The environmental behaviour of beryllium-7 and implications for its use as a sediment tracer

by

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Alex Taylor: The environmental behaviour of beryllium-7 and implications for its use as a sediment tracer

The use of cosmogenic beryllium-7 (^{7}Be) as a soil and sediment tracer relies upon a number of important assumptions which to date have not been fully underpinned by supporting data. As a catchment management tool ^{7}Be offers unique potential to assess the effects of recent land use or climate change but further research is required to provide confidence in key data and elucidate sources of uncertainty. Through a range of laboratory and field studies, this thesis aims to explore knowledge gaps relating to i) the temporal and spatial dynamics of ^{7}Be activity in rainfall which has importance in the context of estimating fallout input during erosion studies ii) adsorption behaviour in soils which is of critical importance when considering tracer stability at the field and catchment-scale and iii) the reliability of erosion estimates using ^{7}Be inventories at the slope-scale to address the current lack of model validation. Findings showed temporal and spatial variability of ^{7}Be fallout emphasising the need for regular site-specific sampling to determine fallout flux during erosion studies. Data supported the assumption of rapid tracer adsorption upon fallout although highlighted the potential for ^{7}Be mobility under changing environmental parameters, thus, raising questions with regard to tracer stability at the catchment-scale. Field investigations demonstrated the potential for current models to overestimate erosion rates by failing to accurately represent key model components, namely, ^{7}Be depth distributions, particle size enrichment and fallout input dynamics. Where these factors cannot be determined directly, a range of erosion estimates should be given based upon realistic sensitivity analysis of model components. In this manner, reported uncertainties will reflect field processes rather than propagated analytical uncertainty alone.

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At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other university award. The research presented here is the work of the author unless otherwise acknowledged.

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Chapter 1. Introduction and thesis overview

Knowledge of the sources and dynamics of sediment redistribution within catchment systems is required to inform management solutions. This is particularly pertinent with regard to Diffuse Water Pollution from Agriculture (DWPA), and in Europe management efforts are increasingly driven by requirements of the Water Framework Directive. Fallout radionuclide (FRN) tracers (^{137}Cs, ^{210}Pb$_{ex}$ and ^{7}Be) have the potential to satisfy the demand for high resolution spatial and temporal data regarding catchment sediment dynamics. In this context, beryllium-7 (^{7}Be), a short-lived, cosmogenic radionuclide has the potential to become a key decision support tool by enabling effects of recent changes in land use and climatic patterns to be assessed. However, the application of FRN tracers is based upon a number of important assumptions, many of which are not fully underpinned by reliable supporting data. This thesis aims to explore some of the assumptions surrounding the application of beryllium-7 as a sediment tracer across a range of temporal and spatial scales through laboratory and field-based experiments. The following introduction provides context for the use of FRN tracers before detailing examples of application and highlighting the current questions surrounding data reliability.

1. Introduction

1.1. The need for soil erosion monitoring

Soil erosion is a major contributor to land degradation and each year it is estimated that 75 billion tonnes of soil are lost as a result of erosion processes; a significant proportion of this is associated with agricultural practice (Ananda and Herath 2003 and references therein). Verheijen et al. (2009) reported mean

soil loss values of 3-40 t ha yr^{-1} for Europe, vastly exceeding the estimated tolerable levels of 0.3-1.4 t ha yr^{-1}. As a contributor, agricultural intensification has placed increased pressure upon the soil resource through use of heavy machinery, removal of field boundaries, autumn cultivation and growth of high erosion risk crops. Further to this, it is possible that water erosion will be exacerbated given the predicted change in climatic patterns (Boardman & Favis-Mortlock, 1993).

Recent reviews (Boardman, 2002; Evans, 2010) discussed soil erosion research in the UK and emphasised the growing recognition in the 1980s of the potential off-site impacts of soil erosion associated with the diffuse inputs of sediment and contaminants. The potential ecological impacts of Diffuse Water Pollution from Agriculture (DWPA) are now well documented (Anderson et al., 2002; Camargo & Alonso, 2006; Weijters et al., 2009) and, in addition, considerable social and economic costs can be entailed (Pretty et al., 2000). The on-site environmental consequences of erosion should also be considered with loss of topsoil ultimately affecting crop yields (Biot & Lu, 1995). Pretty et al. (2000) considered the external costs exerted by UK agriculture with externalities representing costs which are not included in consumer costs, such as those involving water treatment and erosion prevention. The authors provided a conservative estimate of the cost of total UK externalities in 1996 at £2343 m.

In Europe management responses to soil loss have been heavily influenced by the Water Framework Directive (2000/60/EC). The directive was introduced to provide a more coherent movement towards the sustainable use of inland and coastal waters, identifying the need for improved stakeholder participation and a precautionary approach to management. The directive was transposed into UK law in 2003, and since then River Basin Management Plans have been

developed to ensure water bodies achieve the required *good status* by 2015. More recently the European Commission adopted a Thematic Strategy for Soil Protection (COM (2006) 231) to promote sustainable soil use. The strategy aims to halt degradation and restore resources by confronting eight major threats to European soils, erosion being one of the threats identified. The strategy also provides the initiative for establishing a Soil Framework Directive (COM (2006) 232) (EC., 2006). To contribute to meeting the requirements of the Water Framework Directive (and the guidelines of the Thematic Strategy for Soil Protection) the England Catchment Sensitive Farming Delivery Initiative was launched in 2006 to reduce the impacts associated with DWPA. The Initiative operates at the regional scale by providing stakeholders with guidelines for the sustainable use of soils (Defra, 2005). The adoption of Best Management Practice (BMP) is encouraged through incentives from Capital Grant Schemes (within Catchment Sensitive Farming) or from Environmental Stewardship.

A catchment-wide approach to management requires the support of continuing research to monitor the response of sediment within dynamic systems. This entails an interdisciplinary approach and is reflected in the wide range of sediment-water research being carried out globally (Owens & Zhihong, 2011). Within this context, the development of sediment budgets has become a useful tool for considering the dynamics of sediment transport and storage across a range of spatial and temporal scales.

1.2. The role of the sediment budget in catchment management

Early applications of the sediment budget concept (Dietrich & Dunne, 1978; Trimble, 1983) considered components of sediment transfer and storage in conjunction with inputs and yield. Trimble (1983) provided a sediment budget for Coon Creek, Wisconsin for the period 1853-1975 and highlighted that yield did not directly reflect sediment inputs. Because yield is both supply and transport limited, Trimble discussed the potential for yield to be maintained even when inputs and storage had decreased owing to the remobilisation of sediment from storage zones. Trimble, therefore, recognised the role of deposition zones as contaminant sinks with implications for the long-term management of sediment associated contaminants within the system.

Consistent with the need for sediment research to consider linkages within a dynamic system (Owens & Zhihong, 2011), Walling and Collins (2008) identify the importance of management strategies taking a holistic approach in the mitigation of sediment transport. For reliable estimates of system response to land use change or management practice it is necessary to consider the dynamics of storage (locations and times) and remobilisation potential as well as sediment yield (Figure 1.1). Owens (2005) described the river basin as a series of interconnected sub-systems, decisions which affect one area of the system will invariably affect another. In this way, stakeholder interests relying upon sub-systems are also interlinked and the system must be considered as a whole to effectively confront diffuse inputs.
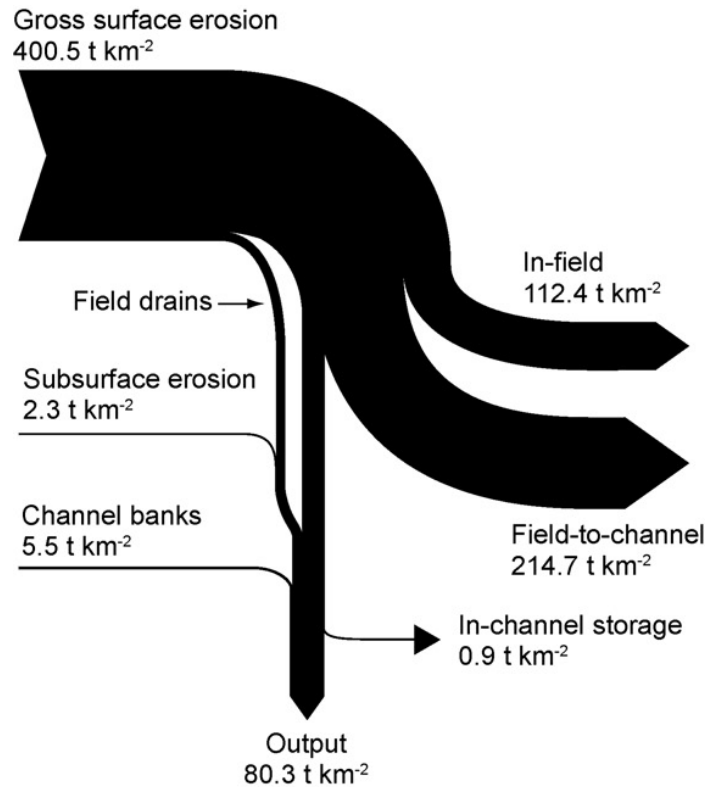
Figure 1.1: Example of a sediment budget constructed for the Lower Simsby catchment, England. Note the significance of storage zones (in-field and field-to-channel). Reprinted from Catena, 47/4, Walling et al., Establishing sediment budgets for two small lowland agricultural catchments in the UK, 323-353., Copyright (2002) with permission from Elsevier.

Numerous studies have documented the use of sediment budgets to aid management decisions (e.g. Minella et al., 2008; Walling et al., 2001; Walling *et al.*, 2002) and often a range of monitoring techniques are required to identify the key components of a sediment budget and how these components may change over spatial and temporal scales. In this regard fallout radionuclide (FRN) tracing techniques have been shown to be a valuable tool for assessing the major components of a sediment system (Owens et al., 1997; Walling, 2004; Walling & Collins, 2005) and can, therefore, provide the basis for the construction of sediment budgets.

