.70	1.40	1.49	1.56	1.37	1.54	1.63	1.56	1.47	1.35	na	1.44	na	1.30	na
C org	wt%	2.78	na	2.48	na	2.64	na	2.79	na	2.44	na	2.56	2.39	2.14	2.27	2.27
CO_3	wt%	0.75	na	0.43	na	0.33	na	0.29	na	0.30	na	0.31	0.31	0.31	0.30	0.29
Rb	ppm	85	85	83	92	90	91	90	88	90	88	88	92	89	91	91
Sr	ppm	151	124	105	103	100	101	100	98	100	101	97	102	100	100	102
Ba	ppm	335	337	357	340	349	347	330	336	338	340	329	351	330	352	344
Br	ppm	157	154	200	226	179	220	204	196	170	156	159	172	159	152	168
I	ppm	93	89	109	114	91	105	95	93	81	70	70	62	66	68	85
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	64	55	55	67	58	59	59	55	57	57	54	59	57	58	62
Ni	ppm	30	29	29	32	31	32	32	30	33	32	31	34	32	33	33
Cr	ppm	106	110	112	119	123	122	115	112	115	115	112	124	119	123	121
Zn	ppm	129	123	117	142	125	134	133	125	129	121	119	134	123	128	136
V	ppm	94	90	87	101	96	104	96	92	103	89	95	99	96	99	100
Y	ppm	25	26	26	33	32	32	31	30	36	35	35	37	37	38	40
Zr	ppm	253	291	293	266	293	268	259	262	280	301	285	294	297	279	270
Nb	ppm	15	15	14	14	16	15	15	15	15	15	16	16	16	16	16
La	ppm	26	29	28	34	34	32	33	30	33	31	32	36	35	36	38
Ce	ppm	49	48	41	52	52	53	53	52	53	51	59	46	53	50	53
^{99}Tc	Bq/kg	217	180	64	37	26	34	27	27	26	32	42	63	69	80	56
^{137}Cs	Bq/kg	803	647	762	1016	1013	1109	1810	2537	3009	4309	5642	8107	10463	9983	11596
^{241}Am	Bq/kg	1367	1004	1110	1458	1430	1438	2197	2394	2836	3040	4285	7762	10956	7785	9374

Depth	cm	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Wet ; Dry Ratio		1.54	1.58	1.58	1.57	1.57	1.54	1.49	1.52	1.48	1.48	1.47	1.49	1.50	1.49	1.46
Total Majors	wt%	100.00	na	100.00	na	99.98	na	100.01	na	100.00	na	100.02	na	99.99	na	100.00
SiO_2	wt%	67.03	na	65.76	na	65.64	na	68.15	na	68.83	na	67.22	na	65.86	na	67.18
TiO_2	wt%	0.71	na	0.70	na	0.71	na	0.70	na	0.69	na	0.73	na	0.74	na	0.73
Al_2O_3	wt%	10.81	na	11.09	na	11.01	na	10.76	na	10.59	na	11.06	na	11.78	na	11.40
Fe_2O_3	wt%	4.54	na	4.63	na	4.64	na	4.23	na	4.57	na	4.88	na	5.27	na	4.78
MnO	ppm	1142	1348	765	629	679	641	600	651	680	762	938	1324	1980	2171	1539
MgO	wt%	2.05	na	2.12	na	2.02	na	1.99	na	1.95	na	2.10	na	2.28	na	2.05
CaO	wt%	1.26	na	1.24	na	1.23	na	1.26	na	1.23	na	1.24	na	1.32	na	1.22
Na_2O	wt%	1.94	na	2.01	na	1.92	na	1.82	na	1.76	na	1.81	na	1.93	na	1.76
P_2O_5	wt%	0.20	na	0.20	na	0.21	na	0.17	na	0.18	na	0.16	na	0.17	na	0.15
LOI	wt%	9.00	na	9.80	na	10.10	na	8.50	na	7.80	na	8.30	na	8.00	na	8.10
S	wt%	0.16	na	0.17	na	0.18	na	0.14	na	0.16	na	0.13	na	0.12	na	0.13
Cl	wt%	1.33	na	1.36	na	1.34	na	1.18	na	1.20	na	1.04	na	1.00	na	0.93
C org	wt%	2.46	2.71	2.83	2.87	2.89	na	2.08	na	2.05	na	2.14	na	2.16	na	2.14
CO_3	wt%	0.30	0.30	0.29	0.31	0.42	na	0.37	na	0.30	na	0.14	na	0.14	na	0.18
Rb	ppm	92	93	91	92	94	94	89	87	89	95	94	97	96	96	92
Sr	ppm	100	102	100	101	103	101	99	98	97	98	101	103	101	102	101
Ba	ppm	362	352	349	355	356	348	347	353	352	367	371	385	386	400	390
Br	ppm	167	182	195	201	195	190	158	166	148	142	136	140	127	125	116
I	ppm	70	74	62	72	70	62	60	68	58	66	64	89	74	81	62
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	63	68	67	69	78	72	62	63	67	78	80	78	82	81	75
Ni	ppm	34	34	32	33	35	34	32	31	32	34	34	37	36	37	34
Cr	ppm	133	140	129	138	156	136	121	119	117	123	122	122	125	121	119
Zn	ppm	139	152	144	150	164	156	136	138	138	149	152	165	164	165	146
V	ppm	101	104	101	100	108	105	89	97	96	102	105	109	108	108	98
Y	ppm	42	41	40	44	53	36	31	33	30	27	29	29	28	27	27
Zr	ppm	286	284	299	293	287	284	306	312	301	298	296	291	284	293	293
Nb	ppm	15	15	15	16	15	16	16	16	16	16	16	17	17	17	16
La	ppm	36	37	37	38	41	33	32	31	32	33	34	34	34	29	31
Ce	ppm	52	53	52	55	55	57	51	53	51	57	55	52	53	52	49
^{99}Tc	Bq/kg	50	66	85	115	141	35	45	32	22	36	25	32	32	32	27
^{137}Cs	Bq/kg	13969	15224	12540	8884	8085	na	4292	na	2122	na	915	na	627	na	316
^{241}Am	Bq/kg	13511	19419	24673	12100	10492	na	2538	na	516	na	58	na	24	na	9

Depth	cm	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Wet ; Dry Ratio		1.5	1.5	1.5	1.5	1.4	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Total Majors	wt%	na	na	100.0	na	na	100.0	na	na	100.0	na	na	100.0	na	na	100.0
SiO_2	wt%	na	na	66.7	na	na	68.0	na	na	68.8	na	na	68.5	na	na	68.7
TiO_2	wt%	na	na	0.7	na	na	0.7	na	na	0.7	na	na	0.7	na	na	0.7
Al_2O_3	wt%	na	na	11.5	na	na	11.4	na	na	10.7	na	na	10.9	na	na	11.1
Fe_2O_3	wt%	na	na	4.8	na	na	4.5	na	na	4.5	na	na	4.6	na	na	4.5
MnO	ppm	1971	2099	2056	1848	1790	1756	1934	1973	1916	1820	1874	1930	1814	1574	1449
MgO	wt%	na	na	2.14	na	na	2.07	na	na	2.02	na	na	2.06	na	na	2.05
CaO	wt%	na	na	1.27	na	na	1.28	na	na	1.27	na	na	1.24	na	na	1.28
Na_2O	wt%	na	na	1.77	na	na	1.80	na	na	1.81	na	na	1.77	na	na	1.77
P_2O_5	wt%	na	na	0.15	na	na	0.16	na	na	0.15	na	na	0.15	na	na	0.15
LOI	wt%	na	na	8.30	na	na	7.50	na	na	7.50	na	na	7.40	na	na	7.30
S	wt%	na	na	0.14	na	na	0.12	na	na	0.11	na	na	0.11	na	na	0.12
Cl	wt%	na	na	0.96	na	na	0.97	na	na	0.90	na	na	0.90	na	na	0.86
C org	wt%	na	na	na	1.91	na	na	na	1.92	na	na	na	1.91	na	na	na
CO_3	wt%	na	na	na	0.14	na	na	na	0.14	na	na	na	0.16	na	na	na
Rb	ppm	92	94	95	94	92	94	91	87	91	92	91	93	91	86	92
Sr	ppm	101	102	101	101	101	97	98	98	100	98	98	98	98	96	98
Ba	ppm	371	376	372	386	376	370	375	383	380	386	375	375	362	358	357
Br	ppm	116	121	121	115	105	106	95	82	88	95	84	79	79	75	80
I	ppm	74	78	74	72	74	79	83	62	78	70	68	78	66	60	68
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	71	73	70	73	65	66	67	68	71	74	69	68	64	60	65
Ni	ppm	35	36	36	34	33	32	34	32	33	33	32	34	33	30	32
Cr	ppm	111	114	124	113	108	107	110	111	101	107	106	108	102	103	113
Zn	ppm	147	153	150	148	137	135	130	122	126	129	126	126	123	112	125
V	ppm	101	107	105	110	101	95	99	93	98	103	99	103	99	88	100
Y	ppm	25	26	26	26	24	25	25	24	24	24	25	25	24	24	24
Zr	ppm	291	284	281	274	290	270	278	313	295	283	295	296	290	294	284
Nb	ppm	17	16	16	16	16	15	16	16	15	16	15	16	16	15	16
La	ppm	31	30	31	31	29	32	30	28	31	30	26	32	31	23	24
Ce	ppm	50	52	57	51	56	48	52	44	52	56	44	60	54	49	52
^{99}Tc	Bq/kg	22	5	1	2	0	0	na	3	na	1	na	0	na	0	na
^{137}Cs	Bq/kg	na	182	na	90	na	61	na	34	na	na	na	na	na	10	na
^{241}Am	Bq/kg	na	4	na	na	na	na	na	3	na	na	na	na	na	na	na

