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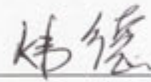
Plutonium as an Environmental Tracer for Erosion Study

A thesis submitted for the degree of
Doctor of Philosophy
at The Australian National University

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This thesis contains no material which has been accepted for the award of any other degree or diploma in any university. To the best of the author's knowledge and belief, it contains no material previously published or written by another person, except where due reference is made in the text.



Wee Teck HOO
25 September 2013



Preface

The erosion of soil is a natural process that involves the detachment of soil particles from the soil mass and their transport by erosive agents such as running water and wind. Problems arise only if the rate of soil erosion greatly exceeds the rate of soil formation, and excessive soil loss can be attributed to human activities such as deforestation, overgrazing, change in land use, and non-sustainable farming practices etc. Fortunately, such human-induced erosion can be prevented or mitigated through an appropriate strategy of effective soil conservation, but this requires a sound understanding of the erosion process and more importantly reliable quantitative data on the extent and rates of soil erosion. Classical methods of measuring soil loss are able to provide data for only a small area, and hence lack the capability to provide data at the larger spatial scale that is critical to the implementation of an effective soil conservation programme. Over recent years, the quest for alternative means to complement the existing methods has focussed attention on the use of environmental radionuclides as tracers to assess the transport of soil and deposition of sediment.

Fallout radionuclides, including anthropogenic ^{137}Cs and natural ^{210}Pb and ^7Be , have been used for many years as environmental tracers for erosion studies. The use of fallout plutonium (Pu) has not been exploited in the past due to the difficulties of detection using the conventional means of alpha-particle spectrometry. However, recent advances in the technique of accelerator mass spectrometry (AMS) allows plutonium isotopes to be readily detectable at the femtogram (10^{-15} g) level with higher sensitivity and shorter analytical times than for ^{137}Cs . These advances allow low-level plutonium measurement in environmental samples and thereby facilitate its use as a tracer for detailed catchment-wide erosion assessment.

Using the AMS technique of detection, this thesis explores the potential of fallout plutonium as a tracer of soil transport and sediment deposition for assessment of erosion, based on two case studies in areas close to Canberra, Australia. The AMS measurements were carried out using the 14UD pelletron accelerator operated by the Department of Nuclear Physics at the Australian National University. Some

complementary gamma-ray measurements were carried out at the Land and Water division of the Commonwealth Scientific and Industrial Research Organisation (CSIRO), also in Canberra, Australia. Assistance with the data analysis and interpretation of the results presented here was received from Professor L. K. Fifield and Dr S. G. Tims.

Publication

The following publication, directly related to the work in this thesis, has been published:

“Using fallout plutonium as a probe for erosion assessment” W. T. Hoo, L. K. Fifield, S. G. Tims, T. Fujioka and N. Mueller, Journal of Environmental Radioactivity, Volume 102, Issue 10, October 2011, pages 937-942.

Conference

The following conference presentation, directly related to the work in this thesis, has been given:

“Using plutonium as a probe change in erosional process” 10th South Pacific Environmental Radioactivity Conference, 24-27 November 2008, New Zealand.

Acknowledgments

The completion of this thesis shares the anguish, joys and fulfilment in life. It reminds me of the bond and encouragement from family and friends, to many of whom I wish to express my thanks.

I am greatly indebted to my supervisors Professor Keith Fifield and Dr Steve Tims. No matter how busy their day may have been, they always found time for me. Especially for Professor Keith Fifield, without whose frequent encouragement, supervision and guidance, I would not have come this far. Be it out in the field or in the laboratory, Dr Steve Tims was always there to guide me along. Both are remarkable people that I will always remember.

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I wish to express my appreciation to the staffs from the Research School of Earth Sciences in ANU and the Land and Water division of the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Canberra, who helped me with the sample preparation works in ^{137}Cs gamma ray spectrometry and the ^{14}C dating measurement. Thanks to Dr Stewart Fallon, Shane Paxton, Gary Hancock, Chris Leslie and Colin McLachlan.

My PhD programme was converted to a part-time basis due to the commitment of a full-time job in Singapore. Amid the frantic, hectic pace of life in Singapore, we always strive for things in a highly competitive and achievement-orientated world, and very often we lose sight of our priorities. I used to expect things to always turn out as I envisaged, and when they did not, stress crept upon me,

until my wife shared with me a principle which goes: “Have faith that things will work out, maybe not how you planned, but just how they are meant to be, for success come with perseverance and passion”. Here, I wish to express my gratitude to my wife, Mui Fang Pui who has been an understanding and caring person. She devoted her time unselfishly to look after the family and our two girls, Sherine Hoo and Shanice Hoo, while allowing me to work on my thesis. Lastly, I must not forget my close friends, Toshi Fujioka and Francis Chiew who were always there to share their concerns and to urge me to complete the programme.

Abstract

The main focus of this thesis is to explore the feasibility and practicality of fallout plutonium as an environmental tracer for erosion study, based on measurements carried out by the highly sensitive ion counting technique of Accelerator Mass Spectrometry (AMS). A number of improvements were made to the sample preparation process with the aim to improve the statistical precision of the plutonium measurements by increasing the count rate and to facilitate the sample preparation process through modification of the preparatory procedure. A simple model is also developed to provide a quantitative estimate of soil loss at a specific study site using the difference between the plutonium inventories at a reference site and the study site, and information about the depth profile of the plutonium in the soil.

Using the methodology established in this thesis, fallout plutonium is applied as an environmental tracer for the assessment of erosion at two case study sites, located within the Australian Capital Territory (Cotter River catchment) and New South Wales (Burra Creek catchment) respectively. The Cotter catchment is a highly disturbed environment that has been influenced by forestry operations and had recently experienced a catastrophic bush fire, whereas the Burra study area is under native vegetation and has been lightly impacted by land use since at least 1950, before the period of fallout from atmospheric nuclear testing.

Plutonium inventories and depth profiles were measured at six study sites across the lower Cotter catchment, as well as at an 'undisturbed' reference site. Comparison of the measured inventories at the study sites with the reference inventory shows that, with the exception of one site, there has been minimal soil loss across much of the pine-forested area since the early 1960s. Locally a loss of ~6 cm of topsoil has been identified at the Pago site. The temporal variation of erosional activity in the Cotter catchment has also been explored based on the study of a 1.2 m deep sediment pit that was collected from the upper reaches of the Cotter dam lake. The plutonium results together with a compilation of dates derived from Carbon-14 dating, indicates an average sedimentation rates of 1-4 cm/yr and 20 cm/yr over the pre-fire period (1990-2003) and the post-fire period (2003-2006) respectively.

At the hillslope study sites in the Burra catchment, the extent of soil erosion ranges from mild to severe. The analysis showed a high erosion rate of 16 t/ha/yr at the vicinity of a steep hillslope, whereas the nearby gentle hillslope terrain is associated with a much lower erosion rate of 0.4 t/ha/yr.

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Chapter 1 Introduction

This chapter presents a general overview of the background information relevant to this study. It includes a brief description on the impacts of erosion, the use of environmental radionuclides, and the potential of fallout plutonium as a tracer to assess the redistribution of soil and deposition of sediment. An outline of the objectives and structure of the thesis is presented.

1.1. Impact of soil erosion

Soil erosion in the 21st century has assumed greater importance in view of its recognition as a global sustainability issue [Lal, 1998; Morgan, 2005; Owens and Collins, 2006; Zapata, 2002]. In many parts of the world, the intensification of agricultural activity has enhanced the soil loss rate and threatened the long term sustainability of the global soil resource. An alarming depletion rate of 7% per decade of the global soil resource has been reported [Zapata, 2003]. It has been estimated that about 80% of the world's agricultural land suffers from moderate to severe erosion and that worldwide, non-sustainable farming practices have resulted in ~120 000 km² of arable land (about the size of the North Island of New Zealand) being destroyed or abandoned annually [Walling, 2002]. Montgomery [2007] highlighted that conventional tillage of agricultural fields has resulted in erosion rates that are on average 1-2 orders of magnitude greater than rates of soil production.

The impacts of erosion are detrimental both at the site of the erosion and away from it. The on-site effects are an excessive loss of soil and nutrients that can cause a reduction in the cultivated soil depth and soil fertility of agricultural land. This ultimately leads to poor crop productivity. Presently the global per-capita food supply is declining owing to the combined effects of such erosion-induced loss of productivity and population growth [Walling, 2002]. The off-site issues are often more evident and predominately associated with problems arising from sedimentation [Lal, 1998; Walling, 2002; Zapata, 2003]. Sedimentation leads to siltation of both reservoirs and waterways. This shortens the design life of reservoirs, and reduces the capacity of rivers and drainage ditches, thereby enhancing the risk of flooding and causing blockage of irrigation canals.

Erosion is known to remove soil organic carbon (SOC) from the site of formation and results in its burial in depositional sites [Oost *et al.*, 2007]. Recent findings have identified that such processes, together or separately, may influence the net flux of carbon between the soil and atmosphere via three key mechanisms:

1. Inputs of carbon from plants to replace the SOC at eroding site.
2. Enhanced decomposition of SOC attributed to the chemical or physical breakdown of soil during erosional process.
3. Deep burial of SOC at depositional sites inhibit its decomposition process.

As a result, the magnitude of the erosion-induced carbon sink or source is determined by several factors such as the rate at which SOC is replaced at sites of erosion, changes in the reactivity of SOC as a result of transport and burial, and the rates of soil erosion and deposition. Depending on the assumptions made, different global assessments of the influence of erosion and deposition on carbon dynamics have come to opposite conclusions, with some finding a net release of carbon, while others find a net gain [Oost *et al.*, 2007]. Hence some commentators argue that soil erosion is a contributor to global warming in the context of the climate change debate [Morgan, 2005]. For instance, Lal [1995] estimated that an annual release of 1.14 GT (Gigaton) of carbon to the atmosphere could be attributed to global soil erosion. This amount is equivalent to ~20% of anthropogenic carbon emissions (fossil fuel burning) indicated in the Global Carbon Budget based on the Intergovernmental Panel on Climate Change (IPCC) assessment [Schimel *et al.*, 2001]. Others, however, dispute this conclusion, and instead see soil erosion as a global sink of atmospheric carbon [Oost *et al.*, 2007]. While its relationship with the global carbon cycle remains contentious, the ominous fact that soil erosion has a detrimental effect on agricultural productivity and the surrounding environment is obvious and undeniable. Hence, curbing erosion is of paramount importance for the benefit of the global environment in the future.

1.2. Erosion assessment technique - The trend toward tracing

Soil erosion can be successfully prevented or mitigated by effective soil conservation programmes. The effectiveness of erosion control measures relies very much, however, on the selection of appropriate strategies for soil conservation. This in turn requires a thorough understanding of the erosion processes and reliable quantitative data on the extent and rates of soil erosion [Walling, 2002; Zapata, 2003, 2002].

Many empirical and theoretical mathematical models such as the Universal Soil Loss Equation (USLE) [Wischmeier and Smith, 1978] and the Sediment River Network Model (SedNet) [Prosser *et al.*, 2001] have been developed to estimate soil redistribution and sedimentation. However, these models tend to identify erosion problems at large spatial scale with limited information about the variability of soil loss within the region [Zapata, 2002]. The fact that environmental conditions vary in both time and space makes it essential to identify the spatial patterns of erosion and re-deposition. Moreover, conservation programmes are most effective at the smaller scale where the control of soil structure can be properly assessed and improved [Higgit, 1991]. The classical methods of assessment such as the use of erosion plots and surveying techniques (Table 1.1) are able to satisfy some of these requirements. They involve direct field measurements and hence are more reliable than modelling in providing realistic data for soil loss. However they are hampered by their limitations in terms of cost, labour intensiveness and operational constraints [Higgit, 1991; Loughran, 1989]. Also, their application requires long term monitoring and the gathered data are typically representative of only a small area and are therefore unsuitable for extensive spatial interpretation purposes [Ritchie 1998; Walling 2002, 1998; Zapata, 2003].

Over recent years, the quest for alternative means to complement the existing methods of assessment has turned to radionuclides as tracers for assessing the transport of soil and sediment [Ritchie, 1998; Walling 2002, 1998; Zapata 2003]. This growing trend towards the use of tracers is strongly motivated by their ease of application and their ability to provide detailed spatially-extensive data. These

advantages offer considerable potential to satisfy the need to verify the new generation of distributed erosion and sediment yield models and also to provide the link to interface with current developments in the application of GIS (Global Imaging System) and geostatistics data in this field [Walling, 1998].

Table 1.1: Common classical soil measurement techniques [Source: Loughran, 1989]

<u>Technique</u>	<u>Description</u>
Plots and trap	In this technique, the runoff and sediment that originated from a designated plot area are caught in a trough or tray and led through pipes to collecting tanks which retain all or a fixed proportion of the plot output, thereby allowing soil loss to be quantified accordingly.
Surveying	<p>This technique involves the setting of a datum against which erosion (or deposition) can be measured.</p> <p>Example:</p> <p>(i) Erosion pins in the form of nails or steel rods are inserted into the ground that serve as a datum against which “ground advance” and “ground retreat” can be measured.</p> <p>(ii) Profilometers consist of frames, resting on permanent benchmarks, with a number of vertical sliding rods which can be lowered to the soil surface. This allows the surface level to be assessed.</p> <p>(iii) Photogrammetry involves the construction of detailed topographic maps with precise contour interval from aerial photographs. Changes in surface elevation (erosion/deposition) can be determined by comparing the photographs.</p>

1.3. Radionuclides as environmental tracers

Several man-made radioisotopes, mainly gamma ray emitters (^{51}Cr , ^{59}Fe , ^{110}Ag , ^{198}Au etc.), have been used as tracers in soil erosion research [Zapata, 2003], although non-radioactive tracers such as chemical markers or coloured paints have also been employed [Loughran, 1989]. The use of radionuclide tracers overcomes many of the problems associated with the traditional approach to soil assessment [Ritchie, 1998; Walling, 1998]. By artificially labelling soil particles with the appropriate radionuclides, it is able to provide location-specific soil measurement, particularly in areas where long term monitoring cannot be established [Ritchie, 1998]. However, the tracing technique can be problematic if it requires the tracer to be added to the environment in the first place, due to radiological concerns. To avoid this, another variant of this technique involves the use of environmental radionuclides which are already present in the environment.

Fallout radionuclides

In the context of erosion research, the term ‘environmental radionuclides’ generally refers to fallout radionuclides that are commonly occurring and widely distributed in the environment or landscape [Walling, 1998]. They are present as both artificial and natural radionuclides in the atmosphere, and are deposited on the earth’s surface by dry or wet precipitation. Upon contact with the soil materials, these radionuclides have the ability to rapidly adsorb firmly to either the mineral or organic components. Subsequent redistribution of the soil materials may then be quantified by measurement of either the radioactivity of a particular isotope [Owens and Collins, 2006] or of the concentration of the radionuclide itself. An illustration of this application using fallout plutonium isotopes is presented in Chapter 2.

Environmental radioisotopes can also be used as chronological markers to estimate the sedimentation rate in reservoirs [Carroll and Lerche, 2003]. This has previously been demonstrated using ^{137}Cs [Heit and Miller, 1987], $^{239+240}\text{Pu}$ [Krishnaswami *et al.*, 1980], ^{238}Pu [Everett, 2009] and ^{228}Th [Hancock and Hunter, 1999]. Eroded soils from the catchment accumulate on the bed of a reservoir, together with a range of environmental indicators including fallout radionuclides. These sediments preserve the chronological order in which they were laid down and

form a natural archive containing a record of events in the environmental history of the reservoir and its catchment [Oldfield, 1975]. Thus by dating the sediment, it is possible to derive and reconstruct the integrated record of erosion events in the catchment on timescales ranging from a few decades to many centuries [Zapata, 2002]. In this study, a preliminary attempt has been made to date a sediment pit sample using the ^{14}C bomb-pulse dating technique and is described in Chapter 5.

The first documented study using an environmental radionuclide as a tracer for erosion studies was carried out in 1960 using fallout ^{90}Sr [Menzel, 1960]. Since then, many other radionuclides such as fallout ^{137}Cs , natural ^{210}Pb , cosmogenic ^7Be , and others ($^{239,240}\text{Pu}$, ^{14}C , ^{26}Al , ^{32}Si , ^{36}Cl etc.) have been exploited to assess soil erosion, deposition patterns in water bodies and other related problems depending on the time-scale [Zapata, 2003]. Presently those most commonly employed in studying recent rates of erosion include the anthropogenic ^{137}Cs and the natural ^{210}Pb (excess) and ^7Be [Wallbrink and Murray, 1993; Walling, 2004; Zapata, 2003, 2002]. Applications and limitations of these three isotopes are highlighted below.

(i) Caesium-137

Among the commonly used radioisotopic tracers of soil movement, ^{137}Cs is the most widely used and well-studied [Ritchie and Ritchie, 2008; Ritchie *et al.*, 1974]. The success of ^{137}Cs as a valuable tracer is attributed to its rapid and strong adsorption by fine soil particles, particularly clay minerals and humic materials [Bachhuber *et al.*, 1982; Brisbin *et al.*, 1974]. It was produced by atmospheric nuclear weapons tests, principally in the 1950s and 1960s and hence its fallout is well defined in time. Since it is a γ -ray emitter, measurement of its concentration in soils by γ -ray counting is relatively straightforward [Zapata, 2003]. There are, however, two significant drawbacks to the general application of this tracer. The first arises from complications introduced by inputs of Chernobyl-derived ^{137}Cs in many parts of Europe, while the second is that concentrations are declining as a consequence of its 30-year half-life. Already, more than 60% of the deposited ^{137}Cs has decayed, and this has already led, and will continue to lead, to a progressive reduction in the detection sensitivity for ^{137}Cs by gamma-ray spectroscopy, particularly in areas such as the Southern Hemisphere where fallout levels were low [Walling *et al.*, 1995].

(ii) Lead-210 (unsupported or excess) and Beryllium-7

Unsupported or excess ^{210}Pb and ^7Be are useful tracers and are frequently used in conjunction with ^{137}Cs [Matisoff *et al.*, 2002; Morgan, 2005; Walling, 1998]. Both are naturally-occurring radionuclides and in contrast to ^{137}Cs , their fallout input can be considered constant through time since they are being continually replenished in the atmosphere. Successful attempts to use excess ^{210}Pb in soil erosion assessment have been reported by Wallbrink and Murray [1996] and Walling and He [1999]. Similarly, several erosion studies have also been carried out using ^7Be [Blake *et al.*, 1999; Wallbrink and Murray, 1996, 1993; Walling *et al.*, 1999].

Lead-210 has a half-life of 22 years and is derived from the decay of the gaseous ^{222}Rn (decay daughter of ^{226}Ra). A small quantity of ^{222}Rn diffuses from the ground into the atmosphere where it decays to ^{210}Pb . This ^{210}Pb attaches to aerosols and its subsequent fallout provides an input of this radionuclide to the surface soil. This fallout component is termed as “unsupported” or excess ^{210}Pb , since it is over and above what would be expected from the decay chain $^{226}\text{Ra} \rightarrow ^{222}\text{Rn} \rightarrow ^{218}\text{Po} \dots \rightarrow ^{210}\text{Pb}$ within the soil itself. The excess ^{210}Pb can then be calculated by subtracting the total measured ^{210}Pb from the in-situ component as determined from the ^{226}Ra concentration under the assumption that the ^{222}Rn is locally retained [Zapata, 2003]. To the extent that this assumption is not valid, and of course the method depends on some ^{222}Rn being lost (although not at the sampling site), the $^{210}\text{Pb}_{\text{excess}}$ will be underestimated, and indeed can even be negative. This uncertainty rather limits the usefulness of ^{210}Pb as a tracer of soil loss and transport.

Beryllium-7 is constantly produced in the atmosphere via the spallation (fragmentation into lighter nuclei) of nitrogen and oxygen nuclei by cosmic rays. “Fresh” fallout ^7Be is continually replenishing the rapidly decaying supply, owing to its short half-life of 53 days. Hence ^7Be is mainly found in the uppermost layer (~2 cm) of the soil. The short half-life offers both the advantage as well as the restriction to the study of short term or single runoff events [Walling, 2002].

(iii) Plutonium

Like ^{137}Cs , the plutonium isotopes (^{239}Pu and ^{240}Pu) originated from the atmospheric nuclear weapons tests in the 1950s and early 1960s. In contrast to ^{137}Cs , however, very little has decayed due to their longer half-lives (24,110 and 6561 years, respectively). Plutonium has the added advantage that almost six times as many plutonium atoms were deposited in fallout as ^{137}Cs atoms.

In the past, these advantages of plutonium were not fully exploited due to the difficulties of detection using the conventional means of alpha-particle spectrometry. As a result there have been only very few attempts to use plutonium as an erosion tracer [Schimmack, 2001]. Recent advances in the technique of accelerator mass spectrometry (AMS) at the Australian National University have, however, transformed the detection of plutonium isotopes, and they can now be readily detected at the femtogram (10^{-15} g) level, resulting in smaller sample sizes, higher sensitivity and shorter analytical times. These advances allow precise analysis of low-level plutonium in environmental samples (soil / sediment) to be carried out with confidence and ease, and therefore facilitate its use as a tracer for detailed catchment-wide erosion assessment.

Earlier work at the ANU by Everett [2009] and Everett *et al.*, [2008] demonstrated an excellent correlation between plutonium and ^{137}Cs in soil and sediment samples. Hence, plutonium can be used in the same way as ^{137}Cs , thereby building on a wealth of experience with the latter isotope for determining modern rates of erosion, but with substantial advantages in terms of sensitivity and throughput.

1.4. *Scope of thesis*

The main focus of this thesis is to explore the feasibility and practicality of using fallout plutonium as an environmental tracer for erosion study, based on measurements carried out by the highly sensitive ion counting technique of AMS. This serves to establish the hypothesis to ascertain the usefulness of using fallout plutonium as an environmental tracer with the aims to accomplish the following objectives:

1. Enhance the efficiency of plutonium measurements using the AMS technique by improving the measurement sensitivity and the sample preparation procedure.
2. Examine the erosional activity and derive quantitative estimates of soil loss at specific study sites from the measurement of plutonium isotopes.

The thesis is structured as follows:

Chapter 2 provides the background information for fallout plutonium. It covers its sources and its application as an environmental tracer for the assessment of soil erosion and sedimentation.

Chapter 3 describes the methodology employed in this study. It includes procedures pertaining to (i) field sampling, (ii) sample preparation, and (iii) AMS operation. It also covers the experimental investigations that were undertaken to explore possible improvements to the efficiency of the overall sample preparation process.

Chapters 4 and 5 constitute the core analytical content and focus on the assessment of erosion of a study area located within the Australian Capital Territory (Cotter River catchment). The Cotter catchment presents a highly disturbed environment that has been influenced by forestry operations and had recently experienced a catastrophic bush fire. It also examines the erosional history and explores the temporal variation of erosional activity in the Cotter catchment based on the study of a 1.2 m deep sediment pit that was collected from the upper reaches of the Cotter dam lake.

Chapter 6 explores the erosional activity at a hillslope site (Burra Creek catchment) located within New South Wales. In contrast to the Cotter catchment site, the Burra study area has been very lightly impacted by land use since the period of fallout from nuclear tests in the 1950s and 1960s.

Chapter 7 is the concluding chapter and summarises the findings. It reviews the objectives highlighted in Chapter 1 and identifies the issues that require further research.

Chapter 2 Fallout plutonium

This chapter aims to provide information about fallout plutonium with the emphasis on its main source of origin (nuclear weapons testing) and application as an environmental tracer.

2.1. Introduction

Plutonium is a rare transuranic radioactive element and the half-lives of its isotopes are much shorter than the age of the Earth. Thus, any plutonium that was present at the formation of the Earth ($\sim 4.5 \times 10^9$ years ago) would have long since decayed. There may, however be some traces of ^{244}Pu in nature as remnants of supernovae [Hoffman *et al.*, 1971]. To date, twenty isotopes (listed in Appendix A3) have been synthesized with half-lives ranging from ~ 1.1 sec (^{228}Pu) to 80 Ma (^{244}Pu). The lighter isotopes such as $^{232-237}\text{Pu}$, are formed by (α , n) reactions while those with mass greater than 238 are formed by neutron irradiation. The primary reaction is the (n, γ) reaction with ^{238}U , which results in the production of ^{239}Pu . This in turn absorbs additional neutrons to build up the heavier isotopes of plutonium. Only those shown in Table 2.1, however, are sufficiently long-lived to be potentially important in the context of environmental radioactivity.

Table 2.1: Characteristics of the long-lived plutonium isotopes

Isotope	Half-life, years	Decay process, (Energy, MeV)	Thermal cross section, barn		Critical mass, kg
			Capture	Fission	
^{238}Pu	87.7	α (5.499)	500	17	0.531
^{239}Pu	2.41×10^4	α (5.155)	271	742	
^{240}Pu	6.56×10^3	α (5.168)	290	<0.08	
^{242}Pu	3.76×10^5	α (4.901)	19	0.2	
^{244}Pu	8.26×10^7	α (4.589)	1.7	-	

[Source: F. Habashi (1997). "Handbook of extractive metallurgy - Volume 3", pg 1685, Wiley Heidelberg, Germany.]

Reviews describing the aspects of the chemistry of plutonium have been given by Clark *et al.*, [2008] and Clark [2000]. In the periodic table, plutonium is found near the middle of the actinide series, which is characterised by the presence of 5f electrons in the valence shell. Elements to the left of plutonium have delocalized (bonding) electrons, while elements to the right exhibit more localized (nonbonding) character. Plutonium is poised in the middle; the valence electrons appear to be in a complex state of being neither fully bonding nor localized, a property that leads to novel electronic interactions and unusual physical and chemical behaviour. Particularly in aqueous solution, its behaviour is complicated. Five oxidation states, Pu(III), Pu(IV), Pu(V), Pu(VI) and Pu(VII), can be readily prepared and stabilized in aqueous solution under the appropriate conditions. Such behaviour is attributed to the small energy separations between the various oxidation states and the extreme oxophilic nature of plutonium cations. This phenomenon is illustrated in the Pourbaix diagram (Eh vs pH) shown in Appendix A5 which highlighted plutonium in water containing the two most environmentally relevant ligands, the hydroxide (OH^-) and carbonate (CO_3^{2-}) ions. In this simple aqueous system, plutonium can exist in four oxidation states. The normal range of natural waters is outlined in Figure A5.1 and it overlaps with the stability fields of plutonium in the III, IV, and V oxidation states. Within this range, plutonium exhibits two triple points, where species in three different oxidation states are in equilibrium. The lower oxidation states, Pu(III) and Pu(IV), are generally more stable in acidic solution (low pH) while the higher oxidation states, Pu(VI) and Pu(VII), are favoured under alkaline conditions (high pH).

Thus far the tetravalent plutonium is the most stable and consequently the most studied, followed by plutonium in the trivalent and hexavalent states. Following the discovery that ^{239}Pu was fissile and hence of interest for nuclear weapons, detailed study of its solution chemistry was highly motivated by the need to separate plutonium from mixtures of actinides and fission products in multiple oxidation states under highly acidic conditions. In the context of the present work, the nature of the oxidation state is crucial for understanding and predicting the migratory behaviours of plutonium in the environment. It also imposes a challenge in the isolation of plutonium during the sample preparation process for measurement.

The most efficient separation technique of plutonium from other actinides is adapted from its unique chemistry behaviours. Plutonium is known to readily adsorb by both cation and anion exchangers from an acid media. The degree of adsorption varies depending on the oxidation state of plutonium, (decreasing in the order $\text{Pu(IV)} > \text{Pu(III)} > \text{Pu(VI)}$), and the acid concentration (decreasing with increasing acid molarity). The common practice is, therefore, to adsorb plutonium from a relatively dilute acid and elute it with a concentrated acid. The separation procedural detail is outlined in Appendix A1.

The chemistry characteristic of plutonium which primarily defined by its oxidation state can lead to complex interactions in the environment. It is noted that the site-specific conditions which include the groundwater pH, the presence of complexants (e.g., carbonate and humic acids) and soil characteristics will determine which plutonium species predominate as well as each specie overall transport and migration characteristics. In most natural waters, the pH is relatively neutral (pH 5 to 9), with a wide range of redox potentials (from -300 to $+500$ millivolts) and low salinities (ionic strengths ≤ 1 molal). Under such condition, plutonium favours the IV oxidation state. Once plutonium is in solution, the dominant reactions governing its fate and mobility in the environment is dominated by a variety of processes, such as oxidation/reduction, precipitation/solubility, complexation/hydrolysis and sorption/desorption. There are many naturally occurring materials that can cause the valence state of plutonium to change when in contact in the subsurface environment. For example, it has been reported that natural dissolved organic matter carbon (e.g., fulvic and humic acids) has been shown to reduce plutonium from the +6 state to the +4 state [Nelson *et al.*, 1987; Choppin *et al.*, 1997]. Similarly, naturally occurring Fe-oxides have been reported to reduce plutonium from the +5/+6 state to the +4 oxidation state. Conversely, Mn-oxides have also been shown to potentially oxidize plutonium from the +4/+5 state to the +6 state [Duff *et al.*, 1999]. Research activities also indicated that microbes can affect the plutonium migration, either through direct association or by helping to maintain a reducing environment. Hence, it will require a strong multidisciplinary foundation in environmental chemistry, molecular science, and interfacial science in order to gain an in depth understanding to this complex set of interacting processes.

2.2. Plutonium in the environment

Traces of plutonium that occur in the environment are predominately of anthropogenic origin. Their origins and environmental distribution were well reviewed by Harley [1980]. On the global scale, plutonium essentially originated as fallout from the series of atmospheric nuclear weapon tests that were conducted by the Soviets and the United States in the 1950s and 1960s. These are described in more detail in the following section. Fallout plutonium is expected to comprise principally the isotopes $^{239,240}\text{Pu}$, with only a very small amount of the heavier plutonium isotopes, ^{242}Pu and ^{244}Pu , produced mainly by post explosion decay of heavy uranium isotopes that were created by multiple neutron captures on the ^{238}U of the tamper. Typically the isotope ratios of $^{242}\text{Pu}/^{239}\text{Pu}$ and $^{244}\text{Pu}/^{239}\text{Pu}$ are in the order of 0.2% and 0.0002% respectively, which are to be compared to typical $^{240}\text{Pu}/^{239}\text{Pu}$ ratios of 20% in global fallout.

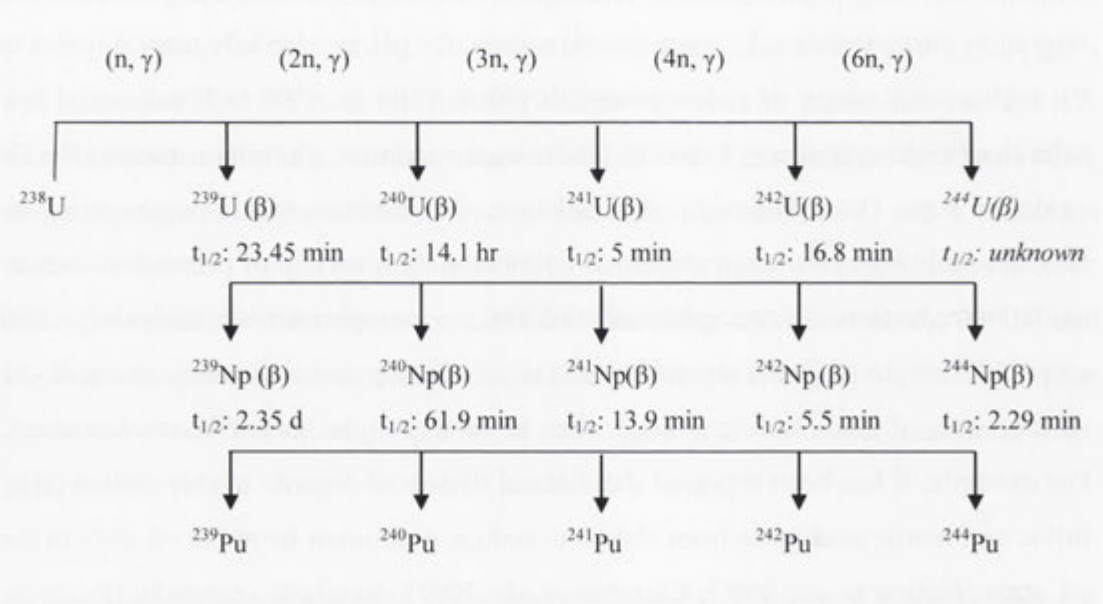


Figure 2.1: Possible multiple pathways of heavy plutonium isotopes produced from nuclear explosion.

In addition to the bomb-produced isotopes, a significant amount of the shorter-lived ^{238}Pu was deposited as the result of the burn up of a nuclear powered satellite (containing 630 TBq of ^{238}Pu) over the Indian Ocean in 1964. Also, there were several other isolated incidents which mainly contributed to local-scale land contamination. They include crashes of B-52 bombers carrying nuclear weapons in Greenland (Thule, 1968) and Spain (Palomares, 1966), and accidental releases from nuclear facilities, including the nuclear power facility at Chernobyl in Ukraine and the fuel reprocessing plant at Rocky Flats in United States. In addition, coastal waters have been contaminated with plutonium radioactive wastes, discharged by the French at Cap de la Hague, the British at Windscale / Sellafield and the Indians at Trombay. Taking these various sources into account, and based on measurement at more than 60 worldwide locations, Hardy *et al.*, [1973] arrived at the global fallout inventory of $^{239+240}\text{Pu}$ and ^{238}Pu in the top 30 cm of the earth's crust shown in Table 2.2, and the average measured fallout $^{239+240}\text{Pu}$ deposited in each latitudinal band is plotted in Figure 2.2.

Table 2.2: Global fallout inventories^a of $^{239+240}\text{Pu}$ and ^{238}Pu isotopes

	$^{239+240}\text{Pu}$ (PBq)	^{238}Pu (PBq)
Northern Hemisphere	9.5±1.2	0.34±0.04
Southern Hemisphere	2.6±0.5	0.46±0.08
Global	12.1±1.3	0.80±0.09

^a These inventories have been derived by multiplying the average activity per area for each ten degree latitude band by the latitude band area.

[Source: Hardy *et al.*, 1973]

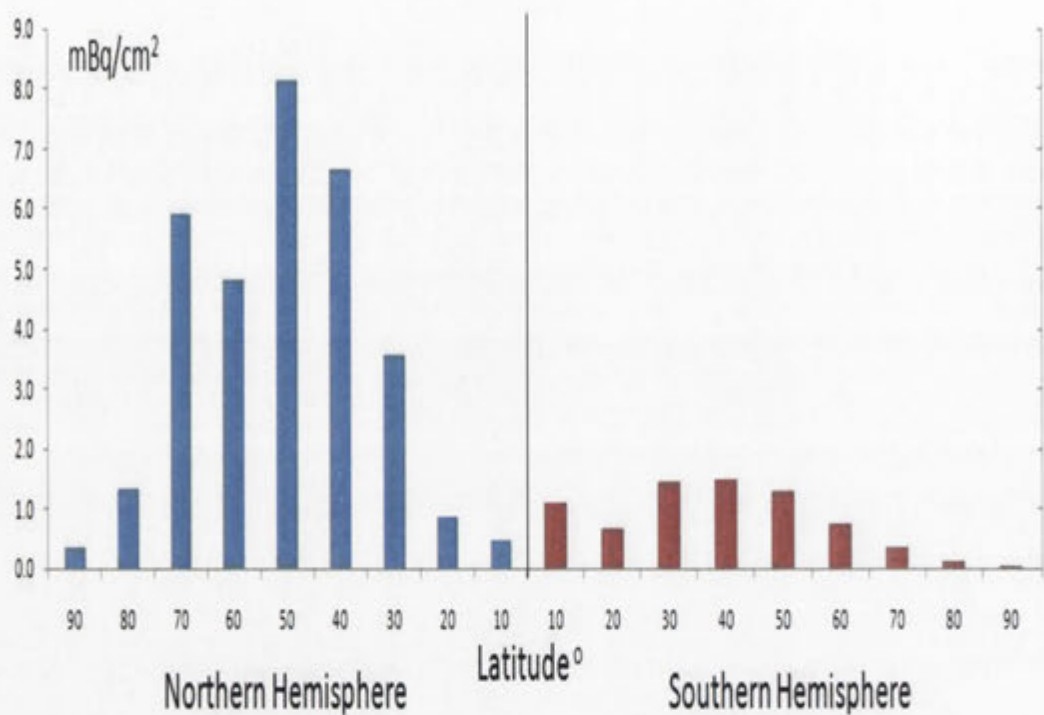


Figure 2.2: Average latitudinal distribution of measured fallout $^{239+240}\text{Pu}$.
[Source: Hardy *et al.*, 1973]

Plutonium-239 is also known to be produced naturally in uranium ore by neutron capture on ^{238}U followed by two subsequent β decays (see Figure 2.1). The neutrons necessary for the formation of ^{239}Pu arise from spontaneous fission of ^{238}U and from (α, n) reactions on light elements in the ore, particularly sodium and aluminium. The existence of ^{239}Pu in nature was first reported by Seaborg and Perlman [1948] who managed to isolate it from a pitchblende concentrate. The atom ratio $^{239}\text{Pu}/^{238}\text{U}$ in natural uranium ore lies in the order of 10^{-11} [Taylor, 2000; Wilcken *et al.*, 2008]. In the wider environment, i.e. away from uranium ore bodies, this ratio is estimated to be $\leq 10^{-14}$ and hence may usually be ignored compared to the much larger quantities of anthropogenic plutonium that were introduced into the environment.

2.3. Atmospheric nuclear weapon testing

From 1945 until 1980, a total of 543 atmospheric nuclear tests with a cumulative yield of 440 MT (Megaton) were carried out by the United States, Russia, the United Kingdom, France and China [UNSCEAR, 2000]. The most active periods of testing were 1954 to 1958 and 1961 to 1962. Following the Limited Test Ban Treaty in 1963, all subsequent United States and Soviets tests were carried out in underground testing facilities. The French and Chinese were not signatories to the Treaty, and continued atmospheric testing until 1974 and 1980 respectively, although they too progressively moved to underground tests.

Nuclear weapons

Nuclear weapons fall into two categories, fission and fusion (also known as thermonuclear or hydrogen weapons). A comprehensive discussion of these devices is available in Bodansky [2004] and Mark [1993].

(i) Fission device

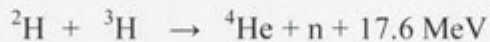
A fission device derives its explosive force from the energy released when a heavy nuclide such as ^{235}U or ^{239}Pu is induced to fission, i.e. split into two roughly equal-mass components, by the absorption of a neutron. The total energy released in the fission of ^{235}U and ^{239}Pu are 195 MeV and 202 MeV respectively. On average, two neutrons are released in the fission process and if on average more than one of these induces another fission, then a chain reaction occurs, leading to the rapid release of a large amount of energy. Uranium-235 may be produced by enriching uranium from its natural ^{235}U abundance of 0.7% to greater than 90%. Plutonium is produced in a nuclear reactor from the neutron bombardment of ^{238}U and may be chemically extracted in a reprocessing plant. As the ^{239}Pu builds up, ^{240}Pu is produced inevitably from it by neutron capture. The heavier isotope has a higher rate of spontaneous fission and this produces unwanted background neutrons that may cause premature initiation of a chain reaction in a bomb. Such a process is known as predetonation and it causes the bomb to fizzle i.e. explode with a smaller yield. Technically, nuclear weapon designers prefer to work with plutonium containing less than 7% of ^{240}Pu to avoid this undesirable occurrence. The world's first fission bomb contained ~6 kg of plutonium and was exploded in the Trinity test in New Mexico in

July 1945 [Mark, 1993]. Its reported explosive yield was 18.6 kT which corresponded to a fission efficiency of about 20% [Bodansky, 2004]. This basic device is limited in explosives yield because the core blows itself apart rapidly before the rest of the fissile fuel can be fissioned.

In a normal detonation process, the sub-critical fissile material is compressed with conventional explosive to trigger the fission chain reaction. Any plutonium in the weapon that is not fissioned ($^{239,240}\text{Pu}$) together with the heavier plutonium isotopes (mass number >239) that are created during detonation eventually return to the ground as fallout materials. It is noted that in some fission devices, the fissile material is surrounded by an optional layer of dense material (depleted uranium). Under such circumstance, some fallout plutonium could be produced from the post explosion decay following neutron capture by ^{238}U .

(ii) Fusion boosted device

A more efficient utilisation of fissile materials to boost the fission yield can be achieved using a small amount of fusion fuel consisting of the heavy isotopes of hydrogen, deuterium (^2H) and tritium (^3H). The fusion fuel is introduced into the core of a fission weapon and the high temperature generated from the fission process is then used to ignite the fusion process:



The energy released from the fusion process is ~ 17.6 MeV which is about one tenth of the energy released in a fission process. Thus the importance of fusion in these bombs is not as an additional source of energy but as a source of neutrons to increase substantially the fraction of the fissile material that undergoes fission. By such means, the explosive yield of a fission bomb can be increased to several hundred kT.