1.3. The use of fallout radionuclide (FRN) tracers in soil erosion investigations

The use of FRN tracers has the potential to provide distinct advantages over traditional monitoring techniques by enabling retrospective estimates of soil redistribution from fewer site visits. Relatively simple and efficient sampling programmes can achieve estimates of a high spatial resolution which are unlikely to be obtained using traditional methods (Loughran, 1989). Moreover, the sampling techniques involve minimal disturbance to the study site and are, therefore, unlikely to affect erosion processes (Mabit et al., 2008a; Zapata, 2003). Nuclear techniques enable the individual components of conservation practice to be assessed more rigorously and application of tracer techniques over longer time periods offers the potential to investigate the sustainability of agricultural systems. The most commonly employed FRN tracers are caesium-137 (^{137}Cs), excess lead-210 (^{210}Pb$_{ex}$) and beryllium-7 (^{7}Be). Of these the use of ^{137}Cs, representing the foundation of FRN tracing, will be discussed below in brief together with detailed discussion of the use of ^{7}Be and current challenges.

1.3.1. The use of ^{137}Cs as a soil tracer

Caesium-137 (^{137}Cs) ($t_{1/2} = 30.2$ years) is the most widely employed FRN tracer to date with examples of use including assessment of hill slope soil redistribution (e.g. Quine et al., 1999; Walling & Quine, 1991), quantification of erosion sources (e.g. Owens et al., 1997; Wallbrink, 2004) and determination of sediment transport distances within a system (e.g. Matisoff et al., 2002). ^{137}Cs is an artificial radionuclide produced during nuclear fission and its stratospheric input was largely the result of nuclear weapons testing from the 1950s to 1970s,

although the northern hemisphere experienced a significant input to the troposphere as a result of the Chernobyl incident in 1986. Fallout ^{137}Cs was largely associated with wet deposition with latitudinal spatial variation occurring due to predominance of weapons testing in the northern hemisphere (Mabit *et al.*, 2008a). Early studies investigated the partitioning of ^{137}Cs within the soil profile following deposition and its subsequent loss from erosion plots in association with soil transport (Rogowski & Tamura, 1965; Tamura, 1964). Later, ^{137}Cs was applied to quantify soil erosion and redistribution patterns based on the relationship between soil loss (calculated from the Universal Soil Loss Equation) and ^{137}Cs loss (Ritchie & McHenry, 1990; Ritchie et al., 1974). Because ^{137}Cs has been widely used in soil erosion investigations to date, a large volume of literature exists on its application and effectiveness as a tracer (Mabit *et al.*, 2008a; Poreba, 2006; Ritchie & McHenry, 1990; Zapata, 2003). With a half-life of 30.2 years, ^{137}Cs can, potentially, provide estimations of medium-term rates (*c* 40 years) of soil redistribution.

Determining soil redistribution using FRNs involves comparison of the radionuclide inventory (Bq m^{-2}) at a sampling location to that of a reference location which is assumed to be stable with regard to soil movement. Erosion is indicated by the inventory of the sample point being below that of the reference baseline, whereas deposition is reflected in the sample inventory exceeding the reference inventory (Figure 1.2). The key assumptions involved in the use of FRN tracers, are i) that fallout to the sample site is spatially uniform, ii) upon fallout FRNs rapidly adsorb to soil particles and iii) adsorption to particles is irreversible, thus, changes in radionuclide inventories can be related directly to soil movement. To quantify soil redistribution, conversion models are used,

taking into account the distribution of the FRN with depth and particle size (Quine *et al.*, 1999; Walling & Quine, 1991).
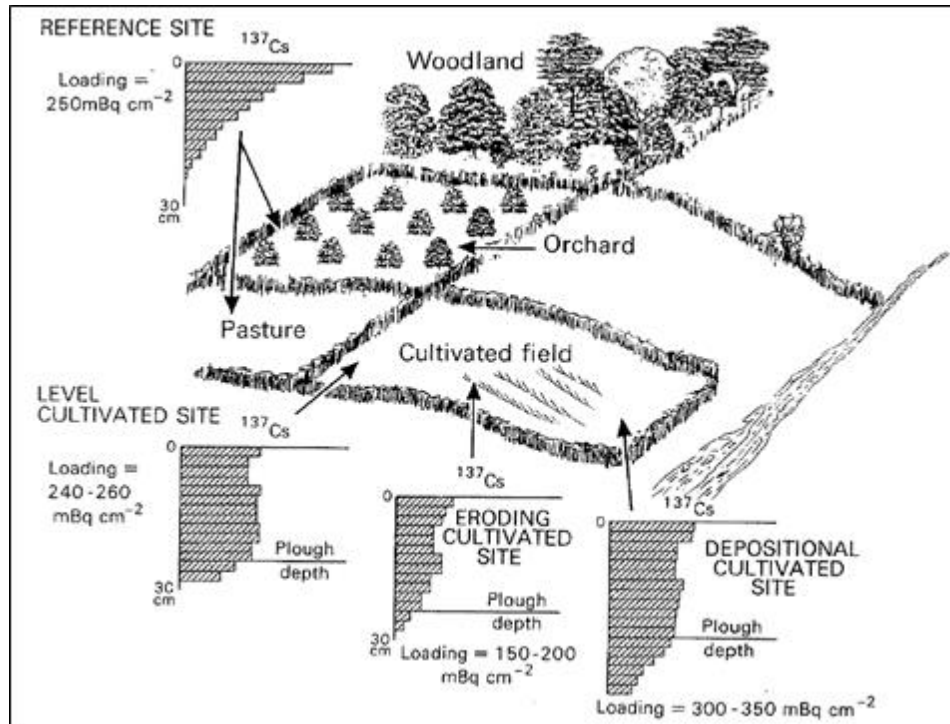
Figure 1.2: Comparison of ^{137}Cs inventories to baseline inventory at stable a reference location. The lower inventory on the cultivated slope indicates erosion and excess inventory at the footslope indicates deposition. Note the exponential decrease in activity with depth at the reference location and the uniform depth distribution displayed at the cultivated site owing to mixing through the plough layer. Reprinted from European Journal of Soil Science, 42, Walling and Quine, Use of ^{137}Cs measurements to investigate soil erosion in arable fields in the UK: potential applications and limitations, 147-165, Copyright (1991) with permission from John Wiley and Sons, Inc.

Despite its widespread application as a tracer to date, Parsons and Foster (2011) questioned the reliability of some ^{137}Cs tracing studies owing to insufficient data to underpin the key assumptions. The authors provided detailed accounts of situations where the uniformity of fallout may not be assumed with confidence owing to variability in local rainfall patterns and infiltration rates across a field site. The latter point is also considered as a possible factor affecting the displacement of inventory independent of soil transport, particularly where infiltration excess overland flow has occurred during the main period of fallout. There is also evidence to suggest that ^{137}Cs partitioning behaviour in

soils may contribute to tracer mobility under some conditions, thus, undermining the assumption of irreversible adsorption. Also criticised are the conversion models which do not always sufficiently account for site-specific factors and fail to consider erosion processes, particularly with regard to the transport of particle size fractions. Parsons and Foster further conclude that uncertainties associated with field sampling methods and sample processing are often overlooked and acceptable levels of analytical uncertainty are not standardised.

Although Parsons and Foster focused explicitly upon the application of ^{137}Cs as a tracer, many of the questions raised apply to the use of FRN tracers in general and, thus, these issues will be considered here with respect to the use of ^{7}Be. ^{7}Be has potential to become a powerful tool in sediment tracing studies owing to its half-life (53.3 days) enabling estimates of soil redistribution over shorter timescales. This is likely to be of particular relevance when assessing the effects of land use change or variation in future climatic patterns. ^{7}Be also provides the benefit of constant, natural production, an important consideration given the finite nature of ^{137}Cs inventories without replenishment from atmospheric fallout.

Accordingly, the use of ^{7}Be as a tracer is detailed below, firstly by reviewing current knowledge regarding production and fallout dynamics followed by its distribution behaviour within soils. These are important precursors to ^{7}Be application as a tracer at the field and catchment-scale and, here, as well as a general introduction to these factors, potential uncertainties relating to key assumptions will be highlighted. The use of ^{7}Be as a tracer at the field-scale is then described with an explanation of conversion models and examples of application. Again, emphasis is placed upon key model parameters and current lack of knowledge regarding the reliability of model estimates. A range of

catchment-scale applications are then outlined followed by a detailed review of the current knowledge regarding ^{7}Be adsorption behaviour and research needs. This knowledge is critical to underpin the assumption of irreversible adsorption and, therefore, the application of ^{7}Be as a tracer at the catchment-scale (Mabit *et al.*, 2008a).

1.3.2. The use of ^{7}Be as a soil tracer

1.3.2.1. ^{7}Be production and fallout

Beryllium-7 (^{7}Be) ($t_{1/2}$=53.3 days) is a cosmogenic radionuclide produced in the stratosphere and troposphere as a result of cosmic ray interaction with nitrogen and oxygen (Brost et al., 1991) . Rates of production are dependent upon solar activity (Kikuchi et al., 2009) and can, thus, be influenced by latitude with increased production occurring at the poles owing to cosmic ray deflection towards polar regions. Production is also affected by altitude with higher levels of production in the stratosphere than in the troposphere (Feely et al., 1989). Variation according to the 11-year solar cycle can also occur with reduced production during the solar maximums owing to reduced flux of cosmic rays to the Earth's atmosphere (Kaste et al., 2002).