Depth	cm	**46**	**47**	**48**	**49**	**50**	**51**	**52**	**53**	**54**	**55**
Wet ; Dry Ratio		1.44	1.43	1.45	1.44	1.41	1.40	1.37	1.37	1.37	1.36
Total Majors	wt%	na	na	100.00	na	na	100.00	na	na	100.01	na
SiO_2	wt%	na	na	69.16	na	na	71.19	na	na	72.48	na
TiO_2	wt%	na	na	0.70	na	na	0.66	na	na	0.63	na
Al_2O_3	wt%	na	na	11.37	na	na	10.32	na	na	9.64	na
Fe_2O_3	wt%	na	na	4.76	na	na	4.27	na	na	3.90	na
MnO	ppm	1825	1665	1794	1484	1366	1632	1400	1374	1426	1431
MgO	wt%	na	na	2.14	na	na	1.89	na	na	1.77	na
CaO	wt%	na	na	1.30	na	na	1.22	na	na	1.16	na
Na_2O	wt%	na	na	1.79	na	na	1.72	na	na	1.65	na
P_2O_5	wt%	na	na	0.15	na	na	0.15	na	na	0.13	na
LOI	wt%	na	na	6.00	na	na	6.10	na	na	6.20	na
S	wt%	na	na	0.17	na	na	0.13	na	na	0.11	na
Cl	wt%	na	na	0.91	na	na	0.95	na	na	0.91	na
C org	wt%	1.66	na	na	na	1.95	na	na	na	na	na
CO_3	wt%	0.15	na	na	na	0.14	na	na	na	na	na
Rb	ppm	95	90	91	91	88	89	85	81	82	79
Sr	ppm	98	96	98	99	97	94	94	92	94	91
Ba	ppm	367	349	361	359	349	343	356	345	350	353
Br	ppm	82	80	95	89	74	80	67	64	62	61
I	ppm	62	78	72	78	64	68	56	62	64	56
As	ppm	na	na	na	na	na	na	na	na	na	na
Pb	ppm	69	64	69	64	57	60	57	55	54	na
Ni	ppm	33	32	34	32	30	32	28	28	28	na
Cr	ppm	113	110	106	103	105	110	107	97	101	101
Zn	ppm	131	121	128	126	114	119	107	104	102	na
V	ppm	107	99	105	100	96	96	92	89	83	87
Y	ppm	25	24	24	25	24	23	23	23	23	22
Zr	ppm	281	304	289	296	309	310	316	311	297	312
Nb	ppm	16	15	17	15	15	15	14	15	14	15
La	ppm	29	28	29	28	27	29	29	25	26	25
Ce	ppm	50	54	47	46	46	54	48	44	41	41
^{99}Tc	Bq/kg	na	na	na	na	na	na	na	na	na	na
^{137}Cs	Bq/kg	na	na	3	na	na	na	na	na	na	11
^{241}Am	Bq/kg	na	na	na	na	na	na	na	na	na	10

Sequential extraction data

Sequential extraction Data in Bq/kg.

Sample	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5
Rc7-2	9	9	23	106	23
Rc7-12	3	2	16	22	19
Rc7-13	3	6	14	34	11
Rc7-14	6	7	12	33	16
Rc7-17	17	23	12	11	5
Rc7-18	21	30	14	16	5
Rc7-19	44	34	13	16	12

Fraction 1: Water wash. 12 Hours at room temperature.

Fraction 2: Leach in 0.11 M Acetic acid for 12 hours at room temperature.

Fraction 3: Leach in 0.1 M Ammonium Hydoxyl Choloride + 400 µl for 12 hours at room temperarure

Fraction 4: Leach in two sequential 10 ml aliquots of 15% H_2O_2 at 80°C until dryness. Leach in 1M Ammonium acetate at pH 2 for 4 hours at room temperature

Fraction 5: Leach in 8 M HNO_3 for two hours at 90°C.

A2.2.4. Core R-96-008

Stable and Radionuclide data

Depth	cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Wet ; Dry Ratio		1.30	1.30	1.30	1.31	1.31	1.31	1.30	1.31	1.31	1.31	1.38	1.34	1.36	1.36	1.34
Total Majors	wt%	100.00	100.00	100.01	100.01	100.00	99.98	99.99	99.99	100.00	100.01	na	100.00	na	99.99	na
SiO_2	wt%	74.57	72.87	74.27	72.93	72.18	72.18	72.26	73.11	73.37	72.84	na	71.95	na	71.36	na
TiO_2	wt%	0.54	0.55	0.54	0.53	0.57	0.56	0.55	0.54	0.54	0.54	na	0.57	na	0.58	na
Al_2O_3	wt%	7.85	8.74	8.20	8.75	8.69	8.79	8.67	8.57	8.39	8.59	na	8.97	na	9.34	na
Fe_2O_3	wt%	3.12	3.32	3.25	3.35	3.47	3.41	3.40	3.24	3.19	3.33	na	3.42	na	3.59	na
MnO	ppm	746	737	817	1035	1176	1355	1064	923	900	815	na	594	na	723	na
MgO	wt%	1.43	1.58	1.47	1.60	1.58	1.58	1.56	1.50	1.48	1.51	na	1.58	na	1.66	na
CaO	wt%	2.77	2.88	2.63	2.82	2.84	2.95	2.91	2.93	2.92	2.96	na	2.83	na	2.69	na
Na_2O	wt%	1.47	1.51	1.47	1.54	1.49	1.57	1.56	1.54	1.55	1.57	na	1.57	na	1.63	na
P_2O_5	wt%	0.14	0.15	0.16	0.16	0.17	0.17	0.17	0.16	0.17	0.17	na	0.16	na	0.17	na
LOI	wt%	6.11	6.34	5.92	6.16	6.77	6.57	6.73	6.25	6.35	6.38	6.77	6.75	7.10	6.97	6.67
S	wt%	0.14	0.15	0.12	0.12	0.12	0.13	0.19	0.41	0.13	0.14	na	0.14	na	0.21	na
Cl	wt%	1.54	1.23	0.78	1.17	2.11	1.23	2.27	0.94	1.35	1.87	na	0.92	na	0.97	na
C org	wt%	0.67	0.89	0.76	na	0.98	na	0.93	na	0.52	0.83	0.74	1.26	0.99	1.50	0.88
CO_3	wt%	1.90	2.20	2.04	na	2.32	na	2.31	na	1.94	2.22	2.13	2.53	2.28	2.74	2.18
Rb	ppm	71	76	74	75	75	74	75	72	71	73	na	76	na	78	na
Sr	ppm	116	119	115	118	120	123	124	121	119	121	na	119	na	118	na
Ba	ppm	301	308	298	303	304	303	314	316	312	313	na	299	na	306	na
Br	ppm	73	86	72	75	78	75	84	75	78	81	na	93	na	109	na
I	ppm	44	48	44	61	61	61	70	46	55	44	na	48	na	51	na
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	43	47	47	47	48	51	47	46	47	49	na	52	na	54	na
Ni	ppm	23	26	23	23	25	25	25	23	23	23	na	24	na	26	na
Cr	ppm	102	98	99	101	105	116	112	110	102	106	na	119	na	121	na
Zn	ppm	88	99	95	101	107	108	104	99	96	103	na	111	na	120	na
V	ppm	71	73	77	80	74	77	80	75	72	75	na	81	na	83	na
Y	ppm	25	28	27	27	30	33	31	28	30	29	na	30	na	31	na
Zr	ppm	411	346	358	367	347	342	360	366	374	359	na	347	na	317	na
Nb	ppm	12	12	12	12	12	12	13	12	12	12	na	13	na	13	na
La	ppm	27	29	27	26	30	34	29	27	26	27	na	25	na	29	na
Ce	ppm	50	45	45	37	43	58	41	29	28	35	na	41	na	37	na
^{99}Tc	Bq/kg	84	107	71	na	42	na	35	na	36	47	69	95	140	158	76
^{137}Cs	Bq/kg	5214	6295	6672	7877	9182	9529	9847	9817	9251	9592	9340	9103	8455	7587	5775
^{241}Am	Bq/kg	16570	5920	5990	7760	8520	11860	9850	10660	11750	14140	15150	15240	11540	10950	8570