(iii) Thermonuclear device

Higher yields than those achievable with fusion boosted devices are possible by separating the fission and fusion components so that much more fusion fuel can be used, leading to the making of a thermonuclear device (Figure 2.3). Explosive yields can be very large, being dependent on the amount of fusion fuel in the device. Such devices operate in 2 stages using the Teller-Ulam radiation implosion principle [<http://nuclearweaponarchive.org>]. The intense X-ray flux produced by the primary fission explosion ablates the outer surface of the heavy tamper that surrounds the fusion fuel, causing the remainder of the tamper to implode, thus compressing the fusion fuel to high pressure and temperature and initiating the fusion reaction. As noted earlier, the fusion process generates an intense flux of fast neutrons (14 MeV). If the tamper is made from depleted uranium ($>99.9\%$ ^{238}U), then not only does the very dense metal enhance the effectiveness of the implosion, but also a substantial amount of extra energy is released due to the fission of ^{238}U by the fast neutrons. Explosive yields in the MT range are thereby achieved. For thermonuclear weapon with explosive yield in the range of 0.1-5 MT, fusion contributes about 50% of the total energy released. In contrast, for the largest ever test, which had a total yield of 50 MT and was conducted by the former Soviet Union in 1961, fusion contributed 97% of the total yield and fission only 3% [UNSCEAR, 2000].

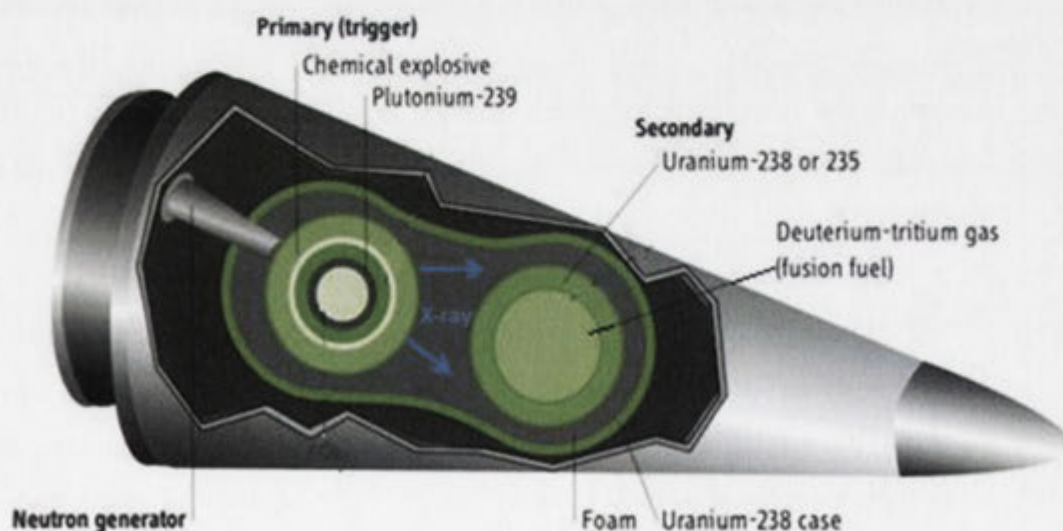


Figure 2.3: A typical thermonuclear device.
[Source: Encyclopaedia Britannica]

Twenty five of such high yield (>4 MT) thermonuclear devices were tested and accounted for nearly 66% of the total explosive yield attributed to all the atmospheric weapon tests conducted [UNSCEAR, 2000]. Much of the global fallout was contributed by these tests, mainly carried out by the Soviets at Novaya Zemlya and by the United States at the Bikini and Eniwetok atolls. Notably, the fallout plutonium that originated from thermonuclear devices mainly comes from the post explosion decay of neutron-rich uranium isotopes that were produced via multiple neutron capture processes on ^{238}U as shown in Figure 2.1. Uranium isotopes up to ^{255}U were created by the intense neutron flux [Diamond *et al.*, 1960].

Dispersion and deposition of nuclear fallouts

The debris (inclusive of radioactive particles) resulting from nuclear weapon tests were carried by the characteristic mushroom cloud produced in the explosion into the atmosphere. The partitioning of the radioactive debris injected at various altitudes is dependent on the height of the cloud formation which is determined by the total explosive yield and the height of the burst. Low-yield nuclear tests (<0.05 MT) introduced materials primarily into the troposphere, whereas high-yield (>1 MT) tests introduced greater proportions into the stratosphere [Peterson, 1970].

The subsequent dispersion and deposition of the nuclear fallouts are then determined by the air mass circulation patterns in the atmosphere. These materials may be transported great distances by local and large-scale air movements. The large-scale mixing processes and air movements in the atmosphere were presented in the UNSCEAR reports [2000, 1982]. Briefly, circulation of air within the troposphere is dominated by circulation cells which increase and decrease in size and move latitudinally with season. During winter, gaps that are present in the tropopause region at the temperate latitudes will facilitate the downward air movement and carry materials from the stratosphere across the tropopause into the troposphere. Air movement in the lower stratosphere is caused by the random eddy diffusion, and is more stable than in the stratosphere. Material movement is dominated by gravitational settling in the upper stratosphere. The time periods that the materials remain airborne depend on the latitude, time of year and height of injection into the atmosphere. Typical residence time in the troposphere and lower stratosphere are

~1 month and 1-3 years respectively [Bennett, 2002]. The removal processes include gravitational settling and dry deposition, and incorporation into rain drops with subsequent washout by falling precipitation. The physical and chemical characteristics of the materials themselves, such as particle size and chemical and physical forms, also influence the removal rates.

Following atmospheric deposition, the fate and transport of plutonium are determined by a variety of environmental factors, such as type of vegetation, amount and characteristic of organic matter present in soil, soil type, and climatic conditions at the site. It has been shown that the deposited plutonium migrates very slowly downwards through the soil. Typical migration rates of about 1 cm per year have been reported for climatic conditions of southern Germany [Bunzl *et al.*, 1995; 1994].

Harley [1980] estimated that approximately 15 000 TBq of $^{239+240}\text{Pu}$ were released in the form of oxide particles from the atmospheric nuclear weapon tests. Most of these materials were distributed worldwide, with only about one fifth of the weapon debris falling out close to the test sites (see Figure 2.4). Based on the relative areas of land and sea, about two thirds of this fallout plutonium would have been deposited in the oceans. The deposition in the northern hemisphere was more than three times greater than that in the southern hemisphere [Harley 1980]. This is expected as most of the nuclear weapons tests sites were located in the northern hemisphere. The tests of France in the Pacific and the United Kingdom in Australia dominated the few conducted in the southern hemisphere. Also, due to the preferential exchange of air between the stratosphere and troposphere in the mid-latitudes of the hemisphere and the air circulation patterns in the troposphere, there is enhanced deposition in the temperate regions and decreased deposition by a factor of two in the equatorial and polar regions [UNSCEAR, 2000].

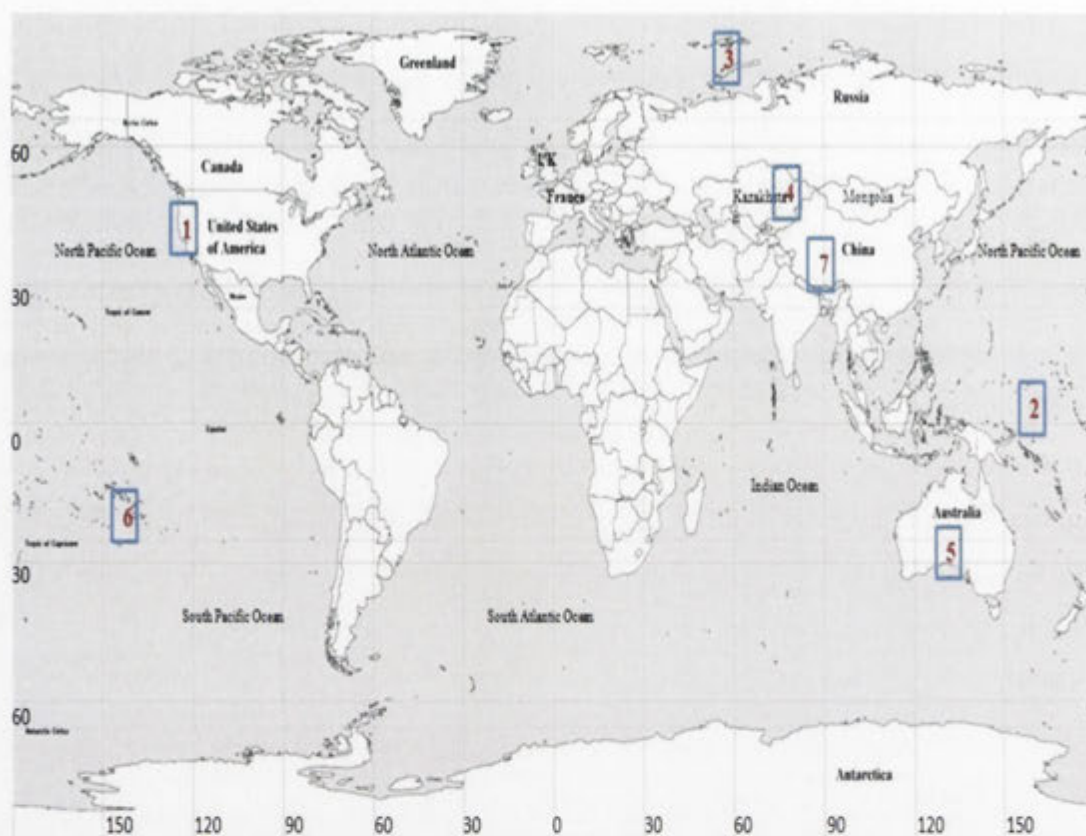


Figure 2.4: Locations of major nuclear test sites – (1)^{US} Nevada, (2)^{US} Bikini and Enewetak, (3)^{RUSSIA} Novaya Zemlya, (4)^{RUSSIA} Semipalatinsk, (5)^{UK} Maralinga and Emu, (6)^{FRANCE} Mururoa and Fangatafu, (7)^{CHINA} Lop Nor.

The plutonium isotopic ratio ($^{240}\text{Pu}/^{239}\text{Pu}$) is an important signature of the source of plutonium in the environment. For nuclear power reactors, the ratio depends on reactor design, and ranges from 0.23 to 0.67 [Carson *et al.*, 1988]. Weapons grade plutonium, on the other hand, has a low ratio of <0.07 . Fallout from nuclear weapons depends on the specific design of the weapons, the period and the scale of explosion, and the ratio ranges from 0.09 to 0.34 [Koide *et al.*, 1985]. Fallout from the Nevada test site is characterized by a low ratio which averages 0.035 [Buesseler and Sholkovitz, 1987; Hicks and Barr, 1984]. Elevated ratios ranging from 0.21 to 0.36 from the Pacific Proving Grounds have also been reported [Koide *et al.*, 1985; Noshkin, 1978]. Higher ratios can be generated from the higher neutron flux associated with an increase in the yield of a thermonuclear detonation. Also, the ratios could have increased over the history of weapons testing as a result of higher implosion speed, allowing the use of higher concentrations of ^{240}Pu without predetonation issues. The average global fallout ratio reported by Krey *et al.*, [1976]

is 0.176 ± 0.014 . This value was comparable with the $^{240}\text{Pu}/^{239}\text{Pu}$ results derived from the samples that were collected from the sampling sites at the Cotter and Burra catchments. There has been no significant variation in the $^{240}\text{Pu}/^{239}\text{Pu}$ results from the samples and thus implies that the plutonium source is mainly originated from global fallout.

Another important signature of global fallout is the $^{137}\text{Cs}/^{239+240}\text{Pu}$ activity ratio. The time-averaged activity ratio determined from the studies of ice cores from Greenland and Antarctica are 29.3 ± 2.2 and 25.9 ± 2.1 respectively (corrected for decay of ^{137}Cs to 2007) [Koide *et al.*, 1982, 1979].

2.4. A probe for erosion assessment

Fallout plutonium (^{239}Pu and ^{240}Pu) is known to associate with organic matter present in the soils [Bunzl *et al.*, 1994; Livens *et al.*, 1987], while others have shown strong associations of plutonium with the hydrous oxides (sesquioxides of iron, manganese and aluminium) coating of the soil particles [Ibrahim and Morris, 1997]. It has been found that once these long-lived radionuclides have infiltrated into the soil and attached to soil particles, they are relatively immobile over long period of time [Smith and Beresford, 2005]. This relative immobility of plutonium in soil has been demonstrated by measurements presented by Bunzl *et al.*, [1995, 1994] for undisturbed grassland in Germany in 1990. Almost 30 years after its deposition onto the soil, much of the $^{239+240}\text{Pu}$ remained in the upper 15 cm of the soil profile. Further, it is believed that the long term vertical migration of plutonium is mainly caused by bioturbation of the soil rather than diffusion in solution [Anspaugh *et al.*, 2002]. These observations suggest that plutonium should be highly suitable as a marker to trace the movement of soils. Successful demonstrations of the use plutonium isotopes in erosion studies are few, but have been reported by Schimmack *et al.*, [2002] and Everett [2009].

Analytical strategy

The principle of using fallout plutonium as an environmental tracer to assess soil distribution is essentially the same as that for ^{137}Cs which is well documented in Ritchie and McHenry [1990], and Walling [1998]. In brief, the analytical strategy was to compare the plutonium inventories (sum of ^{239}Pu and ^{240}Pu) at a number of study sites with the inventory at an undisturbed reference site. The reference site was selected on the basis that it had experienced negligible erosion or deposition of sediment or aeolian material over the last 50-60 years, and hence should retain the full inventory of plutonium fallout in this region. In contrast, sites that have lost or gained topsoil as a result of disturbance by erosion, deposition or human activity will have a different plutonium inventory. Thus, the measured deviation from the reference level allows the extent of disturbance at a disturbed site (a study site) to be evaluated. Illustrations of the translation of this difference in plutonium content onto soil loss or gain are described in Chapter 3, section 3.4.

Also, the plutonium concentration in the sediment present in a gully may be used to apportion soil loss between surface and gully erosion. For instance, isotope rich sediment indicates erosion activity that is dominated by loss of topsoil and hence likely to be generated from sheet and rill processes operating at the surface, whereas loss of subsoil by channel and gully erosion leads to negligible or low isotope concentration. This provides the means to allow the severity of gully erosion at a specific study site to be assessed appropriately.

Assumptions and limitations

Although the basis for the use of plutonium as an environmental tracer in soil studies is attractive in its simplicity, it is predicated on several key assumptions with potential limitations. Nevertheless by understanding and reducing the effects of these limitations, the measurement of plutonium can be confidently translated into valuable information concerning erosion as discussed below.

Two important issues with implications for the investigations in this thesis are as follows:

(i) Spatial variation

One of the assumptions is that the study area and the reference site have experienced a closely similar plutonium fallout history, and that the total plutonium inventories (in mBq/cm^2) were therefore essentially identical originally. In this context, studies of ^{137}Cs have shown that there is strong correlation between rainfall and fallout level [Zapata, 2003]. This implies that variations in rainfall could affect the fallout pattern and / or inventory level of plutonium as well. Walling [1998] commented that the assumption can, however, be readily justified by taking into consideration the extended period of input associated with bomb fallout (1954-1962), which would have embraced many individual rainfall events, such that local variability associated with individual precipitation events is likely to disappear when the input associated with a large number of precipitation events are averaged.

Ideally, a technique that is based upon a tracer such as plutonium or ^{137}Cs that falls out in rainfall is best suited to application in open terrain where the fallout can

be realistically assumed to be spatially homogeneous. In contrast, both the case study sites discussed in Chapters 5 and 6 are typical forested terrain where spatial heterogeneity in fallout plutonium distribution is possible due to interception and subsequent redirection of rain by the canopy. Evidence of such spatial variation in ^{137}Cs inventories at undisturbed forested sites has been reported by Wallbrink *et al.*, [1994]. The variation can be attributed to the mix of species in a forest that lead to varied interception rates of the fallout radionuclide due to different leaf areas and densities. Alternatively, the canopy could redirect some of the rain down the stems of plant, which tends to concentrate the radionuclides around the tree trunks. Clearly, under such circumstances the best approach is to collect several samples over an extended area at a single reference site or to sample multiple reference sites and to average the results in order to reduce the effect of local spatial variability on the reference inventory level.

(ii) Preferential mobility of soil fractions

The denudation of surface soil may be associated with preferential mobilisation of specific grain size fractions (fine versus coarse) or components (mineral versus organic) of the soils. Generally, in the process of quantifying the soil loss using the measured inventory, the preferential partitioning of radionuclides (tracer) between soil components or size fractions is ignored for simplicity. This could lead to an over or under estimation of the loss of soil, and might be expected to be more significant in forested terrain where the surface litter layer intercepts a large proportion of the fallout materials. It is therefore important to address the issue of partitioning of the radionuclides between the organic and mineral fraction. Thus it is essential to have a clear understanding of plutonium behaviour in term of its affinity toward the specific soil components in order to interpret the measured data appropriately. This issue is further addressed in Chapter 5, section 5.4.

Chapter 3 Methodology and experimental work

This chapter outlines the methodology employed in this study. It includes the procedures pertaining to field sampling, sample preparation and AMS operation, and the approach to translating the experimental data in terms of plutonium concentration into soil loss. It also covers the experimental investigations that were undertaken to explore possible improvements to the efficiency of the overall sample preparation process.

3.1. Sampling

Soil / sediment samples were collected from two study areas, located within New South Wales (Burra Creek catchment) and the Australian Capital Territory (Cotter River catchment). Three sampling field trips, each with a similar sampling strategy, were carried out during the course of this project. The main strategy was focused on obtaining information on the total inventory and the depth-distribution of the fallout plutonium. This was to allow comparison of measured inventories (total activity per unit area) at individual sampling sites with a reference inventory from an 'undisturbed site' that represents the cumulative input from atmospheric fallout within the area. At most sampling sites, a pit was excavated down to the top of the underlying saprolite. Typically the pits were ~20-30 cm in depth. Loose surface vegetation and leaf litter were cleared, and representative soil samples were then taken from a vertical face of the pit in 3-5 cm depth increments (Figure 3.1a). Surface soils were also collected with a trowel at specific sites in the Cotter catchment. Usually, multiple samples were collected over an area and were combined in order to produce a composite sample that was representative of the area. In addition, sediments were collected from gullies and creek banks, and again multiple samples were combined to obtain a representative sample.

Although it would have been possible in principle to have determined the average density of each sample from a pit by carefully measuring the dimensions of the sample, and accounting for any losses due to material falling to the bottom of the pit, in practice this was not done. Since knowledge of the density is crucial when converting plutonium concentrations in atoms/g to an inventory in atoms/cm²,

separate sampling specifically to obtain the density was required. In future, the sampling protocol will be adapted so that both density and plutonium concentrations will be available for the same material. Two sampling procedures were employed to determine soil density.

1. The first involved three techniques to sample the soil at different depths. For the top 10 cm, a scraping tool within a rectangular metal frame (see Figure 3.1b) of dimension 35 cm x 21 cm was used to sample in 2 cm increments. A metal tube of internal diameter 10 cm was then driven to a depth of 5 cm and the enclosed soil was removed with a small hand auger to sample the 10-15 cm interval. Finally, a 5 cm diameter polythene tube was driven in as far as it would go in order to sample the soil below 15 cm. This tube was dug out, and the soil transported in the tube.
2. The second procedure involved the use of several metal tubes of different length (3 cm, 5 cm, 8 cm, 10 cm and 15 cm), each of internal diameter 3.5 cm. Based on the depth interval sampled at the preceding sampling trips, a combination of different length metal tubes were driven into the surface of the ground and the enclosed soil removed to sample the top 10 to 15 cm (see Figure 3.1c). The top layer soils were then removed with a spade in order to sample the soils that were below 15 cm using the metal tube of suitable length.

a(i)



a(ii)



Figure 3.1a: Typical sampling process. Photograph (i): A paint-scraper was inserted horizontally at a known depth and a metal ruler was used to cut the outline of a block of sample. Photograph (ii): The paint-scraper was used as base support to transfer the soil sample from the pit to a sample bag.

b(i)



b(ii)



Figure 3.1b: Soil bulk density measurement – Procedure I. Photographs (i-ii): A set of sampling tools used for the purpose of soil bulk density measurement. It includes a scraping device, a metal cylinder (with cap for hammering), and auger.

c(i)



c(ii)



Figure 3.1c: Soil bulk density measurement – Procedure II. Photograph (i): A stainless steel tube was driven into the ground for the purpose of soil bulk density measurement. Photograph (ii): A paint scraper was inserted to the base of the stainless steel tube to prevent the sample from falling out.

3.2. Sample preparation

Several sample preparation techniques for determining plutonium in soils and sediments have been reported. Specifically the technical document [BS ISO 18589-4, 2009] published by the International Organisation for Standardization, is intended for the determination of plutonium radioactivity in soil by alpha spectrometry for environmental study purposes. It contains a detailed description of the plutonium desorption methods, broadly classified into either simple leaching in nitric acid or dissolution in a mix of acids. In some cases, fusion with a flux such as lithium borate is required to digest the sample. The fusion method is known to produce a high salt content that may complicate the plutonium purification process [Nygren, 2003].

In this project, the procedure adopted is a modified form of the leaching method used by Everett *et al.*, [2008] which has been adapted for AMS measurements. It closely resembles the simple nitric acid leaching procedure described in the ISO document. The method uses nitric acid to leach the plutonium from the surfaces of the soil or sediment grains, and has been further developed to optimise the overall sample preparation process. Global fallout plutonium that is present in soil is easily and readily leachable in nitric acid [Krey and Bogen, 1987; Sill, 1975] since it is typically comprised of small particles in the nanometer range which are readily dissolvable. Hence the acid leaching method employed should not compromise the full recovery of plutonium from the sample. It is noted, however, that there are studies which show that plutonium may convert into a refractory plutonium oxide compound when it is subjected to high temperature ($\sim 1000^{\circ}\text{C}$) [Sill, 1975]. More complex treatment would be required to separate the plutonium in this case. Plutonium can be incorporated into fused silicate particles, which are themselves highly refractory and may be present close to an explosion site, but such compounds are not expected to contribute to global fallout [Krey and Bogen, 1987]. Sill [1975] highlighted that the exceptionally high temperature in the range of million degrees, in a nuclear explosion would certainly not permit the existence of the more highly oxygenated and refractory plutonium compounds. Recent work by Tims *et al.*, [2013] shows that tropospheric fallout from the British nuclear tests in Australia (Maralinga) are contributing to the plutonium inventory in large parts of the

continent. However the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio derived from the samples that were collected in this project indicated that the source is mainly originated from global fallout. Hence the acid leaching procedure is suitable to apply on the samples.

The original procedure was as follows:

- (i) A known amount (~ 4 pg) of ^{242}Pu spike was added to typically ~ 4 g of dried and ground sample.
- (ii) The spiked sample was dried for 12 hrs (minimum) at 70°C before ashing at 450°C for 8 hr to remove the organic components, leaving only the soil/sediment matrix behind.
- (iii) Plutonium was leached for 24 hrs in 15 ml of 8M nitric acid on a hotplate at 70°C , and the solution was separated by centrifugation.
- (iv) Typically 1 g of sodium nitrite (oxidising agent) was added to ensure that the plutonium was in the required +4 valence state.
- (v) The solution was then loaded on to an anion exchange column of 7 mm diameter, packed with ~ 1.7 g of BioRad AG, 1-X8 100-200 mesh chloride resin. Contaminating elements such as uranium and thorium were removed by sequential elution with 25 ml of 8M nitric acid followed by 70 ml of 12M hydrochloric acid. Plutonium was finally eluted from the column with 25 ml of warm 0.1M ammonium iodide in conc. hydrochloric acid solution. The elutant was taken to dryness over a hot plate at 85°C .
- (vi) Further purification of the plutonium-containing residue was carried out with the addition of small amounts of conc. nitric and hydrochloric acid to remove iodine and ammonium nitrate respectively, and the solution was evaporated to dryness.
- (vii) The final residue was then re-dissolved in conc. nitric acid and iron (~ 1 mg) in the form of iron nitrate solution was added. After drying down, the resulting solid was converted to iron-oxide by baking at 800°C in a furnace for 8 hr. Finally, the iron-oxide material was mixed with silver powder, in the ratio 1:4 by mass, and pressed into an aluminium sample holder.

3.2.1. Modified procedure

A detailed step-wise description of the modified procedure, including pre-treatment process is outlined in Appendix-A1. In brief, three main improvements were made to the original procedure outlined above:

- (i) the sample size was increased from 4 g to 20 g,
- (ii) the ²⁴²Pu spike / tracer was added to the sample after the ashing process, and
- (iii) both silver nitrate and iron nitrate were added to the final solution before drying down and baking.

The increase in sample size was motivated by a desire to improve the statistical precision of the plutonium measurements by increasing the count rate. The latter modifications were designed to facilitate the preparation process. Test samples were prepared and compared using the original and modified procedure. The overall results as shown in Table 3.1 are in good agreement in terms of the deduced ²³⁹⁺²⁴⁰Pu activities, thereby validating the modified procedure.

Table 3.1: Experimental results obtained from the sub-samples of CDP 72-75 (Cotter Dam pit, 72-75 cm), using the original (O) and modified (M)^a procedure

Sample code	²³⁹⁺²⁴⁰ Pu (mBq/g)	²³⁹ Pu (counts/sec)	LOI (%)	Experimental parameters		
				Ashed sample size (g)	Ashing duration (hr)	Amount of leaching acid (ml)
Test-1 (O)	0.531±0.015	6	21	4	8	15
Test-2 (M)	0.544±0.019	7	22	4	8	15
Test-3 (M)	0.544±0.008	65	23 ^b	20	16	100

^a Modified procedure include ashing the sample before adding the ²⁴²Pu spike and adopting the (Fe-Ag) dry down technique.

^b Only 16% of LOI (loss on ignition) was achieved when the 20 g sample was ashed for 8 hr.

Increase of sample size

The increase in the sample size ultimately required other changes to the sample preparation protocol. For instance, more nitric acid (~100 ml) is needed for the leaching process. This generates a larger volume of leached solution that must be passed through an ion exchange column. Consequently, to minimize the possibility of getting the column blocked, an additional filtration step was introduced into the procedure. This helps to remove any fine suspended material from the leached solution that cannot be effectively removed by the centrifugation process. Cellulose filter paper was used because it gave an adequate flow rate and was sufficiently resistant to the 8M leaching acid. Although teflon membrane or glass-fibre type filter paper might have been preferable from the point of view of their durability and inert nature, the flow rate through them was found to be slow. It is noted that the plutonium tracer was added prior to the filtration process and thus any potential loss of plutonium onto the filter paper will affect all three plutonium isotopes equally and hence will not affect the isotope ratios from which the concentrations are derived.

The required ashing duration depends on the amount of organic material present in the sample as well as the geometry of the container. Thus the increase in sample size also extended the duration for the ashing process. Typically 16 hr is sufficient to ensure the complete removal of the organic component in a ~20 g sample. Experience showed that samples that had completely ashed were usually characterised by a distinct light yellowish orange-pigmentation. Occasionally, soot was present in the ashed sample which could be easily removed by further ashing. Un-removed soot tends to turn the leached solution a dark-tea colour, making it difficult to determine a change in the colour of the solution when the oxidising agent sodium nitrite is added. In practice sodium nitrite is added until the solution turns bluish-green due to the formation of nitrous acid which is deemed as an end-point indicator. The presence of soot makes the colour detection difficult and this may lead to an excessive amount of sodium nitrite being added. Unreacted sodium nitrite creates an effervescence during passage through the ion-exchange column and may lead to blockage in the column.

Addition of ^{242}Pu spike / tracer – after ashing versus before ashing

The ashing process essentially incinerates and removes the organic components that were present in the samples. This is intended to release any of the plutonium that was incorporated into or bound on to organic material, making it accessible to the leaching acid. Equally importantly, it removes organic compounds that may otherwise have complicated the plutonium separation process. However there is a concern that the ashing process might lead to the possible loss of plutonium along with the removal of organic components. In order to investigate this, experiments were carried out on samples where the plutonium tracer was added either before or after the ashing process. The agreement in the results as shown in Table 3.1, indicated that the ashing process leads neither to loss of plutonium nor to the formation of refractory plutonium that is not accessible to leaching.

In the original protocol, the tracer was added to the sample contained in a baking crucible before ashing was carried out. After the ashing process, the sample was transferred into a 30 ml Teflon vial to leach the plutonium using nitric acid. Additional nitric acid was then added to the crucible and heated on a hot plate for ~1 hour before adding the solution to the Teflon vial containing the sample. This was to ensure that no tracer or residual plutonium was left behind in the crucible. If instead, the tracer was added directly to the ashed sample only after it had been transferred to a Teflon beaker, this cleaning step could be, and was, omitted, leading to a simplified protocol.

Preparation of an intimate mixture of plutonium, iron oxide and silver

The original protocol for preparing plutonium samples for the ion source involved adding ~1 mg of iron as iron nitrate solution to the plutonium eluate from the ion exchange column, drying this down, and firing the resulting solid at 800°C to produce an intimate mixture of the plutonium dispersed in iron oxide. This was then mixed with silver powder. Iron is added to increase the bulk of the extracted plutonium for the ion source sputtering process, whereas the role of silver is to enhance the sample conductivity. The mixing was done on weighing paper with a spatula after breaking up the iron oxide by folding the paper over it and pressing with the spatula. This method was time-consuming, and there was potential for loss of sample due either to charging up of the iron oxide or small hard grains of iron oxide jumping off the paper during mixing. In addition, uneven mixing may lead to short-term variations in the PuO⁺ output from the ion source during the AMS measurement.

In view of the unsatisfactory aspects of mixing the iron oxide and silver after baking, an alternative method which produces an intimate mixture of plutonium, iron oxide and silver without the need for physical mixing was explored. This method was modelled on a method developed by Stone *et al.*, [2004] for ¹⁰Be and ²⁶Al AMS samples. In this improved procedure, silver is added in the form of a weighed amount (~ 7 mg) of silver nitrate crystals which dissolve readily in the ferric nitrate solution, prior to the drying down and baking process. Typical Ag:Fe ratios are 4:1 by mass. In the course of baking, the iron nitrate decomposes to iron oxide, and the silver nitrate to metallic silver. Initially, a problem was encountered in that some of the material would fuse with the glaze of the crucible during the baking process, thereby reducing the recovery of the plutonium-containing material. Although this problem had been observed previously in the original procedure, it was generally less severe. Four separate measures were taken to alleviate this effect. The first was to ensure that the samples were thoroughly dry before transfer to the crucible. Samples were dried in 30 ml Teflon vials in a heating block at 80°C for at least 48 hours. The second measure was to minimise the surface contact between sample and crucible. This was accomplished by taking care during transfer not to break up the small dried pellet of sample that had formed in the round or conical base of the Teflon vial. The third measure was to reduce the ramp rate of the baking oven so as to allow the

decomposition of silver nitrate to take place gently. Finally, it has been observed that the presence of ammonium nitrate enhances the severity of adhesion. Hence, care is taken to ensure complete removal of ammonium nitrate after the plutonium elution step, using an excess amount of hydrochloric acid if required. As shown in Figure 3.2, a marked improvement in terms of the final recovery has been achieved through this combination of measures and sample handling skill gained through experience.

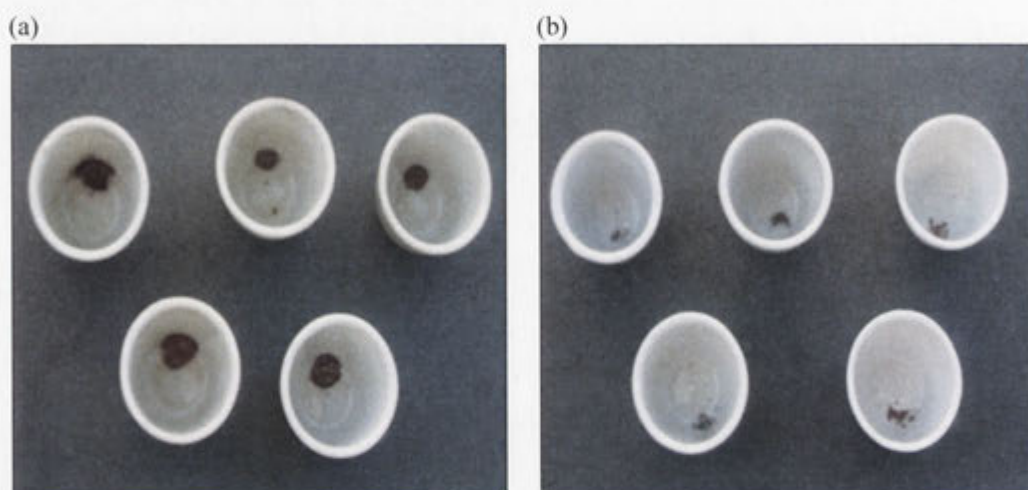


Figure 3.2: Stains of residues left on the crucible surface that could not be removed after the baking process. Photograph (b) indicates a marked improvement after adopting the optimum operational parameters specified above.

3.3. Methods of detection

A number of different techniques are available for the measurement of the plutonium isotopes. Traditionally the most widely used has been the radioanalytical technique that involves α -particle spectroscopy (ideal for ^{238}Pu) or liquid scintillation radiometry (typical for the β counting of ^{241}Pu) [Becker *et al.*, 2004]. The major advantage of α -particle spectrometry is the relatively low equipment cost and the high sensitivity due to low background and the high selectivity for α particle against other types of radiation [Vajda and Kim, 2010]. The efficiency of radioanalytical techniques depends upon the half-life of the radioisotope of interest and feasible counting times. Hence in the analysis of long lived radionuclides such as $^{239,240}\text{Pu}$, long counting times are needed. These can range from days to several weeks depending on the required sensitivity and precision [Boulga *et al.*, 2003]. In α -particle spectrometry, owing to the short range of α -particle radiation, the typical source thickness should not exceed a few μm , otherwise the alpha spectrum becomes degraded [Vajda and Kim, 2010]. Hence it requires a complete separation of plutonium from the sample components through tedious radiochemical procedures in order to obtain a desirable thin alpha source. In addition, the determination of the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio by α -particle spectroscopy is difficult due to the closeness of the α -particle energies of ^{239}Pu and ^{240}Pu (5.155 MeV and 5.168 MeV respectively) which are not resolved by the silicon detectors that are employed for α -particle spectroscopy. Hence, in practice, only the sum of the ^{239}Pu and ^{240}Pu activities is measured, and the concentrations are typically reported as $^{239+240}\text{Pu}$ Bq/kg. This difficulty can be partially surmounted in favourable cases by using silicon detectors that have been optimised for the best possible resolution together with suitable deconvolution software [Povinec, 2004; Vintro *et al.*, 1996]. Based on realistic counting periods, the detection limit of this technique is estimated to be $\sim 50 \mu\text{Bq}$ [O'Donnell *et al.*, 1997]. This limit corresponds to $\sim 20 \text{ fg}$ of ^{239}Pu .

Mass spectrometry techniques

Mass spectrometry is an alternative technique that counts the atoms themselves rather than depending on the radioactive decay process. It is applicable to both stable and unstable isotopes, and can be highly advantageous for the determination of radionuclides with low specific activities such as plutonium. In mass spectrometry the atoms in a sample are converted to ions and then separated according to their mass under the influence of electric and magnetic fields. This allows the specific isotopes of interest to be analysed individually. Several advanced mass spectrometric techniques such as accelerator mass spectrometry (AMS), thermal ionisation mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS) and resonance ionisation mass spectrometry (RIMS) have been developed to provide accurate isotopic ratio information and ultra trace level measurements of plutonium. Among the plutonium isotopes, the analysis of ^{238}Pu is the most problematic and least favourable. The main technical issue is the severe interference from its naturally-occurring isobar ^{238}U , which cannot be effectively resolved by mass analysis, and is always present in the ion source and /or in the sample itself. Additionally, the analysis of ^{239}Pu is also troubled by the presence of $^{238}\text{UH}^+$ ions and the tailing of $^{238}\text{U}^+$ ions. Other limiting factors that could affect the accuracy of plutonium determination include interference from molecular ions of lead or rare earth elements, which can be expected in the actinide mass range (e.g., PbO_2^+ , PbN_2^+) [Becker, 2005]. Povinec [2004] reported that the precisions of $^{239+240}\text{Pu}$ measurements achieved by AMS, ICP-MS and α spectrometry were 10%, 7% and 5% respectively. AMS and RIMS are superior to ICP-MS with respect to the detection limit of plutonium isotopes, and TIMS is better than sector-field ICP-MS in the precision of plutonium isotopic ratio [Kim *et al.*, 2007]. The detection limits of the various mass spectrometric techniques are shown in Table 3.2.

Table 3.2: The detection limits of various mass spectrometry techniques for the determination of plutonium isotopes in environmental samples

Technique	Detection limits (^{239}Pu)	References
AMS	$< 10^6$ atoms	Ketterer and Szechenyi, 2008
RIMS	10^6 to 10^7 atoms	Ketterer and Szechenyi, 2008
TIMS	10^7 to 10^{11} atoms	Kurosaki <i>et al.</i> , 2006

(i) Thermal Ionisation Mass Spectrometry (TIMS)

In TIMS, as its name implies, atoms are ionised as they are released from a metal surface (usually rhenium) that is heated to high temperature (800-2000 °C) and the ions of different mass are accelerated to energies of a few keV and separated by a magnet. The technique of TIMS is well established for the accurate and precise measurement of actinide ratios and has been recognised as the reference method for the certification of many analytical standard materials. Most International Union of Pure and Applied Chemistry (IUPAC) recommendations for the standard atomic weights are based on isotope abundance measurement by TIMS [Walczyk, 2004]. The early study of plutonium in the environment using TIMS required the isolation of plutonium from relatively large, kg-size soil samples in order to counter the low ion source efficiency [Ketterer and Szechenyi, 2008]. Over the years, improvements in ion-source efficiency have allowed the utilisation of smaller amounts of raw sample. This is demonstrated by the work of Kelley *et al.*, [1999], who used as little as ~1 g of soil sample in their studies of the global distribution and inventories of fallout plutonium. Although TIMS offers a higher sensitivity than ICP-MS for plutonium isotopes and interferences due to U traces are less significant [Vajda and Kim, 2010], the sample preparation process is time-consuming, particularly to produce the measurement source in the form of a thin filament. Further, high quality chemical separation of the analyte and the use of ultra pure reagents are needed to avoid isobaric contaminants. In terms of operation, careful heating is also essential to obtain a stable ion beam and the ionisation efficiency (typically < 1%) is not as impressive compared to ICP-MS.

(ii) Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

In ICP-MS, the sample is volatilised and injected into a plasma (Argon) where it is ionised at a temperature as high as 10,000 K. The merits of this technique include good sensitivity, short analysis time, reasonable cost and relatively straightforward operation [Becker, 2005, 2004]. Nygren *et al.*, [2003] highlighted that the common single ion collector ICP-MS that utilises either the quadrupole or sector field focusing systems is generally less precise than TIMS due to the instability of the ion source. However multi-collector devices that allow simultaneous detection of the different isotopes have been shown to reach the same level of precision as TIMS. Of the single collector devices, the double-focusing sector-field ICP-MS offer higher mass-resolution and provides higher sensitivity compared to the conventional quadrupole based system.

Over recent years, the analysis of plutonium using ICP-MS has been increasing steadily as a result of the improvement of detection limits based on new designs in the detection system, such as the dynamic reaction cell ICP-MS, double focusing sector-field high resolution ICP-MS and multi-collector ICP-MS [Kim *et al.*, 2007]. Additionally the development of easy and compatible sample loading systems by means of direct and indirect injection of aqueous or solid sample is also a motivating factor. Although a plasma ion source offers a high ionisation efficiency, other atomic and molecular ions are also formed in the plasma which can potentially interfere with the ion species of interest. Thus in spite of the significant advances in ICP-MS, the accurate determination of plutonium is still hampered by polyatomic interferences expected in the mass range of 239-242, and the tailing of ^{238}U . Moreover, demanding chemical separation is essential in order to achieve reliable measurements for plutonium at concentrations between pg/g and fg/g that are typical of environmental soil and sediment samples. Kim *et al.*, [2007] noted that the effects of interferences from ^{238}U are relatively high in comparison with those from other interferences, despite the best efforts of the chemist to remove uranium from the sample.

(iii) Resonance Ionisation Mass Spectrometry (RIMS)

The basis of the RIMS technique is the selective ionization of atoms or molecules of a particular element such as plutonium by resonant multi-photon excitation using lasers. Undesirable species such as ^{238}U are not resonant and are therefore not ionised, thereby eliminating the associated isobaric interferences. Hence RIMS has the ability, for example, to determine the low abundances of ^{238}Pu present in the environment. The early work of RIMS for plutonium measurements was summarised by Ruster *et al.*, [1989]. These workers reported an overall atom counting efficiency of $\sim 2 \times 10^{-6}$ with a detection limit of ~ 1 fg for ^{239}Pu . Despite the apparent advantages of RIMS, its application is limited to only a number of specialised laboratories [Becker, 2005]. This could be due to high capital costs, especially for the laser system, and the requirement for a highly-skilled operator. Nevertheless, the introduction of easy-to-use and reliable solid state laser systems may simplify the RIMS technique in the near future [Wendt *et al.*, 1999].