Following its formation, ^{7}Be becomes associated with aerosols and is, thus, subjected to atmospheric transport processes which can exhibit seasonal variations. Higher rates of ^{7}Be production in the stratosphere and longer residence times create a stratosphere-troposphere concentration gradient (Doering & Akber, 2008b) and this gradient can be reduced during folding of the tropopause which encourages exchange of ^{7}Be from the stratosphere to the upper troposphere; this process is enhanced during the spring months at mid-

latitudes (Caillet et al., 2001; Daish et al., 2005). Vertical mixing within the troposphere may also occur through convective circulation during warmer months, which transports ^{7}Be enriched air from the upper troposphere to the lower troposphere (Feely *et al.*, 1989; Ioannidou et al., 2005). ^{7}Be is removed from the troposphere predominantly by precipitation scavenging (Ioannidou & Papastefanou, 2006) and, therefore, concentrations of ^{7}Be in air can be influenced by seasonal climatic conditions (Feely *et al.*, 1989). Wet deposition is the dominant pathway of ^{7}Be delivery to the Earth's surface with dry deposition accounting for around 10 % to total fallout (Doering & Akber, 2008a; Ioannidou & Papastefanou, 2006; Wallbrink & Murray, 1994). On an event basis deposition (Bq m^{-2}) is correlated to the amount of rainfall received and, therefore, seasonal depositional fluxes reflect monthly rainfall volumes (Ayub et al., 2009; Doering & Akber, 2008a; Gonzalez-Gomez et al., 2006; Wallbrink & Murray, 1994).

Knowledge of ^{7}Be activity in rainfall (Bq L^{-1}) is required for estimates of deposition (fallout input) at a field site and is a key component of the soil redistribution model suggested by Walling et al. (2009) (section 1.3.2.3). Here, the authors assume a constant ^{7}Be activity in rainfall across an autumn-winter period. However, aside from atmospheric transport processes influencing seasonal activity variation, ^{7}Be activity in rainfall is not shown to be constant during an event with activity found to decrease through an event owing to washout from the troposphere (Ioannidou & Papastefanou, 2006; Wallbrink & Murray, 1994). Event magnitude and rainfall rate have also been found to influence ^{7}Be activity, with higher activity occurring with low rainfall volumes and low rainfall rate. This is likely to reflect the availability of ^{7}Be-bearing aerosols

(i.e. the extent of washout) and the efficient scavenging of fine rain droplets (Caillet *et al.*, 2001; Ioannidou & Papastefanou, 2006).

A complex combination of factors including solar activity, stratosphere-troposphere exchange and varying climatic conditions can, therefore, influence the temporal variability of depositional fluxes by determining the concentration of ^{7}Be available for scavenging in the troposphere. This is highlighted in the global range of rainfall activity and depositional values detailed in Table 1.1. Spatial variability of ^{7}Be activity in rainfall is also evident given the monthly concentrations reported by Mitchell (2009) for areas of the UK in 2009. Values for Chilton, Oxfordshire were markedly lower than those of Aberporth, Wales with mean annual values of 0.75 Bq L^{-1} and 1.27 Bq L^{-1} respectively. ^{7}Be fallout data for the UK is generally lacking and given the temporal and spatial variability of ^{7}Be rainfall activity and fallout input, further datasets are required to quantify variability in a wider range of locations. This is of particular importance when applying ^{7}Be as a tracer over extended timescales (following Walling et al., 2009).

Location	^{7}Be rainwater activity (Bq L^{-1})	Annual deposition (Bq m^{-2})	Event deposition (Bq m^{-2})	Source
[a]Central Argentina	0.70-3.20	1140	1.10-120	(Ayub *et al.*, 2009)
[b]Texas, USA	0.09-21	2000-3833	nv	(Baskaran et al., 1993)
[a]Geneva, Switzerland	0.93-10	2087	2.00-180	(Caillet *et al.*, 2001)
[a]N. Greece	[c]< 1- > 10	458-1164	0.09-124	(Ioannidou & Papastefanou, 2006)
Chilton, England	0.30-2.41	431	[d]8.16-80	(Mitchell, 2009)
Aberporth, Wales	3.00-0.18	1086	[d]21-223	(Mitchell, 2009)
Windermere, England	1.23-3.55	3912	nv	(Short et al., 2007)
[a]SE Australia	0.02-5.90	1030	0.03-108	(Wallbrink & Murray, 1994)

Table 1.1: ^{7}Be rainwater activity concentrations and deposition flux at global sites
[a] Values derived from event samples
[b] Values for Galveston Station
[c] Approximate values obtained from graphical representation
[d] Values of monthly deposition

1.3.2.2. ^{7}Be distribution in the soil column

Following deposition, the shallow depth profiles displayed by ^{7}Be in a range of soil types is well established with distributions generally extending to around 20 mm with activity decreasing exponentially from the surface (Blake et al., 2009; Blake *et al.*, 1999; Schuller et al., 2006; Schuller et al., 2010; Wallbrink & Murray, 1994). This is in contrast to longer-lived FRNs such as ^{137}Cs ($t_{1/2}$ = 30.2 years) and ^{210}Pb ($t_{1/2}$ = 22.3 years) which display deeper profiles owing to the effects of diffusion and bioturbation through time. Distribution of these FRNs can extend to depths of around 160 mm in undisturbed soils and can be

uniformly distributed to depths of approximately 300 mm where cultivation has occurred (He & Walling, 1997).

Characterising the depth distribution across a field location is vital for accurate determination of soil redistribution using current modelling approaches (Walling et al., 1999; Walling et al., 2009) (section 1.3.2.3). These approaches rely upon an exponential decrease in activity with depth and have to assume that the shape of the profile, as characterised, is uniform across a given location. However, slight deviations from the exponential decrease in ^{7}Be depth distribution have been reported for some soils owing to changes in textural characteristics. Wallbrink and Murray (1996) showed a uniform distribution in the upper 4 mm of eucalypt soil which was attributed to coarse grain size encouraging high infiltration and, therefore, less contact/adsorption time. Below this depth, an exponential decrease in activity was displayed. Shallow depth profiles (< 5 mm) were found in bare alluvial soils owing to surface crusting and smaller grain size reducing infiltration capacity. Depth distribution in grass covered plots displayed spatial variability with the extent of distributions ranging from 5-20 mm. Greater depths were attributed to preferential transport through root channels. It was suggested that a clay rich (30-40 %) soil layer at depths of 15-20 mm reduced infiltration and, thus, penetration of ^{7}Be at this depth. Owing to the importance of characterising ^{7}Be depth distributions for erosion estimates, spatial variability owing to textural characteristics should be considered during field investigations.

In the same study, Wallbrink and Murray found ^{7}Be to be negligible in surface soils of a eucalypt forest with the majority of fallout remaining within the litter layer. The hydrophobicity of the acidic eucalypt leaf litter encouraged water retention and evaporation leading to higher ^{7}Be activity and this is supported by

findings from Blake et al. (2009). It is also of interest to note the effect of vegetation upon soil inventories. Wallbrink and Murray found that longer grass appeared to lower soil surface concentrations owing to the nature of raindrop interception. The importance of vegetation type and length should, therefore, be taken into account particularly where uniform plant cover does not exist. Doering et al. (2006) also found ^{7}Be to have a greater association with the vegetation layer than ^{210}Pb and findings from Pourcelot et al. (2003) further support the association with vegetation and litter layers. Bettoli et al. (1995) carried out leaching investigations to determine the extent of ^{7}Be remobilisation from vegetation surfaces. Under simulated natural conditions, around 30 % of intercepted ^{7}Be was released into solution. This is likely to be of importance when establishing a reference baseline at stable sites under vegetation. The extent of uniformity in vegetation cover is likely to contribute spatial variability in ^{7}Be inventories at reference locations (c.f. Owens & Walling, 1996) and should, therefore, be considered in sampling strategies.

Walling et al. (2009) discussed the potential for temporal changes in ^{7}Be depth distributions and effects upon the relaxation mass depth (h_0), that is, the depth at above which 63 % of the ^{7}Be inventory can be found. Walling et al. suggested that h_0 may increase with time over a wet period or season and a linear change could be assumed. The authors do highlight, however, the lack of data regarding temporal change and identify the need for further research to quantify any variation. Schuller et al. (2010) documented temporal variation in h_0 at reference sites in Chile and an example is given in Figure 1.3. Quantifying temporal change in h_0 is of importance for application of ^{7}Be as a soil erosion tracer over extended timescales (section 1.3.2.3.).
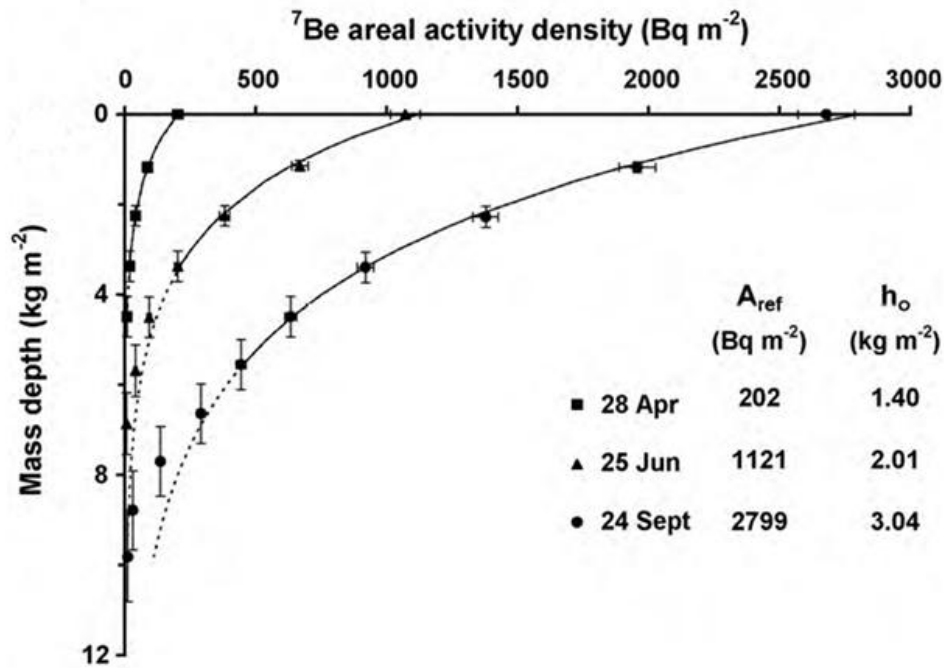
Figure 1.3: Temporal change in ^{7}Be depth distribution over a 5 month period at a reference location (harvested forest area) in southern Chile. Reprinted from Soil and Tillage Research, 110/1, Schuller et al., Use of beryllium-7 to study the effectiveness of woody trash barriers in reducing sediment delivery to streams after forest clearcutting, 143-153., Copyright (2010) with permission from Elsevier.