Depth	cm	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Wet ; Dry Ratio		1.32	1.33	1.33	1.32	1.33	1.31	1.32	1.36	1.33	1.33	1.37	1.40	1.39	1.37	1.35
Total Majors	wt%	100.00	na	99.99	na	99.99	na	100.00	na	100.01	na	100.02	na	99.98	na	100.00
SiO_2	wt%	72.82	na	72.71	na	72.95	na	74.15	na	73.10	na	73.08	na	72.90	na	73.81
TiO_2	wt%	0.54	na	0.53	na	0.52	na	0.51	na	0.53	na	0.53	na	0.53	na	0.50
Al_2O_3	wt%	8.51	na	8.64	na	8.60	na	8.09	na	8.48	na	8.65	na	8.92	na	8.32
Fe_2O_3	wt%	3.27	na	3.25	na	3.16	na	2.95	na	3.16	na	3.18	na	3.39	na	3.09
MnO	ppm	1342	na	973	na	1186	na	955	na	1198	na	780	na	1178	na	722
MgO	wt%	1.44	na	1.46	na	1.46	na	1.39	na	1.44	na	1.52	na	1.52	na	1.42
CaO	wt%	2.57	na	2.65	na	2.76	na	2.72	na	2.70	na	2.74	na	2.54	na	2.73
Na_2O	wt%	1.54	na	1.56	na	1.60	na	1.57	na	1.63	na	1.70	na	1.63	na	1.56
P_2O_5	wt%	0.17	na	0.16	na	0.15	na	0.13	na	0.15	na	0.14	na	0.15	na	0.14
LOI	wt%	6.39	6.70	6.34	6.23	6.34	6.08	6.19	6.59	6.44	6.55	6.97	7.05	6.57	6.60	6.17
S	wt%	0.15	na	0.13	na	0.13	na	0.13	na	0.13	na	0.14	na	0.46	na	0.12
Cl	wt%	1.50	na	1.12	na	0.62	na	0.62	na	0.72	na	0.70	na	5.85	na	0.62
C org	wt%	na	0.65	na	1.01	na	1.91	na	1.77	na	1.22	na	1.31	na	0.99	na
CO_3	wt%	na	1.96	na	2.06	na	3.06	na	2.74	na	2.07	na	2.12	na	2.04	na
Rb	ppm	72	na	71	na	72	na	69	na	69	na	71	na	74	na	72
Sr	ppm	118	na	116	na	119	na	116	na	115	na	116	na	112	na	116
Ba	ppm	316	na	312	na	296	na	300	na	310	na	310	na	325	na	319
Br	ppm	90	na	91	na	91	na	83	na	105	na	120	na	139	na	101
I	ppm	67	na	53	na	53	na	57	na	59	na	46	na	61	na	42
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	51	na	50	na	48	na	44	na	47	na	51	na	53	na	48
Ni	ppm	24	na	22	na	23	na	22	na	23	na	25	na	24	na	22
Cr	ppm	120	na	111	na	104	na	94	na	95	na	105	na	106	na	96
Zn	ppm	110	na	103	na	100	na	93	na	97	na	100	na	107	na	93
V	ppm	76	na	70	na	73	na	67	na	68	na	72	na	73	na	67
Y	ppm	34	na	28	na	25	na	22	na	26	na	25	na	23	na	21
Zr	ppm	355	na	343	na	327	na	309	na	301	na	284	na	300	na	282
Nb	ppm	12	na	12	na	12	na	12	na	12	na	12	na	11	na	11
La	ppm	31	na	26	na	23	na	22	na	20	na	23	na	24	na	23
Ce	ppm	35	na	39	na	50	na	44	na	28	na	34	na	24	na	27
^{99}Tc	Bq/kg	54	52	36	28	23	20	14	16	na	12	na	12	na	16	na
^{137}Cs	Bq/kg	4464	3890	3062	2510	2181	1710	1500	881	1128	1128	1142	1036	911	809	553
^{241}Am	Bq/kg	6770	6400	4590	3174	3255	2160	1859	934	1194	1182	1031	986	797	647	358

Depth	cm	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Wet ; Dry Ratio		1.35	1.36	1.40	1.41	1.37	1.41	1.42	1.40	1.39	1.36	1.37	1.37	1.40	1.43	1.41
Total Majors	wt%	na	99.99	na	99.99	na	99.99	na	99.99	na	100.00	na	100.01	na	100.00	na
SiO_2	wt%	na	73.93	na	71.31	na	70.34	na	71.32	na	73.40	na	72.74	na	70.16	na
TiO_2	wt%	na	0.51	na	0.54	na	0.57	na	0.53	na	0.50	na	0.49	na	0.58	na
Al_2O_3	wt%	na	8.40	na	9.53	na	9.62	na	9.15	na	8.24	na	8.34	na	9.49	na
Fe_2O_3	wt%	na	3.12	na	3.46	na	3.56	na	3.43	na	3.03	na	3.03	na	3.60	na
MnO	ppm	na	526	na	557	na	627	na	662	na	625	na	700	na	855	na
MgO	wt%	na	1.43	na	1.65	na	1.71	na	1.64	na	1.43	na	1.44	na	1.69	na
CaO	wt%	na	2.74	na	3.30	na	3.55	na	3.54	na	3.13	na	3.21	na	3.49	na
Na_2O	wt%	na	1.56	na	1.63	na	1.69	na	1.70	na	1.59	na	1.65	na	1.68	na
P_2O_5	wt%	na	0.14	na	0.15	na	0.13	na	0.11	na	0.10	na	0.10	na	0.11	na
LOI	wt%	na	6.46	na	7.21	na	7.43	na	7.43	na	6.38	na	6.59	na	7.19	na
S	wt%	na	0.15	na	0.28	na	0.40	na	0.54	na	0.46	na	0.55	na	0.44	na
Cl	wt%	na	0.67	na	1.00	na	1.17	na	0.73	na	1.17	na	1.03	na	1.93	na
C org	wt%	0.95	na	0.82	na	0.95	na	0.60	na	0.58	na	0.39	na	0.46	na	0.48
CO_3	wt%	2.26	na	2.30	na	2.62	na	2.34	na	2.19	na	1.97	na	2.04	na	2.12
Rb	ppm	na	71	na	77	na	78	na	74	na	70	na	70	na	78	na
Sr	ppm	na	118	na	130	na	135	na	137	na	128	na	128	na	137	na
Ba	ppm	na	313	na	318	na	331	na	326	na	301	na	299	na	326	na
Br	ppm	na	69	na	67	na	61	na	58	na	54	na	58	na	61	na
I	ppm	na	29	na	44	na	46	na	46	na	40	na	44	na	44	na
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	na	52	na	57	na	59	na	59	na	51	na	51	na	56	na
Ni	ppm	na	24	na	26	na	27	na	25	na	24	na	22	na	27	na
Cr	ppm	na	103	na	104	na	100	na	95	na	83	na	91	na	100	na
Zn	ppm	na	105	na	118	na	124	na	125	na	103	na	99	na	118	na
V	ppm	na	76	na	80	na	80	na	76	na	69	na	67	na	84	na
Y	ppm	na	21	na	21	na	22	na	20	na	19	na	18	na	20	na
Zr	ppm	na	266	na	288	na	267	na	259	na	292	na	290	na	301	na
Nb	ppm	na	12	na	13	na	12	na	12	na	12	na	12	na	13	na
La	ppm	na	23	na	25	na	20	na	21	na	22	na	20	na	20	na
Ce	ppm	na	30	na	41	na	31	na	33	na	36	na	41	na	40	na
^{99}Tc	Bq/kg	19	na	16	na	12	na	15	na	15	na	14	na	22	na	16
^{137}Cs	Bq/kg	485	746	1092	512	361	324	261	193	173	151	184	171	247	442	412
^{241}Am	Bq/kg	223	232	241	245	175	164	172	66.5	47.6	36.8	32.4	31.5	27.9	22.8	17.1

Depth	cm	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61
Wet ; Dry Ratio		1.41	1.42	1.41	1.39	1.40	1.39	1.39	1.36	1.34	1.29	1.31	1.30	1.28	1.29	1.27	1.28
Total Majors	wt%	100.01	na	100.01	na	100.01	na	100.01	na	99.98	na	99.99	na	100.00	na	100.01	na
SiO_2	wt%	71.41	na	71.94	na	73.59	na	73.42	na	75.09	na	76.97	na	78.36	na	78.77	na
TiO_2	wt%	0.56	na	0.56	na	0.53	na	0.51	na	0.43	na	0.35	na	0.33	na	0.34	na
Al_2O_3	wt%	9.04	na	8.88	na	8.46	na	8.33	na	7.40	na	6.54	na	5.83	na	6.20	na
Fe_2O_3	wt%	3.42	na	3.39	na	3.12	na	3.14	na	2.63	na	2.22	na	1.98	na	2.07	na
MnO	ppm	740	na	913	na	710	na	653	na	613	na	493	na	472	na	559	na
MgO	wt%	1.62	na	1.56	na	1.44	na	1.45	na	1.19	na	1.01	na	0.90	na	0.94	na
CaO	wt%	3.45	na	3.16	na	3.02	na	2.93	na	2.56	na	2.24	na	2.16	na	2.32	na
Na_2O	wt%	1.69	na	1.66	na	1.62	na	1.63	na	1.44	na	1.33	na	1.22	na	1.24	na
P_2O_5	wt%	0.11	na	0.11	na	0.10	na	0.10	na	0.08	na	0.07	na	0.07	na	0.07	na
LOI	wt%	7.07	na	6.62	na	6.17	na	6.30	na	5.15	na	4.47	na	3.85	na	4.12	na
S	wt%	0.40	na	0.35	na	1.27	na	0.35	na	0.31	na	0.31	na	0.28	na	0.34	na
Cl	wt%	1.35	na	1.77	na	9.19	na	1.46	na	0.78	na	0.74	na	0.65	na	0.91	na
C org	wt%	na	0.50	na	0.60	na	0.60	na	na	na	na	na	na	na	na	na	na
CO_3	wt%	na	2.10	na	2.10	na	2.10	na	na	na	na	na	na	na	na	na	na
Rb	ppm	73	na	73	na	69	na	70	na	65	na	62	na	58	na	na	na
Sr	ppm	136	na	127	na	124	na	122	na	112	na	103	na	99	na	na	na
Ba	ppm	303	na	323	na	297	na	297	na	293	na	255	na	249	na	270	na
Br	ppm	55	na	52	na	70	na	51	na	42	na	37	na	31	na	32	na
I	ppm	32	na	30	na	30	na	36	na	17	na	19	na	15	na	23	na
As	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Pb	ppm	55	na	55	na	49	na	46	na	41	na	34	na	31	na	na	na
Ni	ppm	25	na	25	na	23	na	24	na	21	na	17	na	15	na	na	na
Cr	ppm	96	na	98	na	83	na	96	na	74	na	71	na	77	na	69	na
Zn	ppm	112	na	109	na	97	na	97	na	84	na	70	na	59	na	na	na
V	ppm	77	na	76	na	71	na	71	na	66	na	52	na	48	na	55	na
Y	ppm	20	na	19	na	19	na	18	na	15	na	12	na	13	na	na	na
Zr	ppm	285	na	307	na	313	na	290	na	262	na	217	na	217	na	na	na
Nb	ppm	12	na	13	na	11	na	12	na	10	na	9	na	10	na	na	na
La	ppm	23	na	22	na	18	na	22	na	19	na	17	na	13	na	13	na
Ce	ppm	41	na	40	na	41	na	37	na	23	na	31	na	23	na	23	na
^{99}Tc	Bq/kg	na	13	na	na	na	na	na	na	na	na	na	na	na	na	na	na
^{137}Cs	Bq/kg	329	263	187	154	115	102	127	103	132	251	409	508	693	826	1014	1247
^{241}Am	Bq/kg	na	na	na	na	na	2.8	8	na	na	na	5.14	na	3.1	na	na	44.9