(iv) Others

Other specialised forms of mass spectrometry, including Secondary Ion Mass Spectrometry (SIMS) and Glow Discharge Mass Spectrometry (GDMS) are less frequently used in plutonium measurement. Betti *et al.*, [1999, 1996] were among the few who successfully demonstrated the use of these techniques to analyse plutonium. Both techniques are important forms of 'solid-source' mass spectrometry that allows direct analysis of the sample material without the necessity of chemical separation or dissolution. This helps to reduce the possibility of contamination. The quantification of solid state mass spectrometry, however, is more difficult than in chemically treated samples, often due to the lack of suitable standard reference materials [Becker and Pickhardt, 2000]. Detection limits in the range of ng/g – pg/g have been achieved by optimising the integration time and mass resolution [Betti *et al.*, 1999, 1996]. SIMS has been used in nuclear forensic investigations to characterise and identify the origin of plutonium particles [Betti *et al.*, 1999]. It has a significant potential as a technique for studies of distribution and transport of 'hot' particles in the environment. Similarly, the GDMS technique can be employed for direct analysis in high plutonium activity samples, but it is unlikely to be suitable for analysis in raw samples at fallout level [Ketterer and Szechenyi, 2008].

3.3.1. Accelerator mass spectrometry (AMS)

AMS is a highly sophisticated analytical technique that incorporates a tandem electrostatic accelerator into the mass-spectrometric system. The advantage of AMS compared to TIMS and ICP-MS is the ability to provide a high level of discrimination against molecular interferences. AMS is able to suppress the contribution of molecular isobars (e.g., $^{238}\text{UH}^+$ for ^{239}Pu) by many orders of magnitude by accelerating the ions to MeV energies and passing them through a gas or foil stripper to remove electrons. If three or more electrons are removed, the resulting positively-charged molecules are unstable and rapidly dissociate into their component atoms. The ability of AMS to offer immunity to molecular interferences enables it to be used for ultra-high sensitivity detection of actinides, such as plutonium isotopes, down to sub-femtogram levels. Technical complexity and cost are the main issues that have prevented the widespread use of AMS for plutonium measurements [Tuniz *et al.*, 1998], but with the demonstration that plutonium could be measured using smaller (<1 MV) accelerators [Fifield *et al.*, 2004], and a growing number of plutonium-capable small AMS systems, these inhibiting factors are diminishing in importance.

In the course of this study, plutonium measurements were carried out using the 14UD pelletron tandem accelerator at the Australian National University (Department of Nuclear Physics). The methodology for measuring plutonium using AMS is well established and is described in Fifield [2008]. The operation is best described with reference to Figure 3.3, which shows the schematic layout of the tandem accelerator.

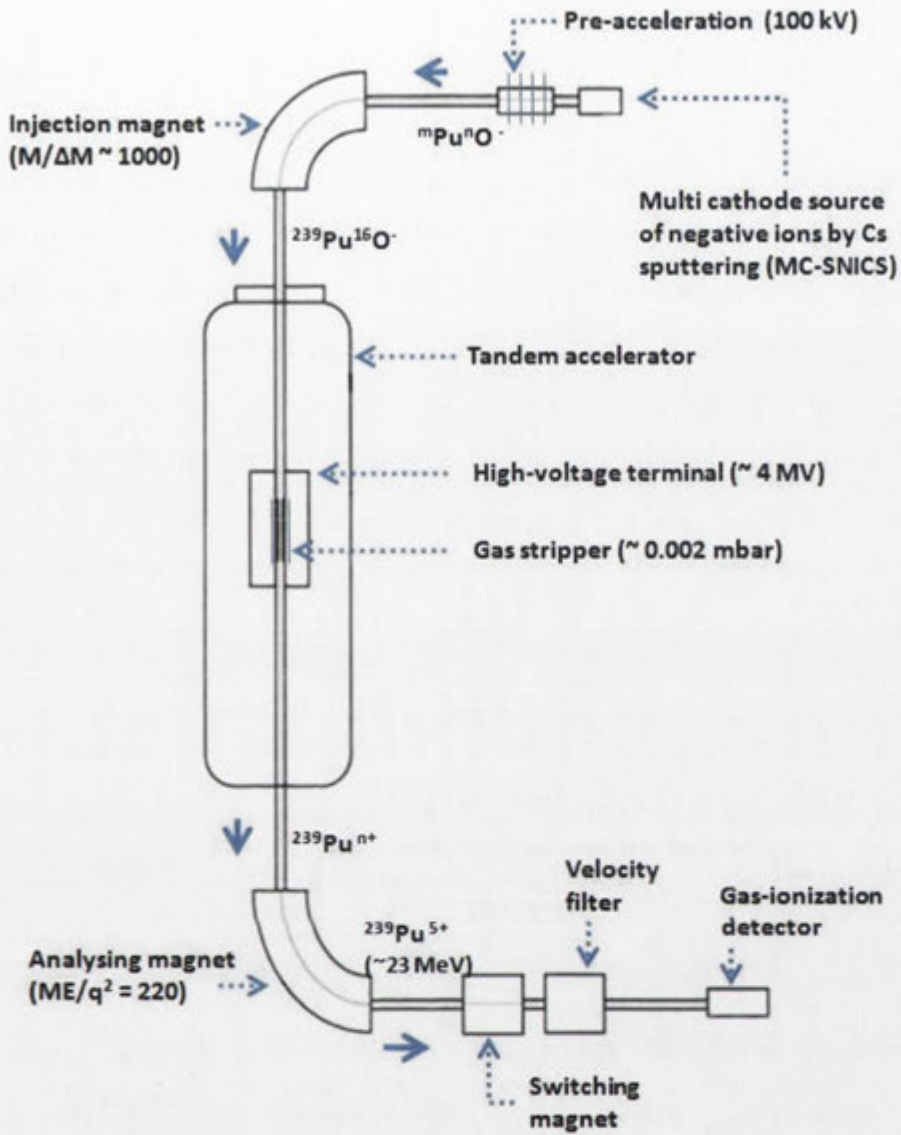


Figure 3.3: AMS system for the measurement of plutonium isotopes.

Ion source (MC-SNICS)

Briefly, negative ions are created from the sample at the ion source using a Cs^+ beam to sputter atoms out of the sample and Cs vapour as an electron donor. A typical ion source (Figure 3.4) consists of a heated Cs reservoir and a delivery outlet located between the cooled cathode and the heated ionizer. During operation, Cs vapour condenses on the surface of the sample while a portion is ionized on a hot hemispherical tantalum surface. The ionized Cs^+ accelerates towards the cathode, sputtering atoms from the sample in the cathode holder through the condensed Cs layer. The Cs atoms on the surface of the sample serve as electron donors to the sputtered atoms, thereby forming negative-ions. The negative-ion beam intensity depends on the Cs^+ ion beam intensity which can be optimized by increasing the temperature of the Cs oven and/or the current to the ionizer heater, while still allowing the condensation of Cs vapour on the sample surface to take place.

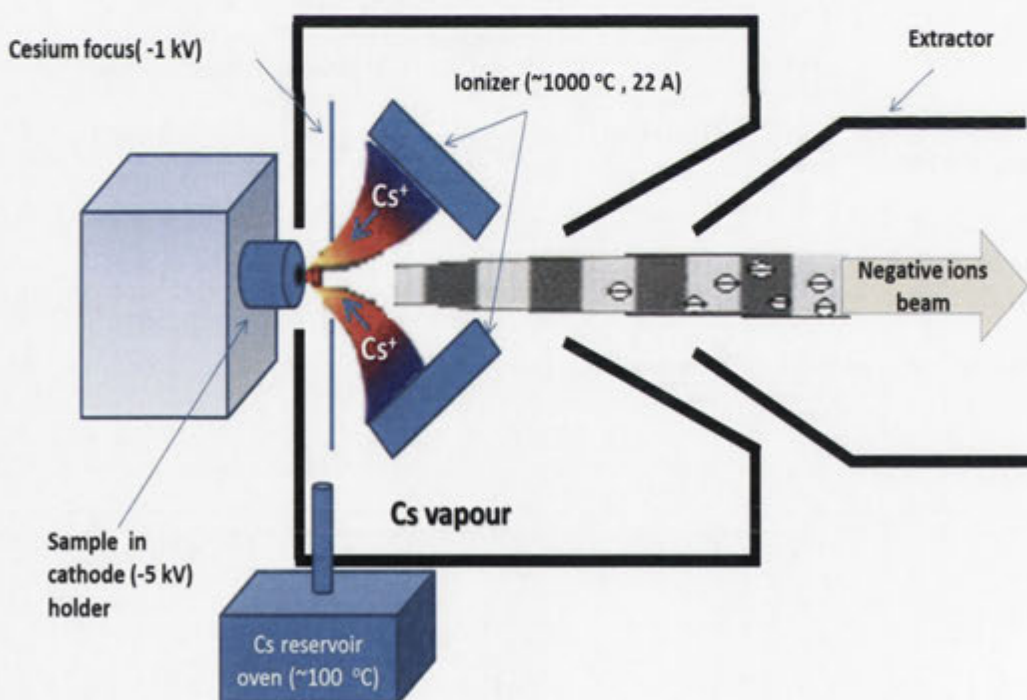


Figure 3.4: Schematic diagram of a typical ion source (Multi Cathode-Source of Negative Ion by Cs Sputtering).

[Source: National Electrostatics Corp's website, <http://www.pelletron.com/source.htm>]

Acceleration, mass analysis and detection

The negative ions are pre-accelerated through ~100 kV, enter an injection magnet (90° dipole bending magnet) and are deflected according to their radii of curvature given in equation (3.1):

$$r = \frac{\sqrt{2mE}}{Bq} \quad (3.1)$$

where m is the mass of the ion, E is the energy, q is the charge on the ion and B is the magnetic field strength. At this stage all the ions have the same energy and charge state (-1), and different masses can be selected for injection into the accelerator by varying the magnetic field. PuO^- molecular ions instead of Pu^- atomic ions are selected due to their relatively higher intensity (two orders of magnitude higher). These negative ions are then injected into the accelerator and accelerate towards the positive high-voltage terminal. The molecular species are subsequently dissociated and stripped to Pu^{n+} ions by a differentially pumped gas stripper located in the accelerator high-voltage terminal, which is operated at ~4 MV for plutonium measurements. Multiply-charged plutonium atomic ions are then further accelerated to the exit of the accelerator and separated by a 90° analysing magnet. Unlike the injection magnet, the analysing magnet is operated at a constant magnetic field strength. It has the ability to bend ions with mass-energy product (ME/q^2) up to 220 MeV-amu and, for plutonium measurements, it is operated at maximum field. Plutonium ions of a specific charge state (+5) and energy (~23 MeV) are selected by the analysing magnet for subsequent analysis. The choice of charge state is determined by the optimal compromise between stripping yield and transmission through the accelerator. For higher charge states (≥ 3), the stripping yield decreases with increasing charge state. For example, the yield of Pu^{5+} is a factor of two higher than Pu^{6+} . Although the stripping yield to Pu^{4+} is higher than to Pu^{5+} , it requires the accelerator to operate at 3 MV in order for the analysing magnet to deflect the ions appropriately. At this voltage, transmission through the large 14UD accelerator is significantly reduced, even relative to Pu^{5+} at 4 MV.

Following the analysing magnet, the Pu^{5+} ions pass through a Wien (velocity) filter which allows ions of definite velocity to pass un-deflected into a propane-filled ionization detector. The combined effect of both analysing magnet and velocity filter effectively prevents any interfering background ions with different M/q ratio to the Pu^{5+} ions of interest from reaching the detector. Ions with closely similar M/q ratios to the Pu^{5+} ions will, however, reach the detector, but are readily separated from the plutonium ions on the basis of their energy (see Figure 3.5). The detector employed is equipped with a $0.7\text{ }\mu\text{m}$ mylar window of diameter 13 mm. It has a resolution of $\Delta E/E = 3\%$ which is adequate to separate plutonium from the other lighter-mass, lower-charge state background ions.

Typical energy spectra for the $^{242,240,239}\text{Pu}$ isotopes are shown in Figure 3.5. These isotopes were measured using a slow cycling procedure where switching between the individual isotope was effected by changing the injection magnetic field strength, the terminal voltage of the accelerator and the electric field of the Wien filter. Typical measurement durations were 1, 3 and 2 minutes for ^{242}Pu , ^{240}Pu and ^{239}Pu respectively. A complete measurement usually consists of two cycles, and ends with a third ^{242}Pu measurement. The raw data from the AMS measurement are the $^{239}\text{Pu}/^{242}\text{Pu}$ and $^{240}\text{Pu}/^{242}\text{Pu}$ atom ratios which are readily converted into ^{239}Pu and ^{240}Pu concentrations (atoms/g of sample) using the known mass of ^{242}Pu spike added to each sample and the mass of soil that was leached. In order, however, to facilitate the comparison with earlier studies that employed conventional radioanalytical methods, which are unable to discriminate between ^{239}Pu and ^{240}Pu , the concentrations are also expressed as the sum of the specific activities of the two isotopes in mBq/g.

In this thesis, the measurement of $^{239}\text{Pu}/^{242}\text{Pu}$ and $^{240}\text{Pu}/^{242}\text{Pu}$ atom ratios of a certified reference material (UKAEA Certified Reference Material No. UK Pu 5/92138) is used to validate the analytical method and to determine the performance characteristic of the AMS system.

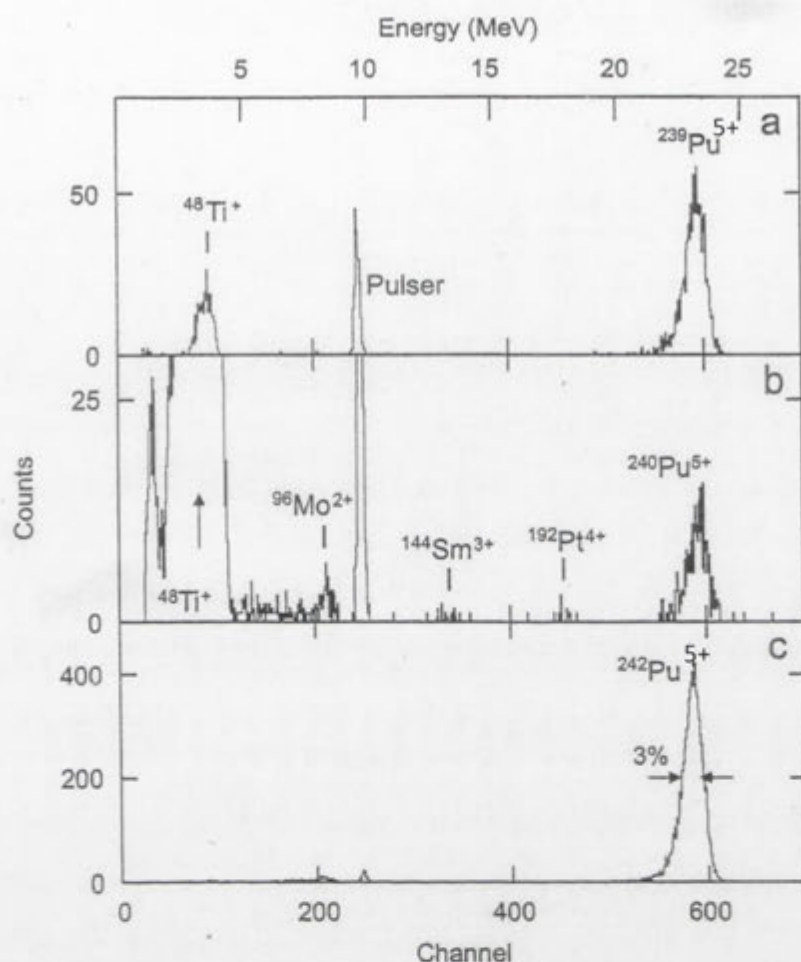


Figure 3.5: Typical energy spectra taken for (a) ^{239}Pu , (b) ^{240}Pu and (c) ^{242}Pu measurements from a soil sample. ^{242}Pu ($\sim 4\text{pg}$) was added to the sample as a spike for normalisation purposes and the pulser is used to monitor dead-time in the electronics and data acquisition systems. The ^{240}Pu spectrum in particular, show peaks at lower energy that arise from fragments of molecules that were dissociated in the gas stripper and subsequently passed the high energy analysis.

3.4. Quantification of soil loss / gain

Plutonium inventories, in mBq/cm^2 are derived from plutonium concentrations per unit volume (mBq/cm^3) in each depth interval, using measured plutonium concentrations per unit mass (mBq/g) and dry bulk soil densities (g/cm^3), determined from dry sample mass and *in situ* volume. To be consistent, both the density and the plutonium concentrations (mBq/g) should be expressed relative to the unashed mass. All measurements in this thesis are so expressed unless otherwise stated.

The loss (or gain) of plutonium inventory from a study site i , $N_{\text{loss/gain}}^i$, is calculated as the difference between the measured plutonium inventory from the study site i , N_{measured}^i , and the plutonium inventory from the reference site, $N_{\text{measured}}^{\text{ref}}$ as:

$$N_{\text{loss/gain}}^i = N_{\text{measured}}^{\text{ref}} - N_{\text{measured}}^i \quad (3.2)$$

Although this result provides only qualitative information indicating that a study site had been subjected to either erosion ($N_{\text{loss}}^i > 0$) or deposition ($N_{\text{gain}}^i < 0$), it can be further translated into net soil loss / gain as outlined below.

Fallout plutonium is generally concentrated in the top ~ 10 cm of the soil, and falls off rapidly below that depth. The distribution of plutonium with depth in a soil column is most likely controlled by the movement of soil grains due to bioturbation activity by worms and ants or by movement down root channels. Hence, undisturbed profiles are likely to be similar in terms of the distribution of plutonium with depth. Therefore, where soil has been lost to erosion, a quantitative relationship can be established between the measured inventory and soil loss under the assumption that the plutonium depth profiles were originally the same at the reference and study site. Plutonium depth profiles in term of plutonium concentrations per unit volume (mBq/cm^3) in undisturbed soil may be approximated by an exponential function, $f(x) = ae^{-\beta x}$. The depth, D , of soil loss is then related to the measured inventory by the equation:

$$N_{\text{measured}}^i = \int_D^{\infty} f(x)dx = \int_D^{\infty} \alpha e^{-\beta x} dx \quad (3.3)$$

where the parameters α and β are determined from an exponential fit to the measured plutonium depth profile at the reference site. Combining equations (3.2) and (3.3) into the following expression (3.4) leads to equation (3.5) for D :

$$\frac{\text{Plutonium inventory at study site } i}{\text{Plutonium inventory at reference site}} = \frac{N_{\text{measured}}^i}{N_{\text{measured}}^{\text{ref}}} \quad (3.4)$$

$$= \frac{\int_D^{\infty} f(x)dx}{\int_0^{\infty} f(x)dx}$$

$$D = \frac{-1}{\beta} \ln \left(\frac{N_{\text{measured}}^i}{N_{\text{measured}}^{\text{ref}}} \right) \quad (3.5)$$

Equation (3.5) is used in this thesis to estimate the depth of soil loss at specific study sites.

The above treatment assumes that the soil depth profile of plutonium has not changed with time, and is equal to the profile at the present day. This is not strictly correct because the profile does evolve with time, from being essentially all at the surface immediately after fallout, to being distributed over a depth of 20 cm or more with an approximately exponential falloff at the present day. Thus it is expected that erosion that occurred close in time to the fallout period would have removed substantially more plutonium than would the same amount of erosion occurring today. The model does not take this into consideration and hence tends to overestimate the erosion.

3.5. Experiments

Simplicity was recognised as the primary consideration in any modifications to the protocol that were intended to enhance the efficiency of sample preparation. To ensure that the modified protocol did not compromise the reproducibility of the measurements, several experiments were carried out independently to address and investigate the following issues:

- (i) Sample homogenisation
- (ii) Tracer treatment
- (iii) Redox process

Sample homogenisation

Sample homogenisation is critical to ensure that the materials under investigation are mixed and distributed randomly throughout the sample, and that any subsample is therefore representative of the sample as a whole. It is noted that the original procedure specified that all samples be ground to achieve homogeneity. However in this project, all the sediments and some of the soil samples were not ground in order to retain the option of separating them into different particle sizes. Information on the distribution of plutonium among the different particle sizes is crucial for apportioning the sources of sediment between surface and sub-surface (gully) erosion, for example, since the distribution of grain sizes is different for soil and sediment, and since plutonium concentration can vary with grain size.

It was initially anticipated that the sediment samples from the Cotter Dam pit would be well-mixed in the natural environment under the action and influence of flowing water. Hence in the early stage of the project, no attempt was made to homogenise the entire bulk sediment samples, which each consisted of a few kilograms of sediment. Rather analyses were carried out on sub-samples obtained randomly from the bulk sample. Each subsample was, however, thoroughly homogenised before splitting for the various test measurements. As discussed in section 3.5.1, discrepancies among the plutonium concentrations from sub-samples indicate that the assumption of good mixing may not in fact be valid. Unlike the

sediment sample, individual soil samples were typically less than 500 g each. Hence all the soil samples that were not ground were ‘mixed’ thoroughly in bulk. Mixing was carried out by intense shaking and stirring of the materials vigorously in a large sampling bag.

To assess the effectiveness of this manual mixing process, the plutonium concentrations obtained from well-mixed bulk soil and sediment samples were compared with values derived from measurements on the full range of grain sizes. After a subsample had been removed from the bulk soil (well-mixed) for the bulk plutonium measurement, the remaining bulk sample was sieved and separated into a full range of grain sizes samples. A subsample of each individual grain size sample was measured for plutonium concentration.

The agreement in the results as shown in Table 3.3(a) and (b) indicates that representative plutonium concentrations can be obtained by mixing the sample (applicable to both soil and sediment) in bulk without grinding.

Table 3.3(a): Experimental results obtained from the soil sample: Cref-A-5/10 (Cotter catchment reference site pit A, 5-10 cm) in different ranges of grain size, separated using standard dry sieving technique

Sample code	Particle size (μm)	LOI (%)	Bulk % component	$^{239+240}\text{Pu}$ (mBq/g)
CREF-A-5/10 [250]	$250 < x < 3\text{mm}$	9	50	0.141 ± 0.008
CREF-A-5/10 [125]	$125 < x < 250$	15	22	0.181 ± 0.010
CREF-A-5/10 [64]	$64 < x < 125$	14	16	0.193 ± 0.010
CREF-A-5/10 [40]	$40 < x < 64$	12	9	0.198 ± 0.011
CREF-A-5/10 [<40]	$x < 40$	11	4	0.151 ± 0.009
Bulk $^{239+240}\text{Pu}$ (mBq/g) derived from the activity concentrations of the individual grain sizes:				0.163 ± 0.008
$^{239+240}\text{Pu}$ (mBq/g) measurement obtained from bulk sample (well mixed):				0.181 ± 0.013

Table 3.3(b): Experimental results obtained from the sediment sample: CDP-24/27 (Cotter dam pit, 24-27 cm) in different range of grain size, separated using standard dry sieving technique

Sample code	Particle size (µm)	LOI (%)	Bulk % component	²³⁹⁺²⁴⁰ Pu (mBq/g)
CDP-24/27 [250]	250<x<3mm	57	1	0.738±0.041
CDP-24/27 [125]	125<x<250	27	9	0.486±0.027
CDP-24/27 [64]	64<x<125	11	27	0.297±0.017
CDP-24/27 [40]	40<x<64	6	48	0.171±0.009
CDP-24/27 [20]	20<x<40	7	14	0.142±0.007
CDP-24/27 [<20]	x<20	8	1	0.208±0.011
Bulk ²³⁹⁺²⁴⁰ Pu (mBq/g) derived from the activity concentrations of the individual grain sizes:				0.234±0.013
²³⁹⁺²⁴⁰ Pu (mBq/g) measurement obtained from bulk sample (well mixed):				0.231±0.014

In addition, the results also highlighted that the plutonium concentrations vary significantly with grain size, particularly in the sediment sample. Generally, one would expect a higher plutonium concentration to be associated with the smaller size grains since the finer-grained materials have a relatively large surface area and thus are able to retain more plutonium than the coarser grains. But such a trend was not observed in either the soil or the sediment samples. Rather, plutonium concentrations in the sediment samples were found to decrease with respect to the reduction in grain size. Similarly the amount of organic materials present in the samples also decreased with the reduction in grain size. Subsequent investigations revealed that there is a strong correlation between the plutonium activity and the organic content of the sample. This is discussed in detail in Chapter 5, section 5.4.

A high proportion of organic materials were found to be present in the larger grain-size fractions of the sediment. This would be expected since the organic material is less dense than the mineral material, and thus a large size organic fraction would be prone to be mobilised and washed away, compared to the mineral faction of the same size.

The distribution in grain size was rather different in the soil and sediment samples. About 50% of the bulk soil samples were found in the 250 μm - 3 mm fraction, whereas 50% of the sediment samples were found in the 40 μm - 64 μm fraction. Clearly, finer particles are selectively transported through the river system. It is also noted that during the sieving process, careful inspection revealed that fine materials tend to aggregate and become larger fraction grains, particularly in the soil samples. This shows that the dry sieving method is an imperfect way to separate the sample grains into the respective size range fraction. Although the wet sieving and settling method employed by Everett [2009] is more likely to disaggregate the grains, it does not completely solve the 'agglomeration' issue.

Tracer treatment

In the original protocol, the sample is dried after adding the ^{242}Pu tracer. Presumably the drying process allows the tracer to bind to the soil/sediment surface via a similar mechanism to the fallout plutonium. This process is deemed essential as it helps to establish an equilibrium between the different oxidation states of plutonium that should be the same for both the tracer and the fallout plutonium. The current practice does not, however, ensure that the tracer is uniformly mixed with the sample before drying since typically only 0.2 ml of tracer solution is added and this wets only a small volume of the soil or sediment sample. This has been a concern as it allows the possibility of differential leaching between the tracer, which is attached to only a small subsample, and the fallout plutonium, which is spread throughout the sample. In order to check whether this might be an issue, test samples were prepared by adding an adequate amount of Milli-Q water (just enough to cover the sample) after dispensing the tracer. A careful stir of the resulting slurry produced a well-mixed tracer-laced sample, which was then gently dried down. This additional step has the significant disadvantage of requiring a much longer drying time (~2 days at 70 °C). The results are presented and discussed below.

It is also noted that drying of the sample after addition of tracer is not specified in the ISO 18589-4:2009 protocol. Rather, tracer is simply added to the solution after the addition of nitric acid, following which the sample proceeds to leach on a hot plate. This approach is not considered satisfactory since it requires 100% leaching efficiency which cannot be guaranteed. In the earlier part of the project, some of the analyses omitted the tracer drying step, and the leaching acid solution was added to the soil immediately after the tracer.

Results of experimental tests with the different tracer treatments outlined above are presented in Table 3.4. The three different methods are seen to yield equivalent $^{239+240}\text{Pu}$ concentrations, implying that neither the drying process nor complete dispersal of the tracer is critical. It appears that the highly acidic leaching environment is sufficient to create and guarantee an equilibrium condition between the tracer and fallout plutonium. Nevertheless, the ‘standard’ drying process is still adopted in the protocol as a precautionary measure to ensure that valence equilibrium

is maintained. On the other hand, the time-consuming procedure of completely wetting the sample to ensure uniform distribution of the tracer has not been adopted, on the basis that it should not be necessary provided that the soil sample has been well-homogenised.

Table 3.4: Comparison of the plutonium activity concentration between different tracer treatment procedures^a carried out independently on two different sediment sub-samples: CDP 60/63 and CDP 96/99 (Cotter dam pit, 60-63 cm and 96-99 cm respectively), measured in AMS wheel no. M416

Sample code	Tracer treatment procedure	²³⁹⁺²⁴⁰ Pu (mBq/g)
CDP 60/63-d	Dried, standard	0.316±0.016
CDP 60/63-d-m	Dried, MQ	0.294±0.016
CDP 60/63-w	Wet	0.325±0.017
CDP 96/99-d	Dried, standard	0.438±0.023
CDP 96/99-d-m	Dried, MQ	0.454±0.023
CDP 96/99-w	Wet	0.432±0.022

^aTracer treatment procedure:

- (i) Dried, standard – The tracer was added directly to the sample and dried before carrying out the leaching process. This is the standard protocol adopted in this thesis as specified in Appendix A1.
- (ii) Dried, MQ – The tracer was added directly to the sample, followed by copious amount of MQ water to cover the sample. The slurry solution was stirred thoroughly and dried before carrying out the leaching process.
- (iii) Wet – The tracer was added directly to the sample and immediately followed by the leaching process without drying the tracer.

Redox process

Plutonium is known to exist in different oxidation states (III to VI) in aqueous medium [see Chapter 2]. During the plutonium separation process, only the Pu(IV) species is effectively retained on the anion exchange column, while the III, V and VI oxidation states of plutonium are poorly retained, and pass through the column with the nitric acid. Such loss can be minimised by applying a reduction-oxidation (redox) cycle to optimise the Pu(IV) concentration and ultimately enhance the plutonium recovery in the anion ion-exchange separation process. A redox procedure involves an initial stage of reduction to convert plutonium in high oxidation states (IV-VI) into the III state, followed by an oxidation stage to convert Pu(III) to Pu(IV). This also ensures that the different plutonium isotopes (spike ^{242}Pu and fallout $^{239,240}\text{Pu}$) have identical oxidation-state distributions and are not therefore fractionated in subsequent chemical steps. Several reducing agents including ammonium iodide (NH_4I), ferrous sulfamate ($\text{Fe}(\text{NH}_2\text{SO}_3)_2$) and hydroxylamine ($\text{N}_2\text{H}_5\text{OH}$), and oxidizing agents such as sodium nitrite (NaNO_2) and hydrogen peroxide (H_2O_2) have been employed to manipulate the plutonium oxidation state.

Nevertheless in the standard protocol of Everett *et al.*, [2008], only a single oxidation step was performed prior to the ion exchange process. Since plutonium is known to exist preferentially in its III and IV states in acidic medium, a single oxidation step was deemed sufficient to ensure that essentially all of the plutonium was in the IV oxidation state before loading on to the anion exchange column. A single oxidation step cannot, however, guarantee identical oxidation-state distributions between the fallout $^{239,240}\text{Pu}$ isotopes and the ^{242}Pu tracer and thus the valence equilibrium condition may be affected.

Several experiments were carried out to explore this concern. In these experiments, the oxidation step (using NaNO_2) in the standard protocol was replaced by a redox procedure. Two independent redox procedures were used. One of these was adapted from the method used by Wilcken [2006] and utilised ammonium iodide as the reducing agent and sodium nitrite as the oxidising agent. The other procedure used by Child [2000], utilises ferrous sulfamate and sodium nitrite as reducing and oxidising agent respectively. The experimental results were then compared with

those obtained from the standard protocol, as shown in Table 3.5. Although there is a tendency for the redox treatments to yield lower $^{239+240}\text{Pu}$ concentrations, it is barely statistically significant, implying that the redox process is not critical and thus can be avoided. Moreover the procedure that involves the redox process tends to complicate the subsequent ion-exchange process. It is noted that a strong effervescent effect occurred during the redox process in both the procedures described above. The effect would eventually subside but mild bubbling still occurred periodically during the ion-exchange process, and the gas bubbles severely clogged the column and prolonged the plutonium separation process.

It is also noted that, in common with previous experience, the ^{242}Pu count rates varied substantially from sample-to-sample and run-to-run despite an essentially constant amount of ^{242}Pu tracer being added to each sample. Presently this is not understood and certainly requires further investigation.

Table 3.5: Comparison of the measured plutonium concentrations with and without a redox procedure during sample preparation, for three different samples. Sample identifiers CDP 54/57, CDP 60/63 and CDP 96/99 refer to the Cotter dam pit 54-57 cm, 60-63 cm and 96-99 cm respectively. The samples were measured in the AMS wheel no. specified in the sample code

Sample code	Experimental procedure ^a	^{242}Pu counts/sec	$^{239+240}\text{Pu}$ (mBq/g)
CDP 60/63-s-M411	Standard	4	0.472±0.036
CDP 60/63-r(I)-M411	Redox(I)	7	0.424±0.026
CDP 96/99-s-M411	Standard	14	0.465±0.026
CDP 96/99-r(I)-M411	Redox(I)	13	0.446±0.025
CDP 54/57-s-M425	Standard	28	0.430±0.023
CDP 54/57-r(II)-M425	Redox (II)	81	0.390±0.020

^a Experimental procedure:

- (i) Standard - This is the standard protocol adopted in this thesis as specified in Appendix-A1. It involves a single oxidation step using NaNO_2 .
- (ii) Redox (I) - This protocol incorporates a redox process and uses NH_4I and NaNO_2 as the reducing agent and oxidising agent, respectively.
- (iii) Redox (II) - This protocol includes a redox process and uses $[\text{Fe}(\text{NH}_2\text{SO}_3)_2]$ and NaNO_2 as the reducing agent and oxidising agent, respectively.

Ashed versus unashed samples

In order to investigate the necessity for ashing and the consequences of not ashing, experiments were carried out on both unashed and ashed samples. Particularly organic-rich samples from two depths in the Cotter dam pit that had been concentrated by floating on water were chosen for this study. Since the enriched organic samples were only a few grams each, the amount of leaching acid (8M nitric acid) used for these experiments was reduced to ~20 ml. The results are shown in Table 3.6, and suggest that the present plutonium extraction and separation protocol can equally be applied to unashed samples. It is also observed that the unashed samples yield a relatively higher ²⁴²Pu count rate compared to their ashed counterparts. A possible explanation for this observation is given below.

Table 3.6: Measured plutonium activity concentrations obtained from samples^a with and without ashing

Sample code	Mass of ²⁴² Pu tracer (pg)	Ashing process	Mass of unashed sample (g)	LOI (%)	²⁴² Pu (cps)	²³⁹⁺²⁴⁰ Pu (mBq/g) ^b
CDP 24/27-o-ua	3.5586	omitted	3.09	-	97	0.751±0.055
CDP 24/27-o-a	3.8753	carried out	5.15	55	20	0.818±0.066
CDP 81/84-o-ua	3.7365	omitted	5.03	-	94	0.359±0.026
CDP 81/84-o-a	3.7597	carried out	7.58	81	17	0.315±0.066

^a Samples were enriched organic materials floated off from the Cotter dam pit samples, CDP 24/27 and CDP 81/84 of depth 24-27 cm and 81-84 cm respectively, and measured in wheel M431

^b Plutonium concentration is expressed relative to the unashed masses.

The ashing process helps to break down the macromolecular organic components in the sample, thereby facilitating the release of other chemical sub-components that are incorporated into or bound on to the organic complex structure, making them accessible to the leaching acid. Thus more impurities were eventually leached along with the plutonium and might get into the final processed sample. Ion source output can be affected by the presence of impurities in the sample, and the incorporation of additional impurities as a result of ashing may reduce the plutonium counting efficiency in ashed samples.

Although the exclusion of the ashing process may seem attractive, it is not encouraged. The leaching of unashed samples tends to cause the leached solution to become viscous and impede the flow in the ion exchange column. This causes delay and prolongs the plutonium separation process. Moreover, as highlighted earlier, the presence of organic materials also causes the leached solution to turn a dark-tea colour, making it difficult to detect the colour change in solution (end-point determination) when sodium nitrite is added, which could lead to an undesirable excess of sodium nitrite in the leachate.

3.5.1. A puzzle resolved – variations in plutonium concentration due to inhomogeneity in sediments

In the course of the above tests, several measurements were performed on different subsamples of the various bulk sediment samples from the Cotter Dam pit. These measurements are summarised in Figure 3.6. Although there is generally good agreement among splits of the same subsample as noted above, there are clearly inconsistencies in the determined plutonium activity concentration between some of the subsamples.

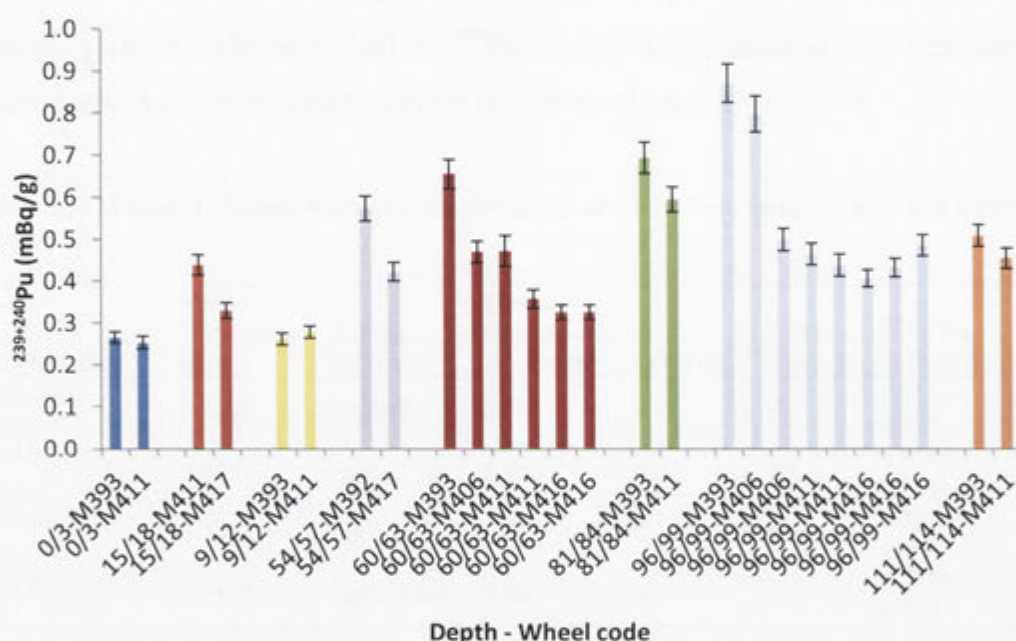


Figure 3.6: Plutonium activity concentrations from repeat measurements on samples from a range of depths in the Cotter dam pit. Samples were labelled with depth and with the AMS wheel number in which they were measured. Samples with the same wheel code were prepared from splits of the same (homogenised) subsample unless otherwise stated^a. Note that there are significant discrepancies between individual measurements for the 60-63 cm and 96-99 cm samples.

^a The 96-99 cm samples from the Cotter dam pit analysed in M411 and M416 were all from splits of the same subsample, whereas those measured in M406 were taken from different subsamples. Samples from depth 60-63 cm analysed in M411 were also taken from different subsamples.

In order to test the possibility that the discrepancy could be due to variations in the leaching duration and temperature during different batch preparations, a series of samples were prepared from a well-mixed subsample of the 96-99 cm sediment from the Cotter dam pit. Both the leaching time and leaching temperature were varied independently. The results are shown in Figures 3.7(a) and (b), and indicate that variations in the leaching conditions were not responsible for the observed discrepancies. An additional observation is that the ^{242}Pu count rate increases with both the temperature and duration of leaching, suggesting that leaching efficiency improves with higher temperature and longer duration. As noted above, however, other factors can also influence ion source efficiency and hence ^{242}Pu counting rates.

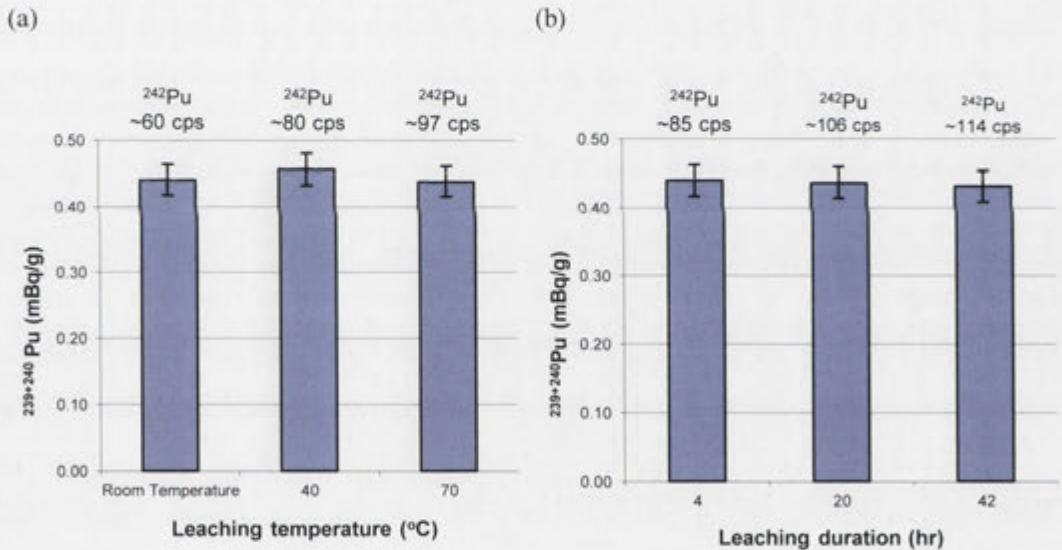


Figure 3.7

(a): A study of the effect of variation in leaching temperature on the plutonium activity. The leaching duration was ~20 hr.

(b): A study of the effect of variation in leaching duration on the plutonium activity. The leaching temperature was ~70 °C.

These tests were carried out on the sediment sample collected from the Cotter dam pit at a depth of 96-99 cm, and were measured in wheel M416.

Since the discrepancies that are evident in Figure 3.6 are invariably between different subsamples whereas splits of the same subsample are generally in agreement, the most plausible explanation is that the discrepancies are due to inhomogeneity within the sediment samples themselves rather than any inadequacies of the analytical method. As highlighted earlier, the ~3 kg sediment samples were not mixed in the bulk before subsampling, but individual subsamples were thoroughly mixed before splitting further. With hindsight, it is not difficult to imagine scenarios that would lead to an inhomogeneous distribution of plutonium in the sampled sediment. Each sample consisted of 3 cm of deposition, and was likely to represent many individual rainfall events of widely-varying intensity. Particularly heavy but short rainfall is more likely to mobilize material from gullies and from stored sediment upstream than gentler but more sustained rainfall. The plutonium concentrations of the deposited sediment could be rather different in these two cases because the former may mobilize deeper material that contains little or no plutonium. This could result in significant inhomogeneities across the 3 cm thickness of the bulk samples.