1.3.2.3. Quantifying hill slope soil redistribution using ^{7}Be

Documenting soil redistribution using ^{7}Be can be categorised in terms of use at the event-scale and use over extended timescales of a few months or wet seasons. Blake et al. (1999) demonstrated the potential use of ^{7}Be to investigate short-term soil movements associated with a period of intense rainfall at a cultivated site in east Devon, UK. The short half-life of ^{7}Be provides a distinct advantage over longer lived radionuclides by enabling change associated with rainfall events or land use to be assessed. Aside from meeting the assumptions listed in section 1.3.1, an important consideration here is that the pre-event inventory at the eroding site under investigation is uniform. In the Blake et al. study this requirement was satisfied owing to i) the soil inventory being reset by ploughing prior to the commencement of the study and ii) the occurrence of low magnitude, low intensity rainfall prior to the erosive event

causing no significant soil redistribution whilst allowing the ^{7}Be soil inventory to be established. A reference baseline inventory was estimated from neighbouring stable locations, against which, slope inventories could be compared. A profile distribution model, which considers the ^{7}Be depth distribution in the soil (h_0, determined from stable in-field sites), was used to convert changes in inventory with respect to the reference baseline, to quantitative rates of erosion. Results returned a sediment delivery ratio (net/gross erosion) of 0.8 indicating high levels of soil export from the site as a consequence of the intense rainfall event and compacted soil conditions. Characterisation of medium-term (~ 45 years) estimates of soil redistribution using ^{137}Cs at the same site (Walling *et al.*, 1999) revealed long-term rates which were ~ 5 times lower than those associated with the intense event detailed by Blake et al. The authors concluded that this identified the extreme nature of the single event and highlighted the benefits of combined use of FRNs.

Sepulveda et al. (2008) used combined ^{7}Be, ^{137}Cs measurements to determine the effects of stubble burning upon soil redistribution at a site in southern Chile. Estimates using ^{7}Be, again, apparently identified the effects of an extreme event upon soil erosion in comparison to long-term estimates derived using ^{137}Cs. The combination of an extreme event and land use change meant it was difficult to isolate the effects of burning although data did suggest that long-term erosion rates under the no till with burning system would be lower than under conventional tillage. Blake et al. (2009) also used ^{7}Be in conjunction with ^{137}Cs and ^{210}Pb to determine post wildfire sediment budgets at hill slope sites in southeast Australia. Results highlighted the potential for deterioration in post fire water quality owing to increased sediment-nutrient loading in channels. Data

identified major sediment source areas and the implications of wildfire for water quality management. Schuller et al. (2006) demonstrated the potential benefit of using [7]Be to document the effects of recent forest clearance upon slope soils in a timber harvesting region of Chile. By using [7]Be, the use of mitigation strategies could be assessed and, in this case, a significant delivery ratio indicated the need for further soil conservation strategies.

Although the use of the [7]Be to document soil redistribution at the event-scale appears to have clear benefits, the method is limited because the given event may not be representative of longer-term patterns in rainfall. This can be seen in the example of Sepulveda et al. (2008) where the study event was an extreme example and it was, therefore, difficult to interpret the effects of management practice.

To overcome this limitation, Walling et al. (2009) developed a method for extending the use of the profile distribution model to periods covering a few months or wet seasons. The basis of the model remains similar to the conventional approach whereby sample point inventories are compared to a reference baseline and the depth distribution of [7]Be is taken into account. The approach differs because it considers changes in the inventory of a given sample point on an event basis throughout the study period by estimating the relative erosivity of an event, additional [7]Be deposition during the event and on-going decay. If these factors are not considered over longer time frames, considerable underestimation in redistribution rates can be expected by failing to account for the effects decay upon estimation of inventory change relative to the reference value. The potential benefit of using this approach was demonstrated by Schuller et al. (2010), whereby the effectiveness of a mitigating strategy during forest management was shown to be markedly

reduced over a longer time period which included a range of rainfall events. Attention could then be focussed upon suitable measures to improve the mitigating methods, which may have been ignored if event-scale data had been used.

Clearly, [7]Be has the potential to be a valuable decision support tool for catchment managers but estimates of soil redistribution using the profile distribution model rely upon establishing a reliable reference baseline and accurately determining the [7]Be depth distribution in the soil. It is also vital that the selective transport of particle size fractions is considered during events given the association of [7]Be to fine soil fractions. Owing to a larger surface reactive area across fine particles, [7]Be (and ^{137}Cs and ^{210}Pb) will preferentially adsorb to fractions < 63 μm (Blake *et al.*, 2009; He & Walling, 1996; Wallbrink & Murray, 1994). Failure to account for preferential adsorption to fine particles can lead to overestimation of soil redistribution. Given the importance of these factors and the likelihood for variability in [7]Be depth distributions and inventories across a field site, suitable validation of model estimates should be undertaken. This is likely to be of particular importance for the extended timescale approach given the need to consider a wider range of variables over a greater period of time. Of the published literature documenting the use of [7]Be as a soil erosion tracer, little attention has been given to validating procedures by comparing model estimates to those derived from alternative methods.

Schuller et al. (2006) attempted to validate redistribution estimates by comparison with values derived from the use of erosion pins. Close agreement was found between estimates made using erosion pins and those derived using [7]Be although the disadvantages surrounding the use of erosion pins should be considered i.e. estimates relate to single points and there are often problems

with installation and disruption. Similarly Walling et al. (2009) compared estimates of redistribution using the extended timescale approach to erosion pin estimates and found disparity of up to an order of magnitude between some sample point estimates, although overall mean erosion values were comparable (0.81 kg m^{-2} and 1.08 kg m^{-2} for model and pin estimates respectively). The authors acknowledged the difficulty of directly comparing pin and model estimates.

Sound validation of the profile distribution model will require comparison of radionuclide estimates of soil loss to the direct capture of soil exported from a site and, currently, there are limited examples of such studies. Liu et al. (2011) found close agreement between estimates of deposition rate and the mass of soil deposited at the exit of a small plot. Shi et al. (2011) provided (to the best of the author's knowledge) the only example of direct validation of event-scale redistribution estimates using the profile distribution model. Estimates of net soil loss from a plot (5 x 20 m) using ^{7}Be were 14 % lower than the known mass of soil captured at the plot exit. To the best of the author's knowledge no such validation data exists for estimates of soil redistribution over an extended time period and clearly more studies are required to address validation concerns over a range of temporal scales and field conditions.

As an alternative to the profile distribution model, Wilson et al. (2003) validated an inventory balance approach which avoids the need for a stable reference location and, to some extent, overcomes the need to consider selective transport of particle size fractions (if eroded sediment is analysed directly). The method was validated at the plot-scale by comparing the mass of soil flux from the plot to erosion estimates, with results showing very close agreement (0.058 g cm^{-2} and 0.059 g cm^{-2} for estimated and captured mass respectively).

However, given the need for repeat sampling at the eroding site, the increased labour required and high disturbance to the site are major disadvantages of the approach and it is unlikely, therefore, that this technique will be widely employed to assess hill slope soil redistribution.

1.3.2.4. The use of ^{7}Be as a tracer at the catchment-scale

With regard to sediment tracing beyond the slope boundary, to date, ^{7}Be has been applied to assess i) sources of channel sediment, ii) sediment transport distance and residence time and iii) deposition rates.

i. ^{7}Be fingerprinting as an indicator of sediment source

Aside from providing quantitative estimates of soil redistribution, the contrasting depth distributions and, therefore, signatures of ^{7}Be, $^{210}Pb_{ex}$ and ^{137}Cs in parent soils can be used to determine the source and pathways of mobilised sediment. An early study by Burch et al. (1988) demonstrated the use ^{7}Be and ^{137}Cs signatures to identify sediment from surface and gully sources. Wallbrink and Murray (1993) used ^{7}Be, $^{210}Pb_{ex}$ and ^{137}Cs signatures to assess the contributions of sheet, rill and gully erosion to entrained sediment during rainfall simulation experiments on hill slope plots. High concentrations of all radionuclides were found in the early stages of simulation on a uniform plot indicating the predominance of surface material and, thus, sheet erosion. With continued rainfall the activity of ^{7}Be and $^{210}Pb_{ex}$ decreased while ^{137}Cs activity remained uniform indicating rill sources. Gully sediment was found to be deficient in all radionuclides. The research of Wallbrink and Murray has been further developed by Yang et al. (2006) and Liu et al. (2011) , where plot-scale

simulation was carried out to enable the formation and relative contribution from rills to be quantified at fine temporal scales.

Within channels, this fingerprinting technique has been used to identify contributions to suspended sediment loads providing valuable data with regard to major sediment sources, thus, assisting with management planning (Blake *et al.*, 2002; Evrard et al., 2011; Whiting et al., 2005).

ii. *The use of ^{7}Be to estimate sediment transport distance and residence time*

Bonniwell et al. (1999) suggested that estimates of transport distance could be determined by considering an exponential decrease in the ^{7}Be activity of source material with distance downstream and comparing activity in suspended sediment at a given point to that of the source material decay curve. This approach was used by Matisoff et al. (2002) and Whiting et al. (2005), with the former study demonstrating rapid transfer of material to the catchment outlet during a storm event. Matisoff et al. suggested, therefore, that the system would be likely to show an active response to mitigating strategies aimed at reducing yield.

Matisoff et al. (2005) and Salant et al. (2007) used a ^{7}Be/^{210}Pb$_{ex}$ ratio to determine the age of suspended sediment in channel samples. A reduction in the ratio can provide an indication of increased sediment age since ^{7}Be will decay at a much greater rate than ^{210}Pb$_{ex}$. However, the ratio can also decrease by the introduction of material with low or negligible ^{7}Be signature, thus, diluting the activity concentration in bulk suspended sediment samples. The sources of this low activity sediment could reflect i) recently eroded material with low signature i.e. from channel banks or material from below the ^{7}Be depth distribution, ii) recently mobilised channel bed sediment which has been stored

for a time sufficient for decay of original surface activities (i.e.> 3 half-lives) or iii) remobilisation of channel sediment of which the original source had low activity concentration. The authors recognised that it was not possible to distinguish between these scenarios with the method applied.