A2.2.5. Inventory Cores

Stable element and Physical data

Sample		Ric 1	Ric 2	Ric 3	Ric 4	Ric 5	Ric 6	Ric 7	Ric 8	Ric 9	Ric 10
Location		Y 7.5	Y 5.5	E 4.5	Y 2.5	D 4.5	C 6.5	V 6.5	A 4.5	C 2.5	B 4.5
Accumulation Rate	cm/yr	0.57	0.57	0.63	0.85	1.09	0.94	1.05	0.90	0.87	0.77
Wet ; Dry Ratio		1.39	1.52	1.49	1.60	1.61	1.53	1.59	1.55	1.67	1.73
Density wet	g/cm^3	1.40	1.22	1.29	1.28	1.00	1.26	0.99	1.34	1.37	1.32
Total Majors	wt%	91.68	97.58	96.29	102.14	96.60	97.54	97.57	98.62	94.23	103.29
SiO_2	wt%	64.49	66.43	63.72	66.13	60.21	64.50	61.17	61.25	59.91	63.76
TiO_2	wt%	0.56	0.68	0.71	0.75	0.74	0.71	0.75	0.79	0.70	0.81
Al_2O_3	wt%	8.45	10.76	11.68	12.68	11.90	11.37	12.57	13.12	11.94	13.86
Fe_2O_3	wt%	3.42	4.38	2.98	5.10	4.90	4.70	5.29	5.61	4.94	5.42
MnO	wt%	0.12	0.14	0.16	0.17	0.16	0.16	0.17	0.17	0.11	0.14
MgO	wt%	1.75	2.07	2.25	2.46	2.19	2.27	2.37	2.26	2.11	2.62
CaO	wt%	1.68	1.17	1.18	1.19	1.10	1.34	1.10	0.70	0.76	1.12
Na_2O	wt%	2.05	1.98	2.49	2.63	2.51	2.45	2.65	2.71	2.51	2.79
P_2O_5	wt%	0.07	0.07	0.09	0.07	0.11	0.07	0.06	0.05	0.08	0.11
S	wt%	0.12	0.17	0.15	0.15	0.21	0.15	0.15	0.15	0.12	0.19
Cl	wt%	1.35	1.73	1.55	1.46	1.70	1.56	1.58	1.47	1.23	1.88
C org	wt%	2.04	2.81	2.40	2.31	3.58	2.29	2.70	3.09	2.71	3.67
CO_3	wt%	0.18	0.11	0.18	0.18	0.18	0.25	0.15	0.02	0.11	0.14
Rb	ppm	102	96	82	99	99	96	108	98	97	96
Sr	ppm	106	119	126	106	101	102	102	101	112	987
Ba	ppm	303	332	352	336	327	344	341	339	314	337
Br	ppm	96	151	122	114	163	120	137	159	162	201
I	ppm	68	89	87	101	95	83	126	105	78	91
As	ppm	21	18	14	23	20	19	23	20	18	19
Pb	ppm	78	65	50	76	72	67	82	68	66	65
Ni	ppm	35	34	26	34	33	31	37	32	33	31
Cr	ppm	95	98	111	103	112	112	110	108	103	107
Zn	ppm	157	151	117	207	148	149	163	136	151	132
V	ppm	71	91	103	104	109	99	114	123	111	118
Y	ppm	32	32	28	32	30	30	30	28	35	28
Zr	ppm	255	249	286	258	267	262	250	263	261	274
Nb	ppm	17	17	14	17	17	16	18	17	16	17
La	ppm	25	32	33	33	36	34	36	37	30	37
Ce	ppm	53	56	49	63	57	64	68	67	61	68

Sample		Ric 11	Ric 12	Ric 13	Ric 14	Ric 15	Ric 16	Ric 17	Ric 18	Ric 19	Ric 20
Location		V 2.5	B 1.5	A1.5	A3.5	A5.5	A7.5	A9.5	D7.5	E1.5	E3.5
Accumulation Rate	cm/yr	0.97	0.62	0.89	0.70	0.90	0.82	1.31	0.85	0.95	0.58
Wet ; Dry Ratio		1.55	1.70	1.86	1.80	1.69	1.57	1.58	1.50	1.69	1.52
Density wet	g/cm^3	1.01	1.20	1.40	1.22	1.29	1.28	1.00	1.26	0.99	1.34
Total Majors	wt%	96.99	96.07	100.00	98.48	97.14	103.72	98.84	98.88	97.63	95.41
SiO_2	wt%	60.70	61.46	61.16	60.27	58.80	67.41	63.42	67.78	62.83	62.43
TiO_2	wt%	0.74	0.73	0.77	0.78	0.75	0.77	0.71	0.63	0.71	0.71
Al_2O_3	wt%	12.24	11.72	12.67	13.03	12.45	13.02	11.63	9.82	11.66	11.81
Fe_2O_3	wt%	5.26	4.86	5.50	5.56	5.23	5.29	4.81	3.83	4.90	4.94
MnO	wt%	0.17	0.09	0.08	0.08	0.17	0.18	0.15	0.11	0.10	0.16
MgO	wt%	2.36	2.23	2.32	2.34	2.44	2.64	2.41	1.96	2.39	2.22
CaO	wt%	1.24	1.09	0.93	0.85	1.15	1.43	1.48	3.18	1.45	1.06
Na_2O	wt%	2.58	2.50	2.59	2.71	2.59	2.66	2.50	2.13	2.50	2.53
P_2O_5	wt%	0.06	0.01	0.11	0.08	0.06	0.06	0.06	0.09	0.08	0.05
S	wt%	0.16	0.19	0.41	0.27	0.18	0.17	0.16	0.17	0.21	0.18
Cl	wt%	1.41	1.73	2.75	1.47	1.70	1.75	1.68	1.69	2.14	1.45
C org	wt%	3.26	3.76	3.68	4.05	3.39	2.30	2.64	1.76	3.01	2.70
CO_3	wt%	0.16	0.06	0.11	0.06	0.13	0.19	0.35	0.54	0.20	0.12
Rb	ppm	94	98	101	104	99	86	94	103	103	83
Sr	ppm	105	103	153	156	151	132	143	142	142	129
Ba	ppm	333	334	340	343	344	343	335	314	333	342
Br	ppm	154	178	188	180	164	119	114	105	164	111
I	ppm	97	78	83	74	111	105	99	72	95	83
As	ppm	20	20	24	22	24	17	24	24	28	18
Pb	ppm	69	71	95	99	95	72	89	100	104	75
Ni	ppm	32	34	36	38	36	29	35	37	37	28
Cr	ppm	112	112	108	109	115	119	107	92	110	102
Zn	ppm	141	161	226	224	225	188	222	231	250	186
V	ppm	108	106	127	120	116	113	103	84	115	110
Y	ppm	30	30	26	25	25	24	26	26	28	23
Zr	ppm	263	245	216	209	224	206	239	221	218	221
Nb	ppm	17	17	16	17	17	15	16	16	17	15
La	ppm	35	32	37	35	34	33	38	25	37	31
Ce	ppm	62	64	51	68	61	54	59	57	62	54

Sample		Ric 21	Ric 22	Ric 23	Ric 24	Ric 25	Ric 26	Ric 27
Location		W1.5	W3.5	W5.5	W8.5	X1.5	X3.5	X5.5
Accumulation Rate	cm/yr	0.69	0.66	0.55	0.92	0.89	0.52	0.68
Wet ; Dry Ratio		1.51	1.62	1.57	1.57	1.50	1.47	1.66
Density wet	g/cm^3	1.37	1.32	1.01	1.20	1.10	1.20	1.30
Total Majors	wt%	97.94	102.10	101.12	97.24	97.79	98.25	97.15
SiO_2	wt%	65.32	65.53	66.30	64.04	65.82	66.33	61.26
TiO_2	wt%	0.70	0.79	0.76	0.72	0.72	0.69	0.73
Al_2O_3	wt%	11.47	13.56	12.17	11.49	11.37	11.05	11.92
Fe_2O_3	wt%	4.77	5.54	4.95	4.76	4.53	4.61	5.07
MnO	wt%	0.16	0.16	0.15	0.15	0.14	0.15	0.13
MgO	wt%	2.26	2.30	2.04	2.39	2.06	2.14	2.40
CaO	wt%	1.65	1.78	0.98	1.97	1.56	1.33	1.23
Na_2O	wt%	2.47	2.78	2.56	2.49	2.41	2.45	2.53
P_2O_5	wt%	0.05	0.00	0.06	0.01	0.08	0.08	0.06
S	wt%	0.17	0.20	0.20	0.17	0.14	0.15	0.21
Cl	wt%	1.41	1.71	2.01	1.85	1.42	1.56	2.15
C org	wt%	2.89	2.77	2.90	2.34	2.11	2.39	3.81
CO_3	wt%	0.03	0.02	0.09	0.23	0.11	0.12	0.25
Rb	ppm	103	105	108	110	106	89	104
Sr	ppm	136	133	133	132	131	119	132
Ba	ppm	338	328	318	340	321	326	335
Br	ppm	130	169	163	120	132	111	185
I	ppm	89	101	97	97	89	87	87
As	ppm	23	28	31	29	29	21	26
Pb	ppm	103	112	120	123	119	84	113
Ni	ppm	37	40	40	41	39	32	38
Cr	ppm	101	114	101	111	101	102	107
Zn	ppm	234	267	261	298	264	231	260
V	ppm	102	116	103	106	99	101	104
Y	ppm	25	27	27	27	28	24	27
Zr	ppm	226	210	206	212	207	197	226
Nb	ppm	16	16	17	16	16	15	16
La	ppm	29	33	28	37	30	36	32
Ce	ppm	52	66	61	63	56	60	51