In light of the above discussion, complications caused by sample inhomogeneity can be avoided either by grinding the bulk samples or by otherwise thoroughly mixing them in the bulk before subsampling. Such a homogenisation process is critical particularly in the study of sediment cores, if plutonium (or other tracer) concentrations that are representative of the sampled interval are to be obtained. In future, all samples will be homogenised prior to any subsampling in order to avoid the variability observed here.

Chapter 4 Case study I - Assessment of erosion activity in a “highly disturbed” environment

This chapter presents a case study that demonstrates the use of fallout plutonium to assess the erosion activity in a highly disturbed catchment that has been influenced by bush-fire events and pine forestry operations.

4.1. Introduction

Significant rainfall after intense bushfires in forested terrain has been widely recognised as a driving factor of enhanced erosion and sedimentation [Blake *et al.*, 2009; Brown, 1972]. Fire tends to remove ground vegetation cover and litter, and this leaves the soil prone to raindrop impact and also reduces the opportunities for rainfall storage [Shakesby and Doerr, 2006]. Consequently overland flow tends to occur more readily and the enhanced post-fire runoff dynamic may ultimately lead to an increase in sediment transport and deposits in drainage lines. Many researchers regard this as the most important factor leading to enhanced post-fire erosion, where sheet and rill erosion are frequently reported [Shakesby and Doerr, 2006]. Fire is also known to alter sediment sources in river basins. In the absence of fire, gully and riverbank erosion of subsoil are commonly recognised as the source of sediment supply in forested catchment. A recent study by Wilkinson *et al.*, [2009] showed that post-fire erosion caused a switch in sediment sources from 80% subsoil by gully and river bank erosion to 86% topsoil derived from hill slope surface erosion. On the other hand, there are studies which indicate that fire increases channel erosion [Moody and Martin, 2001]. Since specific erosional responses can vary markedly due to the variability in the response between environments and fire intensity, the prediction of catchment scale erosional effects of individual fires is difficult and challenging.

In Australia, many of the fire-related erosion studies have been carried out in sandstone-dominated terrain of the coast and upland of New South Wales in the Sydney Basin, with a smaller number located in the south-eastern region of New South Wales and Victoria [Shakesby *et al.*, 2007]. Most of these studies were based

on small-scale ground-height change measurements or plot scale runoff experiments [Shakesby and Doerr, 2006]. Although these conventional means of assessment are able to provide useful and relevant information, such studies require considerable investment of resources and labour. Further, they are difficult to set up in time for opportunistic fire studies and do not explicitly reveal channel storage or sediment depositional sites [Blake *et al.*, 2009]. As a complement to instrument records, a tracer-based approach offers advantages in terms of its ease of deployment and its independence from monitoring equipment, which is often destroyed in the fire [Wilkinson *et al.*, 2009].

Previous use of tracing techniques employing fallout radionuclides (^{137}Cs , ^{210}Pb and ^7Be), had successfully quantified the post-fire soil redistribution rate and budgets on a hill slope in eucalypt forest in SE Australia [Blake *et al.*, 2009; Wallbrink *et al.*, 2005]. Wilkinson *et al.*, [2009] adopted a similar approach using ^{137}Cs and ^{210}Pb to determine the effect of fire on the contribution of surface and subsurface erosion to catchment sediment yield. In the present work, fallout plutonium is used for the first time as a tool to investigate recent erosional processes on the scale of a catchment of a few hundred km^2 . This catchment was severely affected by a major bush fire event in 2003, and approximately half of it had been significantly disturbed by forestry operations since the 1930s. Forestry activity eventually ceased after the fire catastrophe. The purpose of the present study is to explore the potential of fallout plutonium as a tracer of soil and sediment transport in this highly disturbed environment with the aims to:

- (i) Estimate the soil loss at various study sites.
- (ii) Assess the severity of gullyng at specific study sites.
- (iii) Obtain a better understanding of the use of the plutonium tracer technique in burnt forest terrain.

4.2. Study area

The Cotter River catchment extends over 490 km² with terrain elevation ranging from 470-1900 m above sea level. It serves as the main source of water for Canberra, the capital city of Australia located in the Australian Capital Territory (ACT). Sited within the catchment are three dams, namely Corin Dam, Bendora Dam and Cotter Dam, and each defines a sub-catchment (see Table 4.1 for the dams specification). The upper and middle sub-catchments (Corin and Bendora) are protected in national park, with the consequence that the runoff into the dams was historically of high quality and required minimum treatment. The Cotter catchment is also relatively wetter than nearby Canberra, receiving an average of 950 mm/yr compared with 600 mm at Canberra airport [White *et al.*, 2006].

The study area is the lower Cotter catchment, defined as the catchment between the Bendora and Cotter dams (Figure 4.1). It covers an area of about 192 km², of which ~107 km² lies within the national park and the remaining ~84 km² was within the former ACT Forest Estate, covered mainly by pine plantations prior to the 2003 bush fire.

Table 4.1: Characteristics of the dams located in the Cotter River catchment

Dam	Sub-catchment (km ²)	Constructed	Capacity (GL)
Cotter	Lower Cotter: 192	1912 ^a	4.65 ^a
Bendora	Middle Cotter: 91	1961	10.7
Corin	Upper Cotter: 197	1968	75.4

^a The Cotter dam was constructed between 1912 and 1915 with a volume of 1.85 GL (Gigalitre). The dam wall was raised to its current height between 1949 and 1951 to accommodate a capacity of 4.65 GL.

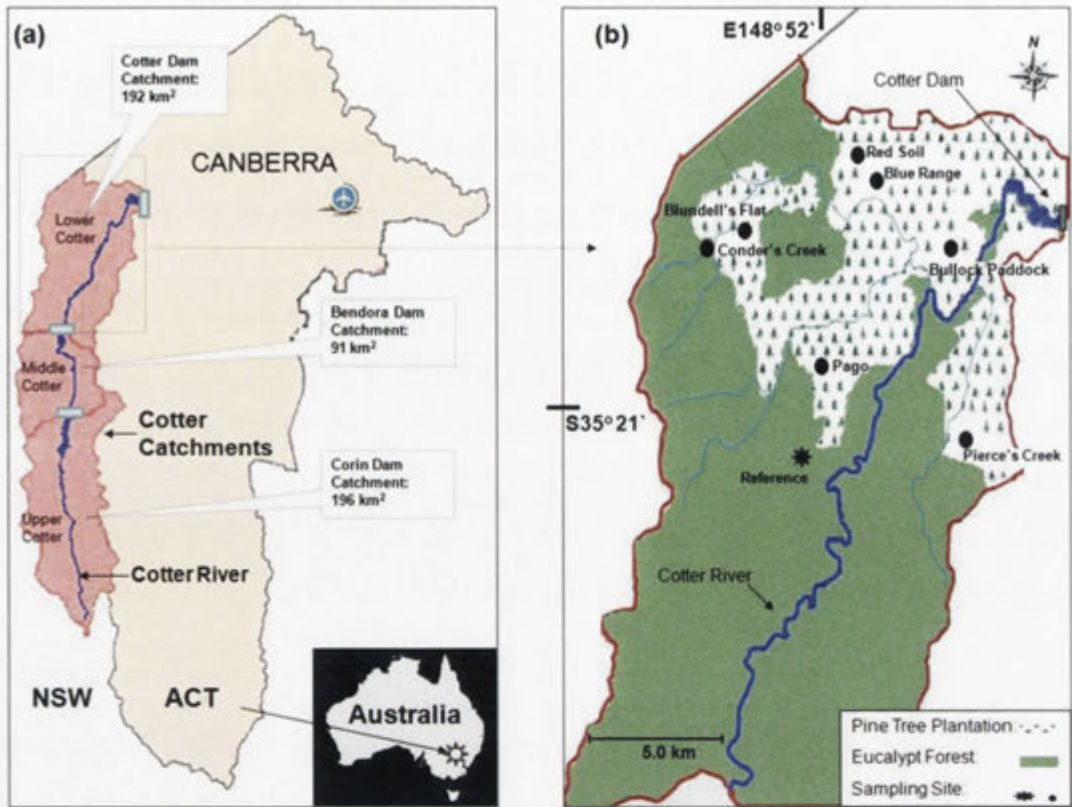


Figure 4.1: Location of sampling /study sites within the lower Cotter catchment (study area).

Erosion history of the lower Cotter catchment

Water quality in the lower Cotter has historically been poorer than the middle and upper catchments, and its condition became worse following the 2003 bush fire [Wale *et al.*, 2008]. As early as the 19th century, the lower Cotter was subjected to a greater degree of disturbance than the rest of the catchment as a result of both human activity and introduced animals. Early human settlements initiated the clearing of native vegetation and over-grazing eventually led to serious soil erosion. The problem was exacerbated by the activity of rabbits reported in 1925 [Rustomji and Hairsine, 2006]. In an attempt to stabilize the erosion, a tree planting programme was initiated in 1931 which grew substantially into a commercial operation. Additional native forest was cleared to make room for the pine industry. Clearing eventually ceased in 1961 under public pressure, at which stage a total area of 84 km² was under pine plantation [ACT Government 2007, *Lower Cotter Catchment Strategic Management Plan*, Department of Territory and Municipal Services, Canberra].

Forestry operations generate and redistribute sediment. Several studies have shown high erosion rates at logging roads, extraction tracks, landings, and harvested areas [Wilson, 1999]. These are consistent with the findings of White *et al.*, [2006], who attributed the major source of the elevated turbidity in the Cotter dam to the road networks that had been established for the commercial pine plantation operations within the catchment. Additionally, the gully networks that were formed during the early phases of clearing within the lower Cotter catchment were also recognised as an important source of sediment [Rustomji and Hairsine, 2006].

Impact of bush fire in 2003

Historically, there have been five major bushfires (see Table 4.2) within the Cotter catchment over the last century, with the recent 2003 event being the most severe [Worthy and Wasson, 2004]. In January 2003, approximately 30 000 km² of forested, agricultural and urban land in eastern Australia was engulfed by a series of unconnected fires. The fire severely damaged almost the entire Cotter River catchment (~98%). Heavy storms that closely followed the fire led to much-enhanced erosion across the catchment and the eroded sediments affected the quality of the dam water. Large pulses of sediment were channelled into the Cotter River. These included ~19 000 tonnes of inorganic sediment and ~2 000 tonnes of organic materials delivered to Bendora Dam as reported in Wasson *et al.*, [2004]. An unprecedented increase (up to 30 times as compared to previous events) in turbidity was observed by White *et al.*, [2006]. This severe degradation of water quality necessitated the construction of a filtration plant for Canberra's water supply where previously none had been required.

While natural re-vegetation in the eucalypt-dominated upper and middle catchments gradually returned the water quality to nearly pre-fire condition, water quality in the lower catchment remains poor [White *et al.*, 2006]. Although the Cotter Dam presently makes only a minor contribution to Canberra's water supply, construction of a much larger dam with a storage capacity of 78 GL (Gigalitre) began in late 2009. Hence, the issue of erosion and water quality in the lower Cotter catchment will assume much greater importance in the future. This increases the

motivation to carry out an erosion assessment in the lower catchment in order to inform amelioration strategies.

Table 4.2: Major fire events in the Cotter catchment since 1900

Year	Affected location	Area of the Cotter catchment that were burnt (km ²)
1920	Upper Cotter, Tidbinbilla valleys	170
1926	Cotter valley	250
1936	Lower and Middle Cotter, Paddy's River valleys	151
1983	Upper Cotter, Licking Hole creek	58
2003	Cotter catchment	475

[Source: White *et al.*, 2005]

4.2.1. Sampling sites

One reference site and seven study sites were selected across the lower Cotter catchment. The locations of the specific sites are illustrated in Figure 4.1 b. The types of sample collected at the sites are summarised in Table 4.3, and include:

- (i) Soil profiles in typically 5 cm increments from hand-dug pits with depths of 25-40 cm.
- (ii) Representative surface soil samples in the form of composite samples from the area surrounding selected pits.
- (iii) Sediments in the form of composite samples from gullies and along a creek (Conder Creek site).

The sampling trips were carried out in August 2007 and January 2008 respectively, and followed the sampling methodology outlined in Chapter 3. The purposes of the follow up visit were to expand the coverage of the catchment and also to determine the total inventory of plutonium at several sites where only surface soils were collected previously. This was to allow the derivation of a more reliable estimate of soil loss across the catchment. Further, additional pit samples were collected at the Reference, Pierce's Creek and Blundell's Flat sites in order to gauge the extent of spatial variability within the study area. Three additional field trips were subsequently carried out between May and July 2010 specifically to obtain the density of the soils required for the derivation of plutonium inventories.

Table 4.3: Location of the study sites in the lower Cotter catchment

Site	Location (Alt.)	Sample type
Reference	35° 22.16'S, 148° 50.95'E (1124 m)	Soils (pit)
Pierce's Creek	35° 21.99'S, 148° 54.31'E (770 m)	Soils (pit and surface), Sediments (gully)
Pago	35° 20.99'S, 148° 51.41'E (784 m)	Soils (pit and surface), Sediments (gully)
Conder Creek	35° 19.42'S, 148° 49.35'E (800 m)	Sediments (creek)
Blundell's Flat	35° 19.28'S, 148° 49.78'E (781 m)	Soils (pit and surface)
Bullock Paddock	35° 19.42'S, 148° 53.74'E (672 m)	Soils (pit)
Blue Range	35° 18.35'S, 148° 52.59'E (686 m)	Soils (pit)
Red Soil	35° 17.86'S, 148° 52.50'E (743 m)	Soils (pit)

A detailed description of the soil groups and their distributions within the Cotter catchment is documented in Talsma [1983]. Five major soil groups were identified on the basis of morphological characteristics and parent material as shown in Figure 4.2. In the vicinity of the Cotter dam area (example: Red Soil and Blue Range study sites), red and yellow podzolic earths were found developed on the Silurian volcanic bedrock. These soils were reported to have low water retention capacity, low permeability and the yellow earths in particular were erosion prone. The red earths were the most erosion resistant soils in the catchment [Rustomji and Hairsine, 2006].

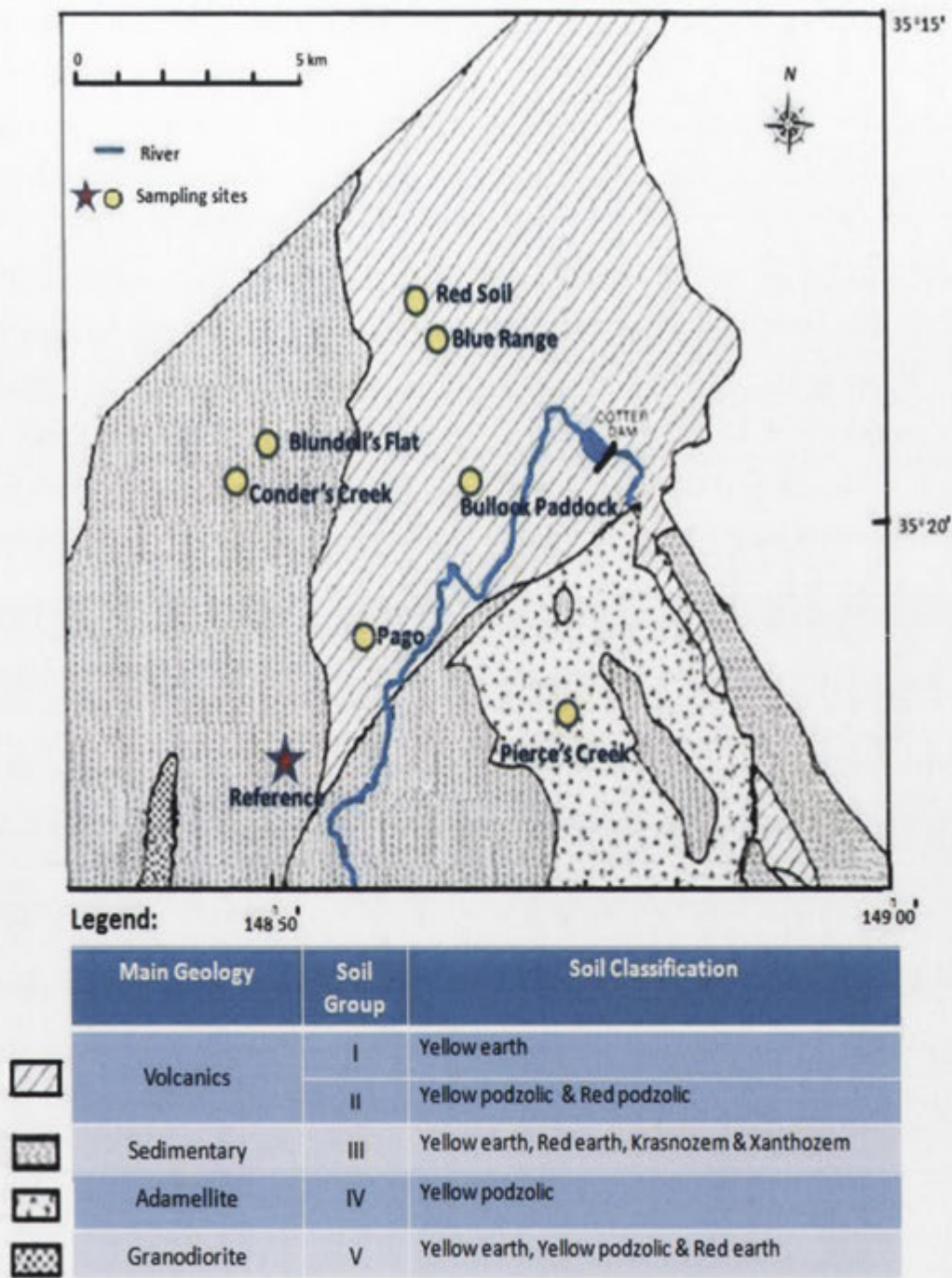


Figure 4.2: Soil classifications and distributions at the lower Cotter catchment area.
[Source: Talsma, 1983]

Talsma [1983] noted that the bulk density of soil groups I and II were rather similar (Table 4.4). The bulk density of group IV soils was high throughout the profile, whereas group III soils on the other hand, were associated with high organic matter and low densities. These findings were generally consistent with the measurements taken at the sampling sites as shown in Table 4.4. Among the sampling sites, the soil bulk density is the highest at the Pierce's Creek site and the lowest at the Reference sites. While the soil density at the Blundell's Flat site was low in the top 10 cm, it was high beyond the 10 cm depth. This was not typical of group III soil, which has a low density depth profile. The soil at the Blue Range site was hard and stony, making it extremely difficult to obtain a sample for soil density measurement at the deeper depth. Nevertheless, one would expect the bulk density to be high and consistent with the typical soil group I & II.

Table 4.4: Soil bulk density at the sampling sites

Sampling site	Soil Group	Depth (cm)	Bulk soil density (g/cm ³)	Sampling site	Soil Group	Depth (cm)	Bulk soil density (g/cm ³)
<u>Red soil</u>	I & II	0-5	1.22	<u>4 sites^a</u>	I	0-10	1.31 ^b
		0-10	1.32			10-20	1.46 ^b
		15-20	1.41			20-30	1.50 ^b
<u>Bullock Paddock</u>	I & II	0-5	1.24	<u>4 sites^a</u>	II	0-10	1.18 ^b
		0-10	1.30			10-20	1.46 ^b
		19.5-24.5	1.25			20-40	1.62 ^b
<u>Blue range</u>	I & II	0-5	1.29				
		0-10	1.27				
<u>Reference: Pit A</u>	III	0-5	0.92	<u>6 sites^a</u>	III	0-10	1.02 ^b
		0-10	0.80			10-25	1.17 ^b
		16-21	1.01			25-40	1.21 ^b
<u>Reference: Pit B</u>	III	0-5	0.74				
		0-10	0.73				
		17-22	1.05				
<u>Blundell's Flat</u>	III	0-5	0.67				
		0-10	0.95				
		13-18	1.58				
<u>Pierce's Creek: Between rip lines</u>	IV	0-5	1.35	<u>2 sites^a</u>	IV	0-10	1.45 ^b
		0-10	1.40			10-30	1.55 ^b
		20-25	1.58				

^a Number of sampling sites of specific soil group referenced in Talsma [1983].

^b The average bulk density for the soil group referenced in Talsma [1983].

Reference site

The reference site was situated on a broad hill top covered by previously undisturbed native eucalypt forest. All of the study sites were within a 7 km radius of the reference site and hence would have experienced a very similar rainfall regime, and hence plutonium fallout history, to the reference site. As the entire study area was ravaged by the 2003 bush fire, it was not possible to locate an appropriate reference site that was not fire affected, and this reference site had clearly been burnt over. The effects of fire were likely to be twofold – loss of organic material from the surface, and the creation of bare soil that was more prone to loss by erosion. It is considered that neither is likely to have had a large impact on the plutonium inventory at the site. Although the organic matter in the surface soil was burnt, any plutonium should have been retained in the ash with the caveat that the ash could have been mobilised by the firestorm. Further, the reference site is almost flat, hence any loss of materials (soil or ash) to erosion would be expected to have been minimal. In order to gauge whether the fire may have had an impact on the plutonium inventory at this reference site, a second pit (Pit B) was sampled that was only about ~10 m from the first (Pit A).

Study sites

The study sites in the disturbed area of the catchment were chosen to reflect important topographic features and different soil types. All except the Conder Creek site were in areas that had been pine plantation prior to the 2003 bushfire. There had been at least one cycle of harvesting and replanting at each site in the past 40 years. In addition, heavy machinery was employed to harvest the dead trees following the bush fire. At most of the sites, the cleared ground was subsequently ripped with a bulldozer to create lines of furrows and ridges along contours in preparation for the replanting of pines, although these replanting plans were later abandoned. At present, the area is largely covered with weeds, but there have been some planting of native vegetation as well as some recolonisation by native bushes, vines and small trees. Photographs of the study sites and a brief description of their surrounding terrains are given below:

1. **Pierce's Creek:** This site was mainly grassed and the nearby gully was 1-2 m deep. The soil in this region is a highly-erodible decomposed granite. The area had been ripped post-fire and the new rip lines were clearly visible. There was also some evidence of earlier rip lines. Samples were collected from different contexts relative to the rip lines such as the swales, ridges and unripped area between the rip lines (See Figure 4.3a).



Figure 4.3a: The Pierce's Creek site. Photograph (i): Looking north east across the north-south trending gully where rip lines and regenerating vegetation were within the line of sight. The soils in this region were highly-erodible decomposed granite and the >3 mm stone fractions were quartz and feldspar rich. Photograph (ii): Looking north west across the gully showing the relative location of the sampling site. Sediments were sampled along the bottom gully area. Photographs (iii)-(iv): A close up view showing rip-lines and space between lines of the sampling sites.

2. **Pago:** This site was selected because of its obviously dynamic nature. The nearby gullies were 2-3 m deep and appeared highly active. The hill slopes coming into the gullies were very steep ($\sim 20^\circ$). The sampling pit was located on a flatter section near the edge of a deeply-incised gully shown in Figure 4.3 b-ii.



Figure 4.3b: The Pago site. Photograph (i): Location of the sampling pit. The deep gully is just out of the photo to the right, and the shot is looking up the steep hill coming down into the gully. A representative surface soil sample was also collected on the slope over an area within tens of meters from the pit. The yellowish surface soils in this region were dry and brittle, and loose coarse pebbly stones were common across the terrain. Photograph (ii): Looking west across the gully (2-3 m deep) about ~ 30 m downstream from the sampling pit. Sediments were collected from this deep gully, although not much loose material was present.

3. **Conder Creek:** This creek was sampled where it ran through native vegetation but close to where it emerged into a pine-forest area. At this point, it drained a catchment that was covered mainly by native vegetation, although it is possible that there may have been some influence of a forestry road that ran along a nearby ridge. It was the only site where creek-borne sediments (banks, log jam etc) were sampled. Photographs of this specific site are shown later in Figure 4.6 of section 4.4.3.

4. **Blundell's Flat:** This former pine-forest site was ~600 m from the Conder Creek site and drained into the creek where it emerged from the native eucalypt forest. The site had been cleared in the 70s/80s and also after the 2003 bush fire. Presently the area was mainly grassed and was the only sampled pine-forest site not to have been ripped after the 2003 bushfire. It was on a gentle slope with a gradient less than 5° . Two pits (C and D) within a few meters of each other were sampled at this site on different occasions in 2007 and 2008 respectively.



Figure 4.3c: Evidence of 'old' rip lines was present at this site. These rip lines were created before 2003. Stony granite pebbles were scattered across the surface and the ground was hard below ~10 cm depth. A representative surface soil sample was collected over an area of (100 x 100) m².

5. **Bullock Paddock, Blue Range and Red Soil:** The terrains of the remaining sites were similar (See Figure 4.3d-i), characterised by gentle slopes ($\sim 5^\circ$) and all had been ripped after the bushfire. The soil properties across these sites were different as highlighted in section 4.2.1. Samples were deliberately collected away from the post-fire rip lines to avoid possible soil disturbance caused by the ripping process.



Figure 4.3d: Photograph (i) was taken looking down from a hill top at the Blue Range site. It depicts a gently-sloping terrain which was similar to other sites (Red Soil and Bullock Paddock). Photograph (ii): Soils at the Blue Range site were yellowish. Small stones were common down the depth profile. Photograph (iii): Soils at the Red Soil site were reddish and sticky. Photograph (iv): Soil at the Bullock Paddock site has a low stone (>3 mm fraction) content.

4.3. Methodology

The application of fallout plutonium as a tracer of soil loss and sediment transport, and the analytical strategy are described in Chapters 2 and 3. The sample preparation and measurement of plutonium isotopes using the AMS technique followed the procedure described in Chapter 3, with further details as highlighted below.

The samples were separated into >3 mm (stones) and <3 mm components, since little of the plutonium was expected to reside on the stones. All of the <3 mm components were analysed, and the >3 mm component of three samples, two from the pit A reference site (0-5 and 5-10 cm depth intervals) and one from the Pago site, were crushed, leached and measured as separate samples. Plutonium concentrations of the >3 mm component averaged about 20% of the concentrations of the <3 mm component, and this average concentration was adopted for the >3 mm proportion of those samples for which the plutonium on the >3 mm component was not measured. The experimental results were corrected to include the plutonium concentrations of both the <3 mm and >3 mm components. Soil densities were determined at all the sites except Pago site which was inaccessible at the time of the visit. The soil density at the Bullock Paddock site was taken to be representative of the Pago site, based on the close similarity of soil type and stone contents. The sampling for soil density measurements was carried out as close as possible to the locations of the sampling pits for plutonium measurements. Since stone content could vary significantly from sample to sample, the densities were determined separately for the <3 mm and >3 mm fractions, and used to derive total inventories from the measured plutonium concentrations.

4.4. Results & discussion

4.4.1. Plutonium inventory and soil loss

Reference site

The plutonium results from the reference site are shown in Table 4.5 and Figure 4.4. Total plutonium inventories at the two sampling sites, Pits A and B, were calculated to be 3.1 and 2.0 mBq/cm² respectively. Typically, 60-70% of the inventory was found in the top 10 cm at both sites, with about 30% and 50% concentrated in the top 5 cm layer of Pit A and Pit B respectively. The observed plutonium depth profiles are most likely the result of the movement of soil grains due to bioturbation by ants and worms or by movement down root channels. There may also be some transport in solution.

Table 4.5: Plutonium inventories of the reference site

Depth (cm)	<3 mm component		²³⁹⁺²⁴⁰ Pu (mBq/g)		²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory (%)
(Pit A)	Density ^a (g/cm ³)	% Composition	<3 mm component	>3 mm component	Bulk 0.223±0.010 0.298±0.015 0.168±0.009 0.095±0.005 0.049±0.003	29.3±1.8 33.8±2.5 18.5±1.4 14.0±1.1 4.1±0.3
0-5	0.63	46	0.42±0.02	0.06±0.01		
5-10	0.61	83	0.34±0.02	0.12±0.01		
10-15	0.88	78	0.21±0.01	0.04 ^b		
15-20	0.88	82	0.11±0.01	0.02 ^b		
20-23	0.88	86	0.06±0.01	0.01 ^b		
					3.14±0.10 [Total]	
(Pit B)					1.08±0.13 0.44±0.06 0.13±0.02 0.22±0.03 0.09±0.015 0.04±0.007 1.99±0.15 [Total]	54.3±7.7 22.1±3.4 6.5±1.1 11.1±1.7 4.5±0.8 2.0±0.4
0-5	0.51	67	0.46±0.04	0.09 ^b		
5-10	0.50	78	0.18±0.02	0.04 ^b		
10-15	0.93	89	0.05±0.01	0.01 ^b		
15-20	0.93	94	0.05±0.01	0.01 ^b		
20-25	0.93	96	0.02±0.01	0.004 ^b		
25-29	0.93	94	0.01±0.01	0.002 ^b		

^aDensity of the >3 mm component ~2.1 g/cm³.

^bPu concentration of the >3 mm component is derived from 20% plutonium concentration of the <3 mm component.

The variation in the plutonium inventory between these two closely-spaced sites is about 40%. Two factors may have contributed to this variation. The first is spatial heterogeneity in the distribution of plutonium deposited on the ground surface due to interception and subsequent redirection of rain by the canopy, particularly in this forested terrain. This issue has been highlighted and discussed in Chapter 2, section 2.4. Secondly, as shown in Chapter 5 section 5.4, plutonium has a preferential affinity for organic materials. Thus plutonium attached to organic matter in the near surface soil could have been redistributed by the fire, since the intense heat of the firestorm would have ignited much of the organic matter at and near the surface, converting it into plutonium-carrying ash that could easily be mobilised by rain water running across the terrain. Further, it has been reported that forest fires may resuspend radionuclides [Garland and Pomeroy, 1994; Paatero *et al.*, 2009]. Since the 2003 fire was driven by a very strong westerly wind, and the area to the west of the reference site is largely undisturbed eucalypt forest, it is possible that resuspended plutonium-carrying surface material could have been re-deposited at the reference site. Thus, the lower plutonium inventory in pit B may reflect natural heterogeneity due to redirection of rain by the forest canopy, or the fire-driven loss of more organic-rich surface material from the Pit B site and /or the accumulation of additional plutonium at Pit A.

In order to ascertain more precisely the reference level in this burnt terrain, there is clearly a need to measure profiles and inventories at other reference sites, preferably sites that were not burnt, although given the extent of the fires, we have been unable to find such a site that is sufficiently close to the study area. As part of another project, however, the plutonium inventory was measured at another site in undisturbed forest that was only 4 km to the south of the reference site studied here. Although the soil densities were not measured, this additional site has the same soil type as our reference site, and hence the average densities of Pits A and B were assumed in calculating its inventory. The result is shown in Table 4.6 and Figure 4.4, and is similar to that measured at Pit B, which may indicate that the inventory at Pit B is more representative of the true fallout than the higher value at Pit A.

Table 4.6: Measurement of plutonium inventories^a of an undisturbed forest site^b located within a 4 km radius from the reference site.

Site (Location)	Distance from reference site (km)	²³⁹⁺²⁴⁰ Pu (mBq/cm ²)
WP021 (35° 22.83'S, 148° 50.95'E)	4	1.84±0.18

^aDerivation of the plutonium inventories at this site was based on average soil density measurements at Pit A and Pit B of the reference site.

^bA schematic map indicating the location of this site relative to the reference site is available in Appendix A4. Additional information such as site description and plutonium concentration measurements are also included.

Nevertheless, the average plutonium inventory derived from the reference and the undisturbed forest sites is 2.32 ± 0.40 mBq/cm² which is comparable with the expected Southern Hemisphere value at the latitude of Canberra (35.3°S) of ~ 1.9 mBq/cm². This expected value, which is close to the plutonium inventory level measured at Pit B, is based on ²³⁹⁺²⁴⁰Pu inventories reported by Hardy *et al.*, [1973] and Kelley *et al.*, [1999] for soil samples collected in 1970-71 over a wide range of latitudes in both the southern and northern hemispheres, and is the average of the measured inventories for Sydney (33.8°S) and Melbourne (37.8°S) of 1.74 and 2.04 mBq/cm² respectively [Hardy *et al.*, 1973].

As an independent check of the plutonium results, the ¹³⁷Cs activities of the 0-5 cm samples from Pits A and B were determined in order to determine the ¹³⁷Cs/²³⁹⁺²⁴⁰Pu activity ratio. Measurements of ¹³⁷Cs were carried out on samples of the <3 mm component using gamma ray spectrometry at the CSIRO Land and Water laboratories in Canberra. These samples, each of ~ 40 g, were ashed, ground, pressed into a cylindrical sample holder of 7 cm diameter and 2 cm depth, and counted over a period of ~ 48 hours using a 125 cm³ high purity germanium (HPGe) co-axial detector of detection efficiency $\sim 3\%$. The measured factors (~ 30) as shown in Table 4.7 agree well with the established global measurements (Cs data for nuclear decay corrected to 01/01/2007) described in Everett *et al.*, [2008].

Table 4.7: Measurement of $^{137}\text{Cs}/^{239+240}\text{Pu}$ activity ratio using samples from Cotter catchment reference site pit A and pit B, 0-5 cm depth

Sample code	^{137}Cs (mBq/g) ^a	$^{239+240}\text{Pu}$ (mBq/g)	$^{137}\text{Cs}/^{239+240}\text{Pu}$ Activity ratio
CREF-A-0/5	15.67±0.53	0.505±0.026	31.0±2.0
CREF-B-0/5	16.18±0.49	0.564±0.047	28.7±2.6

^a ^{137}Cs data has been decay corrected to 01/01/2007

In order to establish a baseline for the estimation of the depth of soil loss at the study sites in the pine-forest area, an exponential regression fit, to the average of the profiles at the reference and the undisturbed forest sites has been used to define the shape of the expected soil profile prior to erosion (Figure 4.4).

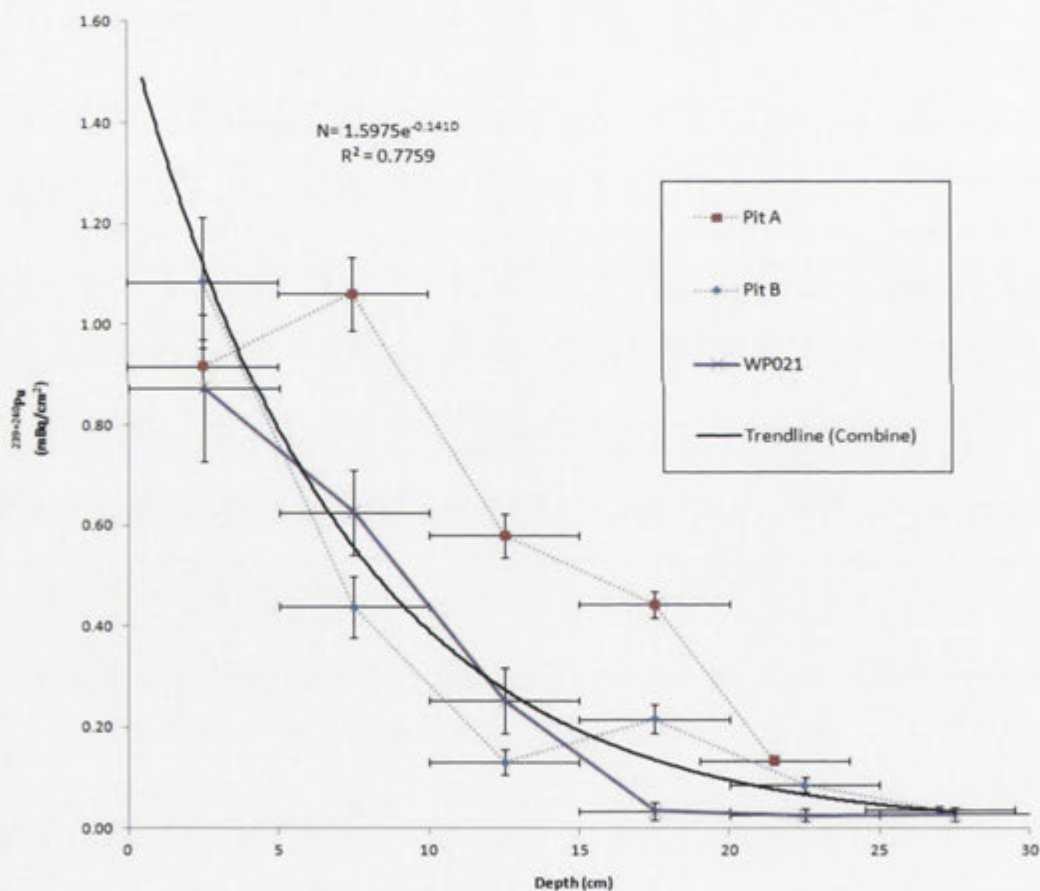


Figure 4.4: Plutonium depth profiles of the two reference pits and another nearby site in undisturbed forest. The y-axis error bars reflect 1 sigma error, whereas the x-axis error bars simply represent the depth interval of the sample. N and D denote $^{239+240}\text{Pu}$ inventory (mBq/cm²) and depth (cm) respectively.

Study sites

Plutonium depth profiles and total inventories from the study sites are shown in Figure 4.5 and Table 4.8. With the exceptions of the Pago and Pierce's Creek sites, all the studied sites look remarkably similar, both in terms of the distribution of plutonium with depth and the surface concentrations. Since these sites are representative of much of the catchment, this similarity implies that eroded surface material will carry a uniform plutonium concentration. Hence it should be possible to apportion sediment reliably between surface erosion and gully erosion sources. Such an investigation has been carried out and is discussed in Chapter 5. As at the reference site, plutonium is generally concentrated in the top 10-15 cm layer of the soil, and falls off rapidly below that depth. Total plutonium inventories at the Blundell's Flat, Bullock Paddock, Red Soil and Blue Range sites are all within the range of the average plutonium inventory derived from the reference and the undisturbed forest sites, indicating that there has been no significant loss of soil from these sites. Moderate loss of topsoil has been identified at Pierce's Creek site where the soil is more erodible. On the other hand, the Pago site has significantly lower plutonium inventories, indicating a substantial loss of soil over the past 50 years, although further investigation will be required to determine how much of the soil loss can be attributed to forestry operations and how much to denudation and subsequent erosion following the 2003 bushfire.

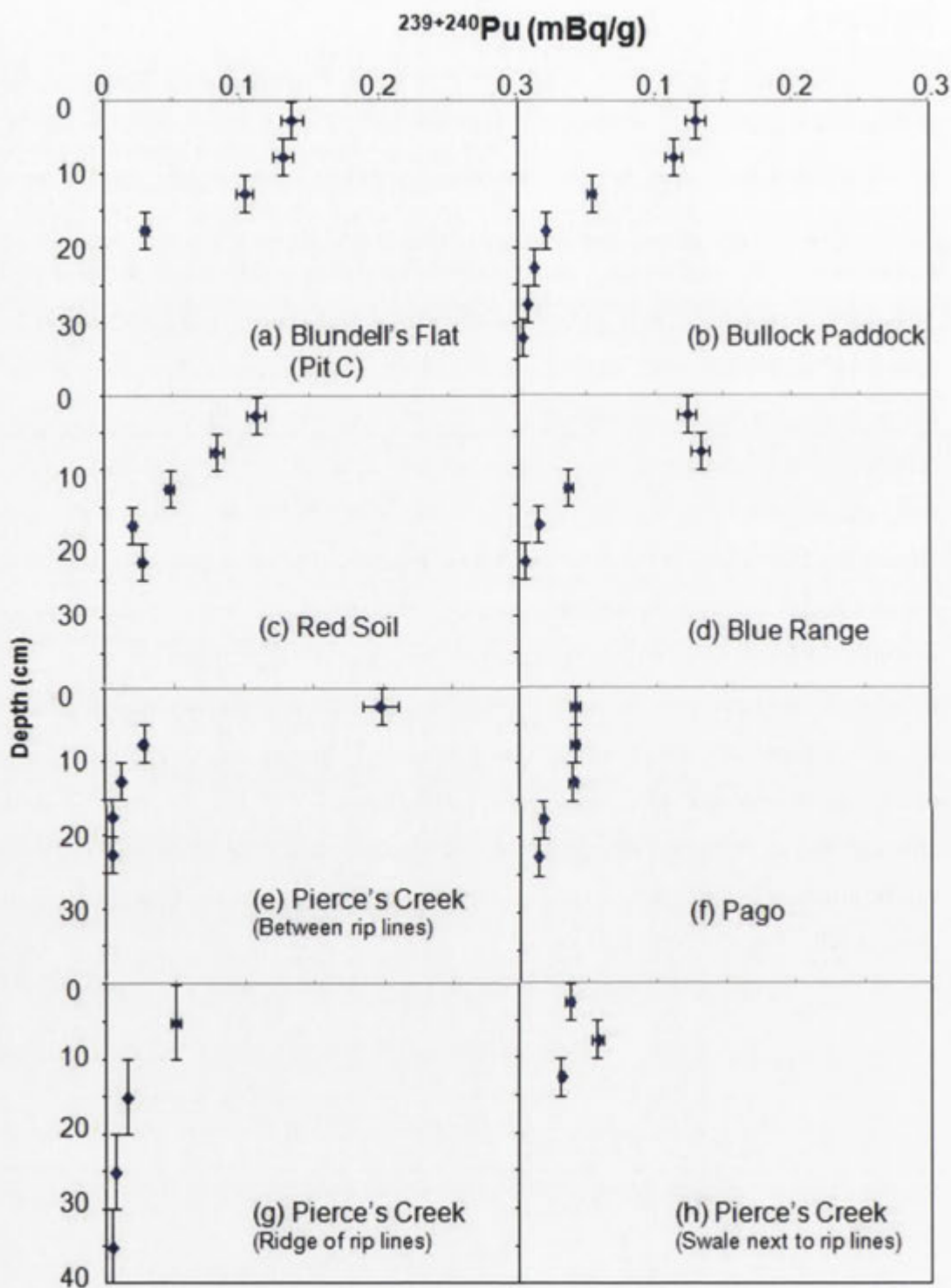


Figure 4.5: Plutonium depth profiles at the study sites. The x-axis error bars reflect 1 sigma error, whereas the y-axis error bars simply represent the depth interval of the sample.