More recently, Saari et al. (2010) extended the use of the ^{7}Be/^{210}Pb$_{ex}$ ratio approach to a saline environment to determine tidal and seasonal influences upon particle-contaminant dynamics in the Gironde estuary, France. Evrard et al. (2010) combined the approaches of Matisoff et al. (2005) with modelling methods developed by Dominik et al. (1987) and Le Cloarec et al. (2007) to determine residence times and suspended sediment age in three sub-catchments in central Mexico. Data provided important decision support for management planning.

iii. *The use of ^{7}Be to estimate rates of deposition*

Blake et al. (2002) used ^{7}Be inventories to determine rates of overbank sedimentation at a site on the River Culm in Devon. By comparing floodplain inventories to a nearby reference site, inventory excess was attributed to overbank events. By considering the ^{7}Be activity of suspended sediment and accounting for particle size composition of deposited material, a mean event deposition rate of 0.24 g cm^{-2} was estimated. The authors emphasised that these low rates of deposition could not be accurately determined using conventional methods. The same approach has also been applied to document sedimentation rates in a tidal marsh (Neubauer et al., 2002). Here, estimates of deposition using ^{7}Be were compared to sediment mass captured on tiles and data showed similar magnitudes of deposition for some sites (e.g. 62-140 g m^{-2} d^{-1} and 128-139 g m^{-2} d^{-1} for tiles and ^{7}Be respectively). The authors highlighted

the difficulty of characterising the suspended sediment ^{7}Be activity in a tidal environment given the large range in activity displayed between tidal cycles; consequently a median value derived from literature was applied. The influence of dissolved ^{7}Be concentrations upon estimations also needed to be considered given that the area was submerged for ~ 12 hours each day. This was accounted for by applying a fallout value to calculations (thus, representing a maximum value of dissolved input) and, therefore, conservative estimates of deposition were provided.

1.4. The adsorption behaviour of FRNs

The studies outlined above demonstrate the broad application of ^{7}Be as a tracer to date. The reliable application of these methods at the catchment-scale requires confidence in the assumption of rapid and irreversible adsorption to soil particles upon fallout. Given that it is likely that environmental parameters will vary throughout the catchment, confidence in this assumption must be demonstrated through suitable study of geochemical behaviour in a range of conditions. Currently, knowledge with regard to the geochemical behaviour of ^{7}Be is lacking. As the most extensively used FRN tracer, confidence in the irreversible adsorption behaviour of ^{137}Cs has been based on early studies documenting its residual adsorption in the mineral matrix of soils. However, recent concerns over the reliability of this assumption have been raised by Parsons and Foster (2011) where numerous studies are documented which suggest the potential for ^{137}Cs mobility in some environments.

As the cornerstone of FRN tracer approaches, attention will be given to the geochemical behaviour of ^{137}Cs here. Although ^{137}Cs behaviour may not be

directly comparable to that of ^{7}Be, the literature underpins the assumptions associated with FRN tracing and provides a platform from which to base further ^{7}Be investigations.

1.4.1. The adsorption behaviour of ^{137}Cs

Early studies carried out by Rogowski and Tamura (1965) documented the adsorption behaviour of ^{137}Cs by demonstrating a linear relationship between soil loss and ^{137}Cs loss from erosion plots. Shortly after fallout, a large proportion (90 %) of ^{137}Cs was found to be held in the upper 20 mm of the soil surface (similar to ^{7}Be). Schultz et al. (1960) investigated ^{137}Cs fixation in five Californian soils and it was suggested that ^{137}Cs becomes incorporated into the crystal structure of clay minerals and cannot be readily displaced by cations including H^+, Na^+ and Ca^{2+}. Thus, these early findings are often cited in support of the assumption for irreversible adsorption. Squire and Middleton (1966) also found that a large proportion of ^{137}Cs entering soils remained in the upper surface layer although differences in ^{137}Cs mobility were found between soil types. The highest rate of adsorption was found in those soils which were low in K^+. Where a high exchangeable K^+ concentration existed, adsorption was reduced and, thus, depth penetration increased. However, contrary to this, Schultz (1960) and Tamura and Jacobs (1960) identified increased sorption of Cs to some clay minerals with the addition of K^+ owing to a favourable change in lattice structure. Both of the afore mentioned studies identify the importance of clay minerals other than kaolinite (namely illite) in the fixation of Cs, a notion supported by Komarneni (1978).

Evidence suggests, therefore, that the mobility of ^{137}Cs can be affected by changes in soil composition. Further to this, Livens and Rimmer (1988) provided

an overview of the physicochemical factors which are likely to influence the mobility of radionuclides in soil. The authors highlighted the role of organic ligands which may inhibit the adsorption of radionuclides owing to complexation. A decrease in pH may also reduce adsorption by lowering the cation exchange capacity at pH dependant exchange sites. Livens and Loveland (1988) reviewed research regarding ^{137}Cs mobility and produced a soil classification based on the immobilisation capacity of soils in northwest England. Properties of soils with a low classification (i.e. high mobility) included presence of vermiculite, montmorillonite and kaolin minerals, high sesquioxide content, organic soils (peat), high ammonium ion (NH_4^+) concentration (resulting from addition of fertilisers or from decomposition in organic-rich soils) and deficiency in free potassium.

Rigol et al. (1998) isolated humic and humic-mineral fractions in a range of soils to determine the role of organic and mineral phases in radiocaesium partitioning. A decrease in the partitioning coefficient (K_d) with the addition of NH_4^+ was identified where adsorption was associated with frayed edge sites in illite owing to competition for binding sites. Desorption experiments showed that low levels of extraction occurred from humic-mineral (illite) samples and high levels where illite was absent, thus, demonstrating the importance of illite for adsorption. This was reflected in high K_d values in the presence of illite. It is of interest to note that K_d values also increased when organic acids were removed implying that these can inhibit adsorption to mineral sites.

Rigol et al. noted the possible temporal influence upon adsorption processes with greater levels of fixation occurring with increased time where binding was associated with clay minerals; this is supported by Rigol et al. (1999) and Chiu et al. (2008). There is likely to be no increase in fixation with time where Cs is

associated with regular binding sites (organic acids) and the radionuclide will, therefore, remain in the exchangeable form. Gil-Garcia et al. (2008) investigated ^{137}Cs adsorption-desorption patterns in a range of Spanish soils. A ratio of K_d to extraction yield was used to indicate the potential for radionuclide mobility with a higher ratio indicating lower mobility. The ratio was found to be influenced by soil solution composition with high cationic concentration in solution reducing the ratio owing to increased competition for exchange sites. This is perhaps reflected in the findings of Foster et al. (2006) where it was suggested that ^{137}Cs mobility in a coastal lake sediment had been influenced by periodic increases in salinity.

1.4.2. The adsorption behaviour of ^{7}Be

The tracer requirement of rapid adsorption upon fallout has largely been assumed from the shallow ^{7}Be depth distributions displayed in a range of soil types (e.g.Wallbrink & Murray, 1996) and high partition coefficients (K_d) in freshwaters (e.g.Hawley et al., 1986). Laboratory batch experiments carried out by You et al. (1989) confirmed the rapid adsorption of ^{7}Be to a range of sediments although similar knowledge with regard to representative agricultural soils remains limited. The effects of reduced infiltration capacity upon the adsorption of ^{7}Be should also be considered following the findings of Dalgleish and Foster (1996). Here, the authors demonstrated the transport of ^{137}Cs in the dissolved phase in overland flow and the subsequent scavenging of the radionuclide by entrained particles, thus, highlighting potential to affect redistribution estimates. The same process was suggested by Wallbrink and Murray (1996) for the loss of up to 50 % of ^{7}Be fallout input from small plots.

Upon fallout, the affinity of ^{7}Be for fine sediment fractions has been demonstrated (Blake *et al.*, 2009; Wallbrink & Murray, 1996) which is consistent with the behaviour of ^{210}Pb$_{ex}$ and ^{137}Cs (He & Walling, 1996). However, limited knowledge exists with regard to ^{7}Be geochemical partitioning behaviour in soil particles. Sequential extraction methods can provide an efficient means of assessing the association of ^{7}Be to geochemical soil fractions, knowledge of which can then be used to determine the potential for mobility under varying environmental conditions (Bacon & Davidson, 2008). Bai et al. (1997) investigated ^{7}Be and ^{137}Cs partitioning in brunisolic and yellow soils using sequential extractions to identify association with soluble and exchangeable, carbonate, organic and Fe-Mn and residual fractions. A large percentage of ^{7}Be was bound to organic and Fe-Mn oxyhydroxide fractions and < 1 % was soluble and exchangeable. This suggested that ^{7}Be mobility was likely to be influenced by changes in redox conditions and solution pH. Given the desire for broader application of ^{7}Be as a tracer at the catchment-scale (Mabit *et al.*, 2008a) (section 1.3.2.4.), further studies are required to assess partitioning in a wide range of soils to determine the potential for mobility in catchment environments.

A number of publications relate to ^{7}Be activity in riverine and estuarine environments. Hawley et al. (1986) studied partitioning in freshwater lakes and demonstrated that ^{7}Be is largely associated with the solid phase at high sediment concentrations (> 100 mgL^{-1}) although an inverse relationship between K_d and suspended particulate matter (SPM) existed under typical environmental SPM conditions (< 30 mgL^{-1}) . The findings did, however, report a large variation in K_d in freshwater and suggested that other factors may influence partitioning, factors which, at the time were unidentified. No correlation was found to exist between ^{7}Be activity and Inorganic Carbon (IC), Particulate

Organic Carbon (POC) or water temperature. Baskaran et al. (1997) studied ^{7}Be partitioning in an estuary and found that suspended particle concentration had no influence upon K_d. Contrary to Hawley et al. (1986), a positive correlation between POC and K_d did exist. Partitioning coefficient values in the Baskaran et al. study were generally low and it was suggested that complexation with Dissolved Organic Carbon (DOC) may have contributed to greater concentrations of ^{7}Be in the dissolved phase in this environment.