Inventory Data

Sample		Ric 1	Ric 2	Ric 3	Ric 4	Ric 5	Ric 6	Ric 7	Ric 8	Ric 9	Ric 10
Location		Y 7.5	Y 5.5	E 4.5	Y 2.5	D 4.5	C 6.5	V 6.5	A 4.5	C 2.5	B 4.5
^{99}Tc	kBq/m^2	31.0	17.8	18.3	15.4	18.7	23.1	14.5	14.4	18.8	16.8
^{137}Cs	kBq/m^2	1480	876	1370	1310	964	1710	1390	965	1350	1240
^{241}Am	kBq/m^2	2110	1020	1230	1100	939	1860	1360	788	1050	1300
^{210}Pb	kBq/m^2	1800	1080	1010	994	820	1190	931	906	1030	945

Sample		Ric 11	Ric 12	Ric 13	Ric 14	Ric 15	Ric 16	Ric 17	Ric 18	Ric 19	Ric 20
Location		V 2.5	B 1.5	A1.5	A3.5	A5.5	A7.5	A9.5	D7.5	E1.5	E3.5
^{99}Tc	kBq/m^2	17.8	15.4	14.1	11.3	24.5	32.9	40.7	142.7	20.7	31.5
^{137}Cs	kBq/m^2	1360	1040	302	1040	1750	2190	760	933	1450	1730
^{241}Am	kBq/m^2	1330	668	474	939	1620	2260	1130	1100	1530	1210
^{210}Pb	kBq/m^2	1110	921	762	898	1180	1450	1290	1410	1210	1220

Sample		Ric 21	Ric 22	Ric 23	Ric 24	Ric 25	Ric 26	Ric 27
Location		W1.5	W3.5	W5.5	W8.5	X1.5	X3.5	X5.5
^{99}Tc	kBq/m^2	23.9	35.0	20.0	44.8	17.2	22.7	26.9
^{137}Cs	kBq/m^2	1210	1320	1020	1480	1070	319	847
^{241}Am	kBq/m^2	1260	1320	839	2200	949	867	1240
^{210}Pb	kBq/m^2	890	1040	798	1480	889	14	1230

Radionuclide Data

Sample		**Ric 1**	**Ric 2**	**Ric 3**	**Ric 4**	**Ric 5**	**Ric 6**	**Ric 7**	**Ric 8**	**Ric 9**	**Ric 10**
Location		Y 7.5	Y 5.5	E 4.5	Y 2.5	D 4.5	C 6.5	V 6.5	A 4.5	C 2.5	B 4.5
^{99}Tc	Bq/kg	61	44	42	39	60	56	47	33	46	44
^{137} Cs	Bq/kg	2924	2178	3150	3260	3110	4160	4490	2237	3290	3230
^{241} Am	Bq/kg	4180	2530	2830	2750	3030	4510	4370	1828	2556	3400
^{210}Pb	Bq/kg	3550	2690	2330	2480	2650	2880	3000	2100	2520	2470

Sample		**Ric 11**	**Ric 12**	**Ric 13**	**Ric 14**	**Ric 15**	**Ric 16**	**Ric 17**	**Ric 18**	**Ric 19**	**Ric 20**
Location		V 2.5	B 1.5	A1.5	A3.5	A5.5	A7.5	A9.5	D7.5	E1.5	E3.5
^{99}Tc	Bq/kg	55	43	45	31	76	72	144	359	57	57
^{137} Cs	Bq/kg	4180	2929	967	2859	5415	4819	2690	2348	4004	3106
^{241} Am	Bq/kg	4080	1888	1516	2591	5013	4960	3986	2777	4211	2176
^{210}Pb	Bq/kg	3390	2600	2440	2480	3660	3190	4570	3540	3320	2200

Sample		**Ric 21**	**Ric 22**	**Ric 23**	**Ric 24**	**Ric 25**	**Ric 26**	**Ric 27**
Location		W1.5	W3.5	W5.5	W8.5	X1.5	X3.5	X5.5
^{99}Tc	Bq/kg	79	80	47	142	36	59	59
^{137} Cs	Bq/kg	4012	3003	2377	4670	2259	3982	1859
^{241} Am	Bq/kg	4185	3005	1966	6970	2007	4054	2721
^{210}Pb	Bq/kg	2950	2360	1870	4670	1880	2920	2700

2.2.6. Miscellaneous

Vegetation Type		**^{99}Tc Activity Bq/kg**
Ascophyllum nodosum		76000
Fucus serratus		20000
Puccinellia maritima		104
Derbesia marina		320
Sea Purslane	Leaves	15
	Stems	47
	Roots	64

A2.3. Carlaverock Saltmarsh

A2.3.1. Core SUTL-331

Stable and Radionuclide data

Depth	cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Total Majors	wt%	na	100.30	na	100.07	na	98.61	na	97.74	na	100.81	na	101.60	na	100.24	na
SiO_2	wt%	na	70.77	na	76.66	na	74.70	na	75.21	na	63.75	na	66.03	na	58.13	na
TiO_2	wt%	na	0.46	na	0.43	na	0.41	na	0.44	na	0.51	na	0.54	na	0.52	na
Al_2O_3	wt%	na	7.62	na	7.01	na	6.86	na	7.01	na	8.18	na	8.67	na	8.62	na
Fe_2O_3	wt%	na	2.71	na	2.23	na	2.22	na	2.16	na	3.00	na	3.38	na	3.30	na
MnO	ppm	1414	1049	904	808	884	750	581	613	572	682	576	804	659	607	519
MgO	wt%	na	1.35	na	1.12	na	0.93	na	0.93	na	1.19	na	1.23	na	1.35	na
CaO	wt%	na	1.30	na	0.88	na	0.61	na	0.57	na	0.58	na	0.55	na	0.61	na
Na_2O	wt%	na	1.50	na	1.52	na	1.57	na	1.66	na	2.11	na	2.01	na	2.16	na
P_2O_5	wt%	na	0.16	na	0.12	na	0.11	na	0.10	na	0.15	na	0.15	na	0.15	na
LOI	wt%	na	12.41	na	8.20	na	9.34	na	7.83	na	19.38	na	17.01	na	23.41	na
S	wt%	na	0.29	na	0.19	na	0.21	na	0.23	na	0.46	na	0.44	na	0.50	na
Cl	wt%	na	0.62	na	0.65	na	0.92	na	1.13	na	3.08	na	2.55	na	3.31	na
C org	wt%	na	3.78	na	2.21	na	2.14	na	2.38	na	6.28	na	5.07	na	9.48	na
CO_3	wt%	na	0.27	na	0.09	na	0.06	na	0.01	na	0.00	na	0.00	na	0.02	na
Rb	ppm	62	58	57	55	57	56	52	56	62	60	58	62	65	64	67
Sr	ppm	100	89	88	81	81	80	77	81	84	87	83	87	88	90	88
Ba	ppm	281	252	274	256	266	251	246	253	255	237	234	253	241	247	255
Br	ppm	183	183	154	127	101	127	85	122	192	341	237	365	388	418	373
I	ppm	16	18	10	14	14	16	14	16	22	27	24	37	43	27	29
As	ppm	8	10	9	7	6	6	6	5	6	8	11	8	11	13	16
Pb	ppm	34	32	25	27	29	27	23	31	41	52	40	55	60	65	61
Ni	ppm	22	18	18	16	17	16	13	17	20	22	19	23	24	24	23
Cr	ppm	142	68	60	58	64	61	58	59	74	75	72	76	73	110	76
Zn	ppm	142	87	73	71	70	76	54	62	82	104	73	86	88	102	87
V	ppm	63	56	45	43	51	47	44	46	64	68	61	69	75	78	79
Y	ppm	17	16	14	15	14	13	13	15	17	19	17	18	17	17	16
Zr	ppm	170	170	200	183	183	180	177	199	210	187	200	183	179	165	153
Nb	ppm	11	11	11	10	11	11	9	11	13	12	11	12	12	12	12
La	ppm	20	19	17	16	13	15	13	13	20	20	18	20	18	20	19
Ce	ppm	30	36	23	17	26	25	22	30	21	30	29	33	40	27	35
^{99}Tc	Bq/kg	40	30	14	10	8	7	7	15	11	20	11	12	11	12	10
^{137}Cs	Bq/kg	382	425	285	379	557	795	488	834	1461	1090	386	307	na	na	na
^{241}Am	Bq/kg	144	161	87	94	115	87	46	104	426	495	91	26	na	na	na