Table 4.8: Plutonium depth profiles and inventories at study sites

Site / Depth (cm)	Density (g/cm ³) ^a <u><3 mm component</u>	% Composition <u><3 mm component</u>	²³⁹⁺²⁴⁰ Pu (mBq/g) <u><3 mm component</u> ^b <u>Bulk</u>			²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory (%)
<u>Blundell's Flat</u>							
(i) Pit C							
0-5	0.640	99	0.138±0.008	0.028	0.137±0.008	0.44±0.04	21.0±2.0
5-10	1.071	97	0.134±0.008	0.027	0.131±0.007	0.71±0.04	33.8±2.1
10-15	1.439	93	0.109±0.007	0.022	0.102±0.006	0.74±0.03	35.2±1.7
15-20	1.439	92	0.032±0.003	0.006	0.030±0.002	0.22±0.01	10.5±0.6
						<u>2.10±0.06 (91%)^d [Total]</u>	
(ii) Pit D							
0-10	0.840	91	0.115±0.006	0.023	0.107±0.006	0.92±0.06	
10-20	1.439	87	0.033±0.002	0.007	0.030±0.002	0.44±0.02	
						<u>1.36±0.06 [Total]</u>	
<u>Bullock Paddock</u>							
0-5	1.236	95	0.136±0.008	0.027	0.130±0.007	0.81±0.04	37.3±2.0
5-10	1.326	93	0.121±0.007	0.024	0.114±0.006	0.76±0.03	35.0±1.6
10-15	1.225	96	0.056±0.004	0.011	0.054±0.003	0.33±0.02	15.2±1.0
15-20	1.225	91	0.022±0.002	0.004	0.021±0.002	0.13±0.01	6.0±0.5
20-25	1.225	95	0.012±0.001	0.002	0.012±0.001	0.07±0.006	3.2±0.3
25-30	1.225	94	0.008±0.001	0.002	0.007±0.001	0.04±0.004	1.8±0.2
30-34	1.225	93	0.004±0.001	0.001	0.004±0.001	0.02±0.002	0.9±0.1
						<u>2.17±0.05 (93%)^d [Total]</u>	

Site / Depth (cm)	Density (g/cm ³) ^a	% Composition	²³⁹⁺²⁴⁰ Pu (mBq/g)			²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory (%)
	<u><3 mm component</u>	<u><3 mm component</u>	<u><3 mm component</u>	<u>>3 mm component^b</u>	<u>Bulk</u>		
<u>Red Soil</u>							
0-5	1.185	95	0.116±0.007	0.023	0.111±0.007	0.66±0.03	34.7±1.8
5-10	1.409	95	0.085±0.005	0.017	0.081±0.005	0.58±0.02	30.5±1.3
10-15	1.390	97	0.049±0.003	0.010	0.047±0.003	0.33±0.02	17.4±1.1
15-20	1.390	98	0.021±0.002	0.004	0.020±0.002	0.14±0.01	7.4±0.6
20-25	1.390	97	0.028±0.002	0.006	0.027±0.002	0.19±0.01	10.0±0.6
						<u>1.90±0.05 (82%)^d [Total]</u>	
<u>Blue Range</u>							
0-5	1.136	70	0.162±0.009	0.032	0.123±0.006	0.75±0.03	42.4±2.1
5-10	0.987	67	0.181±0.010	0.036	0.133±0.007	0.72±0.04	40.7±2.5
10-15	0.987	73	0.046±0.004	0.009	0.037±0.003	0.19±0.02	10.7±1.2
15-20	0.987	78	0.018±0.002	0.004	0.015±0.001	0.08±0.006	4.5±0.4
20-25	0.987	75	0.006±0.001	0.001	0.005±0.001	0.03±0.003	1.7±0.2
						<u>1.77±0.05 (76%)^d [Total]</u>	
<u>Pierce's Creek</u>							
<u>Between rip lines</u>							
0-5	1.324	88	0.219±0.014	0.044	0.198±0.013	1.33±0.06	79.6±4.6
5-10	1.430	87	0.030±0.003	0.006	0.027±0.002	0.20±0.01	12.0±0.7
10-15	1.549	87	0.012±0.001	0.002	0.010±0.001	0.08±0.006	4.8±0.4
15-20	1.549	88	0.004±0.001	0.001	0.003±0.001	0.03±0.003	1.8±0.2
20-25	1.549	85	0.004±0.001	0.001	0.003±0.001	0.03±0.003	1.8±0.2
						<u>1.67±0.06 (72%)^d [Total]</u>	

Site / Depth (cm)	Density (g/cm ³) ^a	% Composition	²³⁹⁺²⁴⁰ Pu (mBq/g)			²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory (%)
	<u><3 mm component</u>	<u><3 mm component</u>	<u><3 mm component</u>	<u>>3 mm component^b</u>	<u>Bulk</u>		
<u>Pierce's Creek</u> <u>Ridge of rip line</u>	0-10	83	0.057±0.004	0.011	0.049±0.003	0.628±0.034	65.4±4.5
	10-20	84	0.017±0.002	0.003	0.015±0.001	0.175±0.014	18.2±1.6
	20-30	83	0.007±0.001	0.001	0.006±0.001	0.094±0.008	9.8±0.9
	30-40	79	0.005±0.001	0.001	0.004±0.001	0.062±0.006	6.5±0.7
						<u>0.96±0.04 [Total]</u>	
<u>Pierce's Creek</u> <u>Swale of rip line</u>	0-5	82	0.042±0.004	0.008	0.036±0.003	0.251±0.016	32.2±2.4
	5-10	88	0.063±0.005	0.013	0.056±0.004	0.339±0.022	43.5±3.3
	10-15	73	0.038±0.003	0.008	0.030±0.002	0.185±0.009	23.7±1.5
						<u>0.78±0.03 [Total]</u>	
<u>Pago</u>	0-5	88	0.044±0.004	0.040±0.003	0.009	0.25±0.02	26.9±2.3
	5-10	86	0.045±0.004	0.040±0.003	0.009	0.27±0.02	29.0±2.3
	10-15	89	0.042±0.004	0.038±0.003	0.008	0.24±0.02	25.8±2.3
	15-20	86	0.018±0.002	0.016±0.001	0.004	0.10±0.01	10.8±1.1
	20-25	82	0.014±0.002	0.012±0.001	0.003	0.08±0.01	8.6±1.1
						<u>0.93±0.03 (40%)^d [Total]</u>	

^aDensity of the >3 mm component ~2.1 g/cm³.^bPlutonium concentration of the >3 mm component is derived from 20% plutonium concentration of the <3 mm component.^cSurface soil samples were collected with a trowel to typical depths of 3-5 cm. Samples at Blundell's Flat site were collected over an area of ~100 x 100 m².^dNumbers in parentheses indicate percentages relative to the average reference inventory (2.32 mBq/cm²) at the undisturbed sites.

Surface soils at specific study sites were also collected in 2007. These surface samples were sampled randomly over a small area, except at Blundell’s Flat site where a ‘transect’ sampling method was employed to cover a much larger area. The plutonium results obtained from these samples were compared with the top 5 and 10 cm soil samples collected in 2008 from sampling pit sites, and are shown in Table 4.9. It is noted that the sampling pits were sited close to the location where the surface soils were collected previously. The variation of plutonium concentrations in ‘near surface’ soils is then used to gauge the spatial variability at a specific study site. In particular, with the exception of the ‘between rip-lines’ Pierce’s Creek site, all of the surface soil samples have higher plutonium concentrations than the 0-5 or 0-10 cm samples. This is reasonable, indeed expected, since the surface samples were generally less than 5 cm deep and the plutonium concentration peaks near the surface.

Table 4.9: Comparison of ‘surface’ soil samples with ‘top 5 cm’ soil samples from sampling pits at specific study sites.

Site	²³⁹⁺²⁴⁰ Pu (mBq/g) ^a (surface soil samples) ^b	²³⁹⁺²⁴⁰ Pu (mBq/g) ^a (top 5 cm soil samples) ^c
Pierce’s Creek, Between rip lines	0.122±0.007	0.219±0.014
Pierce’s Creek, Swales next to rip line	0.060±0.003	0.042±0.004
Pierce’s Creek, Ridges of rip-line	0.079±0.005	0.057±0.004 ^d
Pago, on hill slope about 10 m away from edge of gully	0.080±0.005	0.044±0.004
Blundell’s Flat, open area	0.172±0.010 ^e	0.138±0.008 (Pit C), 0.115±0.007 ^f (Pit D)

^a Plutonium concentration refers to the <3 mm soil components.
^b Surface soil samples were collected with a trowel to typical depths of 3-5 cm.
^c Top 5 cm of a pit depth profile, except otherwise noted.
^d Top 10 cm slice of a pit depth profile.
^e Samples were collected over an area of ~100 x 100 m².
^f Top 10 cm slice of a second pit depth profile.

Blundell's Flat, Bullock Paddock, Red Soil and Blue Range sites

Over the past 50 years since the peak of the fallout from nuclear weapons testing, the Blundell's Flat, Bullock Paddock, Blue Range and Red Soil sites have experienced both extensive pine forestry operations and the major perturbation of the 2003 bush fire. The Blundell's Flat site was not ripped after the 2003 bushfire, whereas the other three sites were ripped. Despite being subjected to these disturbances, the plutonium inventories at these four sites are within 24% of the average reference plutonium inventory at the undisturbed sites, indicating that any loss of top soil over the past 50 years due to forestry operations and/or bushfires has been minimal. The gently sloping terrain that is a common feature among these sites is likely to have been a contributing factor to minimising soil loss.

Among all the study sites, Blue Range site has the highest stone content (30%) in the top 5 cm of soil. This site was selected because its slope and history were similar to the nearby Red Soil site, but the soil type is different. Rustomji and Hairsine, [2006] highlighted that the yellow earths found at this site were less permeable and more erosion prone than the red earth soils at the nearby Red Soil site. Of the four sites, this site has the lowest plutonium inventory, which might offer some support to this expectation.

There is rather poor agreement between the two sampling pits, C and D (Table 4.8), of the Blundell's Flat site, with the plutonium inventories of 2.1 and 1.4 mBq/cm² respectively differing by 40%. As this site was subjected to forestry operations, it is possible that the Pit D could be sited on an old rip line that has deflated over time, or is in an old swale. It is noted the concentration of 0.172 mBq/g measured in the representative surface soil sample (Table 4.9), which was collected by taking a 2-3 cm deep scoop of soil with a trowel on a 10x10 m² grid over an area of 100x100 m², is higher than the average 0-5 cm concentration of 0.138 mBq/g in Pit C. This indicates a probable gradient in plutonium concentration even in the top 5 cm. But the average 0-10 cm concentration of 0.136 mBq/g in Pit C is significantly higher than in the equivalent depth range at Pit D (0.115 mBq/g), which lends support to Pit C being more representative than Pit D.

(i) Pierce's Creek site

The sample taken between the post-fire rip-lines at the Pierce's Creek site showed the second lowest plutonium inventory among all the study sites (Table 4.8). The estimated plutonium loss is ~28%, which represents ~2 cm loss of surface soil. Furthermore, it is highly unusual in that its plutonium concentration in the 0-5 cm depth interval is distinctly higher than any of the other disturbed sites (Figure 4.5e), and 80% of the inventory is found in this interval (Table 4.8). It is also higher than the surface grab sample taken in its vicinity (Table 4.9), and about equal to the surface concentration at Reference Pit A. The soil at this site is a highly-erodible decomposed granite, and the sampled pit was intermediate between two post-fire rip lines, which were ~3 m apart. The higher surface plutonium concentration might therefore be attributable to contributions of fine-grained material washed in from the rip line above which have accumulated at this point. Support for this hypothesis is provided by the 'representative surface soil' sample, which was also collected between the ridge lines but over an area of ~50x2 m². In contrast to all of the other surface grab samples, it has a plutonium concentration that is less than, and indeed only ~50% that in the top 5 cm of the pit. Hence, it is likely that the actual soil loss may be greater than that estimated from the measured plutonium inventory of the pit. If the plutonium concentration in the surface grab sample is taken to be more representative of the 0-5 cm depth interval, then the inventory would drop from 1.67 to 1.09 mBq/cm², corresponding to a loss of ~5 cm of soil at this site.

Plutonium inventories in the swale and on the ridge of the rip line are similar (Table 4.8). *A priori*, one would have expected the inventory in the swale to be significantly lower than the ridge since the surface material has been piled / shifted up into the ridge. During ripping, however, it is likely that a significant amount of surface material from the edges of the rip-line itself will fall into the groove behind the ripper, which would explain the higher-than-expected observed inventory in the swale. Some support for this interpretation is provided by the depth profile, which does not peak at the surface and is relatively flat down to 15 cm. The 'representative' surface grab sample collected along ~50 m of swale, in common with almost all of the surface grab samples, shows a somewhat higher plutonium concentration than the

0-5 cm sample from the pit. This may indicate a small contribution from surface material washed in from the slope above.

Further, the rip-line ridge should have been deposited on top of the original surface, and thus if the sampling pit had intersected the original surface, the plutonium concentration would have been expected to be high at that specific depth, and a spike should be observed in the depth profile. It would be of considerable interest to find such a buried soil, because it would not have been subject to any erosion since the bush fires, and hence would provide an estimate of the immediate pre-fire inventory. However the results (Figure 4.5g and Table 4.8) did not show this feature. Since we did not have this in mind when sampling, it is possible that the 40 cm depth of the pit on the rip line ridge was not sufficiently deep to intersect the previous surface. Alternatively, the ripping process may not be perfectly understood. Nevertheless, the total inventory of 0.96 mBq/cm^2 in the ridge line pit is similar to, but less than, the adjusted inventory of 1.09 mBq/cm^2 (see discussion above) from the pit between the rip-lines, which supports the idea that some material has been washed off the ridge line and transported down-slope.

In view of the possible soil disturbance and complexity caused by the ripping process, all samples at other study sites were deliberately collected away from rip lines where they could be identified, although as noted above, old rip lines have been substantially deflated and are not always visible.

(ii) Pago site

The Pago site showed the lowest inventory, with only 44% of the plutonium remaining (Table 4.8). This represents the loss of ~6 cm of topsoil. The sample pit was ~2 m from a deep active gully, and although it was relatively flat at the pit itself, the hill slopes coming into the gully were steep. This site was selected because of its clearly dynamic nature, which is reflected in the measured low plutonium inventory. In contrast to the other sites, the plutonium concentration in the top 15 cm is low and uniform (Figure 4.5f), implying that the soil at this site has been disturbed and

mixed, perhaps by deposited material from the surrounding slopes and/or by machinery during the removal of burnt trees after the bushfire crisis.

Table 4.9 shows that the representative ‘surface’ sample collected at this site in 2007 has a plutonium concentration that is almost a factor of two higher than the 0-5 cm sample from the 2008 pit. Although this is a general feature of the table, as noted above, and may be attributed at least in part to the plutonium depth profile being strongly peaked at the surface, the effect is largest at the Pago site, despite the ‘surface’ sample having been collected within a few tens of metres of the pit site. This may reflect local variability in what is clearly a dynamic environment on such steep hill slope terrain. Also, as highlighted earlier, the plutonium depth profile (Figure 4.5f) indicated that the soil at this site may have been disturbed and mixed, perhaps by machinery during the removal of burnt trees after the bushfire crisis. Thus the variation in plutonium concentrations in surface soil could be attributed to such activities.

4.4.2 Plutonium concentrations of sediments in gullies

The comparison of plutonium concentrations in surface soils with sediment in the gullies allows one to determine how much of the sediment is derived from the sides of gullies and how much is from surface erosion. Strictly, a quantitative comparison between surface soil and gully sediment should be based upon a specific size fraction, since finer grains are more readily mobilised than the coarser fractions, and finer grains tend to have higher plutonium concentrations than coarser ones due to their higher surface/volume ratios. The measurements reported here, however, are on bulk samples, with only material greater than 3 mm being sieved out. Nevertheless, useful qualitative information can be obtained. As highlighted in Chapter 2, isotope rich sediment results from erosion activity that is dominated by loss of topsoil and hence likely to be generated from sheet and rill processes operating at the surface, whereas loss of subsoil by channel and gully erosion generally leads to negligible or low isotope concentration. Therefore a comparison of the plutonium concentration in the gully sediment with that from soil surfaces can provide a useful mean to distinguish the source of erosional materials.

Table 4.10: Comparison of surface soil samples with sediment samples in gullies.

Site	²³⁹⁺²⁴⁰ Pu (mBq/g) (surface soil samples) ^a	²³⁹⁺²⁴⁰ Pu (mBq/g) (sediment samples in gullies) ^a
Pago	0.080±0.005	0.034±0.002
Pierce's Creek	0.122±0.007 ^b	0.006±0.001

^a Composite surface soil and sediment samples were collected with a trowel to typical depths of 3-5 cm. ^b Surface soil samples were collected from 'undisturbed' area between rip lines.

Pago site

From Table 4.10, the plutonium concentration in the gully sediment indicates that there is some contribution from the nearby surface soil, but the contribution from the gully walls is dominant. Taking into consideration that the surface materials that were washed into the gully would probably have had a higher plutonium concentration than that in the surface sample, the gully contribution would be at least 60%.

Pierce's Creek site

The sediment in the gully at Pierce's Creek site has very low plutonium concentration compared to the nearby surface soil (Table 4.10), implying that it is mostly derived from the gully walls rather than surface wash. The contribution to the sampled sediment from gullying at this site is at least 95%.

Note, however, that there was little sediment in either gully, and what was there probably represented only the last rainfall event and is unlikely to have been representative. Most of the sediment has been transported further down the drainage system.

4.4.3 Plutonium in sediment and stream banks from a native vegetation catchment: the Conder Creek site

At the Conder Creek site, plutonium concentrations were determined from sediment and stream-bank deposits from a creek that drains a catchment that is under native vegetation. This catchment was completely burnt over by the bush fire in 2003, but has recovered with significant regeneration in term of both understory and mature eucalypts at the time of sampling. The sampling locations were ~100 m upstream from where the creek emerges from the native eucalypt forest (See Figure 4.6). At this point, sediment would have been derived from a catchment almost entirely covered by native forest. The only possible exception might have been some runoff from a forest road that runs along a ridge line above the site. Sediments from a deposition area and log jams were collected at this site. Sediments were also collected from a dry creek bed which is located about 250 m downstream from the Conder Creek sampling site. This dry creek bed only flows at times of high-flow since Conder Creek itself appeared to flow underground at this point.

The results are shown in Table 4.11.

Table 4.11: Plutonium concentrations in sediment samples collected from different locations along a creek at Conder Creek site.

Sampling location	²³⁹⁺²⁴⁰ Pu (mBq/g)
Flat deposition area, downstream	0.242±0.019
Log jam, downstream	0.124±0.008
Bank, upstream	0.122±0.008
Opposite bank	0.129±0.008
Dry creek bed	0.052±0.003 ^c

^c Sediment samples were collected from a dry creek bed indicated in Figure 4.6 b iv.

From these data, the following observations can be made.

1. The plutonium concentration in the sediment from the deposition area (Figure 4.6 b-i) at the bend of the creek is higher than the surface concentrations at any of the pine-forest sites and comparable with surface concentrations at the native-forest reference site. This observation is consistent with the sediment being derived from the native-forest catchment. It was probably deposited

post bush fire, since the high-flow regime produced by the storms shortly after the bush fire are likely to have scoured the sediment from this area.

2. The sediment from the log jam (Figure 4.6 b-ii), however, has only half the plutonium concentration of the deposition site. In contrast to the deposition area, this sediment would have been trapped during high-flow, high-energy events. Its lower plutonium content is essentially identical to that on the banks and may therefore represent material derived from the banks. Alternatively, it may indicate a contribution from the nearby road or preferential gullying even in the native forest at times of high rainfall due to loss of soil cover in the bush fire.
3. The low plutonium concentrations on the banks of the creek (Figure 4.4 b-iii) indicate a substantial loss of surface soil at these locations. This is likely to be a result of the bush fire, since the intense heat would have effectively ashed the organic component of the richly organic surface soil, leaving a powdery soil residue behind that would have been readily removed by the post-fire rainstorm. The observation that the plutonium concentrations are very similar on both banks of the creek is consistent with this picture since similar thicknesses of the organic rich layer would be expected along the banks of this straight section of the creek.
4. The plutonium concentration in the sediment from the dry creek bed (Figure 4.4 b-iv) is typically a factor of two lower than the level measured upstream. The low plutonium concentration is probably an indication of deposition from the creek wall in conjunction to the high-flow events or it may indicate a contribution from the nearby road at times of high rainfall. Further, the site is located downstream of the junction with a major tributary, which partially drains a pine forest area (see map 4.6 a). Hence there is certainly a contribution from the pine forest area at this point.

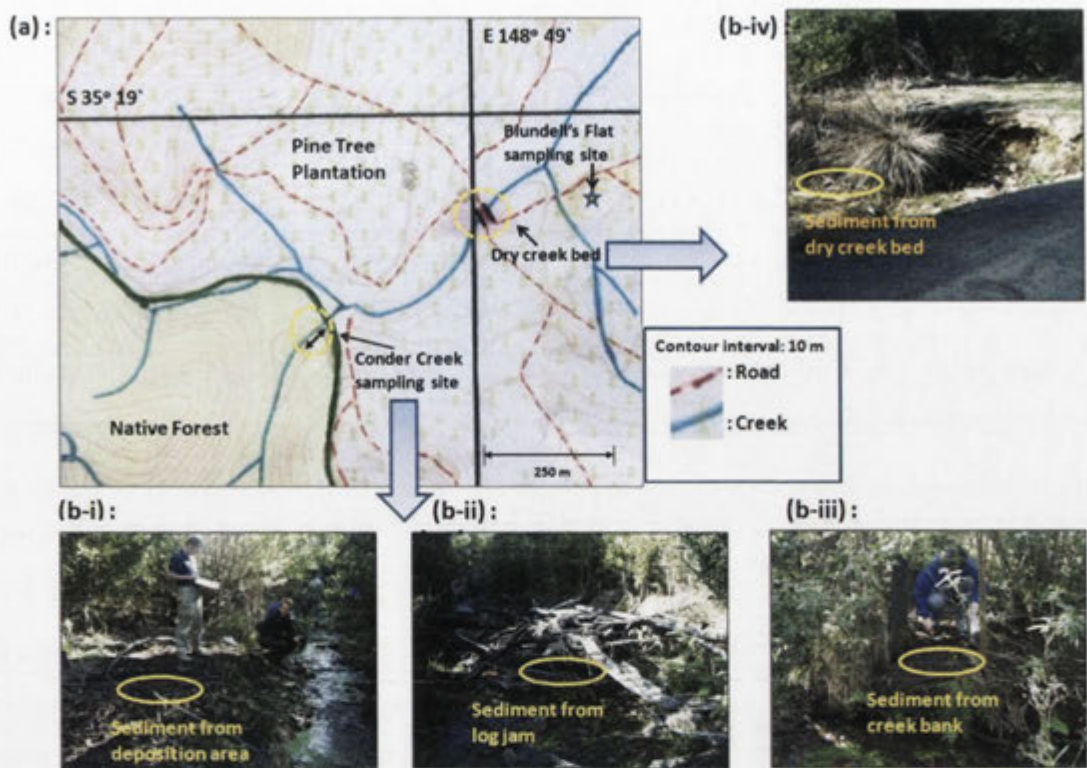


Figure 4.6: Map (a) and photographs (b-i to b-iii) showed the location and surrounding features along Conder Creek sampling site where sediments were collected. Photo (b-iv) showed the site where sediments were collected from the dry creek bed next to a road.

4.5. *Conclusions and summary*

This study has demonstrated the utility of fallout plutonium in investigating recent erosional processes on the scale of a catchment of a few hundred km². It highlights the advantages of plutonium measured by AMS over the more widely-used ¹³⁷Cs measured by γ -ray spectroscopy. Foremost among these is the higher sensitivity of AMS for plutonium which makes possible measurements on 4-20 g samples of bulk soil. In addition, the high throughput of AMS allows measurement of many more samples, which makes detailed whole-of-catchment studies feasible.

Plutonium inventories and depth profiles have been measured at six study sites across a fire-ravaged area that is part of Canberra's water-supply catchment. Prior to a bushfire in 2003, the area was covered by pine plantations. In addition, an undisturbed reference site on a nearby hilltop covered in eucalypt forest was sampled to define the inventory of plutonium that fell out on this area during the nuclear-weapons testing era in the 1950s and 1960s. A second site nearby was also added to determine the reference level in this burnt terrain, and an average plutonium inventory of 2.32 mBq/cm² was determined. Comparison of the measured inventories at the study sites with this reference inventory shows that:

- The total plutonium inventories at four of the study sites (Blundell's Flat, Bullock Paddock, Red Soil and Blue Range) are within the range of the reference inventories, indicating minimum soil loss across much of the pine-forested area since the early 1960s.
- At the Pierce's Creek sites, where the soils are more erodible, between 2 and 5 cm of soil have been lost. Determining the extent to which these losses are due to forestry operations over the preceding 50 years, to heavy rainfall shortly after the bush fire, or to the post-fire use of heavy machinery for harvesting burnt trees and ripping the ground in preparation for replanting, will require further investigation.

- Locally, at particularly dynamic sites such as Pago, loss of ~6 cm of topsoil has been identified. Post-fire use of heavy machinery may have contributed to the higher soil loss.

Additional investigations that involve the comparison of plutonium concentrations in 'near surface' soils and sediment in gullies across specific study sites show that greater than 60% of the sediment presently in the gullies has been derived from gully walls rather than from surface sheet wash, and that this effect is more pronounced at Pierce's Creek than at Pago where the gradients are steeper.

There are several prospects for extending this study. One will be to measure plutonium concentrations in the sediment deposited in the Cotter Dam itself to obtain a depositional history and to chart changes in erosional processes over time. In this regard, a preliminary study has been carried out as part of this thesis and the results are discussed in Chapter 5. Secondly, the study could be extended to the area covered by native eucalypt forest which has not been disturbed by forestry operations. This would allow attention to be focussed on the impact of bush fires on catchments covered by native forest, without the complications associated with prior forestry operations. Thirdly, it would be useful to carry out a tracing investigation to determine the areas which are the principal sources of sediments into the Cotter dam, to allow the implementation of an effective soil conservation programme to mitigate the sedimentation issue. This will require the measurement of plutonium concentrations in different size fractions of the soils and sediments since sediment transport processes fractionate the different grain-sizes in the original soil. Hence, in order to compare like with like, it would be necessary to look at plutonium concentrations in specific size fractions of both the parent soil and the sediment from which it was derived. These studies will require a large number of samples, and could only be realistically tackled with AMS. Complementary data such as rare-earth element ratios will also be required to identify source areas, and some preliminary work in this direction has been reported by Wasson and Worthy [Worthy, 2010].

Chapter 5 A study of catchment erosional response to bush fire using reservoir deposits

This chapter aims to explore the temporal variation of soil erosion activity in the Cotter catchment using sediment samples collected from the Cotter dam.

5.1. Cotter Dam pit sample

As highlighted in Chapter 1, sediments that accumulate on the bed of a reservoir preserve the chronological order in which they were laid down and form a natural archive containing a record of events in the environmental history of the reservoir and its catchment. In this chapter, plutonium concentrations in the sediment deposited in the Cotter Dam are used to study both the depositional history and to chart changes in erosional processes over time in the Cotter catchment. Samples from a 1.2 m deep pit from the upper reaches of the lake behind the Cotter dam were obtained from Martin Worthy of The Fenner School of Environment and Society at the ANU. This pit was dug in July 2006, and exploited an opportunity provided by particularly low water levels at that time. It was sampled in 3 cm increments, each consisting of more than a kilogram of sediment. Figure 5.1 shows the pit, which exhibits the following features:

- Sediments from the top 70 cm (0 to 70 cm) represent those deposited post the 2003 fire. This was inferred from the materials present in the sediment, which was characterized by large quantities of charcoal and other burnt material such as leaves, twigs and pine needles. Sand layers were common in the generally coarse-grained sediments, particularly at 30 cm, 44 cm and a thick layer at 70 cm that marks the transition from pre- to post-fire catchment conditions. This layer contained large quantities of both coarse sand and burnt debris.
- The lower 70 to 120 cm represents sediments that were accumulated prior to the 2003 bush fire. Typically the sediments in this layer were of relatively uniform texture, colour and structure, and only a single thin layer of coarse

grains was evident at a depth of 80 cm. River pebbles were found at the base of the pit which must have been deposited under high-energy fluvial conditions prior to the lake reaching this point.

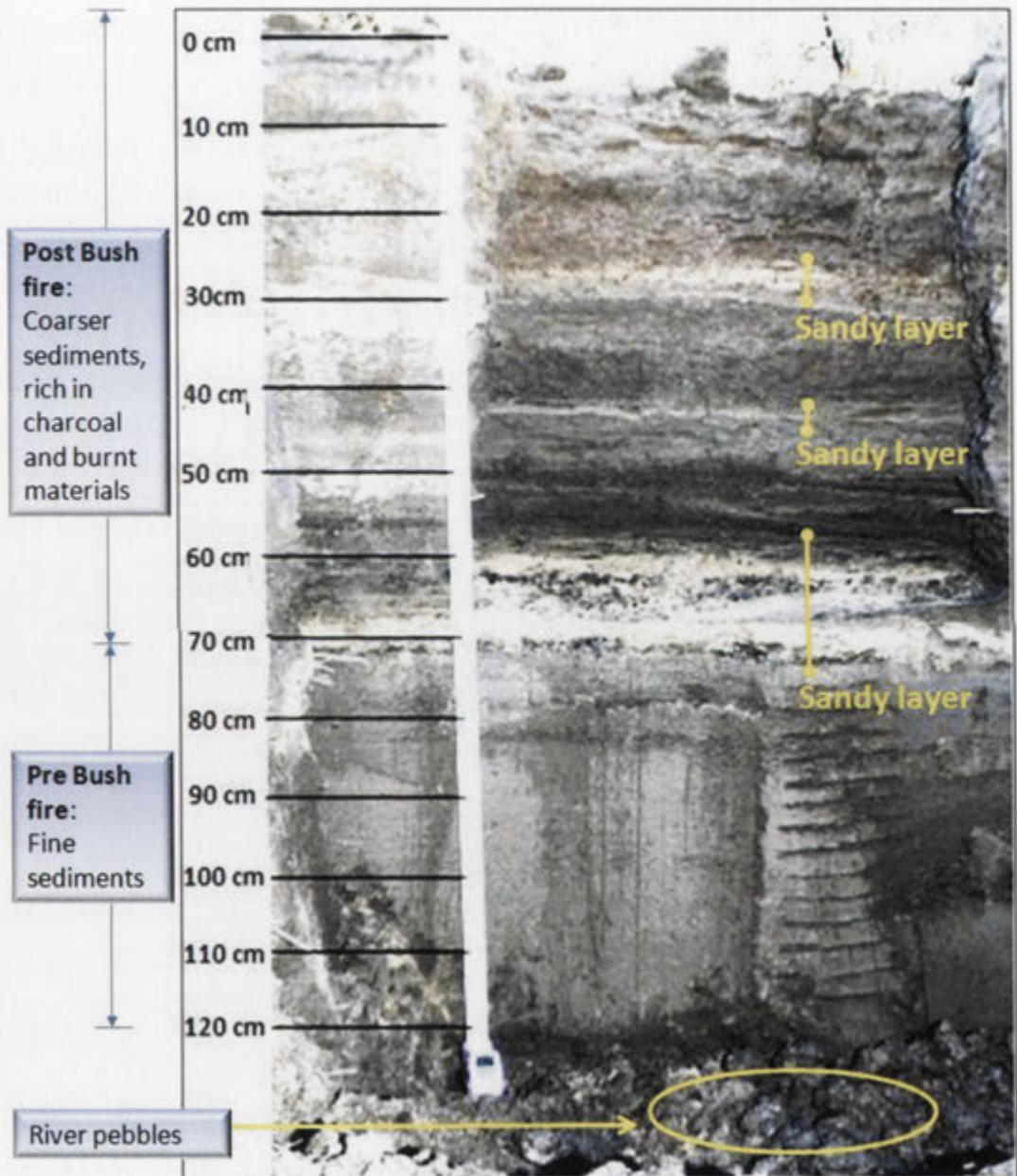


Figure 5.1: A sediment pit sampled at the upper reaches of the lake behind the Cotter dam (S35°18' E148°55') in 2006. Sandy layers are identified at 30 cm, 44 cm and 70 cm.

Cotter Dam is one of three dams within the Cotter catchment and is located approximately 1 km upstream of the confluence of the Cotter and Murrumbidgee Rivers. It was the first dam that was constructed between 1912 and 1915 on the Cotter River and served as ACT's main water supply until the completion of the Bendora Dam in 1961. Cotter Dam was built to hold a volume of 1.85 GL at its initial construction phase in 1915. In view of its low capacity, the resulting lake would not have reached the location of the present sampling pit. The dam wall was eventually raised between 1949 and 1951 from the height of 18.3 m to 26.8 m, increasing the capacity to 4.65 GL [<http://www.actew.com.au>]. At this stage the lake would have reached the position of the sampling pit when full.

5.2. Depth profile measurements

Plutonium concentrations as a function of depth in the Cotter dam pit are shown in Figure 5.2. Several features are evident in these data.

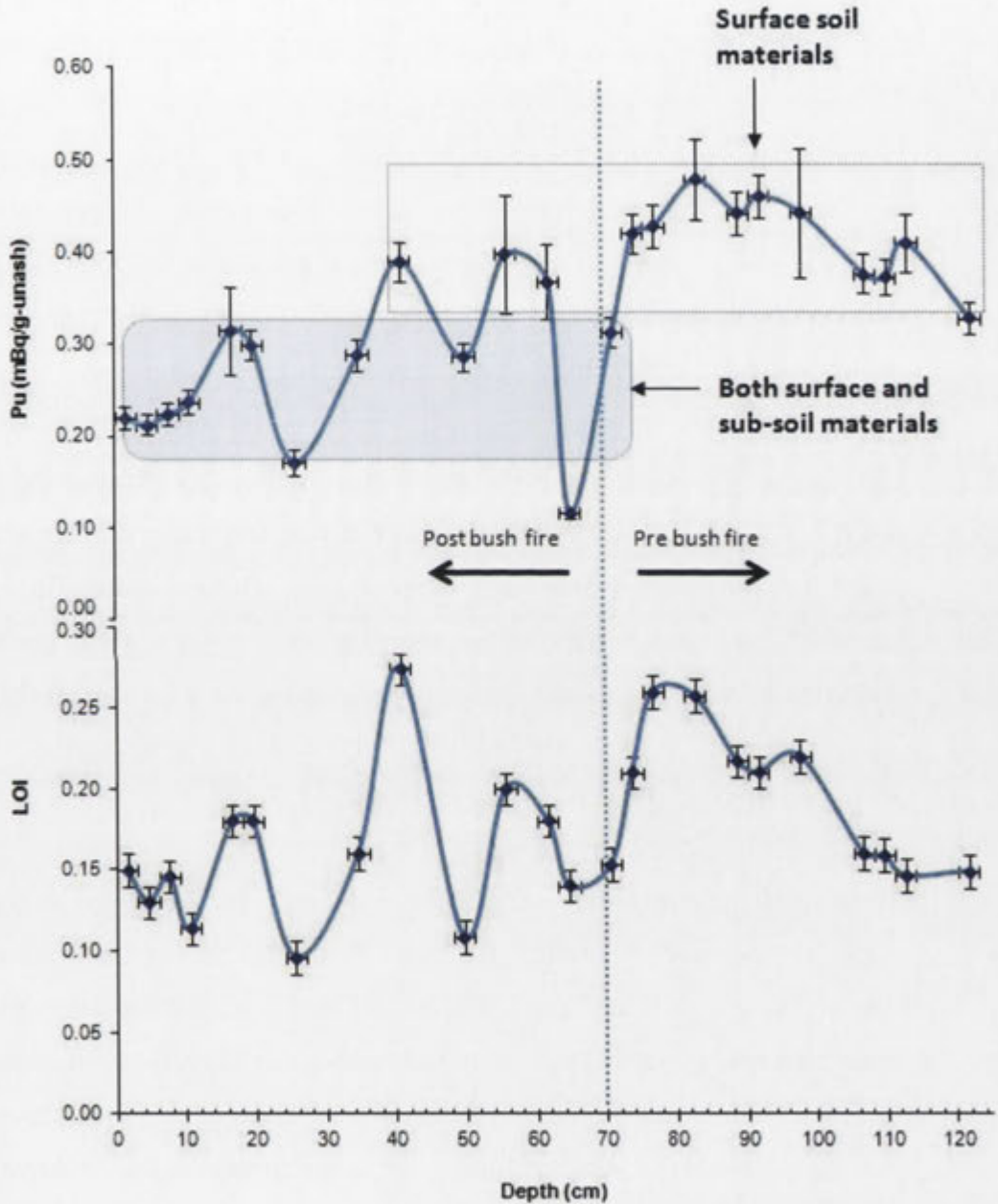


Figure 5.2: Plutonium concentration (upper) and loss-on-ignition (LOI – lower) as a function of depth for the sediments from the Cotter dam pit. The x-axis error bars simply represent the depth interval of the sample. The y-axis error bars for plutonium concentration are 1 sigma and for LOI a constant error of 0.01 has been assumed.

Post-bush fire

1. The post-fire plutonium concentrations are significantly lower than the pre-fire values, although they are still high compared to what is presently found in surface soils across the pine-forest areas. These surprisingly high concentrations can be attributed to two factors; one is the particle-size effect and the other is the presence of soil organic matter. As noted, sediments tend to comprise a high content of fine-grained mud and this is because finer-grained materials are relatively more mobile and likely to be transported to the dam. The finer-grained materials have a larger surface / volume ratio and thus are able to retain more plutonium than the coarser particles. This was demonstrated by Everett [2009] who used a wet sieving and settling procedure to isolate different size fractions, including $<10\ \mu\text{m}$ which showed the most pronounced effect. Attempts to reproduce this in the present work by dry sieving did not show the same contrast, presumably because the finest sieve was $20\ \mu\text{m}$, and because much of the coarser material was actually aggregates of finer grains (see Chapter 3.5). Further, these fine grain sediments are associated with a substantial amount of organic matter as indicated by their LOI result. There is a strong correlation between the LOI and plutonium concentrations and the influence of this organic matter will be discussed in some detail in section 5.4 below.

2. Unlike the pre-fire plutonium concentrations, the post-fire plutonium concentration profile is rather complex. There are distinct high plutonium concentration signals at depth 39-42 cm and 54-57 cm, and dips in plutonium concentrations at depth 24-27 cm and 63-66 cm. This reflects the dynamic response of the catchment in the aftermath of the bush fire. For instance, the sediments associated with high plutonium concentration at the 39-42 cm and 54-57 cm depth region are likely to represent organic-rich surface soils that were washed away more readily shortly after the fires due to lack of vegetation cover. Top soils are generally rich in organic material in contrast to sediment originating from erosion of gully walls which has low or negligible organic content. Thus sediments at the 24-27 cm and 63-66 cm depths could have a significant contribution from materials that were stripped

from gully walls during high-rainfall events. Even so, there is still a considerable quantity of plutonium and organic matter in the sediments indicating that the contribution from surface soil erosion remains significant.

3. Similarly the dip in plutonium concentrations towards the present might indicate the influence of more recently-eroded material. The consistently lower plutonium concentrations and the relatively constant organic contents could be an indication that the catchment is recovering / stabilizing, probably due to re-vegetation. More of the organic matter would then be derived from this post-fire vegetation. Plutonium concentrations are lower because much of the plutonium-labelled organic matter has already been removed. As inferred from the findings in section 5.4, it is noted that organic material that originated from fresh (i.e. post nuclear fallout era) surface vegetation and plant debris would be associated with negligible plutonium content, and thus would be expected to make a negligible contribution to the plutonium concentration in the sediments.

The dip in plutonium concentrations may also be partially attributable to a greater proportion of contributions from gully wall erosion. It could be an indication that there was less top soil erosion as vegetation was re-established whereas most of the active gully network that formed in the aftermath of the fires had not been ameliorated at the time that the pit was dug in 2006.