Dibb and Rice (1989) carried out sorption experiments to investigate the effects of salinity upon stable Be (^{9}Be) adsorption. Sorption was found to increase with increasing salinity, perhaps owing to changes in pH, although the exact mechanisms were not fully identified. The results from these experiments did not translate to field observations of ^{7}Be behaviour. However, field data did identify an interesting trend of increasing sorption along a transect of decreasing suspended sediment and an increase in pH was suggested as a possible influence upon K_d here. This is contrary to the findings of You et al. (1989) where ^{7}Be adsorption rates were reduced in seawater solution and similarly Huang et al. (2011) showed decreasing K_d with increasing salinity. Casey et al. (1986) showed further contrast with no significant change in K_d between salt marsh sediment and pore water of varying salinity. Olsen et al. (1986) found no correlation between suspended particulate ^{7}Be concentration and salinity, particle concentration or particle composition, but, stressed the importance of the amount of time particles remain in suspension and, thus, time available for scavenging. Fe particulate concentrations were found to correlate with K_d suggesting the importance of coprecipitation upon ^{7}Be removal from the aqueous phase. Jweda et al. (2008) also found no correlation between particulate ^{7}Be activity and SPM although a negative correlation between K_d and

SPM was found to exist. Jweda et al. suggested that a Particle Concentration Effect (PCE), involving complexation with colloids, plays a major role in radionuclide partitioning in freshwater; these colloidal fractions would be included in dissolved phase values, thus, reducing K_d. Like Olsen et al. (1986), Jweda et al. also referred to the potential for SPM to scavenge ^{7}Be in the water column.

The lack of consistency between some of the findings in the above studies suggests a complex pattern of ^{7}Be interaction with water and sediment in the natural environment. Many of the studies outlined above focus upon adsorption of ^{7}Be in freshwater and estuarine environments. However, from a tracer perspective it can be argued that greater attention needs to be placed upon the potential for mobility (desorption) in these environments while focussing attention upon K_d at the sediment source (i.e. cultivated slopes). Greater attention to the geochemical behaviour of ^{7}Be is required to firmly underpin its use as a tracer at the catchment-scale (Mabit *et al.*, 2008a).

1.5. Gaps in research knowledge

Current knowledge gaps relating to the use of ^{7}Be as a tracer are largely related to the need to validate assumptions that underpin its use at event and longer-term scales and to quantify associated uncertainties. To the best of the author's knowledge the following areas require attention:

1.5.1. ^{7}Be fallout dynamics

Knowledge of fallout temporal variability is required to assess the reliability of applying a constant value of ^{7}Be activity in rainfall when using the profile distribution soil erosion model for extended timescales. The extent of spatial and temporal variability should be compared between and within regions and, currently, very few data sets are published for southern UK. Further questions relate to the assumption of uniform spatial fallout at the field-scale.

1.5.2. ^{7}Be adsorption upon fallout

Rapid adsorption upon fallout is generally assumed from shallow depth profiles and K_d values from freshwater environments. Data are, however, required which demonstrate the rate of adsorption of Be from solution to agricultural soils to support the fundamental principle of adsorption upon contact with particles. In addition to this, the effect of overland flow upon the translocation of event inventory and subsequent influence upon redistribution estimates requires attention.

1.5.3. ^{7}Be depth distributions in soil

Research should be carried out to determine the key controls upon ^{7}Be depth distributions (h_0) and the extent of spatial variability under common field conditions. Studies are required to quantify variability in a range of cultivated soil types to inform sampling strategies. Knowledge regarding temporal change in h_0 is also required. This knowledge is vital for reliable application of the profile distribution model at the event-scale and over extended time periods.

1.5.4. ^{7}Be geochemical behaviour

Data to evaluate the potential for ^{7}Be mobility under changing environmental conditions are required to underpin the assumption of irreversible adsorption. This is essential to provide confidence in its use as a tracer at the catchment-scale. Currently, no published literature considers the geochemical partitioning of ^{7}Be in agricultural soils and the implications of adsorption behaviour upon tracer estimates.

1.5.5. Validation of the profile distribution soil erosion model

Limited data exists with regard to validating the profile distribution model at the event-scale. No published data attempts to validate the profile distribution approach applied to extended timescales by comparing erosion estimates to a known mass of exported soil. Sensitivity analysis should be undertaken to quantify potential uncertainty associated with controlling factors e.g. h_0, particle size association and fallout input.

1.6. Research aims and thesis overview

1.6.1. Aims and objectives

This thesis aims to explore key assumptions surrounding the application of ^{7}Be as a tracer by addressing current knowledge gaps using a series of research packages. Each research package has a separate aim and set of objectives which are shown below.

Research package 1: *Spatial and temporal variability of ^{7}Be fallout*

Aim: To quantify spatial and temporal variability of ^{7}Be fallout to address i) the current lack of data relating to fallout in southern UK and ii) spatial and temporal variability in fallout dynamics in the context of estimating fallout input for extended timescale erosion studies.

Objective 1: Quantify ^{7}Be activity in regular rainfall samples to provide a monthly fallout record for Plymouth, southwest UK.

Objective 2: Compare Plymouth data to those of wider southern UK sites for the same sample period.

Research package 2: *The adsorption behaviour of ^{7}Be in agricultural soils*

Aim: To investigate the adsorption behaviour of ^{7}Be in representative agricultural soils to address questions regarding the rate and irreversibility of adsorption upon fallout.

Objective 3: Develop a laboratory-based method to improve gamma counting statistics associated with low activity sequential extractions.

Objective 4: Undertake batch experiments to determine the rate of adsorption of Be to soil particles.

Objective 5: Characterise the depth distribution of ^{7}Be in soils exposed to natural fallout under semi-controlled conditions.

Objective 6: Undertake batch experiments to assess ^{7}Be stability in artificial rainwater solutions

Objective 7: Quantify the geochemical association of ^{7}Be in agricultural soils using sequential extractions to determine potential for mobility.

Objective 8: Assess the effect of residence time upon ^{7}Be geochemical association.

Research package 3: *Validation of erosion model estimates*

Aim: To validate estimates of erosion using the profile distribution model at the event-scale and over an extended period of time.

Objective 9: Establish key model components at field locations (^{7}Be reference baselines, depth distributions and particle size enrichment).

Objective 10: Plot-scale rainfall simulation to compare model estimates of event-scale erosion to a mass of exported soil.

Objective 11: Comparison of model estimates of soil erosion over an autumn-winter period at the field-scale to a mass of exported soil.

Objective 12: Undertake sensitivity analysis to evaluate potential uncertainties relating to key model components.

1.6.2. Thesis overview and structure

A simplified diagram of the thesis structure is shown in Figure 1.4. Chapter 2 directly addresses research package 1 by fulfilling the first two objectives. This chapter focuses upon temporal and spatial variability of ^{7}Be activity in rainfall and ^{7}Be deposition with discussion of potential controls. This chapter is cross referenced to chapter 5 owing to the importance of establishing ^{7}Be inventory flux when using the extended timescale approach for estimating soil redistribution.

Chapters 3 and 4 address research package 2 by achieving objectives 3-8. Chapter 3 focuses explicitly upon objective 3 and, thus, provides a detailed report of the method development associated with improving the counting statistics when analysing low levels of ^{7}Be activity using gamma spectrometry. This is a necessary precursor to maximise data quality associated with objective 7. Chapter 4 provides a discussion of objectives 4-8 and is focused upon the major assumption of rapid and irreversible tracer adsorption upon fallout. Each objective is explored in turn with discussion surrounding the implications of the findings for ^{7}Be use as a tracer at the field and catchment-scale.

Chapter 5 directly addresses research package 3 and objectives 9-12. Estimates of soil redistribution using the profile distribution model are compared to a known mass of exported soil and discrepancies between the known and estimated values are discussed with reference to the findings of the previous chapters and wider literature. Practical considerations are highlighted and recommendations for improving model estimates are put forward.