Depth	cm	16	17	18	19	20	21	22	23	24	25	26	27
Total Majors	wt%	99.77	na	99.78	na	99.53	na	99.43	na	100.88	na	na	na
SiO_2	wt%	60.16	na	58.81	na	69.34	na	72.02	na	72.22	na	na	na
TiO_2	wt%	0.53	na	0.51	na	0.54	na	0.49	na	0.56	na	na	na
Al_2O_3	wt%	9.22	na	8.94	na	9.33	na	8.75	na	9.30	na	na	na
Fe_2O_3	wt%	3.18	na	3.13	na	3.06	na	2.95	na	3.55	na	na	na
MnO	ppm	537	623	514	552	543	568	506	648	546	548	580	547
MgO	wt%	1.37	na	1.36	na	1.26	na	1.09	na	1.25	na	na	na
CaO	wt%	0.54	na	0.58	na	0.46	na	0.43	na	0.45	na	na	na
Na_2O	wt%	2.08	na	2.19	na	1.92	na	1.87	na	1.90	na	na	na
P_2O_5	wt%	0.13	na	0.13	na	0.11	na	0.10	na	0.11	na	na	na
LOI	wt%	20.44	na	22.07	na	11.39	na	9.69	na	9.35	na	na	na
S	wt%	0.47	na	0.54	na	0.29	na	0.28	na	0.24	na	na	na
Cl	wt%	3.43	na	3.90	na	2.15	na	1.94	na	2.06	na	na	na
C org	wt%	7.17	na	7.85	na	3.55	na	3.64	na	2.95	na	na	na
CO_3	wt%	0.02	na	0.03	na	0.03	na	0.03	na	0.00	na	na	na
Rb	ppm	71	74	71	73	69	69	65	75	71	69	72	62
Sr	ppm	90	91	93	91	88	87	86	88	87	86	88	83
Ba	ppm	255	264	261	261	268	278	282	278	276	281	286	260
Br	ppm	340	331	376	245	164	158	152	182	137	143	151	82
I	ppm	31	29	31	29	24	25	24	27	31	25	16	16
As	ppm	14	16	13	16	0	0	11	16	14	17	15	8
Pb	ppm	64	70	81	73	60	69	70	96	81	72	78	47
Ni	ppm	24	25	25	25	3	2	21	25	23	22	26	20
Cr	ppm	76	80	78	76	74	77	64	79	78	73	84	68
Zn	ppm	90	100	97	101	31	30	90	126	111	102	113	72
V	ppm	80	84	85	79	72	72	66	86	71	72	76	58
Y	ppm	17	18	18	17	18	17	15	19	18	16	20	16
Zr	ppm	156	151	153	162	163	165	155	173	181	171	195	181
Nb	ppm	12	13	12	13	13	13	12	14	13	12	14	12
La	ppm	21	24	23	22	19	21	16	20	20	19	21	17
Ce	ppm	30	30	31	47	26	35	25	46	38	29	26	29
^{99}Tc	Bq/kg	9	6	8	6	4	5	5	10	7	na	na	na
^{137}Cs	Bq/kg	41	na	14	na	3	na	1	na	2	na	na	na
^{241}Am	Bq/kg	0	na	0	na	0	na	0	na	0	na	na	na

A2.3.2. Core SUTL-332

Stable and Radionuclide data

Depth	cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Total Majors	wt%	na	100.19	na	100.04	na	99.68	na	101.21	na	101.19	na	104.51	na	100.73	na
SiO_2	wt%	na	79.38	na	82.62	na	79.82	na	82.14	na	82.51	na	85.72	na	83.73	na
TiO_2	wt%	na	0.34	na	0.32	na	0.36	na	0.38	na	0.36	na	0.36	na	0.34	na
Al_2O_3	wt%	na	6.28	na	5.59	na	6.12	na	6.53	na	6.31	na	6.43	na	6.08	na
Fe_2O_3	wt%	na	1.79	na	1.57	na	1.65	na	1.80	na	1.79	na	1.63	na	1.57	na
MnO	ppm	785	734	680	605	643	532	600	649	670	705	620	571	548	491	500
MgO	wt%	na	0.95	na	0.82	na	0.91	na	0.97	na	0.95	na	1.00	na	0.89	na
CaO	wt%	na	2.14	na	1.65	na	1.29	na	1.63	na	1.58	na	1.31	na	1.17	na
Na_2O	wt%	na	1.28	na	1.25	na	1.39	na	1.40	na	1.59	na	1.55	na	1.66	na
P_2O_5	wt%	na	0.08	na	0.08	na	0.09	na	0.09	na	0.08	na	0.09	na	0.08	na
LOI	wt%	na	6.12	na	4.32	na	6.27	na	4.44	na	4.17	na	4.56	na	3.38	na
S	wt%	na	0.11	na	0.10	na	0.14	na	0.08	na	0.07	na	0.12	na	0.06	na
Cl	wt%	na	0.11	na	0.08	na	0.09	na	0.09	na	0.11	na	0.18	na	0.16	na
C org	wt%	na	1.21	na	0.44	na	1.01	na	1.32	na	0.66	na	0.77	na	0.64	na
CO_3	wt%	na	0.46	na	0.38	na	0.26	na	0.40	na	0.36	na	0.29	na	0.24	na
Rb	ppm	49	50	51	49	49	49	51	50	50	50	47	49	49	51	50
Sr	ppm	101	100	94	86	83	82	848	87	84	84	81	80	76	79	79
Ba	ppm	238	258	248	245	244	239	260	244	241	240	231	237	240	249	239
Br	ppm	16	27	33	16	31	23	22	23	20	23	21	37	28	16	27
I	ppm	6	10	10	6	8	8	8	8	8	8	8	6	8	4	4
As	ppm	4	5	5	4	4	4	4	4	4	4	3	3	3	3	4
Pb	ppm	19	20	22	16	18	18	19	20	18	19	17	17	18	17	17
Ni	ppm	12	24	13	12	11	12	13	12	12	13	11	12	11	11	12
Cr	ppm	44	95	46	51	46	55	48	44	47	45	46	42	46	38	46
Zn	ppm	142	55	54	46	46	48	48	43	47	46	52	38	39	52	39
V	ppm	32	35	38	29	36	35	36	37	31	32	30	32	32	33	33
Y	ppm	11	11	12	12	12	12	11	12	11	11	12	11	11	10	12
Zr	ppm	138	144	159	172	199	196	154	161	170	144	174	173	171	158	166
Nb	ppm	9	9	10	9	10	10	9	9	10	9	9	9	9	9	9
La	ppm	10	10	15	10	9	12	10	10	9	11	12	10	8	11	11
Ce	ppm	19	16	22	14	15	14	5	12	16	11	18	14	12	15	22
^{99}Tc	Bq/kg	7	12	7	8	8	3	5	7	2	4	2	3	4	2	12
^{137}Cs	Bq/kg	137	191	130	127	140	151	157	161	110	138	148	619	375	184	275
^{241}Am	Bq/kg	43	50	41	27	29	30	31	38	26	48	20	17	23	8	14

Depth	cm	16	17	18	19	20	21	22	23	24	25
Total Majors	wt%	97.84	na	99.19	na	100.05	na	96.25	na	98.47	na
SiO_2	wt%	79.67	na	78.78	na	75.98	na	69.95	na	58.66	na
TiO_2	wt%	0.39	na	0.40	na	0.41	na	0.45	na	0.54	na
Al_2O_3	wt%	6.26	na	6.40	na	6.54	na	7.22	na	8.92	na
Fe_2O_3	wt%	1.64	na	1.86	na	2.01	na	2.46	na	3.48	na
MnO	ppm	477	469	458	490	458	500	520	569	648	620
MgO	wt%	0.94	na	0.88	na	0.73	na	0.85	na	1.22	na
CaO	wt%	0.91	na	0.78	na	0.55	na	0.52	na	0.70	na
Na_2O	wt%	1.39	na	1.48	na	1.46	na	1.47	na	1.52	na
P_2O_5	wt%	0.09	na	0.09	na	0.11	na	0.11	na	0.15	na
LOI	wt%	4.83	na	6.77	na	10.49	na	11.46	na	21.34	na
S	wt%	0.12	na	0.15	na	0.25	na	0.20	na	0.33	na
Cl	wt%	0.29	na	0.36	na	0.48	na	0.58	na	0.76	na
C org	wt%	1.15	na	1.53	na	1.80	na	4.45	na	4.33	na
CO_3	wt%	0.19	na	0.12	na	0.03	na	0.00	na	0.02	na
Rb	ppm	51	50	51	50	51	59	56	59	69	69
Sr	ppm	76	76	78	80	78	80	80	82	86	84
Ba	ppm	252	265	256	237	245	253	244	240	247	251
Br	ppm	37	26	64	167	128	126	125	153	243	214
I	ppm	10	8	10	12	10	17	16	21	23	23
As	ppm	4	4	6	7	6	9	8	11	14	12
Pb	ppm	19	19	24	32	28	41	41	48	67	63
Ni	ppm	14	12	14	16	15	18	18	21	28	25
Cr	ppm	56	42	52	58	56	63	64	68	77	122
Zn	ppm	41	37	45	62	57	71	69	78	101	95
V	ppm	34	33	41	46	45	55	52	60	78	74
Y	ppm	12	11	14	14	13	15	16	17	17	17
Zr	ppm	185	171	198	209	205	204	202	202	180	181
Nb	ppm	10	9	10	10	10	11	11	12	13	13
La	ppm	14	10	14	11	14	16	16	20	20	22
Ce	ppm	14	3	19	20	20	17	24	27	39	34
^{99}Tc	Bq/kg	4	1	6	7	7	4	8	10	6	na
^{137}Cs	Bq/kg	429	291	527	439	288	208	166	100	59	na
^{241}Am	Bq/kg	28	17	95	103	59	16	0	4	0	na