Pre-bush fire

4. The pre-fire plutonium concentrations are consistently high, and the values are about the same as those measured in the undisturbed surface soil at the reference site (see Table 4.5). As noted above, however, the smaller average particle size will tend to increase the plutonium concentration relative to the soil from which it was derived. Note that the LOI of these pre-fire sediments is somewhat higher than even the surface soil (top 5 cm) from the reference site which range from 17-19%, particularly in the 70-100 cm region where LOI is consistently higher than 20%. This could be attributable to two effects. First, most surface soil loss takes place from only the top few mm, which is likely to be more organic rich on average than the top 5 cm. Secondly, the surface soils at the reference site were collected after the bush fire and some of the organic material had probably been removed by the fire.

5. The high plutonium signal is an indication that prior to the 2003 bush fire, the sediments that were accumulated in the dam are likely to have originated from surface soil. It is also likely that much of this sediment was derived from the pine-forest area due to forestry operations. This is inferred from the LOI measurements which indicate that the organic contents in the pre-fire sediment increased gradually over time. The clearing of native vegetation and the harvesting of pine trees in early days would have contributed to the accumulation of organic material in the sediments.

Forestry activities in the Australian Capital Territory (ACT) date from as early as 1914 and arose from a comprehensive scheme of forest conservation and re-afforestation. By the 1950s, over 16,200 hectares of pine plantation was established in ACT, with approximately 5,000 hectares located in the Kowen forest to the east of Canberra and about 8,000 hectares in the lower Cotter catchment. Much of it was on land that had been previously cleared for grazing, although some clearing of native forest also took place. Particularly in the lower Cotter catchment, approximately 3,000 hectares of land were cleared during the early period of settlement in the Canberra region to create grazing land. This was prior to the establishment of the ACT and the

completion of the Cotter Dam in 1915. As early as 1918, overgrazing and infestation by rabbits had resulted in serious soil erosion in this region. In order to stabilise the landscape, a program of tree planting was established and by 1931, pines had been planted over 3,000 hectares. Over time, the plantation, which was never intended to be a purely commercial operation, grew substantially. Eucalypt forest was cleared for pine plantations from 1931 to 1961, but this practice eventually ceased due to community pressure and concerns about the impacts on water quality in the Cotter River and Reservoir. Prior to the 2003 fires, a total of 8,400 hectares of pine plantations were established in the lower Cotter catchment [<http://www.tams.act.gov.au>].

6. The plutonium concentrations remain high to the bottom of the pit. Since significant plutonium fallout from nuclear weapons testing occurred only after 1953, and peaked in 1964 [Koide *et al.*, 1979], the bottom sediments must have been deposited after 1954, which is at least consistent with the observation that sediment would not have been deposited at this location until after the dam wall was raised in 1951. Further, because the plutonium concentrations do not drop significantly towards the bottom of the pit, there is a suggestion that sediment deposition at this site post-dates even the maximum in fallout at ~1964. In order to obtain a better estimate of the time at which deposition was initiated at this site, an attempt was made to radiocarbon-date organic material at a few positions in the pit. This is taken up in the next section.

5.3. Bomb-pulse radiocarbon dating

The principle of bomb-pulse radiocarbon dating is well illustrated by Hua [2009]. In brief, the atmospheric nuclear weapon tests conducted in the 1950s and 1960s produced significant fluxes of neutrons that could react with the nitrogen in the atmosphere to create ^{14}C via the reaction:



This resulted in a doubling of the ^{14}C concentration in the atmosphere of the Northern Hemisphere by 1963. In the Southern Hemisphere, the maximum was delayed by ~ 2 years and attenuated, being only $\sim 70\%$ above pre-bomb levels. After 1965, the levels in both hemispheres became more nearly equal, and declined approximately exponentially due to the exchange between the atmosphere and other carbon reservoirs. Thus for the period since 1950, significant differences in atmospheric ^{14}C levels between consecutive years offer the possibility of dating recent terrestrial samples. This dating technique has been successfully applied on peat land and tree ring studies [Garnett, 2004; Hua *et al.*, 2004, 2000], but has not been commonly used in sediment dating.

Bomb-pulse ^{14}C dating, which is based on rapid changes in the ^{14}C concentration of the atmosphere and hence of the ^{14}C taken up by living plants, differs from conventional radiocarbon dating, which is based on the loss of ^{14}C due to radioactive decay. For the bomb period, measured ^{14}C concentration is usually reported in pMC (percent Modern Carbon) or F (Fraction Modern Carbon) rather than as radiocarbon ages, and a “bomb-pulse” ^{14}C curve (see Figure 5.3) is employed to convert the measured pMC or F values to calendar years.

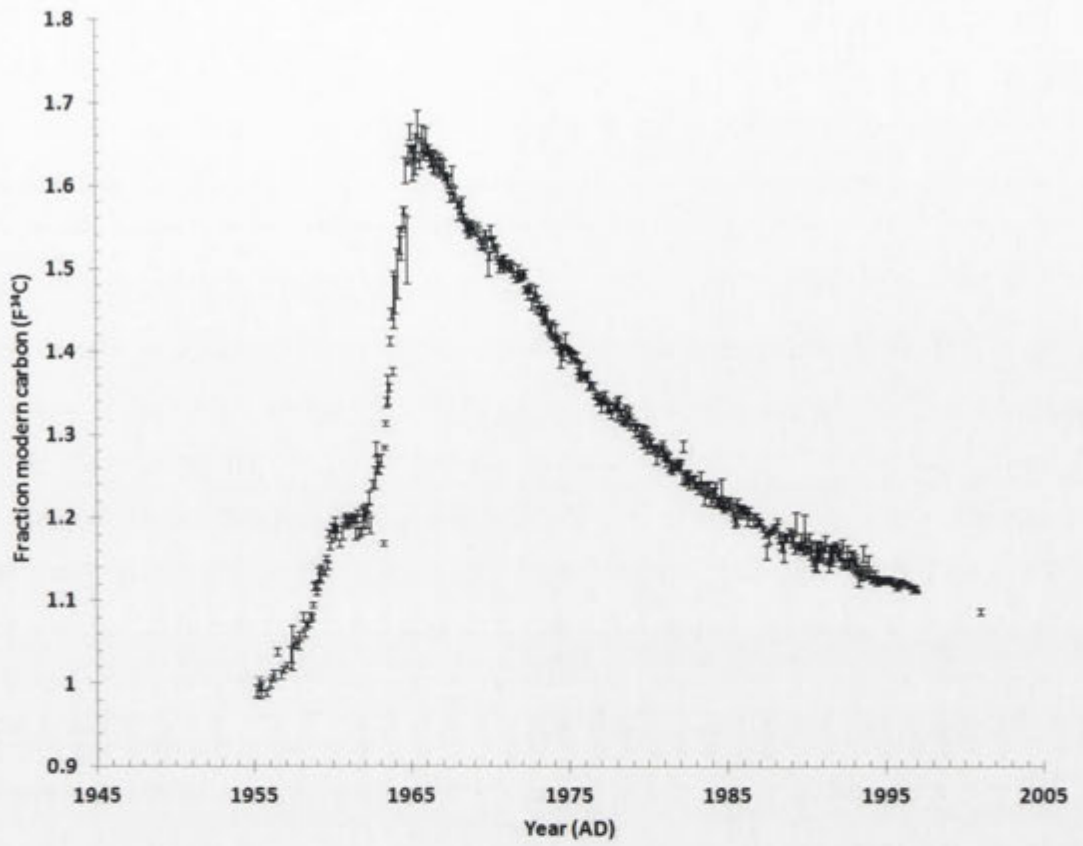


Figure 5.3: Atmospheric ^{14}C concentrations in the Southern Hemisphere for the period 1955-2001. [Source: Hua and Barbetti, 2004]

Radiocarbon measurements

Samples for radiocarbon dating were obtained from the 24-27 cm, 81-84 cm, 111-114 cm and 117-120 cm depth intervals by immersing the sediment in water and stirring it vigorously. Organic rich material such as twigs, leaves, seeds and charcoal will float and may be collected from the water's surface.

There are concerns about twigs and charcoal in particular being stored in the landscape, perhaps for several years, before being mobilised by a rainfall event. In this respect, air-borne pollen or seeds would be more reliable indicators of the year of deposition, but the complexity of pollen extraction and preparation was beyond the scope of the present work. No airborne seeds were found. A few water-borne seed capsules were observed, but insufficient for a radiocarbon sample. Although the year of growth of a twig or a charcoal fragment may not be the same as its year of deposition, it must however precede the year of deposition. Hence, provided that the sample lies on the falling slope of the bomb curve, the measured date must represent the earliest possible date that the sample could have been deposited. For any measured value of the fraction of modern carbon greater than about 1.1, there are, however, two possible dates – one on the rapidly-rising leading edge of the curve between 1959 and 1965, and the other on the trailing edge of the curve from 1965 to the present. Additional information is needed to distinguish between these two solutions.

The samples were selected on the basis of what was available among the floated material as follows:

1. The deepest, and therefore oldest, sediment sampled was from the 117-120 cm interval, only 3 cm above the base of the sediment. The selected organic material consisted of multiple small twigs, each about 3-4 mm long, of total mass 2.0 mg.
2. Single fragments (3-5 mm) of charcoal were selected from two other pre-fire intervals at 111-114 cm and 81-84 cm, of mass 2.7 mg and 3.5 mg respectively.

3. Lastly, the sample from the post-fire 24-27 cm interval was in the form of small fragments (<1 mm) of charcoal with a total mass of about 3.5 mg.

A detailed step-by-step description of the sample preparation procedure is given in Appendix-A2, so only a brief outline will be included here. Both the charcoals and twigs were subjected to a standard acid-base-acid wash procedure and dried before combustion to CO₂. The CO₂ was then converted into graphite on an iron catalyst in a hydrogen atmosphere following a method similar to that described by Vogel *et al.*, [1987]. The ‘Fractions of Modern Carbon’ of these graphite targets were determined using the single stage Accelerator Mass Spectrometer at the Research School of Earth Sciences (ANU).

Table 5.1: ¹⁴C measurement results for samples from the Cotter dam pit of specific depth

Depth (cm)	Sample material	F ¹⁴ C (±1σ)	Year (T ₁) ^a	Year (T ₂) ^b
24-27	charcoal	1.078±0.004	1958	2001
81-84	Charcoal	0.996±0.003	1956	1956
111-114	Charcoal	1.121±0.004	1959	1995
117-120	Twigs	1.184±0.004	1959	1988

^a Year at which the value of F¹⁴C intersects the rising edge of the ¹⁴C bomb pulse curve shown in Figure 5.3.

^b Year at which the value of F¹⁴C intersects the trailing edge of the ¹⁴C bomb pulse curve shown in Figure 5.3.

The ¹⁴C measurements are presented in Table 5.1. The results are reported as Fraction Modern Carbon (F¹⁴C) defined by Stuiver and Polach [1977], and were fitted to the post-bomb Southern Hemisphere atmospheric ¹⁴C calibration curve (Figure 5.3) compiled by Hua and Barbetti [2004]. In order to interpret these data, the following observations are relevant.

1. All 4 samples contain bomb radiocarbon. This is true even for the 81-84 cm sample for which the F¹⁴C is slightly less than unity. Prior to 1950, measurements on annual tree rings show that F¹⁴C does not exceed 0.990 [INTCAL04].
2. The measurement on the twigs from the 117-120 cm depth interval just above the bottom of the pit requires that the sediment in this section cannot have been deposited before 1959 at the earliest. Since sediment higher in the

profile must have been deposited later, this sets the earliest possible date for the start of deposition of the sequence. Note that this is already several years after the completion of the raising of the dam wall in 1951.

3. If instead the twigs were growing in 1988 (year T_2 in Table 5.1), then the sediment, and hence the whole sequence, must have been deposited later than 1988.
4. In order to distinguish between these two scenarios, additional information is needed, and some is available in the plutonium results. In the pre-fire section of the pit, 70-120 cm, the plutonium concentration changes little, and even less after variations due to the organic component are removed. This strongly suggests that the sediment deposition post-dates the era of significant fallout, which spanned the years 1954-1968 [Koide *et al.*, 1979], since the surface soil from which the sediment was derived records cumulative fallout. There are then two possibilities:
 - a. The twigs were growing in 1959, but weren't transported to the pit site until after 1968.
 - b. The twigs were growing in 1988, and arrived at the pit site some time after that date.

Further discussion of this is deferred until the other samples have been discussed.

5. The charcoal from the 111-114 cm section was derived from a tree that must have been growing in either 1959 or 1995. The same arguments as above lead to the possibilities:
 - a. The charcoal origin was from a wood that was growing in 1959, but was not transported to the pit site until after 1968.
 - b. The charcoal origin was from a wood that was growing in 1995, and arrived at the pit site some time after that date.
6. The charcoals from the 111-114 cm and 81-84 cm sections are clearly not in chronological order. Whereas the sample from the 111-114 cm section must have been growing in either 1959 or 1995, there is only a single solution for the year at which the sample from the 81-84 cm section was growing, i.e. 1956. In contrast to a twig, however, charcoal could be derived from larger branches which could represent several years of growth. Hence, the older date

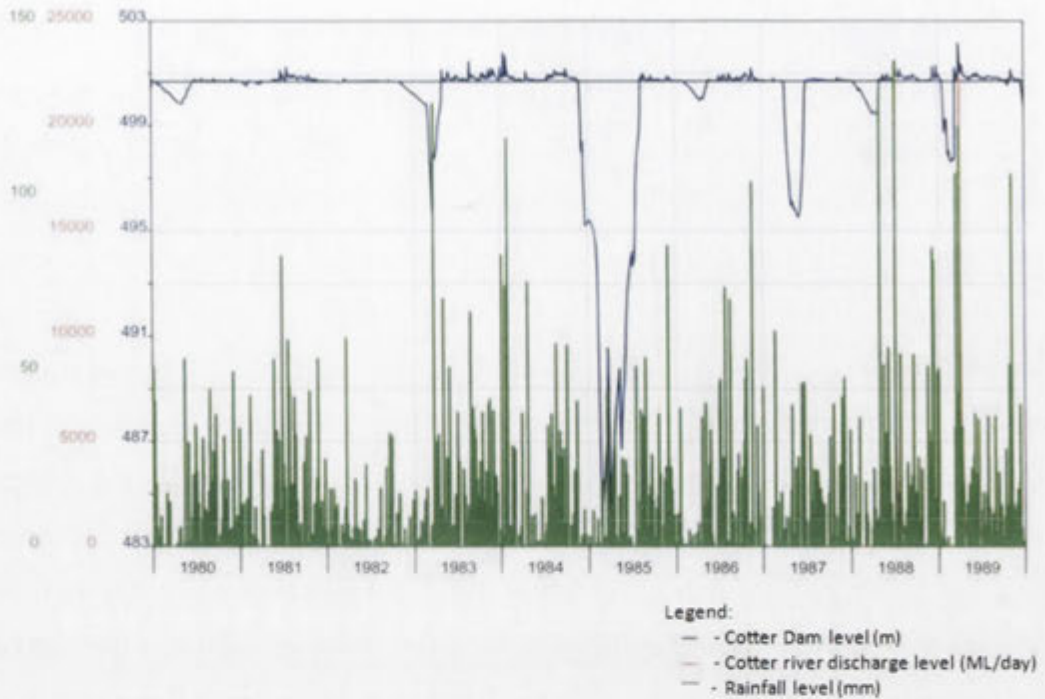
for the 81-84 cm charcoal is plausibly explained in terms of it being derived from a section of tree that was growing in 1956, but wasn't burnt and transported until at least 3 years, and possibly 20 years later. In addition, the sediment in the 81-84 cm interval has a coarse component that indicates that this layer was deposited at a time of high flow and hence high rainfall, which could have mobilized material stored in the landscape, including the charcoal.

7. Deposition of the three samples discussed above all predated the 2003 bush fire. In contrast, the sample from the 24-27 cm section was deposited after the fire, and it is reasonable to assume that the organic debris (charcoal fragments) represents material that was burnt in the fire and transported by the subsequent rainstorm. In this case, the 2001 date obtained from the radiocarbon measurement would be strongly favored over the 1958 date.

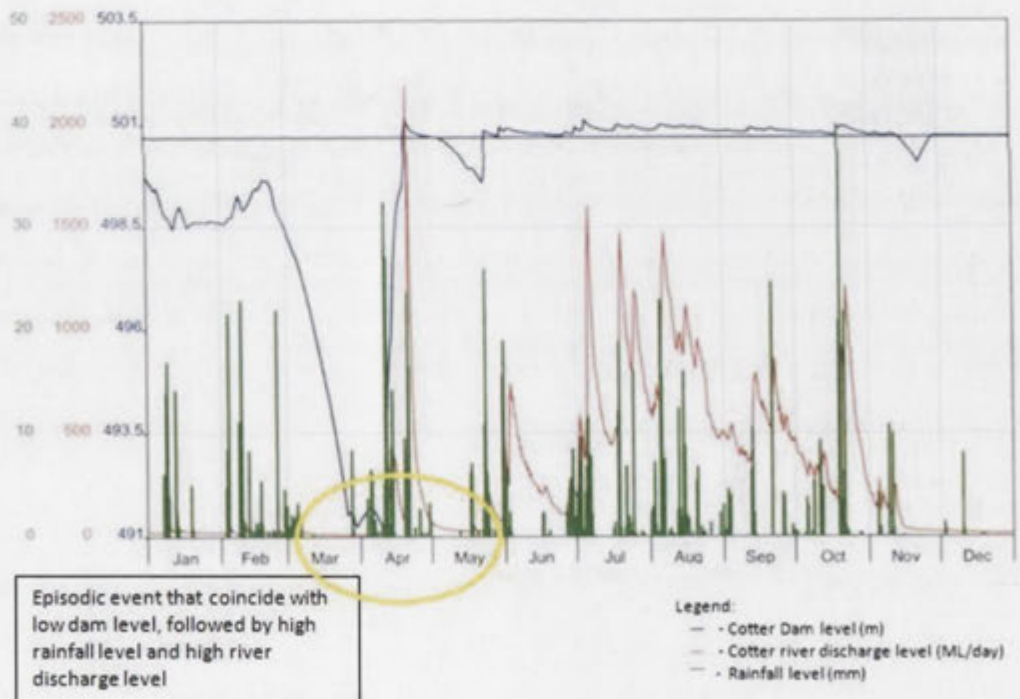
Although it cannot be ruled out that the samples from the 117-120 cm and 111-114 cm sections were both growing at the same time in 1959 before being deposited at different times after 1968, it seems more likely that they were growing in 1988 and 1995 respectively and were deposited closer in time to their growth, the more so since they are in the expected chronological sequence. If this was the case, then the whole sedimentary sequence must have been deposited since 1988. Since the dam wall has been at its present height since 1951, and the lake was often full between then and 1988 as shown in Figure 5.4(a) below, this however raises the question of why there is no sediment prior to 1988 at the location of the pit. A possible explanation is provided by Figure 5.4(b) which shows the water level in the dam, precipitation, and dam discharge rate as a function of time during 1990. Towards the end of March, the dam was almost empty, so the location of the pit would have been exposed because it is only covered by water when the dam is full, and the river would have been flowing across it under low-flow conditions. On 11 April 1990, an average of 60 mm of precipitation (<http://www.bom.gov.au/climate/data/index.shtml>) fell on the catchment and the dam filled very rapidly, indicating high-flow conditions. This high-energy flow would have passed through the location of the pit because there was no lake at that point to slow it down. Hence, it is plausible that it scoured out the sediment that was there

and transported it downstream. Once the lake was full again, sedimentation could restart on top of the river gravels. It is noted that this was an unusual event and Figure 5.3(a) shows that there was no equivalent event in the record of the previous 10 years. Unfortunately, lack of access to the requisite records has made it impossible to ascertain whether another such event might have occurred since 1990.

Nevertheless, if the above interpretation is correct, then ~50 cm of sediment was deposited at this location over the pre-fire period from 1990-2003, implying an average sedimentation rate of ~4 cm/yr. In contrast, 70 cm of sediment was deposited in the 3.5 year post-fire period 2003-2006 implying an average sedimentation rate of 20 cm/yr. According to a bathymetry study of the Cotter Dam [Project Number: AG100062-2005, *GIS Analysis of the Cotter Dam Reservoir Bathymetry*, Report prepared by Ecowise Environmental Pty Ltd (Norm Mueller and Tony Spark) for ACTEW Corporation], approximately 650 000 m³ of sediments were deposited in the dam between 1914 and 2003, and based on the derived storage area (470 000 m²) of the Cotter Dam at its raised height of 26m (500 m above sea level), the average sedimentation rate is ~1.6 cm/yr. As a general comparison, one would expect the sedimentation rate at the sampling pit to be relatively higher, since this is close to where the flow slows down as the river water enters the lake and hence where sediment will be preferentially deposited. Sedimentation may, however have been slower between 1990 and 1995 since if one considers that the sediments at depth 111-114 cm were deposited in 1995 whereas sediments at the base of the pit (117-120 cm) were deposited in 1990, the implied sedimentation rate is ~1 cm/yr which is comparable with the sedimentation rate derived from the bathymetry study.



(a) 10 years record (1980-1990)



(b) Annual record (1990-1991)

Figure 5.4: Rainfall, Cotter dam water level, and discharge rate of water from the Cotter dam as a function of time for the periods (a) 1980-1989, and (b) 1990. Rainfall was measured at Vanity's Crossing within the lower Cotter catchment. The dam level is in metres above sea level – the dam is empty at 491 asl and full at ~500m asl.

[Source: Norm Mueller, The ALS Environmental Division and Ecowise.]

5.4. Study of plutonium in organic materials

A strong affinity between certain fallout radionuclides and organic materials has been reported by a number of authors including Wallbrink [2005] and Blake [2009]. For instance, Blake [2009] reported that ^7Be and ^{210}Pb were closely associated with ash, litter and soil organic material whereas ^{137}Cs was more closely associated with subsurface mineral soil. Similarly, there is evidence that plutonium has a preferential affinity for organic materials [Livens *et al.*, 1987]. In this context, organic materials in the form of ash or charcoal have a tendency to float and thus could be readily mobilized by a post-fire rain storm, particularly in this fire ravaged terrain where the presence of charred organic materials was significant. Moreover, the re-distribution of these organic materials could also lead to spatial variation in the plutonium inventory across a specific study site. Any consequential loss (or gain) of plutonium could lead to an over (or under) estimation of the loss of soil calculated from the plutonium inventory. Furthermore, differences in the affinity of radionuclides between the organic and mineral components may facilitate the study of the soil mobilisation processes. For instance, ^{137}Cs and plutonium could be used in a complementary way to better understand the soil transportation process since the former radioisotope would be sensitive to subsoil mineral soil erosion processes whereas the latter could better reflect the remobilisation of litter, ash and the burnt O-horizon (the organic rich surface layer of the soil). Thus a study of plutonium behaviour in the organic content of the soil would be useful both in understanding experimental plutonium inventories in terms of soil loss, as well as in understanding the soil transportation mechanism.

Investigations of plutonium levels in living plants and in soil organic components were examined separately, using the standard protocol outlined in Chapter 3, with slight modifications. Living plants were represented by a collection of 'fresh' organic materials which included grasses, leaves, branches and tree bark that were gathered from the native forest area of the Black Mountain Nature Park located next to the Australian National University. These materials were first subjected to intense washing, including an ultrasonic bath, to remove any possible contamination from soil materials. They were then ashed at the Australian

Commonwealth Scientific and Research Organization (CSIRO) Black Mountain laboratories by increasing the temperature gradually from 105°C to 450°C over a period of three days to ensure that all of the organic materials were completely ashed.

In contrast to the living plants, the separation of soil organic material is difficult since much of the stable organic material is intimately associated with the mineral particles. The best strategy is then to enhance the soil organic material in a sample instead of separating it, and to compare enriched and un-enriched samples in order to deduce separately the plutonium concentrations on the organic and mineral components of the soil. Samples were therefore soaked in water and the organic rich materials were floated off and removed. Several organic-rich sediment samples from specific depth intervals (24-27 cm, 81-84 cm and 111-114 cm) in the Cotter dam pit, which had a relatively high loss on ignition (LOI), were utilised in this study. Under the assumption that all of the organic material in a sample is removed by ashing, the LOI is a direct measure of the organic content of a sample.

Living plants

The concentrations of plutonium in plants, measured on a dry weight basis are shown in Table 5.2. Typically, the plutonium concentration is about three orders of magnitude lower than that in the soil. This implies that the plutonium uptake by living plants from soil is small. For this reason, the loss of fallout plutonium inventory via uptake by plants is expected to be negligible, and is unlikely to contribute to spatial heterogeneity in plutonium inventories across the catchment. Additionally, surface vegetation and plant debris inclusive of twigs can be removed during sampling or at the sample pre-treatment stage, to avoid diluting the plutonium concentration in a sample.

Table 5.2: Measurements of plutonium concentrations in living plant material

Fresh organic sample	Dry weight (g)	Ashed weight (g)	LOI (%)	$^{239+240}\text{Pu}$ ($\mu\text{Bq/g-dry}$)
Grass	143.5	6.7	95	0.41 \pm 0.07
Sedge grass	44.2	2.2	95	0.04 \pm 0.02
Branches	280.6	2.7	99	0.36 \pm 0.05
Tree barks	431.8	14.3	97	0.67 \pm 0.07
Leaf (from tree)	186.7	3.9	98	0.21 \pm 0.05
Leaf (from ground)	169.0	4.8	97	0.83 \pm 0.09
Typical near surface soil			20	500

Soil organic matter

It was highlighted in the earlier section 5.2 and in Chapter 3, section 3.5 that there is a strong correlation between plutonium concentration and organic content as measured by LOI. The results are reproduced in Table 5.3 for ease of reference.

Table 5.3: Plutonium concentrations in sediment sample: CDP-24/27 (Cotter dam pit, 24-27 cm) in different size fractions, separated using standard dry sieving technique

Sample code	Particle size (μm)	LOI (%)	Bulk % component	$^{239+240}\text{Pu}$ (mBq/g-dry)
CDP-24/27 [250]	250<x<3000	57	1	0.738 \pm 0.041
CDP-24/27 [125]	125<x<250	27	9	0.486 \pm 0.027
CDP-24/27 [64]	64<x<125	11	27	0.297 \pm 0.017
CDP-24/27 [40]	40<x<64	6	48	0.171 \pm 0.009
CDP-24/27 [20]	20<x<40	7	14	0.142 \pm 0.007
CDP-24/27 [<20]	x<20	8	1	0.208 \pm 0.011
Bulk $^{239+240}\text{Pu}$ (mBq/g) derived from the individual grain sizes:				0.234 \pm 0.013
CDP-24/27 [Bulk]	x<3000	10	-	0.231 \pm 0.014 ^a

^a Measured on bulk sample

To further investigate this observation, plutonium measurements were carried out on organic-enriched samples and the results are shown in Table 5.4.

Table 5.4: Plutonium concentrations in samples^a rich in soil organic materials

Sample code	Particle size (µm)	LOI (%)	Wt of dry / unashed sample (g)	Wt of organic (g)	Wt of mineral (g)	²³⁹⁺²⁴⁰ Pu (mBq/g-dry) ^b
CDP24/27 [125]	125<x<250	27	27.64	7.46	20.18	0.486±0.027
CDP24/27 [125] organic	125<x<250	55	5.16	2.84	2.32	0.818±0.066
CDP81/84 [Bulk]	x<3000	26	25.85	6.72	19.13	0.442±0.023
CDP81/84 [250] organic	250<x<3000	81	7.40	5.76	1.44	0.315±0.066
CDP111/114 [Bulk]	x<3000	15	24.08	3.61	20.47	0.387±0.020
CDP111/114 [Bulk] organic	x<3000	70	4.45	3.12	1.34	0.739±0.053

^aThe samples labelled “organic” were concentrated in organic material by flotation. The procedure is described in the text above.

^bThe concentrations are relative to the mass of material before ashing.

There are two observations from these data.

1. Both the 24-27 and 111-114 cm samples show substantial and similar enhancements of the plutonium concentration in the organically-enriched subsamples. Although these were measured on different size fractions, 125-250 µm and bulk respectively, it is clear from Table 5.3 that most of the organic material is found in the size range 40-250 µm, and hence the organically-enriched subsample from the bulk material is probably similar to that in the 125-250 µm fraction alone.
2. In contrast, the 81-84 cm sample actually has a lower concentration of plutonium in the organically-enriched sample. But in this case, the enriched sample was only from the coarsest 250-3000 µm material, whereas the unenriched sample was from the bulk material. Hence, like is not being compared with like in this case. Indeed, a visual inspection of the enriched material shows that it is rich in unburnt twigs and leaf fragments. Such material is likely from recently-living vegetation, and on the basis of the

measurements on living vegetation above, would not be expected to have high plutonium concentrations.

A further point to note is that the organic enrichment process selects only those particles that float, i.e. with average density $<1.0 \text{ g/cm}^3$, and for these to float, much of the volume of the individual particles must be made up of low density organic material. Nevertheless, the LOI of these samples is not 100%, i.e. there must be soil grains attached to the floating organics and these grains must be relatively smaller on average than the soil grains that make up the un-enriched sample. These smaller soil grains could have an intrinsically higher plutonium concentration than the larger ones due to their higher surface/volume ratio [Everett, 2009], which could contribute to the higher plutonium concentrations observed. It is shown below, however, that this effect is unlikely to be significant in the present context.

The total specific activity of plutonium in a sample is the sum of contributions from the mineral and organic components, i.e.

$$A_T = f_o A_o + f_m A_m \quad \text{Eq. 5.1}$$

- A_T : Total plutonium specific activity (mBq/g) present in the sample
 A_o, A_m : Specific plutonium activities of organic and mineral component respectively
 f_o, f_m : Fraction by weight of organic and mineral component respectively

The data from the enriched and unenriched samples then constitute two simultaneous equations that can be solved to yield the specific activities of the mineral and organic components separately. The results are shown in Table 5.5 for the 24-27 and 111-114 cm samples. The 81-84 cm sample is not included for the reasons detailed above. In deriving these results, it is necessary to assume that the specific activity of the mineral grains adhering to the organic material is the same as for the grains of the unenriched sample (see paragraph above). This seems to be a reasonable assumption on the basis of the data shown in Table 5.3, which shows that, within the size range 20-64 μm in which the samples are dominated by the mineral component and which constitute 63% of the total mass, the plutonium concentration is not significantly

influenced by the grain size. This is further supported in a separate project [Everett, 2009], which showed that there was a significant enhancement in plutonium concentration as a function of grain size only for grain sizes less than 20 μm .

Table 5.5: Specific plutonium activity of organic (A_o) and mineral (A_m) component derived from organic enriched and un-enriched samples

Data inputs from samples	LOI of organic-enriched sample	Specific plutonium activity of organic (A_o) (mBq/g)	Specific plutonium activity of mineral (A_m) (mBq/g)
CDP24/27 [125], and CDP24/27 [125] organic	55%	1.34	0.17
CDP111/114 [Bulk], and CDP111/114 [Bulk] organic	70%	0.93	0.29

Data from the different size fractions in Table 5.3 may be used in a similar way to derive specific activities of the mineral and organic components. Taking data from those adjacent size fractions where there is a strong contrast between samples in both LOI and plutonium concentration and where grain-size effects should play a minimal role, i.e. (64-125/125-250) μm and (40-64/64-125) μm , the results shown in Table 5.6 are obtained. Clearly, the concentrations derived in this way from CDP-24/27 are very similar to those obtained from the enriched vs unenriched sample.

Table 5.6: Specific plutonium activity of organic (A_o) and mineral (A_m) component derived from sediment sample CDP-24/27 (Cotter dam pit, 24-27 cm) in different size fractions.

Data inputs from samples	Particle size (μm)	Specific plutonium activity of organic (A_o) (mBq/g)	Specific plutonium activity of mineral (A_m) (mBq/g)
CDP-24/27 [40], and CDP-24/27 [64]	40 < x < 64,	1.15	0.20
CDP-24/27 [64], and CDP-24/27 [125]	64 < x < 125, 125 < x < 250	1.33	0.17

All of these results indicate that plutonium has a high affinity for the organic component of the soil. It is noted that only soil organic matter that was already present at the time of the fallout would have absorbed plutonium. Certainly the early clearing of native vegetation and the subsequent forestry activities would have enriched the surface soil in organic matter and provided the condition for retaining the fallout plutonium in the Cotter catchment.

In an attempt to understand better the catchment response to the bush fire, the organic contributions were removed from the previous data plot of plutonium concentration as a function of depth in Figure 5.2, to carry out an assessment on the specific plutonium activity of the mineral fraction alone, using specific plutonium activity for the organic fraction derived from the 24-27 cm depth data for the post-fire (1.34 mBq/g), and the 111-114 cm depth for the pre-fire (0.93 mBq/g) sections. The results are showed in Figure 5.5.

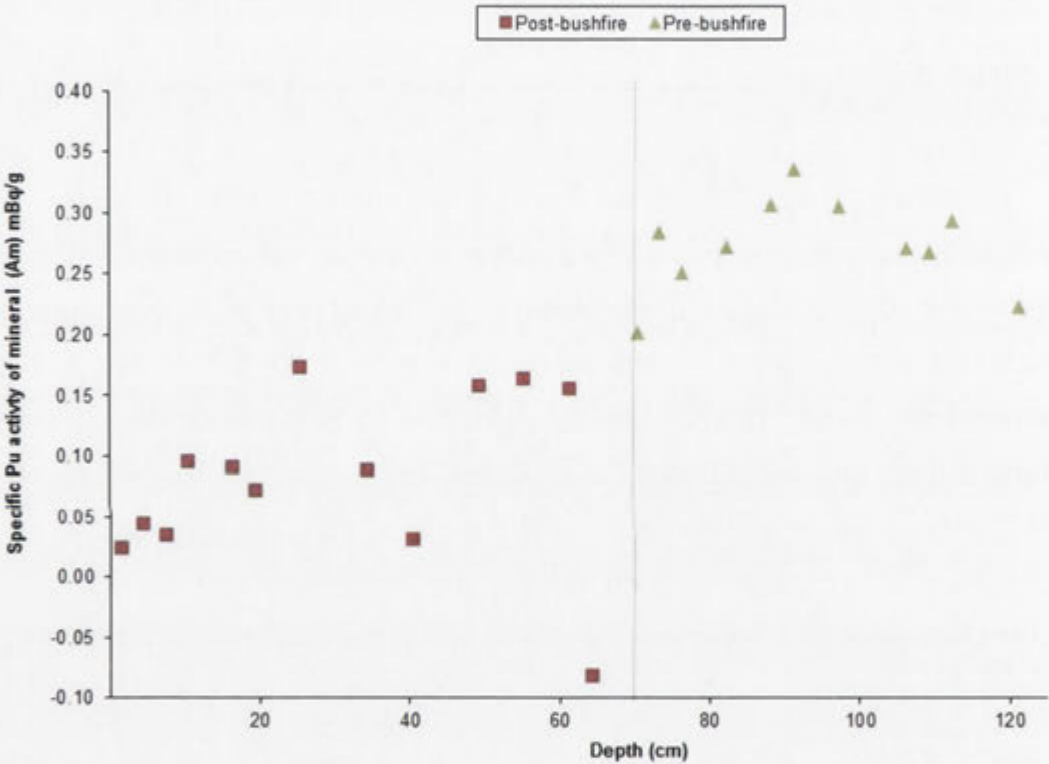


Figure 5.5: Specific plutonium activity of the mineral component (A_m) alone as a function of depth for the sediments from the Cotter dam pit. A_m values for the post-bush fire and pre-bush fire periods were derived using specific plutonium activities for the organic component from Table 5.5 ie 1.34 and 0.93 respectively. The sample for depth 24-27 cm refers to the 125-250 μ m grain size.

The consistently higher specific plutonium activity of the mineral component during the pre-bush fire period and the diminishing specific plutonium activity of the mineral component towards the present provide further evidence of enhanced sub-soil erosion from gullies after the bush fire.

5.5. A summary of the catchment's response to the bush-fire

The catastrophic bush fire event that occurred in 2003 has offered an opportunity to study the effect of a bushfire on the erosional process in the Cotter catchments. It is clear that the intense heat from the fire would have weakened the structure of the top soil and that the destruction of the vegetation cover would have bared the surface soil. The combination of these two factors would have made the soils highly vulnerable to erosion. In addition, once the soil organic matter has been burnt and lost, the soils may become 'hydrophobic' or water-repellent and the tendency for the rainfall to infiltrate into the soil is drastically reduced. Hence over-ground flow (runoff) following a significant rainfall event would be increased in both intensity and velocity, leading to enhanced loss of the already more erosion prone surface soils. Thus the post-fire period is associated with increased stream flows during a rainstorm, compared with a mature forest in the pre-fire period for the same rainfall.

Under these conditions, there will be changes in the two erosional processes which have different effects on the plutonium concentrations in subsequently-deposited sediments. The first is increased sheet erosion of surface soils, which have relatively high plutonium concentrations. The second is enhanced erosion of low-plutonium subsoil due to the formation or deepening of gullies and erosion of river banks due to increased water flows. The balance between these two processes is likely to have been disturbed as a result of the bush fire. Perhaps unsurprisingly, the data from the Cotter Dam pit indicates that the sub-soil contribution from gullies/riverbanks increased post-fire. Nevertheless, there is still appreciable plutonium in the post-fire sediments, indicating that top soil erosion makes an important contribution.

The analysis and investigation works on the Cotter dam pit samples provided substantial insights to the historical erosional process of the Cotter catchments, particularly in response to the 2003 bush fire. This outcome is realised through the complementary AMS measurement of both plutonium and ^{14}C isotopes. Looking forward, it would be of considerable interest to collect a core sample from close to

the Cotter dam wall. This should preserve a sedimentation record dating back to 1915 when the dam first began to fill, and would certainly provide a better understanding of the effect of forestry operations on the catchments. Also, it would be useful to carry out a tracing investigation to determine the areas in the catchments which are the principal sources of sediments into the Cotter dam, to allow the implementation of an effective soil conservation programme to mitigate the sedimentation issue.

Chapter 6 Case study II - Assessment of hillslope erosion

This chapter presents a case study that demonstrates the use of fallout plutonium tracer to estimate the soil loss on a hillslope.

6.1. Introduction

Soil erosion in the form of sheet and rill erosion on hillslopes, as well as gully and stream bank erosion is widespread in Australian landscapes [Hairsine *et al.*, 2009]. While rivers and streams may receive sediment from gully and stream bank erosion, hillslope erosion remains an important mechanism that could indirectly impact on water quality, based on the quantities of nutrients and agricultural chemicals (herbicides, pesticides) that it may deliver into the rivers and streams. Hillslope erosion is a concern in some agricultural lands within Australia and average annual erosion rates of greater than 5 tonnes per hectare per year which is equivalent to the soil removal of 0.4 mm per year, have been identified in a number of regions, as shown in Figure 6.1.

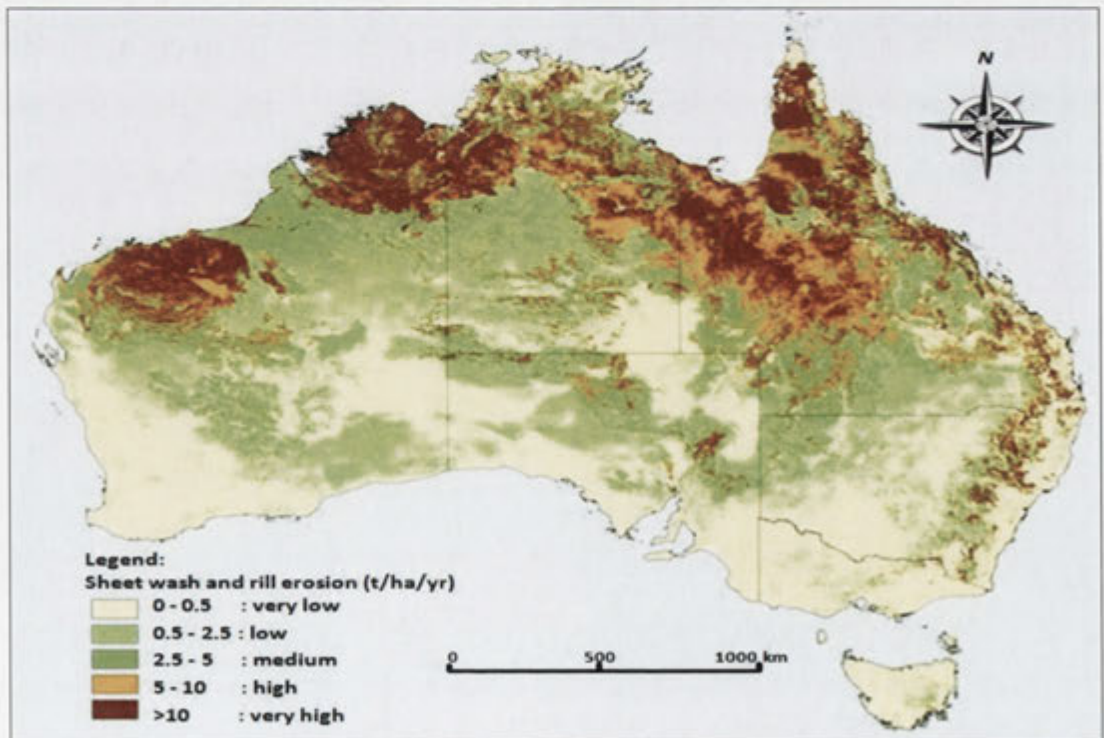


Figure 6.1: Mean annual sheet wash and rill erosion rate.