The final synthesis chapter (6) provides a concise summary of the key findings of the previous chapters and lists recommendations for further research based upon the conclusions. Also listed are the areas of research which were beyond the scope of this study but remain of importance for underpinning the use of ^{7}Be as a tracer.
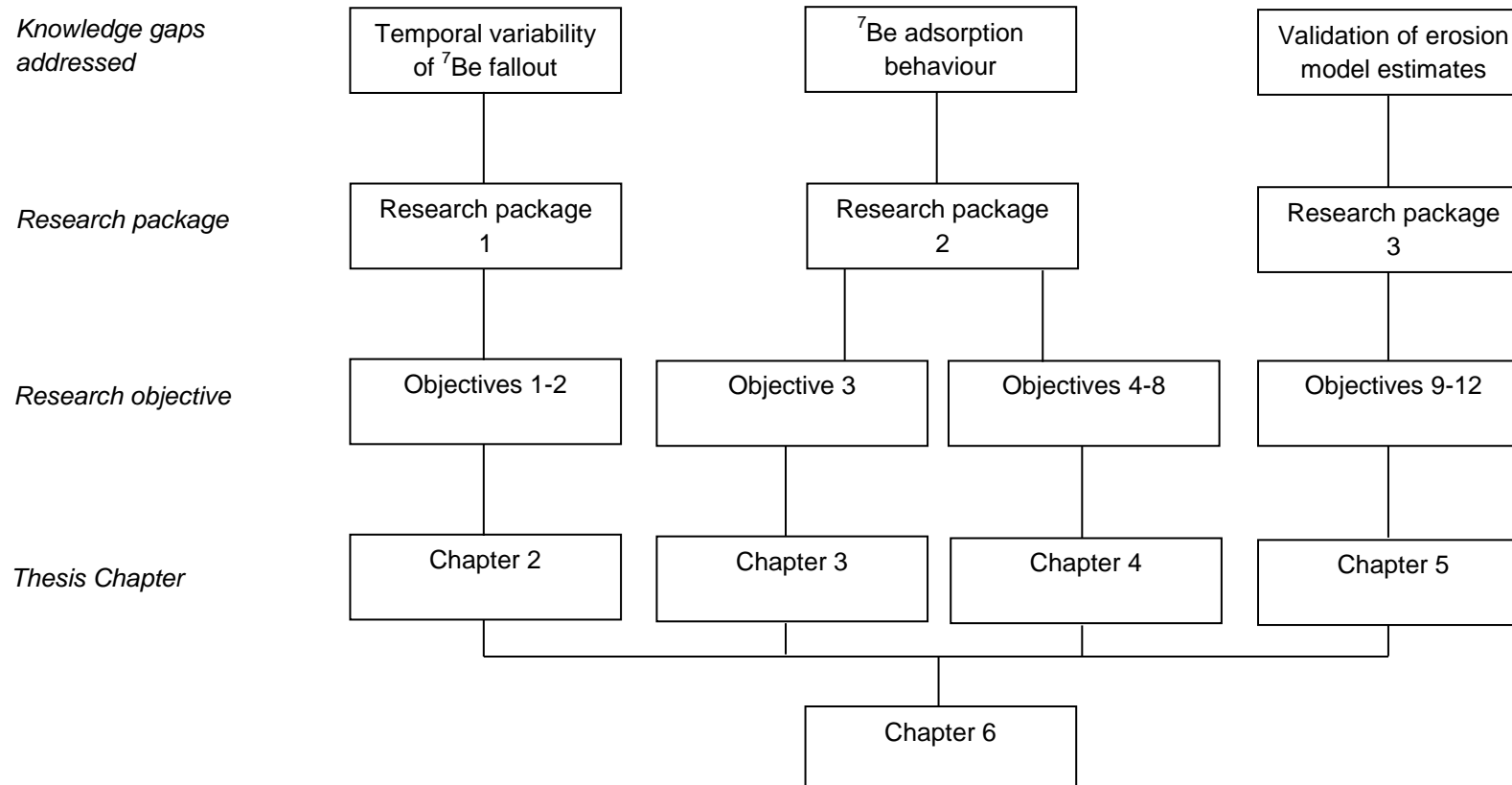
Figure 1.4: Simplified overview of the thesis structure

Chapter 2. Spatial and temporal variability of ^{7}Be fallout in southern UK

2.1. Introduction

^{7}Be ($t_{1/2}$ 53.3 days) is a cosmogenic radionuclide produced in the upper atmosphere by cosmic ray spallation of nitrogen and oxygen. Rates of production are dependent upon cosmic ray activity and, therefore, higher rates of production occur at the magnetic poles owing to cosmic ray deflection towards polar regions (Feely et al., 1989). Production is also affected by sunspot cycles with ^{7}Be concentrations in surface air demonstrating a negative correlation with sunspot number (Ioannidou et al., 2005). ^{7}Be production is largely confined to the stratosphere and to a lesser extent, the upper troposphere.

Following production, ^{7}Be associates with aerosols and the long residence time of aerosols in the stratosphere (~ 1 year half-residence time) is assumed to create a concentration equilibrium with production offset by decay. Shorter residence times in the troposphere (~ 3 weeks) lead to a strong ^{7}Be concentration gradient between the troposphere and stratosphere (Doering & Akber, 2008b). This concentration gradient influences seasonal variation in ^{7}Be concentrations in surface air, with higher concentrations occurring in warmer months owing to convective circulation within the troposphere. This process drives the downward transport of ^{7}Be-enriched air from the upper troposphere, where production rates are higher than surface air and where further enrichment can occur through mixing with stratospheric air during folding of the tropopause (Doering & Akber, 2008b; Feely *et al.*, 1989; Ioannidou *et al.*, 2005). Because ^{7}Be-bearing aerosols are readily scavenged by precipitation (Ioannidou & Papastefanou, 2006), seasonal patterns in rainfall can also

influence surface air concentrations by removing available [7]Be (washout) (Doering & Akber, 2008b; Feely *et al.*, 1989).

Wet deposition is the dominant pathway of [7]Be flux to the Earth's surface with dry deposition accounting for < 10 % (Ioannidou & Papastefanou, 2006; Wallbrink & Murray, 1994). [7]Be deposition (Bq m^{-2}) is, therefore, well correlated with rainfall (mm) (Ayub *et al.*, 2009; Caillet *et al.*, 2001; Doering & Akber, 2008a; Gonzalez-Gomez *et al.*, 2006; Ioannidou & Papastefanou, 2006; Othman et al., 1998; Wallbrink & Murray, 1994) although some variation in depositional flux can be attributed to changes in [7]Be activity in rainwater (Bq L^{-1}) influenced by atmospheric processes such as washout and circulation of enriched air (Baskaran, 1995; Caillet *et al.*, 2001; Gonzalez-Gomez *et al.*, 2006). There is also some evidence to suggest that [7]Be activity can be influenced by rainfall intensity (Ioannidou & Papastefanou, 2006).

The availability of [7]Be in surface air and its subsequent fallout is, thus, influenced by a complex combination of factors which are likely to contribute to spatial and temporal variability in deposition. Knowledge of [7]Be fallout behaviour has been required to document delivery mechanisms, temporal variability within events and spatial variability to underpin its use as an event-scale sediment tracer. More recently, the application of [7]Be as a tracer over extended timescales (wet seasons) (Schuller et al., 2010; Walling et al., 2009) highlights the need for knowledge of fallout variability on a monthly basis. The approach for using [7]Be as a tracer over an extended time period requires a value of [7]Be activity in rainwater (Bq L^{-1}) to enable accurate determination of daily inventory flux (Bq m^{-2}) at the study site. It is assumed that an average rainfall activity value, estimated from soil reference cores, can be applied to the whole study period.

In the UK, data regarding the temporal variability of [7]Be fallout are lacking and to the best of the author's knowledge, no published data exist for southwest England. Data are required to provide a useful baseline against which estimations of fallout activity and deposition can be compared.

This research aimed to quantify spatial and temporal variability of [7]Be fallout in southern UK. To achieve this, rainfall samples were taken at regular intervals, providing a monthly fallout record for Plymouth over a two year period. Primary data were obtained for two other UK sites (Mitchell, 2009) for comparison and potential controls upon spatial and temporal variability are discussed. In addition, fallout data were combined with a high resolution rainfall record to determine temporal variability and controls upon deposition. Data are discussed in the context of estimating deposition when applying [7]Be as a tracer over extended timescales.

2.2. Methodology

Rainfall samples were collected from a flat roof area located ~ 50 m a.m.s.l (~ 15 m above ground level) on the Plymouth University campus (50° 22' 55" N, 04° 08' 34" W). A meteorological station with a tipping-bucket rain gauge (0.2 mm resolution and 10 minute logging intervals) was located adjacent to the sample site. Total (wet and dry) fallout was sampled in two plastic containers (3 L) using 0.05 m^2 area funnels. Prior to deployment, 10 mL HCl (2.5 M) was added to each bottle to prevent adsorption of [7]Be to vessel walls during the sample period. Bottles were exposed for periods of between 3 and 35 days depending upon the frequency and magnitude of rainfall. The majority of samples consisted of fallout from a number of events across the sample period and are,

therefore, referred to as integrated samples. At the point of sampling funnels were rinsed with a known volume of HCl (3 %) and the bottles replaced with acid-cleaned bottles (3 % HCl, 48 hours minimum).

Each sample was pH checked to ensure < 2 and then filtered to remove any coarse debris (Whatman grade number 41 filter papers). [7]Be was then preconcentrated from solution by coprecipitation with MnO_2 following the method of Short et al. (2007). 1 mL of 0.2 M $KMnO_4$ was added per litre of rainwater sample and the pH adjusted to 8-10 using concentrated NH_4OH. Once at the desired pH, 1 mL of 0.3 M $MnCl_2$ was added to the sample whilst stirring. MnO_2 precipitate was then allowed to settle for 24 hours prior to removal by vacuum filtration using 0.45 µm cellulose nitrate filter paper. Filter paper was then air dried, fixed with cellophane and sealed in a 50 mm Petri dish prior to analysis by gamma spectrometry. For each rainwater sample, duplicate 1 L subsamples were treated and the precipitate combined for filtration. Where rainfall samples were low volume, a single 1 L sample was treated. These samples were typically 50 % of the total volume and, therefore, provided a representative sub-sample.

Reproducibility was tested by analysing subsamples separately and Relative Standard Deviation (RSD) was found to be 10 % between duplicates. [7]Be recovery from solution using the coprecipitation method was tested by reprecipitating the filtrate from 3 samples. In each case the [7]Be activity in the filtrate was below Minimum Detectable Activity (MDA). MDA values for these samples were < 10 % of the total activity, suggesting that [7]Be recovery was > 90 %, in agreement with Short et al. (2007). A total of 30 integrated rainwater samples were collected and analysed over a 25 month period from February 2009 to March 2011.

All [7]Be analyses were carried out using high purity germanium (HPGe) Gamma Spectrometry (GEM-FX8530-S Planar, Ortec, UK) in the Plymouth University Consolidated Radioisotope Facility (CORiF) (which operates within ISO 9001:2008 certification). Sample calibration was carried out using a standard of the same geometry as the extract samples. Standards were prepared using QCY58b mixed standard solution (GE Healthcare Life Sciences, Amersham, UK) as a thin-source filter paper (0.45 μm cellulose nitrate). Energy emission of [7]Be (477.6 keV) was interpolated between emission values of [137]Cs (661.7 keV) and [113]Sn (391.7 keV). All sample counts were corrected for background emission and geometry efficiency using Gammavision-32 software. All values were reported as activity (Bq kg^{-1}). Laboratory analytical quality control procedures were carried out in accordance with Wallbrink et al. (2002).