A2.3.3. Core SUTL-333

Stable and Radionuclide data

Depth	cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Total Majors	wt%	na	99.00	na	100.55	na	100.63	na	99.69	na	99.22	na	100.86	na	101.18	na
SiO_2	wt%	na	67.73	na	63.45	na	67.13	na	64.52	na	69.41	na	63.15	na	58.68	na
TiO_2	wt%	na	0.52	na	0.55	na	0.54	na	0.52	na	0.48	na	0.52	na	0.55	na
Al_2O_3	wt%	na	8.40	na	8.97	na	8.27	na	8.51	na	7.69	na	8.39	na	9.42	na
Fe_2O_3	wt%	na	2.94	na	4.31	na	3.05	na	3.22	na	2.60	na	3.21	na	3.86	na
MnO	ppm	1585	1852	1724	1281	962	596	462	551	464	413	454	472	597	596	573
MgO	wt%	na	1.54	na	1.49	na	1.16	na	1.27	na	1.03	na	1.26	na	1.50	na
CaO	wt%	na	1.06	na	0.76	na	0.52	na	0.52	na	0.49	na	0.56	na	0.58	na
Na_2O	wt%	na	1.48	na	1.65	na	1.71	na	1.81	na	1.83	na	2.22	na	2.04	na
P_2O_5	wt%	na	0.16	na	0.22	na	0.16	na	0.15	na	0.12	na	0.15	na	0.16	na
LOI	wt%	na	13.15	na	17.00	na	16.16	na	17.17	na	13.70	na	19.45	na	22.31	na
S	wt%	na	0.30	na	0.33	na	0.44	na	0.47	na	0.45	na	0.52	na	0.53	na
Cl	wt%	na	0.88	na	1.54	na	2.29	na	2.49	na	2.65	na	3.03	na	4.15	na
C org	wt%	na	4.15	na	4.94	na	4.12	na	5.10	na	6.43	na	7.69	na	7.48	na
CO_3	wt%	na	0.20	na	0.04	na	0.00	na	0.01	na	0.00	na	0.00	na	0.01	na
Rb	ppm	65	66	64	67	63	61	63	64	61	58	61	62	66	70	70
Sr	ppm	94	94	93	101	94	89	87	90	89	86	86	89	92	93	91
Ba	ppm	273	273	252	257	267	253	268	255	245	259	253	247	242	259	262
Br	ppm	159	184	290	275	247	200	184	231	243	173	196	223	276	261	252
I	ppm	25	21	51	45	41	27	25	27	27	19	31	39	49	55	49
As	ppm	10	9	11	14	12	10	10	13	11	9	10	12	16	18	15
Pb	ppm	40	38	43	50	46	45	47	51	51	42	50	53	67	70	67
Ni	ppm	25	22	22	25	22	21	23	23	22	19	22	22	25	27	25
Cr	ppm	222	79	72	129	79	71	74	81	70	67	67	72	76	80	67
Zn	ppm	116	91	95	98	86	78	88	96	90	78	90	91	110	108	102
V	ppm	68	69	71	76	67	66	63	71	69	64	66	67	81	84	79
Y	ppm	18	19	18	19	17	18	18	19	17	15	16	17	17	17	17
Zr	ppm	181	197	172	183	191	196	196	187	175	190	182	179	168	166	156
Nb	ppm	13	13	12	13	13	13	12	12	11	12	12	12	13	13	12
La	ppm	22	19	20	24	20	19	18	20	18	20	20	20	18	20	20
Ce	ppm	46	44	42	46	31	34	26	36	45	34	24	39	40	5	40
^{99}Tc	Bq/kg	27	14	12	16	14	12	12	15	15	19	18	11	9	9	7
^{137}Cs	Bq/kg	550	632	957	1121	1910	1287	1558	1933	971	611.5	252	720	382	44	30
^{241}Am	Bq/kg	235	238	301	273	190	164	264	598	473	252.5	32	142	71	0	0

Depth	cm	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
Total Majors	wt%	100.40	na	97.97	na	101.79	na	100.56	na	100.26	na	na
SiO_2	wt%	60.96	na	55.15	na	67.42	na	63.65	na	64.67	na	na
TiO_2	wt%	0.54	na	0.54	na	0.62	na	0.62	na	0.64	na	na
Al_2O_3	wt%	9.33	na	9.70	na	10.68	na	10.68	na	10.95	na	na
Fe_2O_3	wt%	3.60	na	4.50	na	4.13	na	4.22	na	4.29	na	na
MnO	ppm	608	744	918	726	655	657	620	566	603	679	550
MgO	wt%	1.44	na	1.54	na	1.50	na	1.60	na	1.63	na	na
CaO	wt%	0.55	na	0.59	na	0.52	na	0.55	na	0.54	na	na
Na_2O	wt%	2.05	na	2.00	na	1.88	na	1.90	na	1.81	na	na
P_2O_5	wt%	0.14	na	0.16	na	0.13	na	0.13	na	0.13	na	na
LOI	wt%	19.67	na	21.64	na	12.57	na	14.91	na	13.24	na	na
S	wt%	0.47	na	0.43	na	0.25	na	0.29	na	0.22	na	na
Cl	wt%	3.79	na	3.53	na	2.23	na	2.35	na	1.91	na	na
C org	wt%	7.40	na	6.19	na	7.71	na	4.44	na	3.48	na	na
CO_3	wt%	0.08	na	0.04	na	0.00	na	0.00	na	0.01	na	na
Rb	ppm	71	**75**	74	74	77	77	81	82	80	82	80
Sr	ppm	91	**92**	95	89	93	93	95	95	92	95	94
Ba	ppm	257	**267**	261	283	302	285	293	309	292	307	296
Br	ppm	235	**252**	276	164	167	182	188	182	158	153	175
I	ppm	45	**49**	60	41	33	43	43	43	35	39	33
As	ppm	16	**20**	26	17	17	21	22	25	22	22	21
Pb	ppm	68	**73**	88	76	82	101	122	119	99	107	95
Ni	ppm	27	**27**	29	26	27	28	31	30	29	30	37
Cr	ppm	124	**79**	95	87	89	82	86	85	86	89	601
Zn	ppm	106	**113**	126	116	123	132	148	141	125	130	117
V	ppm	80	**87**	91	85	89	85	89	96	91	93	96
Y	ppm	17	**17**	19	19	19	19	19	20	19	20	20
Zr	ppm	156	**150**	146	161	174	170	171	182	171	176	178
Nb	ppm	12	**13**	12	13	13	13	13	14	14	14	14
La	ppm	23	**23**	26	25	23	20	23	27	24	25	23
Ce	ppm	37	**44**	43	39	45	41	49	40	48	54	50
^{99}Tc	Bq/kg	6	6	7	4	6	7	5	6	9	na	na
^{137}Cs	Bq/kg	16	12	8	5	2	0	0	0	1	na	na
^{241}Am	Bq/kg	0	0	0	0	0	0	0	0	0	na	na

A2.4. Ribble Estuary

A2.4.1. Core W-98-001

Stable and Radionuclide data

Depth	cm	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Wet ; Dry Ratio		1.85	1.96	2.04	1.98	1.92	1.76	1.77	1.77	1.71	1.61	1.62	1.62	1.71	1.77	1.84	1.91
Total Majors	wt%	na	99.57	na	99.93	na	98.78	na	98.91	na	98.99	na	96.44	na	99.12	na	99.41
SiO_2	wt%	na	54.34	na	51.87	na	55.87	na	55.46	na	58.16	na	56.58	na	56.34	na	54.43
TiO_2	wt%	na	0.70	na	0.73	na	0.69	na	0.68	na	0.66	na	0.63	na	0.68	na	0.69
Al_2O_3	wt%	na	12.05	na	12.83	na	11.35	na	11.69	na	10.84	na	10.66	na	11.59	na	12.02
Fe_2O_3	wt%	na	5.31	na	5.74	na	4.92	na	5.07	na	4.76	na	4.44	na	4.98	na	5.46
MnO	ppm	1910	1924	2780	2467	2035	1778	1802	1880	1687	1505	1543	1521	1716	1910	1978	2496
MgO	wt%	na	2.57	na	2.82	na	2.47	na	2.54	na	2.33	na	2.30	na	2.49	na	2.65
CaO	wt%	na	4.98	na	5.38	na	5.17	na	5.16	na	5.21	na	4.98	na	5.26	na	5.60
Na_2O	wt%	na	1.34	na	1.53	na	1.24	na	1.45	na	1.38	na	1.46	na	1.52	na	1.72
P_2O_5	wt%	na	0.33	na	0.32	na	0.28	na	0.31	na	0.31	na	0.29	na	0.38	na	0.27
LOI	wt%	na	14.88	na	15.53	na	13.73	na	13.52	na	12.54	na	12.44	na	13.06	na	13.70
S	wt%	na	0.34	na	0.62	na	0.46	na	0.35	na	0.26	na	0.20	na	0.25	na	0.82
Cl	wt%	na	1.34	na	1.10	na	1.13	na	1.20	na	1.04	na	1.15	na	1.39	na	1.66
C org	wt%	na	2.60	na	2.89	na	2.52	na	2.60	na	1.60	na	2.09	na	2.42	na	2.64
CO_3	wt%	na	1.50	na	1.24	na	1.22	na	1.14	na	1.83	na	1.24	na	1.20	na	1.17
Rb	ppm	102	103	108	107	102	98	99	101	97	93	94	91	101	101	99	101
Sr	ppm	192	186	200	201	198	191	190	190	185	194	191	195	199	211	206	194
Ba	ppm	408	399	421	406	389	388	393	397	420	414	416	411	438	420	423	426
Br	ppm	103	115	117	115	100	95	99	96	93	91	94	93	99	100	110	114
I	ppm	76	83	79	81	72	76	79	74	66	72	70	64	68	72	70	68
As	ppm	23	23	24	25	25	23	21	23	24	24	23	20	21	22	25	27
Pb	ppm	120	106	107	106	100	97	103	106	99	100	105	98	105	105	111	100
Ni	ppm	40	40	41	41	39	37	37	38	37	35	34	32	36	36	37	38
Cr	ppm	124	121	122	120	123	117	125	125	123	121	117	119	123	118	127	123
Zn	ppm	271	274	287	281	265	257	266	270	260	246	250	242	268	268	264	260
V	ppm	117	119	125	118	113	119	113	114	109	106	110	106	118	117	121	119
Y	ppm	26	25	27	26	27	26	25	25	26	26	25	24	26	24	25	24
Zr	ppm	315	279	240	236	312	342	313	2912	343	343	315	313	271	255	253	244
Nb	ppm	17	16	16	17	16	16	15	16	17	16	15	15	15	17	16	16
La	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Ce	ppm	61	62	59	61	61	66	64	61	50	51	60	61	57	62	60	55
^{99}Tc	Bq/kg	115	103	120	121	113	110	103	123	117	112	97	86	96	104	104	112
^{137}Cs	Bq/kg	654	622	614	716	659	604	610	696	658	628	1078	633	783	747	762	746
^{241}Am	Bq/kg	311	267	272	317	279	275	250	284	246	270	290	268	323	311	326	315