[Source: National Land and Water Resources Audit 2001, Hairsine *et al.*, 2009]

Soil erosion processes on hillslopes can be complicated, due to the intimate interactions of soil, vegetation, surface cover, and topographic factors that vary with time and space. Likewise the movement and storage of sediment on the hillslope can be mediated by a variety of factors such as land management, rainfall amount and intensity scale of the runoff event. Such complexities in sediment movement were demonstrated in several studies which indicate that the sediments were transported gradually down slopes in a series of erosional and depositional pulses [Saynor *et al.*, 1994]. In recent years, considerable research effort has been focused on the channel response to sediment supply from eroding hillslopes [Harvey, 2001]. In many cases, it has been shown that the steepness of the hillslopes ensures the sediment eroded from the hillslope is being transported through the hillslope and channel system, while in some cases the hillslope sediment may have extended residence time on the hillslope and in the channel system [Hancock and Evan, 2010]. The majority of the above studies were conducted using the ^{137}Cs tracer technique or through the conventional means of erosion pins. As highlighted earlier, these techniques have their limitations in terms of detection sensitivities and labour intensiveness. In the present study, a small scale project was carried out to explore the potential of fallout plutonium as a tracer of soil transport to estimate the soil loss at a hillslope catchment site.

6.2. Study area

The study area is located on a farm near Burra in New South Wales which is about 40 km south of Canberra (Figure 6.2 and 6.3). The mean annual rainfall in this region is ~670 mm. The surrounding landscape is undulating to mountainous with forest coverage on the higher ground giving way to extensively cleared grazing lands and rural residential properties. The vegetation at the study sites is an open eucalypt forest with a grass understory and scattered shrubs. It is observed, however, that most of the trees have similar diameter and that there are essentially no large trees, implying that the land has been cleared at some time since European settlement, presumably for grazing, and has been allowed to revert back to forest. A 1944 aerial photograph shows that the area was already revegetated at that time, and it is known that it has not been cleared since [B. Starr, 2011]. Since significant plutonium fallout from nuclear weapons testing occurred only after 1953, an undisturbed site should retain the full inventory of plutonium fallout in this region. Known land use in the study area over the past 50 years has been light grazing by sheep and cattle, and the land has probably experienced some bush fires.



Figure 6.2: Typical landscapes of the study area. Photograph (a): Grazing farmland across the road from the study site, looking NW. Photograph (b): Typical vegetation of the study area. Note the rather uniform diameter of the mature trees, and the sparseness of the undergrowth, both evidence that the area was formerly cleared and has been allowed to regenerate.

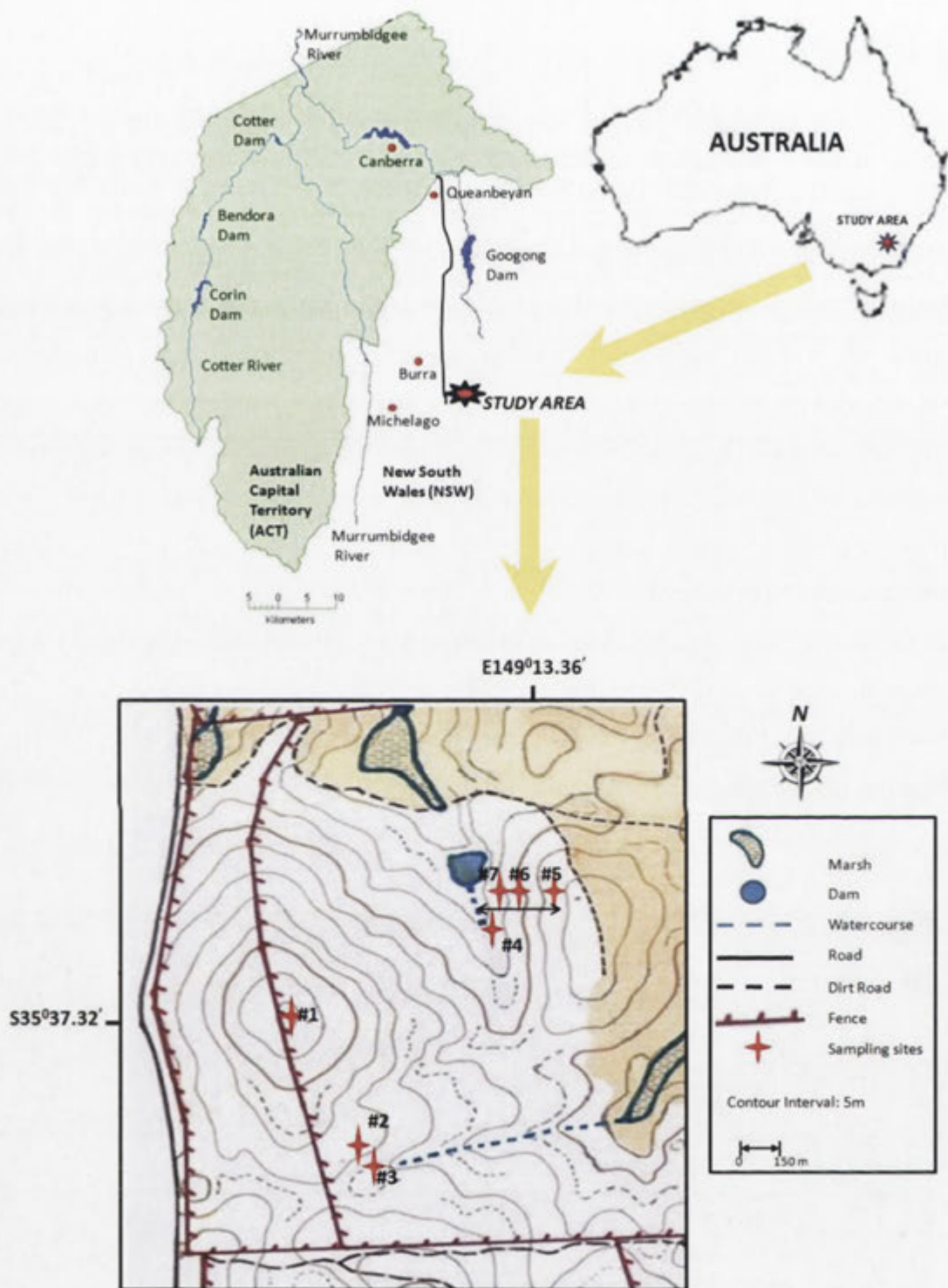


Figure 6.3: Study area near Burra in New South Wales, Australia. The topographic map indicates the sampling locations, which include a hilltop site (#1), and six study sites marked as #2-7. The white area is forested and the yellow area is open farmland. Site #2 was located close to a saddle, site #3 was located at the head of a gully, site 4 was just above a prominent erosion gully, and sites #5, #6 and #7 represent a hillslope transect.

6.2.1. Sampling sites

Table 6.1: Location of the sampling sites in the Burra catchment

Site	Location (Altitude)	Sample
#1: Hilltop	35° 37.32'S, 149° 13.12'E (900 m)	Soils
#2: Gently sloping near saddle	35° 37.47'S, 149° 13.14'E (878 m)	Soils
#3: Head of gully	35° 37.47'S, 149° 13.15'E (873 m)	Sediments
#4: Above erosion gully	35° 37.31'S, 149° 13.29'E (856 m)	Sediments
<u>Hillslope transect</u>		
#5: Upper hillslope	35° 37.27'S, 149° 13.34'E (872 m)	Soils
#6: Middle hillslope	35° 37.26'S, 149° 13.32'E (864 m)	Soils
#7: Lower hillslope	35° 37.27'S, 149° 13.30'E (859 m)	Soils

The locations of the sampling sites, which include a hilltop site (#1) and study sites (#2-7), are shown in Figure 6.3 and Table 6.1. The study sites (#5-7) represent a hillslope transect on a west facing hillslope in a valley. The terrain elevation at the sampling sites range from ~860-900 m above sea level and the bedrock consists of Paleozoic metamorphic rocks, principally phyllites. In accordance to the Australian Soil Classification, the soils found in this region can be described as Red Earths [Fifield *et al.*, 2010]. The samples collected at all sites include soil and sediment profiles in typically 3-5 cm increments from 15-25 cm deep hand-dug pits.

The sampling trip was carried out in February 2009, and followed the sampling methodology outlined in Chapter 3. An additional field trip was conducted in July 2010 specifically to obtain samples for the determination of the soil densities that are required for the derivation of plutonium inventories.

Hill top site

Site #1 was initially identified as a potential reference site. It was situated on a broad hill top covered by regrowth native eucalypt forest. The site was within 350 m of the other sites and hence should have experienced a very similar rainfall regime and hence plutonium fallout history. The ground in this region was dry and hard, and the soil thin. The organic-rich A_o horizon zone extended down to ~3 cm, and saprolite (weathered bedrock) was encountered at ~10 cm.

(a)



(b)



(c)



Figure 6.4: Sampling pit at Hilltop site (#1). Photograph (a-b): show the humus-rich surface layer and the organic-poor stony soil below it. Photograph (c): shows the area surrounding the sampling site littered with leaves and branches.

Study sites

Study sites #2 was ~500 m to the south of the hilltop, and close to a saddle. The gradient at this site was low, and it was not expected to be a site of significant deposition. The surface was covered by a ~1 cm layer of organic rich litter, and the subsequent layer of ~5 cm was reasonably loamy, in contrast to the hilltop soil. The saprolite layer was encountered at a depth of ~15 cm, which determined the depth of the sampling pit.

Site #3 was near the head of a shallow gully ~200 m from the saddle. The channel of a watercourse commenced 40 m down-gully from the sampling site. Sampling pits #2 and #3 were ~150 m apart. At this site, the ground surface was fairly soft and the loamy section extended to a depth of ~10 cm. The saprolite was encountered at a depth of ~20 cm, which determined the depth of the sampling pit. There were stands of vegetation (patches of grass) and trees close to the sampling site, and its surface was covered by a less than 1 cm thick layer of organic rich litter. As expected from its position in a gully, this is clearly a depositional site.

Site #4 was ~900 m down an adjacent gully, and was located ~20 m up-gully from a prominent erosion gully (see Figure 6.5d). The exposure in the erosion gully shows that there is ~80 cm of sediment overlying a distinctive gravel layer at the study site. The vegetation in the gully was mainly grass, with some low shrubs but almost no larger trees. At this site, the surface was covered by a thin layer (< 1 cm) of organic litter and the subsequent loamy section was found to extend down to about 10 cm. The depth of the sampling pit was about 25 cm.

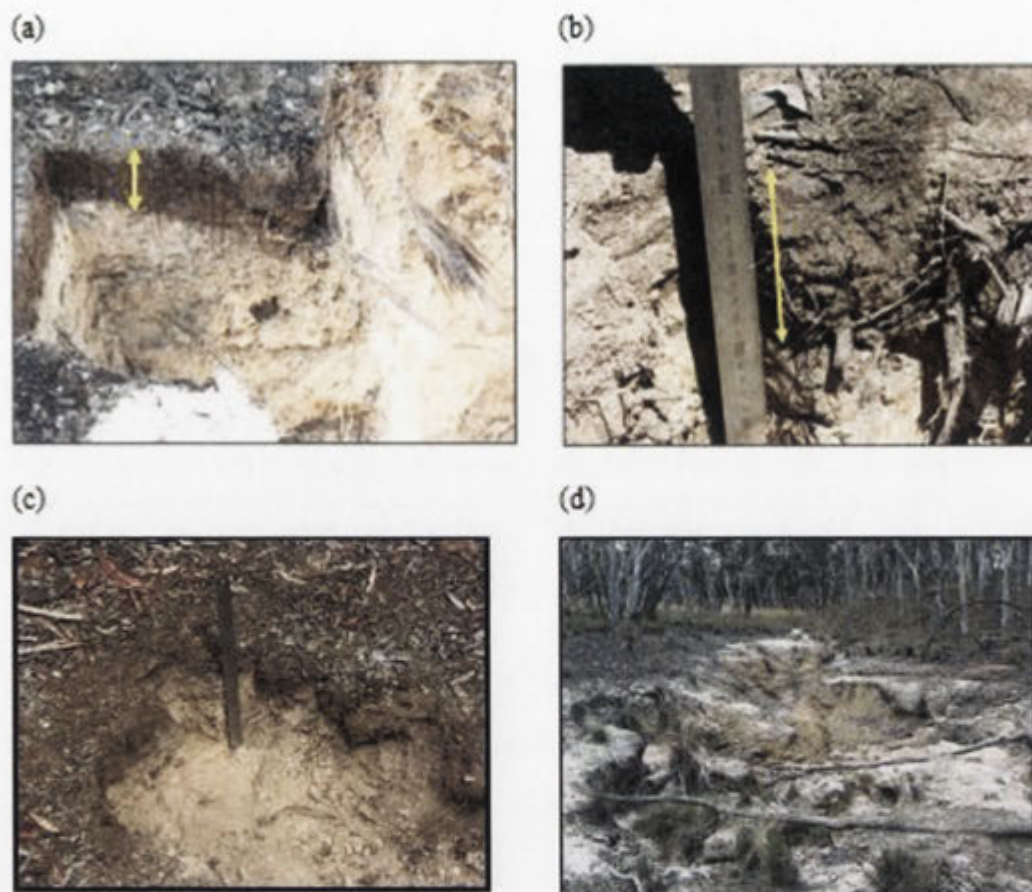


Figure 6.5: Sampling pits at site #2 (near the saddle), at site #3 (near the head of a gully), and at site #4 (~900 km down a gully) are shown in photographs (a), (b) and (c) respectively. The loamy layer at site #2 was only half as thick as at site #3. The pit at site #4 was located ~20 m above the deeply-incised erosion gully shown in photograph (d).

Hillslope Transect

Three soil pits (sites #5-7) at ~30 m apart were sampled along a hillslope transect as shown in Figure 6.6. As evident from the topographic map in Figure 6.3, the hillslope at this site was significantly steeper than the terrain near sites #2 and #3. All three pits exhibit the common feature of a thin (1-2 cm) A_0 horizon at the surface, suggesting active erosion on this hillslope.



Figure 6.6: Upper, middle and lower sampling pits of the hillslope transect are shown in photographs (a), (b) and (c) respectively. Photograph d: Looking northwest overlooking the dam which is ~150 m away from the lower pit (see Figure 6.3).

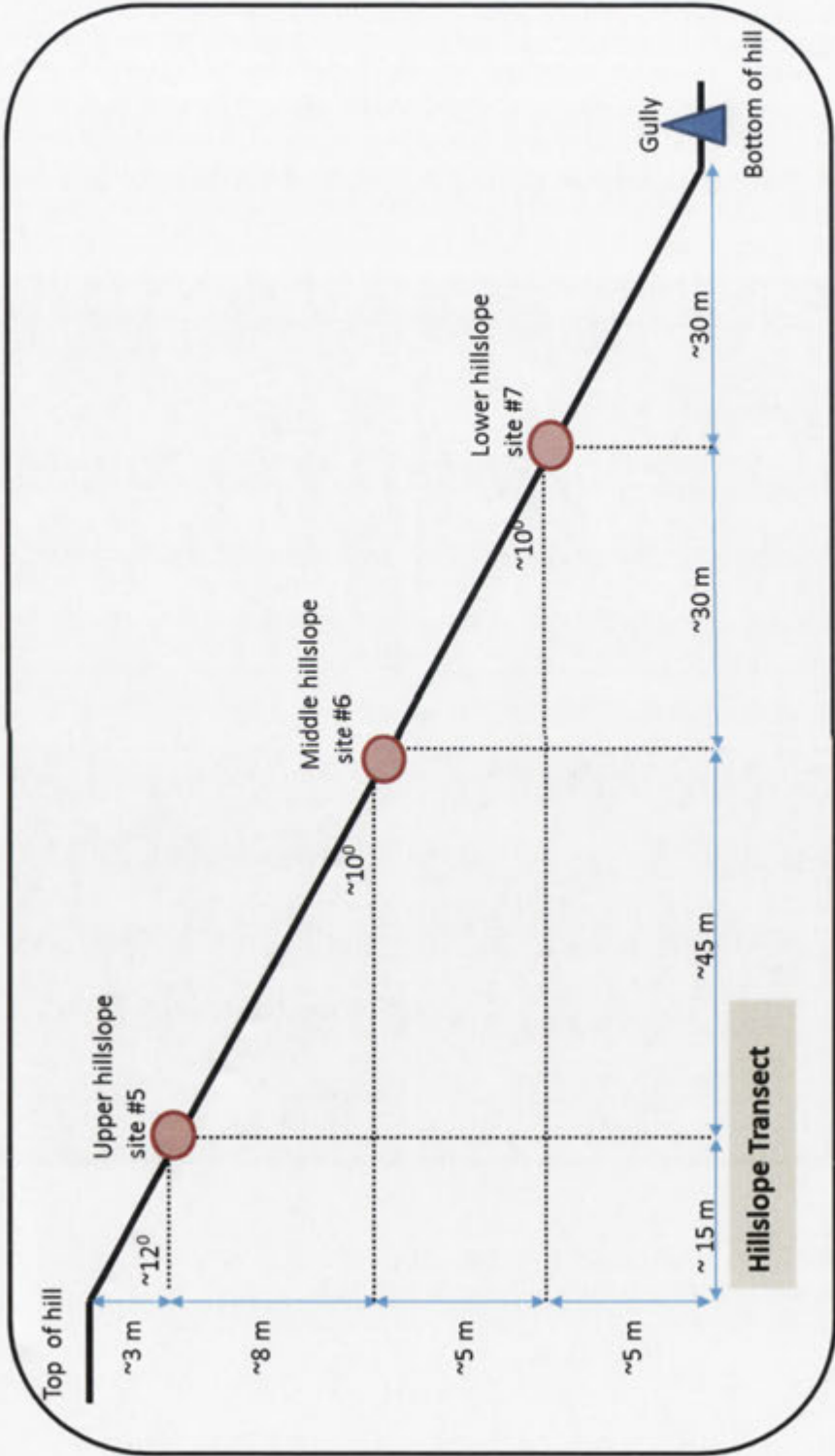


Figure 6.7. Schematic diagram of the hillslope transect sampling sites to illustrate the relative distance and the steepness of the slope at the upper, middle and lower sites.

6.3. Methodology

The application of fallout plutonium as a tracer of soil loss and the analytical strategy are described in Chapters 2 and 3. The sample preparation and measurement of plutonium isotopes using the AMS technique followed the procedure described in Chapter 3, with slight modifications. It is noted that in this particular study, only the determination of plutonium inventory is required, hence the samples were not separated into the >3 mm (stones) and <3 mm components, rather they were all ground and analysed in bulk for simplicity.

6.4. Results & discussion

6.4.1. Plutonium inventory and soil loss

Hilltop site

Table 6.2: Plutonium depth profiles and inventories at the hilltop site #1

Depth (cm)	Bulk Density (g/cm ³)	LOI	²³⁹⁺²⁴⁰ Pu (mBq/g)	²³⁹⁺²⁴⁰ Pu (mBq/cm ³)	²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory in depth interval (%)
0-3	0.468	46%	0.258±0.013	0.121±0.006	0.363±0.019	36.7±2.2
3-6	1.206	12%	0.092±0.005	0.111±0.006	0.332±0.019	33.6±2.2
6-10	1.490	6%	0.018±0.001	0.027±0.002	0.108±0.008	10.9±0.9
10-14.5	1.177	4%	0.012±0.001	0.014±0.001	0.062±0.005	6.3±0.5
14.5-19.5	1.177	3%	0.021±0.002	0.025±0.002	0.123±0.009	12.4±1.0
Total					0.988±0.029	

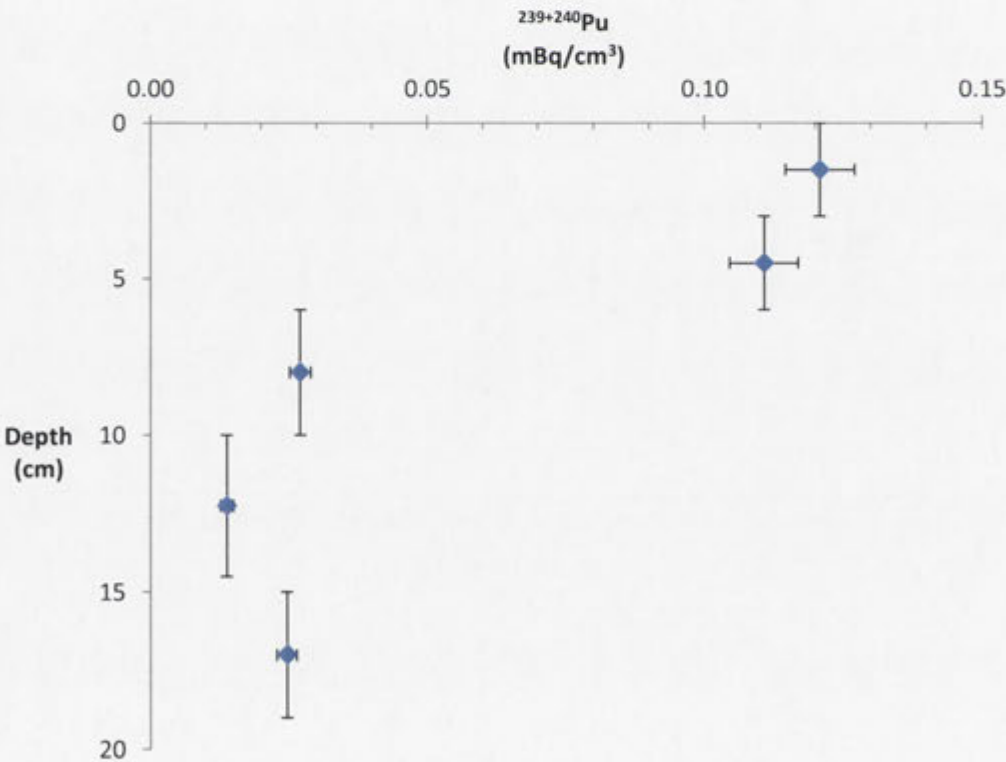


Figure 6.8: Plutonium concentration depth profiles at the hill top site (#1). The x-axis error bars reflect 1 sigma error, whereas the y-axis error bars simply represent the depth interval of the sample.

The plutonium results from the hilltop site #1 are shown in Table 6.2 and Figure 6.8. This site was initially identified as the reference site for this study, since it was on a broad hilltop. The total plutonium inventory at this site, however, is only 0.99 ± 0.03 mBq/cm². More than 70% of the inventory was found in the top 6 cm, with about 37% concentrated in the top 3 cm layer. This top layer consisted largely of leaf and twig litter, as is evident from its high loss-on-ignition. It has a particularly high plutonium concentration, again demonstrating the affinity of plutonium for organic material, and indicating that much of the litter predates the period of fallout.

As noted earlier, the ²³⁹⁺²⁴⁰Pu inventories reported by Hardy *et al.*, [1973] and Kelley *et al.*, [1999] for soil samples collected in 1970-71 over a wide range of latitudes in both the southern and northern hemispheres, were 1.74 and 2.04 mBq/cm² for Sydney (33.8°S) and Melbourne (37.8°S) respectively [Hardy *et al.*, 1973]. Since the study site (35.37°S) is intermediate between the two, it would be expected that its plutonium inventory would fall within this range. The measured plutonium inventory at this site is, however, only about half of what was expected, indicating that some loss of plutonium has probably occurred and that it might not be a suitable reference site. In this context, the atypically thick surface layer of forest litter is very fragile, and would have been easily disturbed by cattle and sheep, making it vulnerable to loss by rainfall.

Alternative reference site

Given the concerns about the suitability of the hilltop site as a reference site, attention turned to site #2 as a possible reference site. Located close to the saddle on a gentle slope, it is unlikely that there has been significant deposition at this site. Further, the layer of forest litter is significantly thinner here, and the depth of soil greater, so it is more likely to have retained the plutonium that fell on it.

The plutonium results from site #2 are shown in Table 6.3 and Figure 6.9. The total plutonium inventory is 1.62 ± 0.04 mBq/cm². This inventory is still slightly lower than the expected range, perhaps due to some loss of plutonium from the easily-disturbed leaf litter layer. In this context, note that the gully site (#3) just down-slope has an excess of plutonium (see below), indicating down-slope migration

of some plutonium-bearing material. Any loss is expected to be minor, however, and in the following it is assumed that this site #2 has retained the plutonium that fell on it, i.e. it is a suitable reference site. The depth profile is strongly peaked at the surface, with 30% of the inventory concentrated in the top 3 cm layer, and almost 60% residing in the top 7 cm. An exponential regression fit (see Figure 6.9) gives an excellent description of this reference site profile, and has been used to define the present-day shape of the soil profile in the absence of erosion, and this has been used to estimate the depth of soil loss at the other study sites. The observed plutonium depth profile is most likely the result of the movement of soil grains due to bioturbation by ants and termites or by movement down root channels. There may also be some transport in solution.

Table 6.3: Plutonium depth profile and inventory at site #2

Depth (cm)	Bulk Density (g/cm ³)	LOI	²³⁹⁺²⁴⁰ Pu (mBq/g)	²³⁹⁺²⁴⁰ Pu (mBq/cm ³)	²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory in depth interval (%)
0-3	1.292	10%	0.126±0.007	0.163±0.009	0.489±0.026	30.1±1.8
3-7	1.389	4%	0.081±0.005	0.112±0.006	0.449±0.025	27.7±1.7
7-10	1.434	2%	0.047±0.003	0.067±0.004	0.201±0.012	12.4±0.8
10-15.5	1.480	2%	0.028±0.002	0.042±0.002	0.230±0.013	14.2±0.9
15.5-20	1.480	2%	0.024±0.001	0.035±0.002	0.157±0.010	9.7±0.7
20-25	1.480	2%	0.013±0.001	0.020±0.001	0.098±0.007	6.0±0.5
Total					1.623±0.042	

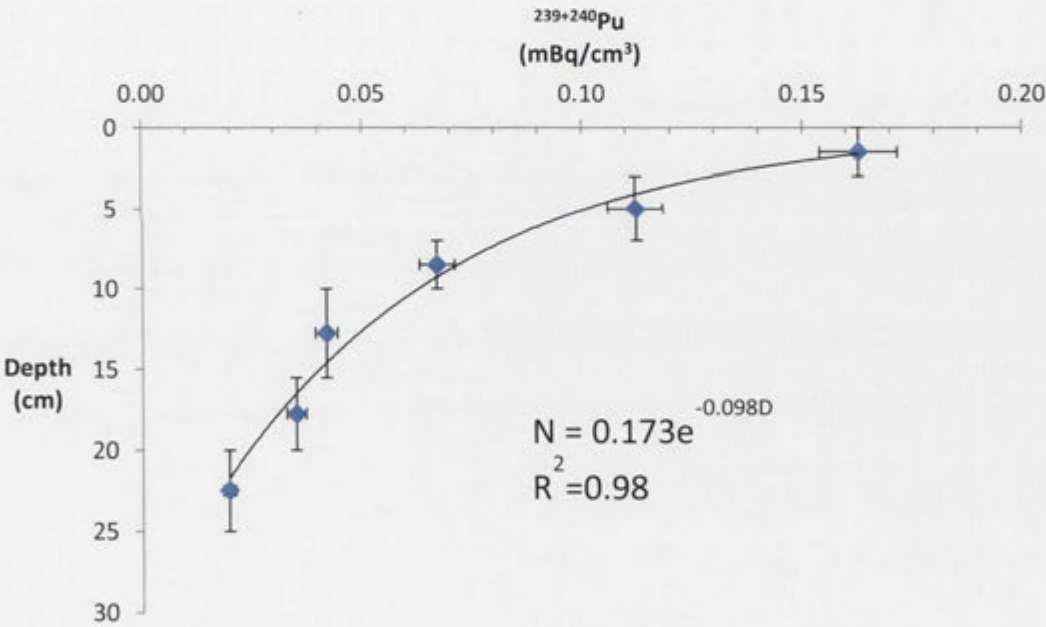


Figure 6.9: Plutonium concentration depth profiles at site (#2). The x-axis error bars reflect 1 sigma error, whereas the y-axis error bars simply represent the depth interval of the sample. The solid line represents an exponential fit to the data. N and D denote ²³⁹⁺²⁴⁰Pu concentration (mBq/cm³) and depth (cm) respectively.

Study sites

Plutonium depth profiles and total inventories from the study sites are shown in Figure 6.10-6.12 and Table 6.4-6.6. Each of these sites is discussed in more detail below.

(i) Head of Gully site #3

Table 6.4: Plutonium depth profile and inventory at the head of gully site #3

Depth (cm)	Bulk Density (g/cm ³)	LOI	²³⁹⁺²⁴⁰ Pu (mBq/g)	²³⁹⁺²⁴⁰ Pu (mBq/cm ³)	²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory in depth interval (%)
0-3	0.967	14%	0.269±0.014	0.260±0.013	0.781±0.040	23.6±1.4
3-6	1.403	8%	0.248±0.013	0.348±0.018	1.044±0.054	31.6±1.8
6-10	1.370	6%	0.190±0.010	0.261±0.014	1.043±0.054	31.5±1.8
10-15	1.048	4%	0.058±0.003	0.061±0.003	0.305±0.017	9.2±0.6
15-20	1.048	3%	0.025±0.002	0.027±0.002	0.133±0.008	4.0±0.3
Total					3.306±0.089	

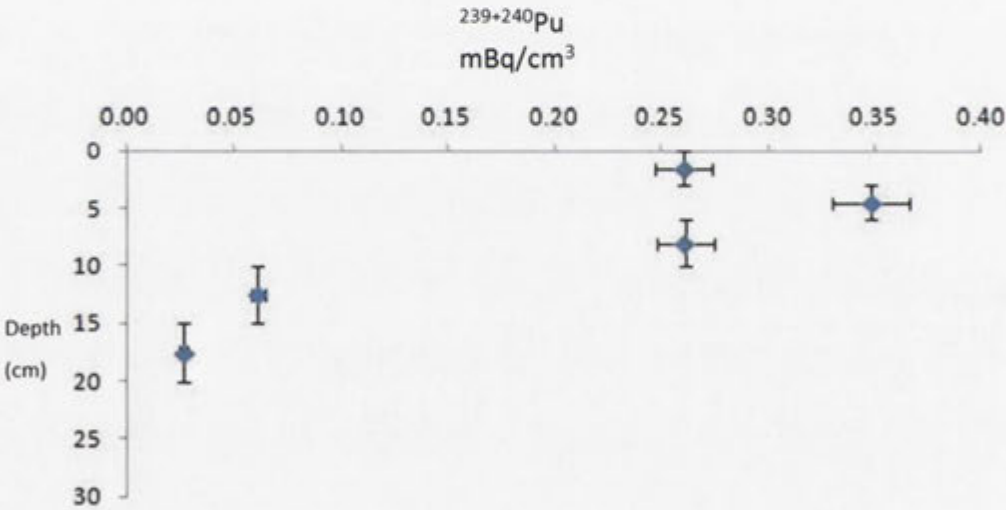


Figure 6.10: Plutonium concentration depth profile at the head of gully site (#3). The x-axis error bars reflect 1 sigma error, whereas the y-axis error bars simply represent the depth interval of the sample.

The plutonium inventory at the gully head site #3 is twice the assumed reference inventory (site #2), indicating that there has been significant post-fallout deposition of sediment at this site from the hillslopes on both sides of the gully. Since the site is essentially at the head of the gully and has a very gentle gradient, it has a very small catchment and any flowing water during rainfall will have low volume and low energy. Hence, any deposited sediment washed down from the hillslopes will likely be retained.

In the top 6 cm, the plutonium concentration in this gully sediment is a factor of two higher than in the top 3 cm of the 'reference' site #2. This could be due to one or both of two factors.

1. Particle size – plutonium preferentially adheres to smaller grains due to their larger surface/volume ratios. Since the smaller grains are more readily transported by water, the deposited sediment would then have a higher plutonium concentration than its parent material.
2. Higher surface concentrations in parent material – the near-surface sampling resolution at site #2 was 3 cm. It is quite possible that the concentration in say the top few mm is higher than the average over the 3 cm sampling interval. Since it is the surface material that is washed into the gully, this could also lead to higher concentrations in the gully sediment.

From the plutonium depth profile shown in Table 6.4, it is deduced that ~5 cm of soil has been deposited at this point in the gully over the past ~50 years. The gully at this point is ~10 m wide, while the south-east and north-west facing hillslopes from which the sediment was derived extend approximately 120 m and 180 m up to the respective ridgelines. Hence, the gully has concentrated the sediment by a factor of 30 ($\{120\text{ m}+180\text{ m}\}/10\text{ m}$). On average, therefore, the hillslope has lost ~1.7 mm of soil (5 cm/30) in the past 50 years, or 0.034 mm/yr. This translates to 0.4 tonnes per hectare per year based on an average bulk density of 1.18 g/cm³. Reference to Figure 6.1 shows that this is right at the low end of the spectrum of soil loss due to sheet wash and rill erosion.

(ii) Gully site #4

Table 6.5: Plutonium depth profile and inventory at the gully site #4

Depth (cm)	Bulk Density (g/cm ³)	LOI	²³⁹⁺²⁴⁰ Pu (mBq/g)	²³⁹⁺²⁴⁰ Pu (mBq/cm ³)	²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory in depth interval (%)
0-3	1.029	12%	0.093±0.005	0.095±0.005	0.286±0.016	22.4±1.4
3-6.5	1.125	5%	0.085±0.005	0.096±0.005	0.335±0.018	26.3±1.6
6.5-10.5	1.362	4%	0.053±0.003	0.072±0.004	0.288±0.016	22.6±1.4
10.5-16	1.455	5%	0.022±0.001	0.031±0.002	0.172±0.011	13.5±0.9
16-20	1.483	4%	0.022±0.001	0.032±0.002	0.128±0.008	10.0±0.7
20-25.5	1.483	3%	0.009±0.001	0.013±0.001	0.065±0.005	5.1±0.4
Total					1.274±0.032	

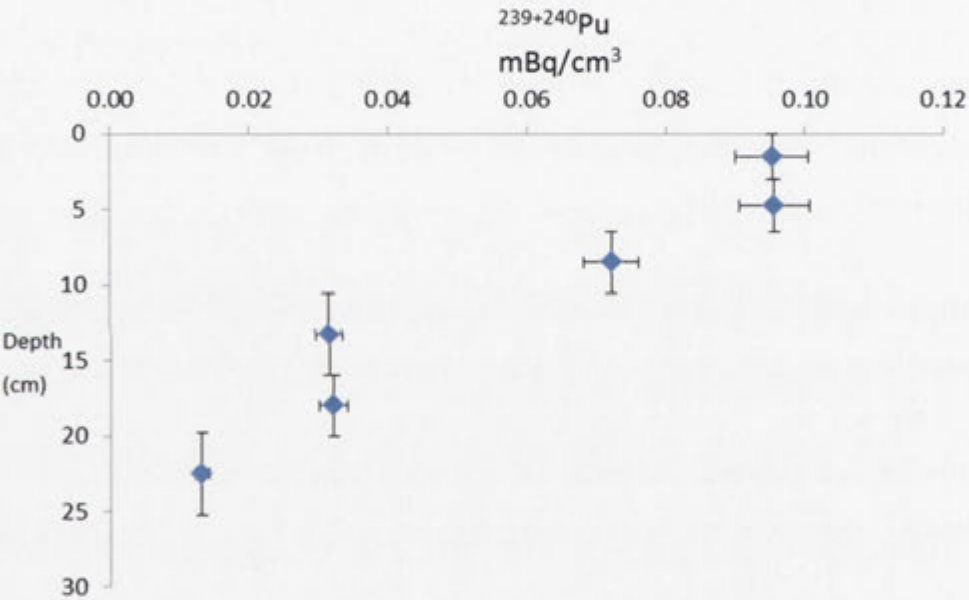


Figure 6.11: Plutonium concentration depth profile at the gully site (#4). The x-axis error bars reflect 1 sigma error, whereas the y-axis error bars simply represent the depth interval of the sample.

In marked contrast to the above site #3, which is clearly an accumulation site, this gully site #4 has a plutonium inventory that is actually lower than the 'reference' site #2. This is despite there being a significant amount of sediment in the gully at this point, and despite there having been appreciable loss of plutonium-bearing soil from the adjacent hillslopes (see below).

Graphic evidence of the processes that have led to this reduced inventory is provided by the deep erosion gully, which is still advancing up-gully and the head of which is just ~20 m down-gully from the sampling site (Figure 6.5d). This erosional feature clearly indicates that there is high-energy water flow down the gully during major rainfall events. In contrast to site #3 which is right at the head of a gully, site #4 is approximately 1 km from its gully head, and hence its catchment area is very much larger. It is also bordered by relatively steeper hill slopes, and the vegetation in the gully is mainly sparse native grasses so that there is little to impede the water flow. These factors contribute to a much higher-volume and higher-energy water flow at this site than at site #3, and it is likely that at present there is no sediment deposition at this point, with the bulk of the sediment transported to the downstream farm dam and beyond in high-rainfall events. Indeed, not only is there no net deposition at this site, but the reduced plutonium inventory relative to the reference inventory indicates that there has been a net loss of ~3 cm of sediment at this site. Given that a metre or more of sediment has been scoured from the erosion gully just downstream, this is perhaps not surprising.

The fact that there is sediment in the gully at the sampling site indicates that the erosional regime was different in the past. Prior to the land being cleared, the forest would have been thicker than at present, with an understory of shrubs that is now largely absent from the regrowth forest, and would have extended into the gully. Hence, the energy of water flow in the gully would have been lower than it is today, allowing deposition of sediment to occur.

(iii) Hillslope Transect

Table 6.6: Plutonium depth profiles and inventories at the Hillslope Transect sites

Site/ Depth (cm)	Bulk Density (g/cm ³)	LOI	²³⁹⁺²⁴⁰ Pu (mBq/g)	²³⁹⁺²⁴⁰ Pu (mBq/cm ³)	²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	Fraction of total inventory in depth interval (%)
<u>#5 Upper hillslope</u>						
0-3	0.998	16%	0.180±0.009	0.180±0.009	0.539±0.028	60.6±3.8
3-7	1.089	4%	0.036±0.002	0.039±0.002	0.155±0.009	17.4±1.2
7-10.5	1.627	3%	0.019±0.001	0.030±0.002	0.107±0.007	12.0±0.9
10.5-15	1.417	3%	0.014±0.001	0.020±0.001	0.089±0.006	10.0±0.8
				Total	<u>0.889±0.031</u>	
<u>#6 Middle hillslope</u>						
0-4	1.181	6%	0.044±0.003	0.052±0.003	0.209±0.012	45.8±3.1
4-8	1.430	3%	0.021±0.001	0.030±0.002	0.119±0.008	26.1±2.0
8-12	1.460	2%	0.011±0.001	0.017±0.001	0.067±0.005	14.7±1.2
12-16.5	1.341	2%	0.006±0.001	0.008±0.001	0.036±0.003	7.9±0.7
16.5-20	1.341	2%	0.005±0.001	0.007±0.001	0.025±0.003	5.5±0.7
				Total	<u>0.456±0.016</u>	
<u>#7 Lower hillslope</u>						
0-3	0.980	15%	0.109±0.006	0.107±0.006	0.321±0.017	41.5±2.5
3-6	1.076	3%	0.032±0.002	0.034±0.002	0.103±0.006	13.3±0.9
6-9	1.152	2%	0.020±0.001	0.023±0.002	0.069±0.005	8.9±0.7
9-13	1.071	2%	0.022±0.002	0.023±0.002	0.093±0.007	12.0±1.0
13-17	1.334	2%	0.017±0.001	0.022±0.002	0.090±0.006	11.6±0.8
17-21	1.334	3%	0.018±0.001	0.024±0.002	0.098±0.007	12.7±1.0
				Total	<u>0.773±0.022</u>	

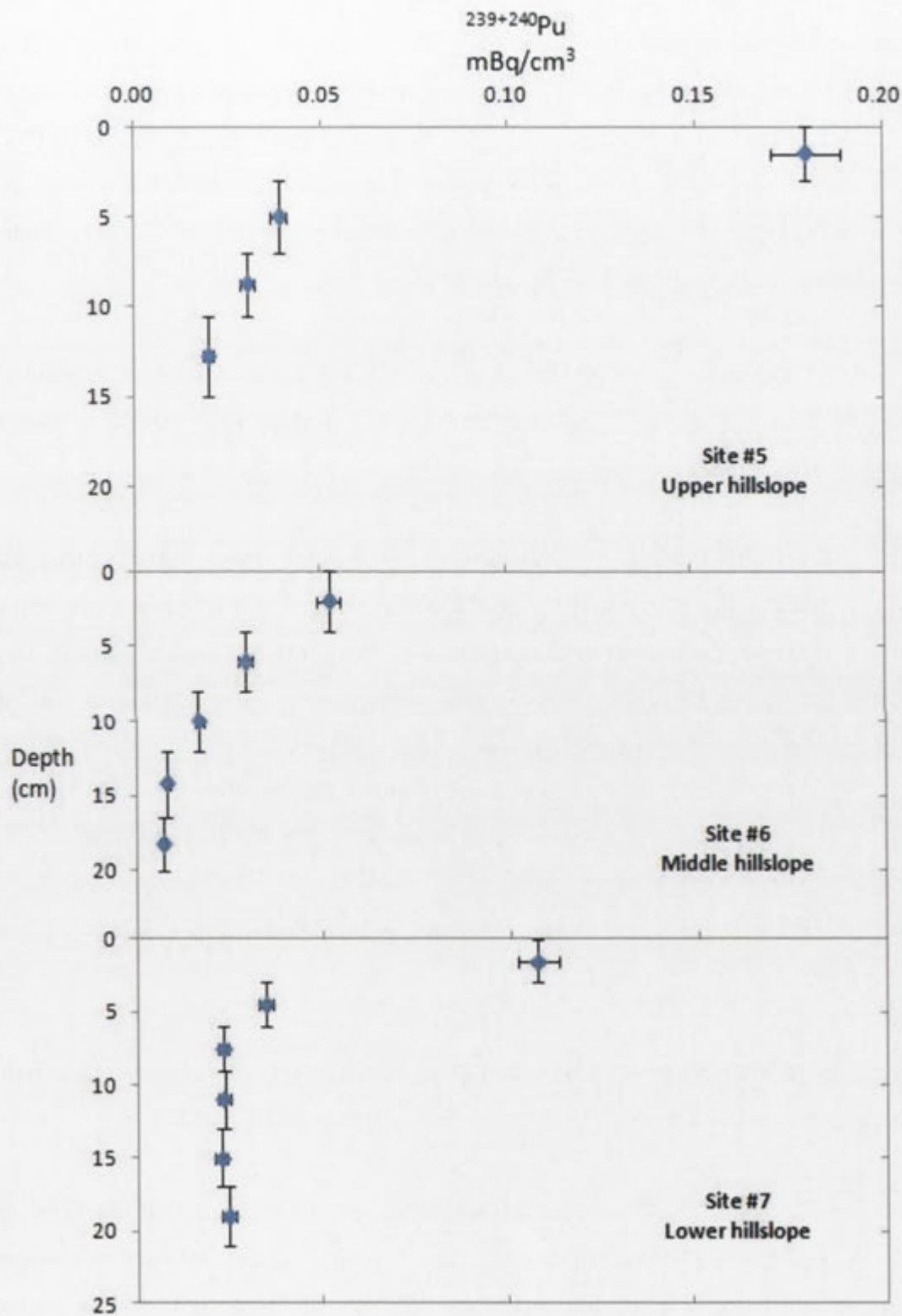


Figure 6.12: Plutonium concentration depth profiles at the Hillslope Transect sites. The x-axis error bars reflect 1 sigma error, whereas the y-axis error bars simply represent the depth interval of the sample.

The plutonium inventories at the top and bottom of the hillslope are ~55% and ~48% of the reference inventory at site #2. Taken at face value, these would indicate losses of 6 to 8 cm of topsoil at these two sites over the past 50 years. This is in stark contrast to the loss of 1.7 mm deduced above for the hillslopes in the vicinity of head-of-gully site #3. A loss of 7 cm of soil in 50 years corresponds to 16 t/ha/yr which is at the very high end of the scale in Figure 6.1. The situation is even more extreme for the mid-slope site (#5) where the inventory is only 28% of the reference inventory implying a loss of 13 cm of topsoil.

There are two factors that would be expected to contribute to substantially enhanced erosion at this hillslope transect relative to that in the vicinity of sites #2 and #3.

1. Proximity to the farm dam makes it likely that this area would have been used much more extensively by stock than the area near sites #2 and #3 which is 1 km away from a water source. The dam was constructed in the early 1970s as part of the Burra Creek soil conservation project funded by the Commonwealth Government, and hence has been in existence since shortly after the peak in plutonium fallout. Although stocks are rarely in this area today, cattle grazing was more intensive during the 1970s and 1980s.
2. This hillslope is also considerably steeper than the hillslopes near sites #2 and #3.

There are, however, additional factors which require that some caution should be exercised in interpreting these data in terms of quantitative soil loss.

1. The present-day soil profiles are the result of ~50 years of soil loss and bioturbation, principally by invertebrates such as ants, termites and worms. Burrowing and feeding activities deliver soil from depth to the surface (Johnson, 1999) leading to a downwardly-migrating, sub-surface concentration peak for fallout plutonium. (Such a peak was observed in an undisturbed soil in northern Queensland at a depth of ~2 cm [Everett, 2009].

Given the sampling interval of 3 cm in the present work, we would not expect to see it in Figure 6.9.) Below this peak the concentrations decline exponentially with depth and become flatter with time, i.e. the soil depth profile of plutonium has evolved with time, from being essentially all at the surface immediately after fallout, to its present shape with a $1/e$ depth of about 10 cm (see Figure 6.9). It follows that erosion that occurred close in time to the fallout period would have removed substantially more plutonium than would the same amount of erosion occurring today.

2. Heavy rainfall events during the fallout period would likely have resulted in significant runoff on this steep slope. This runoff may have carried some of the plutonium with it, resulting effectively in a reduced initial inventory in the soils on this slope relative to areas where the slope is less steep and the water would have been more likely to penetrate the soil so that plutonium could be absorbed.

Both processes will act to reduce the depth of soil lost for a given loss of plutonium inventory. Nevertheless, it is probably still true that soil loss on this hillslope over the past 50 years is at the centimetre scale rather than the millimetre scale that characterises the area in the vicinity of sites #2 and #3, and that the proximity to the farm dam and the steepness of the slope are strong contributing factors. The long-term erosion rate on this same hillslope has been determined previously [Fifield *et al.*, 2010], using ^{10}Be produced in the atmosphere by cosmic rays, and at 0.005 mm/yr, is a factor of two hundreds lower than the recent rate of ~ 1 mm/yr deduced here.

The depth profiles shown in Figure 6.12 provide additional information. Neither the upper nor lower profile shows an exponential depth dependence. Rather, they peak very strongly at the surface. This may indicate that there has been some recent deposition of material washed down from above at these two positions. Given that the area has been largely destocked for at least the past 10 years and that the slope changes subtly at these two points (although this is not obvious for the lower site in Figure 6.7), this is at least plausible. The middle site, where the slope gradient

is uniform, does not show any evidence for deposition, and the depth dependence is much better described by an exponential. Hence, this middle site is probably a better indicator of overall soil loss on the hillslope than the upper and lower sites. A likely scenario, then, is that following the construction of the dam, this hillslope was subject to rapid erosion due to the activities of hard-hooved stock. In this regard, stock activity in the vicinity of the dam would have been most intense in the heat of the summer, when the ground was dry and more readily disturbed, making it more vulnerable to erosion during the summer thunderstorms that are common in this area. Much of the plutonium would have been close to the surface at that time, and hence substantially less soil than deduced above would have been required to result in the measured plutonium inventories.

6.5 Conclusion and summary

This study has demonstrated the feasibility of using fallout plutonium to identify depositional sites and to quantify soil loss on hillslopes. Plutonium inventories and depth profiles have been measured at several study sites across a hillslope catchment, comprising a gully head site #3, a site (#4) about 1 km down a gully, and a transect down a hillslope (sites #5-7). Overall, the investigation demonstrates that sheet erosion has been variable in this region over the past 50 years, and was particularly severe on a steep hillslope near a farm dam, most likely due to the activity of cattle. An inventory of 1.62 mBq/cm^2 was determined as the reference level and comparison of the measured inventories at the study sites with this value shows that:

- Near the heads of gullies as represented by site #3, where water energy during rainfall events is low, much of the material eroded from nearby slopes is trapped in the gully, i.e. these are accumulation sites. In contrast, at site #4, which is 1 km down a gully, the catchment area is much larger and water flow is higher volume and higher energy. Under the present-day vegetation regime in this catchment, that consists principally of eucalyptus trees of a uniform age and little understory, there is little to impede water flow and we find that there is a net loss of sediment from the gully.
- For the hillslope transect, total plutonium inventories at the three sites range from only 30-50% of the reference inventory, indicating that cm of surface soil has been lost from these sites since the early 1960s. It is hypothesised that this is the result of a much enhanced impact by cattle following the construction of a nearby farm dam in the early 1970s. At the upper and lower sites, the plutonium concentration peaks strongly in the top 3 cm of soil, suggesting that there has been some accumulation of soil from higher on the hillslope at these two sites, which may be a consequence of the area having been largely destocked for at least the last 10 years. Quantifying the soil loss is difficult, since much of it may have occurred when the depth profile was much shallower than today, i.e. it is probably not appropriate to use the present-day depth profile defined by the reference site to estimate actual soil loss. Nevertheless, it must have been in the range of centimetre scale.

Chapter 7 Summary and conclusions

This concluding chapter summarizes the findings and outcomes gathered from this thesis. It includes recommendations for future work.

Fallout radionuclides, including anthropogenic ^{137}Cs and natural ^{210}Pb and ^7Be , have been used for many years as environmental tracers for erosion studies. However, measurements of these tracers have been limited by their low concentrations and the low efficiency of the gamma-ray detection technique. In this thesis, studies have been initiated to complement these radionuclides with a new tracer, plutonium. The use of plutonium has not been exploited in the past due to the difficulties of detection using the conventional mean of alpha-particle spectrometry. However, recent advances in the technique of accelerator mass spectrometry (AMS) have allowed plutonium isotopes to be readily detectable at the femtogram (10^{-15} g) level with much higher sensitivity and shorter analytical times. These advances allow the measurement of the low-levels of plutonium in environmental samples and thereby facilitate its use as a tracer for detailed catchment-wide erosion assessment.

In this thesis, a simple model is developed to provide a quantitative estimate of soil loss at a specific study site using the difference between the plutonium inventories at a reference site and the study site, and information about the depth profile of the plutonium in the soil. There is evidence, including from the present work that plutonium adsorbs preferentially to the soil organic component at the time of fallout. Further, plutonium concentrations are higher on the finer grain sizes of the soil due to their larger surface to volume ratios. For simplicity, the above model assumes that erosional processes remove bulk soil, and processes that preferentially remove the organic component or the finer fractions are not considered. The soil depth profile of plutonium does, however, evolve with time, from being essentially all at the surface immediately after fallout, to being distributed over a depth of 20 cm or more with an approximately exponential falloff at the present day. Thus it is expected that erosion that occurred close in time to the fallout period would have removed substantially more plutonium than would the same amount of erosion

occurring today. The model does not take this into consideration and hence tends to overestimate the erosion.

In the course of this thesis, a number of improvements were made to the sample preparation process. In brief, three main improvements highlighted below were made to the original procedure:

- (i) the sample size was increased from 4 g to 20 g in order to improve the statistical precision of the plutonium measurements by increasing the count rate,
- (ii) the ^{242}Pu spike was added to the sample after the ashing process to facilitate the sample preparation process, and
- (iii) silver nitrate as well as iron nitrate was added to the final solution before drying down and baking, so that after baking the plutonium was uniformly dispersed in an intimate mixture of iron oxide and silver metal. This made the final material easier to handle, and removed the need to mix the sample with silver powder after baking.

Using the methodology established in this thesis, fallout plutonium is applied as an environmental tracer for the assessment of erosion at two case study sites, located within the Australian Capital Territory (Cotter River catchment) and New South Wales (Burra Creek catchment) respectively. The Cotter catchment is a highly disturbed environment that has been influenced by forestry operations and had recently experienced a catastrophic bush fire, whereas the Burra study area is under native vegetation and has been lightly impacted by land use since at least 1950, i.e. before the period of fallout from atmospheric nuclear testing.

The temporal variation of erosional activity in the Cotter catchment has also been explored based on the study of a 1.2 m deep sediment pit that was collected from the upper reaches of the Cotter dam lake.

The findings gathered from these two study sites are summarised below.

Cotter catchment

The study conducted at the Cotter catchment has demonstrated the utility of fallout plutonium in investigating recent erosional processes on the scale of a catchment of a few hundred km². Plutonium inventories and depth profiles have been measured at six study sites across a fire-ravaged area that is part of Canberra's water-supply catchment. Prior to a bushfire in 2003, the area was covered by pine plantations. In addition, two adjacent 'undisturbed' reference sites on a nearby hilltop covered in eucalypt forest was sampled to define the inventory of plutonium that fell out on this area during the nuclear-weapons testing era in the 1950s and 1960s. An average plutonium inventory of 2.32 mBq/cm² was determined, which is similar to inventories measured near Sydney and Melbourne in soils that were collected in 1970-71. Comparison of the measured inventories at the study sites with this reference inventory shows that:

- The total plutonium inventories at four of the study sites (Blundell's Flat, Bullock Paddock, Red Soil and Blue Range) are within the range of the reference inventories, indicating minimal soil loss across much of the pine-forested area since the early 1960s.
- At the Pierce's Creek sites, where the soils are more erodible, between 2 and 5 cm of soil have been lost. Determining the extent to which these losses are due to forestry operations over the preceding 50 years, to heavy rainfall shortly after the bush fire, or to the post-fire use of heavy machinery for harvesting burnt trees and ripping the ground in preparation for replanting, will require further investigation.
- Locally, at particularly dynamic sites such as Pago, a loss of ~6 cm of topsoil has been identified. Post-fire use of heavy machinery may have contributed to the higher soil loss.

Additional investigations that involve the comparison of plutonium concentrations in 'near surface' soils and sediment in gullies across specific study sites show that greater than 60% of the sediment presently in the gullies has been derived from gully walls rather than from surface sheet wash, and that this effect is more pronounced at Pierce's Creek than at Pago where the gradients are steeper.

Plutonium concentrations in the sediment deposited in the Cotter Dam were used to study both the depositional history and to chart changes in erosional processes over time in the Cotter catchment. In order to obtain a better estimate of the time at which deposition was initiated at this site, bomb-pulse radiocarbon dating was applied to small twig fragments collected at a few positions in the sediment core. Analysis of the sediment samples indicated that ~50 cm of sediment was deposited over the pre-fire period from 1990-2003, implying an average sedimentation rate of ~4 cm/yr. In contrast, 70 cm of sediment was deposited in the 3.5 year post-fire period 2003-2006 implying an average sedimentation rate of 20 cm/yr.

Burra catchment

The study conducted at the Burra catchment has demonstrated the utility of fallout plutonium in identifying depositional sites and quantifying soil loss on hillslopes. Plutonium inventories and depth profiles were measured at several sites across the study area.

Overall, the investigation demonstrates that sheet erosion has been variable in this region over the past 50 years, and was particularly severe on a steep hillslope near a farm dam, most likely due to the activity of cattle.

Comparison of study sites: Cotter vs Burra catchment

The average plutonium inventory derived from the reference and the undisturbed forest sites at the Cotter catchment was 2.32 ± 0.40 mBq/cm² whereas the plutonium inventory in the Burra catchment was deduced to be 1.62 ± 0.04 mBq/cm². The distance between the two study sites is approximately 40 km and they can be considered in "close" proximity. Thus one would expect the reference plutonium inventory level at these two study sites to be comparable. There are, however,

differences between the two sites that could influence the inventory. Foremost among these is rainfall. Average annual rainfall in the lower Cotter catchment is 780 mm, while at Burra it is 670 mm. It is well known that fallout of plutonium was correlated with rainfall [Everett, 2009]. Hence the lower inventory at Burra may be due in part to the lower rainfall at this site. Differences in land use may also play a role. It was noted that the reference site at the Burra catchment was covered with a thick leaf litter layer which could be easily disturbed by cattle, leading to possible loss of plutonium. Nevertheless, the average plutonium inventory at the two study sites was found to be comparable with the expected Southern Hemisphere value at the latitude of Canberra (35.3°S) of ~ 1.9 mBq/cm². This expected value is based on ²³⁹⁺²⁴⁰Pu inventories reported by Hardy *et al.*, [1973] and Kelley *et al.*, [1999] for soil samples collected in 1970-71 over a wide range of latitudes in both the southern and northern hemispheres, and is the average of the measured inventories for Sydney (33.8°S) and Melbourne (37.8°S) of 1.74 and 2.04 mBq/cm² respectively.

The Cotter catchment is a highly disturbed environment where soil erosion is mainly attributed to land clearing for forestry operation purposes. Although fire was a natural feature of the landscape, it appeared that the 2003 bush fire was dramatic and led to severe erosion across large areas. The resulting soil degradation problem was extreme in some regions, particularly at sites where the soil types were prone to erosion. On the contrary, the study area at the Burra catchment site is under native vegetation and has been lightly impacted by land use. The erosion assessment was conducted at a smaller scale and focused on a typical hillslope terrain where steepness is a crucial factor affecting the severity of erosion. Although sheet erosion has been variable in this region, it is relatively less visible and widespread. Animal activity is identified as a probable contributing factor to erosion in this region.

7.1. Future work

The measurements and analysis reported in this thesis indicate that significant scope still exists for a more in-depth analysis of the erosion process in the Cotter catchment. Although the 2003 fire was very extensive, it should be possible to find an unburnt area under first growth native forest that could provide an indication of whether some loss of plutonium has occurred at the present reference site as a result of the fires. Further, the study could be extended to the nearby area of the Cotter catchment that is covered by native eucalypt forest and has not been disturbed by forestry operations. This would allow attention to be focussed on the impact of bush fires on catchments covered by native forest, without the complications associated with prior forestry operations. Finally, it would be useful to carry out a tracing investigation to determine the areas which are the principal sources of sediments into the Cotter dam, to allow the implementation of an effective soil conservation programme to mitigate the sedimentation issue. This will require the measurement of plutonium concentrations in different size fractions of the soils and sediments since sediment transport processes fractionate the different grain-sizes that were present in the original soil. Hence, in order to compare like with like, it would be necessary to look at plutonium concentrations in specific size fractions of both the parent soil and the sediment from which it was derived. These studies will require a large number of samples, and could only be realistically tackled with AMS.

It would also be of considerable interest to collect a core sample from close to the Cotter dam wall. This should preserve a sedimentation record dating back to 1915 when the dam first began to fill, and would certainly provide a better understanding of the effect of forestry operations on the catchments. Unfortunately, a window of opportunity has been missed here, since the new, enlarged Cotter Dam is presently filling. This will result in a water depth of ~70 m, making the potential coring site less accessible than previously.

The use of fallout plutonium for erosion study on a catchment-wide scale would, in addition, benefit from more detailed studies of the following factors that were outside the scope of the present thesis.

1. The rainfall pattern across the catchment during the fallout period could affect the amount of plutonium deposited at different locations. In a smaller catchment such as that studied here, it is reasonable to assume that the rainfall was uniform across the catchment, but in a larger catchment with considerable relief and rainfall gradient this may not be the case.
2. Further work is required on the mechanisms that lead to the observed depth profiles of plutonium in soils, and the way that the depth profile evolves in time. A more sophisticated model of soil loss than the one used here would take this time dependence into account.
3. A better understanding of the affinity of plutonium for organic material and the role played by this in the evolution of the depth profile and soil loss process would be useful.
4. There is also a case for studying the influence of differing soil type and particle size distributions on the behaviour of plutonium in soils.

In order to pursue such studies, good reference sites spanning a range of soil types and rainfall regimes will be required, supported by enhanced theoretical modelling of the processes involved.

A1. Sample preparation protocol - Plutonium

The procedures below were all carried out in the AMS chemistry laboratories of the Department of Nuclear Physics unless stated otherwise.

Stage 1: Pre-treatment

- (i) Dry sample in an oven to constant weight at ~100°C.
- (ii) Break up clods of earth and remove all plant parts (tufts of grass, roots, etc.).
- (iii) Separate the fine earth from the coarse elements (including rock fragments) using a 3 mm sieve and note their masses. [*Note: This step is omitted for sediment samples as they comprises mainly of fine materials.*]
- (iv) Homogenise sample (the <3 mm portion) by either mixing manually or grinding the material (depending on the application). [*Note: Manual mixing involves shaking the materials vigorously in a large sampling bag. It is carried out with the intention of retaining the particle size information. Grinding is carried out using the hydraulic ring mill in the rock-crushing laboratory of the Research School of Earth Sciences.*]

Stage 2: Ashing

- (i) Weigh sufficient amount (~25 g or more) of dried homogenised sample into a 100 ml porcelain crucible.
- (ii) Weigh the crucible with sample.
- (iii) Re-weigh the crucible after ashing the sample at 450°C for 16 hrs^{*}.

^{*} The exact ashing duration can vary from 8 to 32 hrs, depending on the amount of organic matter present in the sample. To ensure complete ashing, the sample is ashed over an 8-hr cycle. At the end of each cycle, the sample is carefully inspected, stirred and re-weighed. The cycle is repeated until the LOI (Loss On Ignition) difference is less than 1%.

$$LOI = \frac{wt_i - wt_a}{wt_i} \quad \begin{array}{l} wt_i: \text{weight of sample before ash} \\ wt_a: \text{weight of sample after ash} \end{array}$$

Stage 3: **Leaching**

- (i) Weigh a known amount of ashed sample (~20 g) and transfer it into a 500 ml teflon beaker.
- (ii) Add a known amount of ^{242}Pu standard as a spike to the sample and dry for 12 hrs (minimum) at 70°C . [Note: In the work reported here, the amount typically corresponded to $\sim 1 \times 10^{10}$ atoms of ^{242}Pu . The purpose of drying the tracer is to mimic the behaviour of fallout plutonium in the natural environment.]
- (iii) Add ~100 ml of 8M nitric acid to the beaker and leach for 24 hrs at 70°C on a hot plate. [Note: the Teflon lid is placed loosely on the beaker to act as a watch-glass & minimize the loss of liquid. Swirl the beaker occasionally.]
- (iv) Remove the beaker from the heat and allow the solution to cool and stand until the residue settles.
- (v) Slowly decant & filter the “clear” supernatant at the top portion of the solution into a 100 ml conical flask. (Note: Use filter paper of either type: “Whatman 1” or “Adventec 1”. Filtration is essential to remove the fine suspension that stays on the surface of the solution. The decanting procedure need to be carried out carefully without disturbing the residue at the bottom.)
- (vi) Transfer the remaining “supernatant + residue” at the bottom portion of the solution to a 50 ml centrifuge tube. [Note: Rinse the lid and beaker with small amount of nitric acid (8M) and collect into the centrifuge tube.]
- (vii) Centrifuge at 3000 rpm x 5 min. Decant and filter supernatant into the conical flask. [Note: The centrifugation process is to allow the residue to gather at the bottom of the centrifuge tube and this allows the supernatant to be easily decanted without disturbing the residue.]

Stage 4: **Separation**

- (i) Add a small amount (~1 g)[•] of sodium nitrite to the conical flask. [*Note: Caution- vigorous reaction can occur. Allow the reaction to cease completely before proceeding to the next step. Sodium nitrite serves as an oxidising agent to convert the plutonium in the solution to its tetravalent state.*]
- (ii) Pass the solution through a pre-prepared[▼] anion exchange column and allow to drain.
- (iii) Pass a further 25 ml of 8M nitric acid and discard the eluent. This step should elute contaminating elements such as uranium, polonium and iron, while allowing plutonium & thorium to be retained on the column. [*Note: Use the first 5 ml of nitric acid (8M) to rinse the conical flask.*]
- (iv) Elute thorium from the column with 70 ml of conc. hydrochloric acid. [*Note: The elimination of thorium is critical for the analysis of ^{238}Pu using alpha spectrometry due to the energy spectral overlap of ^{232}Th but is less important for AMS measurement.*]
- (v) Place a 30 ml teflon vial under the column. [*Note: Preferably use a flat base type vial.*]
- (vi) Add 25 ml of warm, freshly prepared 0.1M ammonium iodide in conc. hydrochloric acid solution[▲] to the column. [*Note: Ammonium iodide serves as a reducing agent to convert the plutonium from its tetravalent state to the trivalent state; thereby breaking the anionic complex and allowing plutonium to be eluted from the column.*]
- (viii) Place the vial on the hot plate at ~85°C and take the solution to dryness. [*Note: Do not attempt to increase the temperature further as it may lead to boiling. The bubbling splash can cause possible cross contamination between neighbouring vials.*]

[•] Add sufficient amount of sodium nitrite to make the solution turn permanently greenish. Do not attempt to add more than 2 g as it may lead to effervescence and cause the column to block during the ion-exchange process.

[▼] Add ~1.7 g of BioRad AG[®]1-X8, 100-200 mesh chloride resin or equivalent to a clean 7 mm diameter column. Condition the resin by adding 15 ml of 18 MΩ water follow by 15 ml of 8M HNO₃.

[▲] To prepare 0.1M of NH₄I in conc. HCl solution: Add ~0.362 g of NH₄I into 25 ml of conc. HCl and warm on a hot plate at ~40°C.

Stage 5: **Purification**

- (i) Remove the vial from heat and allow it to cool for a minute.
- (ii) Add ~3 ml of conc. nitric acid to the vial. Warm the solution on the hot plate at ~85°C until it turns clear and colourless. [*Note: Caution- vigorous reaction can occur. Add conc. nitric acid moderately to avoid splashing. This warming process is to remove the iodide in the form of iodine gas and the duration usually takes about 30 minutes.*]
- (iii) Reduce heat and add ~3 ml of conc. hydrochloric acid[□] to drive off the ammonium nitrate. [*Note: Temperature should not be more than 75°C to avoid boiling.*]
- (iv) Take the solution to dryness. [*Note: A slight yellow/brown stain residue should remain. Repeat stage 5 if the size of the residue is larger than 1 mm in diameter.*]

Stage 6: **Drying down of Fe-Ag**

- (i) Add ~0.5 ml of conc. nitric acid to dissolve the residue.
- (ii) Add ~7.0 mg of silver nitrate crystal (equivalent to ~4 mg of Ag) and 100 µl of hydrated ferric nitrate solution (equivalent to ~1 mg of Fe). [*Note: Swirl the solution to make sure that it is well mixed.*]
- (iii) Take the solution to dryness at ~85°C. [*Note: A brownish flaky residue should remain. Allow a minimum of 48 hrs drying. It is important that the sample is completely dry before it is baked, otherwise it tends to stick to the crucible.*]

Stage 7: **Baking and Loading**

- (i) Transfer the residue to a freshly pre-prepared* 5 ml crucible and bake at 800°C for 8 hrs. [*Note: The flaky residue should be removed intact from the Teflon vial to ensure minimum contact with the crucible surface. The furnace ramp temperature is set at 2°C/min and 10°C/min between the temperature interval of Room Temperature - 400°C and 400°C - 800°C respectively. This helps to enhance the final recovery from the crucible.*]
- (ii) Crush the residue in the crucible with a spatula before loading and pressing it into an aluminium cathode in preparation for AMS measurement.

[□] It is critical to ensure the complete removal of NH₄NO₃ by adding more HCl if required.

* Crucible pre-heated to 850°C for 8 hrs.

A2. Sample preparation protocol - ^{14}C

These procedures were carried out in the radiocarbon sample preparation laboratories in the Research School of Earth Sciences.

Stage 1: Pre-treatment “Acid-Base-Acid” wash

The sample is pre-treated through a standard Acid-Base-Acid wash to ensure that it is free of residues that may cause contamination.

- (i) Place sample of charcoal or twigs (~20 mg) in a clean test tube.
- (ii) Add 1M hydrochloric acid to fill $\frac{1}{2}$ volume of the test tube and heat at 70°C for 30 mins. [*Note: The acid solution will dissolve carbonates on the sample accumulated from dust or soil.*]
- (iii) Remove acid solution from test tube using disposal pipette.
- (iv) Add 1M sodium hydroxide to fill $\frac{1}{2}$ volume of the test tube and heat at 70°C for 60 mins. [*Note: The base solution will remove any alkali-soluble humics on the sample.*]
- (v) Remove the base solution from test tube using disposal pipette.
- (vi) Repeat steps (iv-v) until base solution turn clear.
- (vii) Again add 1M of hydrochloric acid to fill $\frac{1}{2}$ volume of the test tube and heat at 70°C for 30 mins. [*Note: The acid solution will remove any possible atmospheric carbon dioxide that may have been absorbed during the alkaline wash.*]
- (viii) Remove acid solution from test tube using disposal pipette.
- (ix) Add Millipore (18 $\text{M}\Omega$) water to fill $\frac{1}{2}$ volume of the test tube and heat at 70°C for 5 mins. [*Note: The sample is brought back to neutral pH using Millipore (18 $\text{M}\Omega$) water to get rid of chloride. It is essential to remove the chloride to prevent it from corroding the combustion tube or interfere with the subsequent graphitization process.*]
- (x) Remove water from test tube using disposal pipette.
- (xi) Repeat steps (ix-x) for two or more cycles before proceeding to dry the sample on a hot plate.

Stage 2: **Combustion**

Once the sample is cleaned and dried, it is ready for the combustion process.

- (i) Seal the pre-treated sample (~4 mg) in an evacuated 7 mm diameter Vycor tube (combustion tube), along with ~60 mg [*or ~25 x sample amount*] of wire-formed cupric oxide and a piece of silver wire (~5 mm).
- (ii) Mix the tube contents and heat at 900°C in a muffle furnace for six hours, allowing to cool to room temperature overnight. [*Note: The cupric oxide CuO is reduced to copper metal, which appear as pink residues in the cooled tube. CuO was the source of oxygen for the conversion of any carbon compounds to CO₂. The silver wire acted as a scrubber for sulphur and halogen compounds.*]

Stage 3: **Recovery of carbon dioxide**

- (i) Place combustion tube on a vacuum line and break the tube to recover the desired carbon dioxide.
- (ii) Dry the released carbon dioxide over a “dry ice” trap and freeze it out in a “liquid nitrogen” cooled trap.
- (iii) Pump away any nitrogen gas that is present.

Stage 4: **Graphitization**

- (i) Remove the liquid nitrogen-cooled trap to recover the carbon dioxide gas and note the amount.
- (ii) Transfer the carbon dioxide gas together with ultra-pure hydrogen gas of an amount in excess of the stoichiometric amount needed for the complete reduction [*Note: Typically 2.1 x CO₂ amount.*], into a reaction tube that had been preloaded with ~2 mg of iron catalyst (99% pure -200 mesh powder).
- (iii) Heat the tube to ~570°C to initialise the reduction of CO₂ to graphite on the iron catalyst (~3 hours). [*Note: The oven is left overnight to ensure the process is complete.*]
- (iv) Remove the resultant graphite-coated iron powder and press into the aluminium cathode target for AMS measurement.

A3. Table of plutonium isotopes

Mass Number	Half life	Mode of Decay	Main radiations (MeV)	Method of Production
228	1.1 sec	α	α (7.772)	^{198}Pt (^{37}S , 4n)
229	-	α	α (7.460)	^{207}Pb (^{26}Mg , 4n)
230	2.6 min	α , EC	α (7.055)	^{208}Pb (^{26}Mg , 4n)
231	8.6 min	α (10%), EC (90%)	α (6.72)	^{233}U (^3He , 5n)
232	33.1 min	α ($\leq 20\%$), EC ($\geq 80\%$)	α (6.60) 62%, α (6.542) 38%	^{233}U (α , 5n)
233	20.9 min	α (0.12%), EC (99.88%)	α (6.30), γ (0.235)	^{233}U (α , 4n)
234	8.8 hr	α (6%), EC (94%)	α (6.202) 68%, α (6.151) 32%	^{233}U (α , 3n)
235	25.3 min	α (0.003%), EC ($>99.99\%$)	α (5.850) 80%, γ (0.049)	^{235}U (α , 4n)
236	2.858 yr	α , SF ($1.37 \times 10^{-7}\%$)	α (5.768) 69%, α (5.721) 31%	^{235}U (α , 3n), ^{236}Np daughter
237	45.2 d	EC ($>99.99\%$), α ($4.24 \times 10^{-3}\%$)	α (5.356) 17.2%, α (5.334) 43.5%, γ (0.059)	^{235}U (α , 2n), ^{237}Np (d, 2n)
238	87.7 yr	α , SF ($1.85 \times 10^{-7}\%$)	α (5.499) 70.9%, α (5.456) 29.0%	^{242}Cm daughter
239	2.411×10^4 yr	α , SF ($3.0 \times 10^{-10}\%$)	α (5.157) 70.77%, α (5.144) 17.11%, α (5.106) 11.94%, γ (0.129)	^{238}Np daughter ^{239}Np daughter
240	6.56×10^3 yr	α , SF ($5.75 \times 10^{-6}\%$)	α (5.168) 72.8%, α (5.124) 27.1%	Multiple neutron capture
241	14.35 yr	α ($2.45 \times 10^{-3}\%$), β ($>99.99\%$), SF ($2.4 \times 10^{-14}\%$)	α (4.896) 83.2%, α (4.853) 12.2%, β (0.021), γ (0.149)	Multiple neutron capture
242	3.75×10^5 yr	α , SF ($5.54 \times 10^{-4}\%$)	α (4.902) 76.49%, α (4.856) 23.48%	Multiple neutron capture
243	4.956 h	β	β (0.582) 59%, γ (0.084) 23%	Multiple neutron capture
244	8.08×10^7 yr	α (99.88%), SF (0.1214%)	α (4.589) 81%, α (4.546) 19%	Multiple neutron capture
245	10.5 h	β	β (0.878) 51%, γ (0.327) 25.4%	^{244}Pu (n, γ)
246	10.84 d	B	β (0.15) 91%, γ (0.224) 25%	Multiple neutron capture
247	2.27 d	β		Multiple neutron capture

[Source: D. L. Clark, S. S. Hecker, G. D. Jarvinen, and M. P. Neu (2008). "The Chemistry of the Actinide and Transactinide element - Plutonium", pg 816, Springer, Netherland]

A4. Lower Cotter catchment sampling sites

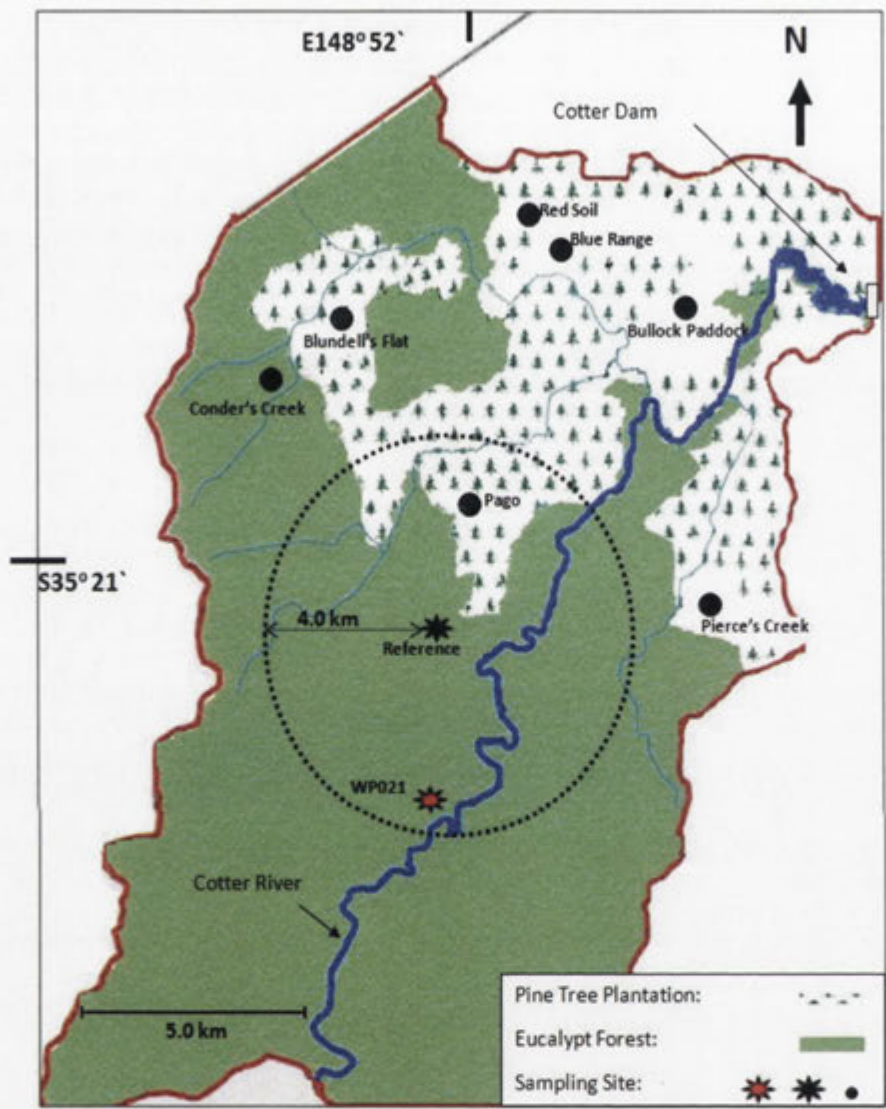


Figure A4.1: Location of sampling sites within the lower Cotter catchment (study area). Site WP021 is located in a thick forest and there are burnt evidences. The soil type is the same as the reference site. Derivation of plutonium inventories at this site (See Table A4.1) is based on average soil density measurements at Pit A and Pit B of the reference site.

Table A4.1: Plutonium inventories of the WP021 site

<3 mm component			²³⁹⁺²⁴⁰ Pu (mBq/g)		²³⁹⁺²⁴⁰ Pu (mBq/cm ²)	
Depth (cm)	Density ^a (g/cm ³)	% Composition	<3 mm component	>3 mm component ^b	Bulk	
0-5	0.566	95	0.31±0.03	0.06	0.30±0.03	0.87±0.15
5-10	0.556	88	0.23±0.02	0.05	0.21±0.02	0.63±0.09
10-15	0.907	91	0.06±0.01	0.01	0.06±0.01	0.25±0.06
15-20	0.907	99	0.008±0.003	0.002	0.008±0.003	0.04±0.02
20-25	0.907	99	0.006±0.003	0.001	0.006±0.003	0.03±0.01
25-30	0.907	99	0.006±0.003	0.001	0.006±0.003	0.01±0.01
Total						1.83±0.18

^a The density of the <3 mm component is based on average soil density measurements at Pit A and Pit B of the reference site, and the density of the >3 mm component ~2.1 g/cm³.

^b Plutonium concentration of the >3 mm component is derived from 20% plutonium concentration of the <3 mm component.

A5. Pourbaix diagram for plutonium

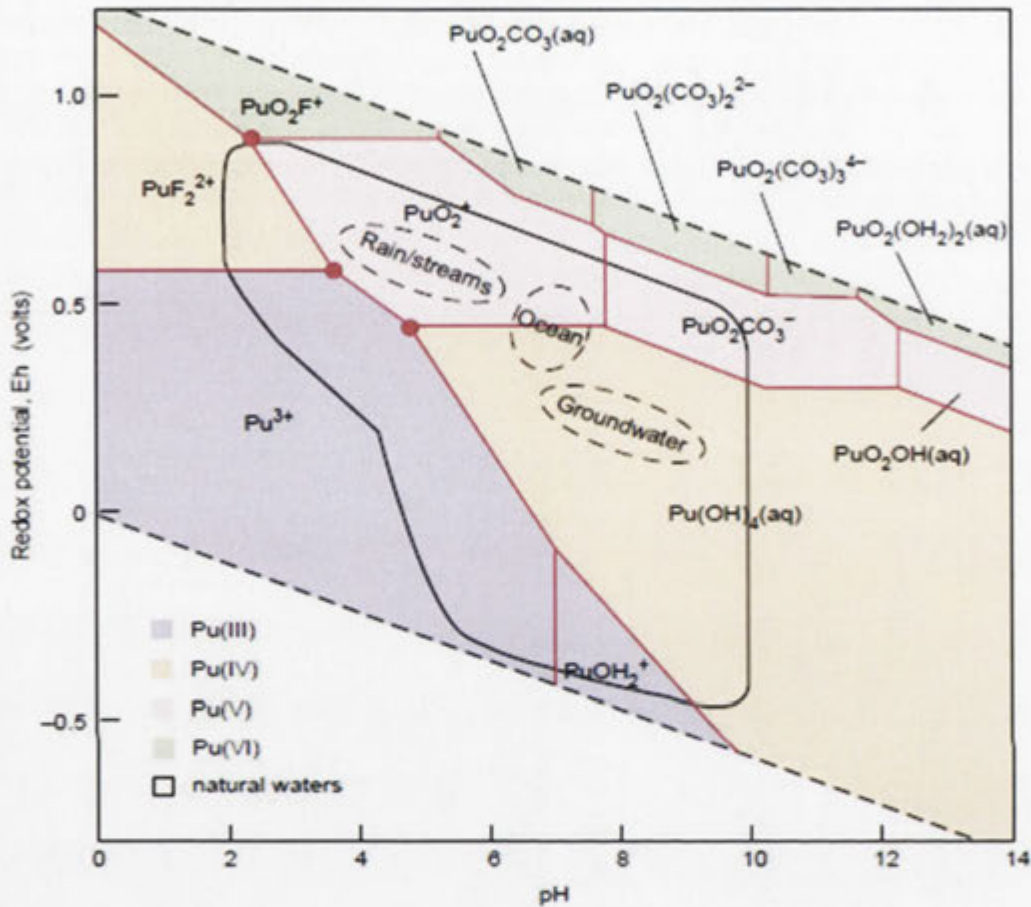


Figure A5.1: The Eh-vs-pH diagram represents plutonium in water containing hydroxide, carbonate and fluoride ion. The red dots are triple points, where plutonium can exist in three different oxidation states. The solid black outline defined the range of Eh/pH values found in natural water. Plutonium is likely to exist as Pu (IV) in ocean water or ground water, while in rainwater or streams, it tends to assume in the Pu (V) state. Other natural environments will favour Pu (III) and Pu (IV) complex state. [Source: Runde, 2000].

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