Depth	cm	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Wet ; Dry Ratio		1.87	1.90	1.92	1.82	1.86	1.87	1.94	1.91	1.89	1.89	1.78	1.79	1.77	1.81	1.82	1.77
Total Majors	wt%	na	100.02	na	99.39	na	99.45	na	99.49	na	99.72	na	99.21	na	99.41	na	99.84
SiO_2	wt%	na	53.57	na	55.66	na	54.14	na	54.08	na	54.03	na	52.96	na	53.50	na	53.66
TiO_2	wt%	na	0.73	na	0.69	na	0.70	na	0.72	na	0.71	na	0.72	na	0.74	na	0.71
Al_2O_3	wt%	na	12.87	na	11.89	na	12.36	na	12.71	na	12.51	na	12.85	na	12.73	na	12.54
Fe_2O_3	wt%	na	5.67	na	5.26	na	5.55	na	5.63	na	5.62	na	5.69	na	5.72	na	5.64
MnO	ppm	2529	2257	2017	1819	1796	1840	1761	1803	1852	1915	2131	2270	2133	1987	1899	2007
MgO	wt%	na	2.85	na	2.63	na	2.72	na	2.80	na	2.73	na	2.83	na	2.80	na	2.73
CaO	wt%	na	5.33	na	5.38	na	5.36	na	5.42	na	5.40	na	5.32	na	5.34	na	5.16
Na_2O	wt%	na	1.71	na	1.74	na	1.59	na	1.58	na	1.91	na	1.59	na	1.61	na	1.62
P_2O_5	wt%	na	0.28	na	0.33	na	0.46	na	0.39	na	0.25	na	0.40	na	0.35	na	0.40
LOI	wt%	na	13.93	na	12.90	na	13.80	na	13.26	na	13.61	na	13.95	na	13.73	na	14.47
S	wt%	na	0.68	na	0.49	na	0.29	na	0.32	na	0.59	na	0.41	na	0.55	na	0.39
Cl	wt%	na	1.61	na	1.62	na	1.87	na	1.63	na	1.86	na	1.60	na	1.66	na	1.68
C org	wt%	na	2.62	na	2.40	na	2.46	na	2.60	na	2.86	na	2.86	na	2.71	na	2.75
CO_3	wt%	na	1.23	na	1.17	na	1.17	na	0.93	na	0.75	na	0.89	na	0.99	na	1.05
Rb	ppm	102	107	107	101	103	103	108	106	104	104	107	106	107	104	107	106
Sr	ppm	195	194	198	197	198	200	197	195	201	197	195	200	198	197	190	180
Ba	ppm	424	460	441	412	415	391	397	401	377	392	395	405	400	419	404	391
Br	ppm	119	131	124	104	111	111	117	107	99	99	106	105	106	106	107	105
I	ppm	72	76	76	70	78	79	83	72	70	74	76	70	74	68	74	76
As	ppm	26	25	25	24	27	26	26	25	26	30	29	27	32	31	30	28
Pb	ppm	103	106	112	113	113	178	131	118	112	122	133	119	118	112	122	119
Ni	ppm	39	40	40	36	39	39	40	39	38	41	40	39	40	39	41	39
Cr	ppm	118	125	123	125	130	122	133	127	125	128	123	129	129	129	131	135
Zn	ppm	266	278	286	271	276	282	287	285	278	301	305	302	319	305	308	293
V	ppm	117	117	123	116	124	125	129	119	118	120	116	126	122	120	120	125
Y	ppm	26	25	26	23	26	26	27	27	26	27	26	26	26	27	26	26
Zr	ppm	235	223	235	276	259	244	225	244	259	250	245	241	234	243	235	306
Nb	ppm	16	16	17	16	16	16	17	16	16	16	17	16	17	15	17	16
La	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Ce	ppm	66	61	62	67	53	68	66	49	62	66	58	58	60	55	61	60
^{99}Tc	Bq/kg	118	114	101	86	98	98	93	71	72	70	71	82	67	72	45	47
^{137}Cs	Bq/kg	740	841	863	723	843	819	829	911	883	877	852	884	883	822	787.5	753
^{241}Am	Bq/kg	312	365	372	306	342	331	354	1072	374	369	351	390	400	349	341	333

Depth	cm	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
Wet ; Dry Ratio		1.74	1.77	1.80	1.83	1.87	1.80	1.69	1.69	1.76	1.90	1.92	1.98	2.04	1.79	1.65	1.70
Total Majors	wt%	na	99.81	na	99.29	na	99.87	na	98.72	na	99.20	na	99.01	na	98.77	na	97.40
SiO_2	wt%	na	53.57	na	52.42	na	55.77	na	58.35	na	53.92	na	51.59	na	56.55	na	56.97
TiO_2	wt%	na	0.73	na	0.72	na	0.70	na	0.66	na	0.71	na	0.74	na	0.65	na	0.64
Al_2O_3	wt%	na	13.07	na	13.13	na	12.30	na	11.17	na	12.59	na	13.53	na	11.62	na	11.03
Fe_2O_3	wt%	na	5.80	na	5.87	na	5.43	na	4.75	na	5.51	na	6.00	na	5.01	na	4.76
MnO	ppm	2326	2876	2691	2516	2233	1825	1700	1737	1929	2049	1996	2136	2003	1825	1590	1652
MgO	wt%	na	2.84	na	2.87	na	2.69	na	2.40	na	2.69	na	2.94	na	2.47	na	2.41
CaO	wt%	na	4.97	na	5.09	na	5.08	na	4.92	na	4.52	na	4.88	na	4.80	na	5.03
Na_2O	wt%	na	1.81	na	1.82	na	1.63	na	1.56	na	1.58	na	1.65	na	1.72	na	1.62
P_2O_5	wt%	na	0.39	na	0.35	na	0.35	na	0.36	na	0.35	na	0.45	na	0.35	na	0.30
LOI	wt%	na	13.52	na	14.10	na	13.14	na	11.96	na	14.43	na	14.22	na	12.81	na	12.00
S	wt%	na	0.29	na	0.36	na	0.30	na	0.27	na	0.44	na	0.41	na	0.55	na	0.45
Cl	wt%	na	1.62	na	1.80	na	1.80	na	1.75	na	1.89	na	2.01	na	1.90	na	1.79
C org	wt%	na	2.90	na	3.12	na	2.87	na	2.30	na	2.50	na	3.25	na	3.32	na	2.10
CO_3	wt%	na	0.87	na	0.78	na	0.92	na	0.91	na	0.88	na	0.64	na	0.20	na	0.97
Rb	ppm	105	106	109	109	109	104	91	91	99	104	106	114	110	94	89	95
Sr	ppm	179	180	184	187	185	187	181	177	173	164	168	182	177	188	181	184
Ba	ppm	394	379	399	393	383	390	367	389	391	397	406	397	396	383	363	381
Br	ppm	110	114	119	126	125	110	93	96	98	104	103	110	116	93	78	88
I	ppm	76	74	72	78	81	78	66	68	74	76	76	81	79	66	64	66
As	ppm	27.1	24.8	28.0	28.1	29.3	27.1	22.3	22.5	26.7	28.1	29.2	30.8	31.8	27.1	23.1	25.2
Pb	ppm	124	120	130	136	138	119	103	114	116	127	130	139	140	115	95.12	101
Ni	ppm	38	40	41.06	40.4	40.28	38.53	31.99	33.07	38.51	40.36	40.2	43.5	44.01	36.47	31.73	33.78
Cr	ppm	132	130	139	130	124	127	119	131	140	134	145	139	141	126	110	123
Zn	ppm	294	288	292	297	297	285	245	254	279	310	307	327	344	292	238	253
V	ppm	120	128	131	135	133	123	107	109	116	121	125	137	134	116	101	116
Y	ppm	27	27	27	26	27	5	24	26	26	26	27	27	26	24	23	24
Zr	ppm	280	268	254	239	231	263	311	319	310	281	251	211	203	272	191	311
Nb	ppm	17	16	17	16	16	17	15	15	16	16	15	17	16	16	15	16
La	ppm	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
Ce	ppm	67	76	63	56	57	75	53	47	62	68	62	82	65	61	51	53
^{99}Tc	Bq/kg	37	37	31	35	27	29	26	23	na	na	na	na	na	na	na	na
^{137}Cs	Bq/kg	760	767	787.5	808	788.5	769	732.5	696	796	758	855	951	857	763	780.5	798
^{241}Am	Bq/kg	326	319	339.5	360	339	318	299.5	281	325	295	360	406	350.5	295	316.5	338

A2.5. Data for Discharge of Radionuclides from BNFL Sellafield

Anthropogenic Radionuclides discharged from Sellafield TBq/year

Year	^{99}Tc	^{137}Cs	^{241}Am	Ingrown ^{241}Am
1952	8	46	0	0
1953	8	46	0	0
1954	8	46	0	0
1955	8	21	0	0
1956	8	160	0	0
1957	8	140	0	0
1958	8	230	0	0
1959	8	73	0	0
1960	8	34	0	0
1961	8	40	0	1
1962	8	74	0	1
1963	8	85	0	2
1964	8	100	4.5	2
1965	8	110	8.1	3
1966	8	180	7.5	6
1967	8	150	17	9
1968	8	370	21	21
1969	8	440	14	24
1970	40	1200	19	33
1971	40	1300	38	59
1972	40	1300	80	62
1973	40	770	110	92
1974	40	4100	120	56
1975	40	5200	36	59
1976	40	4300	12	43
1977	40	4500	3.7	32
1978	180	4100	7.9	60
1979	43	2600	7.8	50
1980	57	3000	8.2	24
1981	5.8	2400	8.8	20
1982	3.6	2000	6.4	16
1983	4.4	1200	2.2	11
1984	4.3	430	2.3	12
1985	1.9	330	1.6	3
1986	6.6	18	1.3	2
1987	3.6	12	0.65	1
1988	4.2	13	0.75	1
1989	6.1	29	1.1	1
1990	3.8	24	0.75	1
1991	3.9	16	0.74	1
1992	3.2	15	0.54	1
1993	6.1	22	0.87	1
1994	72	14	0.38	0
1995	190	12	0.11	0
1996	150	10	0.07	0
1997	84	7.9	0.05	0
1998	0	0	0	

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