Samples were decay corrected over the sample period by considering the relative proportion of total activity contributed by each event. This proportion of activity was then decay corrected for a given number of days to the date of collection. Decay corrected activities using this approach were in close agreement (within uncertainty (~10 %)) of values obtained by correcting to a mid-point in the sample period following Duenas et al. (2005) and Short et al. (2007). The method employed in this study is advantageous since it considers the time and contribution of each event within the sample period unlike the mid-point correction method.

Sample concentrations were assigned to the month which contributed > 70 % of the rainfall to that sample. Where more than one sample was taken in any particular month, a mean value was reported. [7]Be deposition (or inventory) (Bq m^{-2}) was estimated by multiplying the decay corrected rainfall activity (Bq L^{-1}) for the sample period with daily rainfall (L m^{-2}). A cumulative inventory was

estimated following the method of Doering and Akber (2008a), whereby increases in daily inventory as a result of rainfall were considered in conjunction with on-going decay of inventory already in place. These estimates of cumulative inventory were compared to the inventory of soil samples taken from trays exposed over the same period of time and at the same location as the rainfall sampling (Chapter 4). These samples, therefore, represented an independent check upon the cumulative inventory estimates.

2.3. Results and discussion

2.3.1. Temporal variability of [7]Be activity in rainfall

Monthly [7]Be activity in rainfall is shown in Figure 2.1. The range over the study period was 1.56 (± 0.13) to 2.67 (± 0.20) Bq L^{-1} which agrees with values reported for the north of England (1.23 – 3.55 Bq L^{-1} over a 15 month period) (Short et $al.$, 2007). The mean activity for February to December 2009 was 1.95 (± 0.21) Bq L^{-1} and for January to December 2010, 1.97 (± 0.17) Bq L^{-1}. Anova showed no significant difference in [7]Be activity between months at the 95 % level of confidence ($F_{11, 13} = 1.17$, $p > 0.05$).

Despite the lack of statistical significance, observation reveals a general trend of higher activity during the spring/summer months and lower activity during the autumn/winter periods. This corresponds to wider findings of high [7]Be concentrations in air during spring and summer periods owing to decreased stability of air masses encouraging convective circulation within the troposphere (Daish et $al.,$ 2005; Doering & Akber, 2008a; Doering & Akber, 2008b; Ioannidou et $al.$, 2005). This circulation can transport [7]Be-enriched air from the upper troposphere to surface layers where it is readily scavenged by

precipitation (Ioannidou & Papastefanou, 2006). In contrast, periods of low concentration during cooler months may correspond to higher levels of rainfall exceeding the supply of available [7]Be in surface air. Rainfall frequency and magnitude can affect [7]Be air and fallout concentrations by reducing the proportion of [7]Be available for scavenging (Caillet *et al.*, 2001; Feely *et al.*, 1989). Caillet et al. (2001) highlighted the importance of time between events to enable air concentrations to replenish ('reload' time).
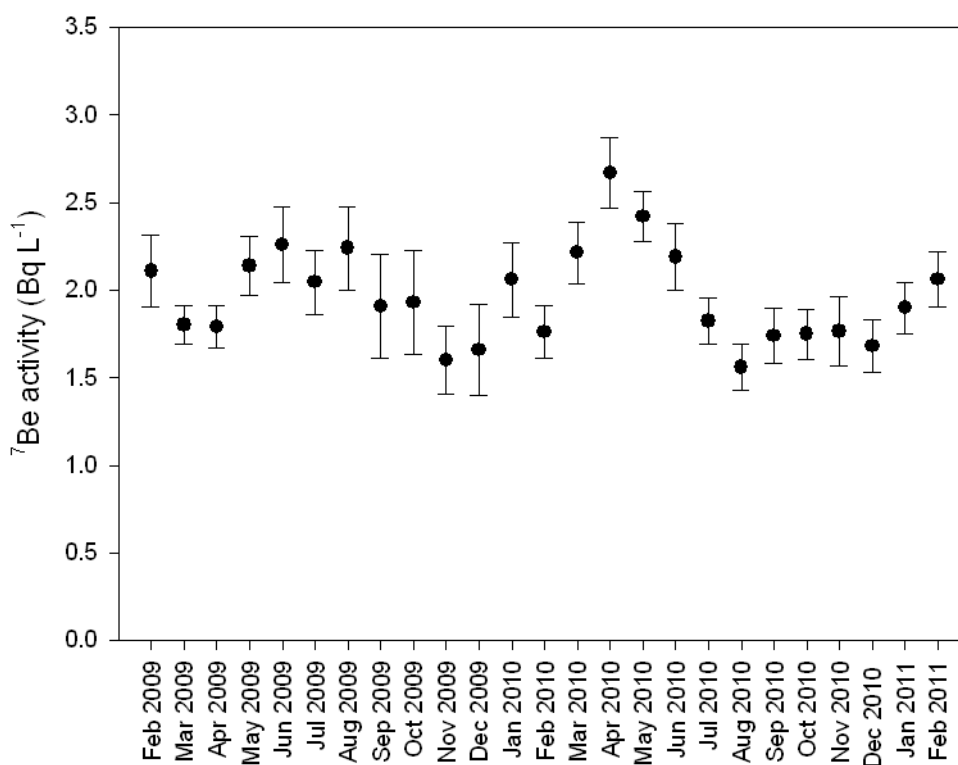
Figure 2.1: Monthly total [7]Be activity in rainfall (Bq L[-1]) in Plymouth, UK. Analytical uncertainties shown as 2σ

The influence of rainfall magnitude upon [7]Be activity is perhaps reflected in the decrease in rainwater activity shown in July, 2009. The highest activities for 2009 were recorded in May, June and August (2.14 ± 0.17, 2.26 ± 0.21 and 2.24 ± 0.24 Bq L[-1] respectively) with July displaying a decrease (2.05 ± 0.19 Bq L[-1]). Rainfall values for the months of May, June and August were 38 mm, 22

mm and 52 mm respectively. July, however, received 144 mm of rainfall and the monthly [7]Be activity value is, therefore, a mean value derived from three samples. Two of these contributing samples displayed activities in agreement to those of May, June and July (2.15 ± 020 and 2.21 ± 0.15 Bq L^{-1}), the third, however, was a reduced value (1.76 ± 0.14 Bq L^{-1}) which may be attributed to the high rainfall (84.8 mm) over this sample period. In particular, 29th July, 2009 received 29.4 mm of rainfall, most of which fell over a 9 hour period with maximum intensities of 9.6 mm hr^{-1}. High magnitude events have been shown to relate to low [7]Be activity in rainfall (Caillet *et al.*, 2001), with an exponential decrease in activity during an event owing to the effect of washout (Ioannidou & Papastefanou, 2006). This low sample value, therefore, reduced the mean monthly [7]Be activity.

Similarly, the highest concentrations for 2010 were recorded from April to June (2.67 ± 0.2 and 2.19 ± 0.19 Bq L^{-1} respectively). Stratosphere to troposphere exchange (STE) can occur during folding of the tropopause and is common at mid-latitudes during spring months (Feely *et al.*, 1989). STE further enriches the upper troposphere and combined with vertical circulation within the troposphere, it is possible that these processes influenced the high [7]Be activities in late spring, early summer 2010. Comparatively low values were recorded for July and August, 2010 (1.83 ± 0.13 and 1.56 ± 0.13 Bq L^{-1}) and, again, this could relate to the high rainfall during these months (87 mm and 98 mm respectively).

Aside from rainfall magnitude and time between events influencing fallout concentrations, rainfall intensity may also affect [7]Be activity in rainfall with low intensity events displaying higher concentration owing to more effective scavenging and increased rates of evaporation associated with small raindrops (large surface area). To determine potential controls upon monthly [7]Be activity,

values were plotted against monthly rainfall (mm) (to represent magnitude), average event intensity during the sample period (mm hr^{-1}), temperature (to represent potential for convective circulation) and the number of dry days in the sample period (to represent the atmospheric 'reload' time). Correlations between [7]Be activity in rainwater and each of the independent variables were not significant at the 95 % level of confidence ($p > 0.05$). To test the relationship with explanatory variables in a more complex model, multiple regression analysis was used. The best model was selected using the lowest Akaike Information Criterion (AIC). The relationship between [7]Be activity and all variables was not significant at the 95 % confidence level (adjusted $r^2 = 0.20$, $p > 0.05$).

It is possible that the integrated samples used in this study would be less likely to isolate the effects of these variables owing to the range of events that contribute to the sample. Considering this, it is of interest to note the weak negative correlations between [7]Be activity and rainfall intensity and magnitude ($r = -0.35$ and $r = -0.34$ respectively, $p = 0.06$ for both), providing some agreement with Caillet et al. (2001) and Ioannidou & Papastefanou (2006) and the weak positive correlation displayed with number of dry days ($r = 0.28$, $p = 0.13$) perhaps suggesting some influence of atmospheric reload time (Caillet et al., 2001).

To quantify the temporal variability of monthly values within a context relevant to [7]Be use as a tracer, mean seasonal values and standard deviations were calculated (Figure 2.2). Relative standard deviation (RSD) values within seasons were generally 10 % with the exception of 15 % in summer, 2010 and 0.7 % in autumn, 2010. The larger variation in summer 2010 can be attributed to the low concentration value returned for August (1.56 Bq L^{-1}) in comparison

to that of June (2.19 Bq L^{-1}). In the warmer months larger variation can be expected given the combination of atmospheric instability promoting enrichment and the occurrence of heavy events promoting washout.

For comparison, event-based values were taken from Caillet et al. (2001) (for events 5-35 mm magnitude) and mean monthly values and relative standard deviations (RSD) calculated. RSD ranged from 12-49 % with greater values displayed in the warmer months. This temporal variability would suggest that it is inappropriate to assign a single rainwater activity value across an extended period. In the context of [7]Be use as a tracer, variability in rainwater activity needs to be considered in conjunction with inventory estimation. The potential effect of not accounting for temporal variability of [7]Be activity in rainfall upon inventory estimations is identified in section 2.3.3.
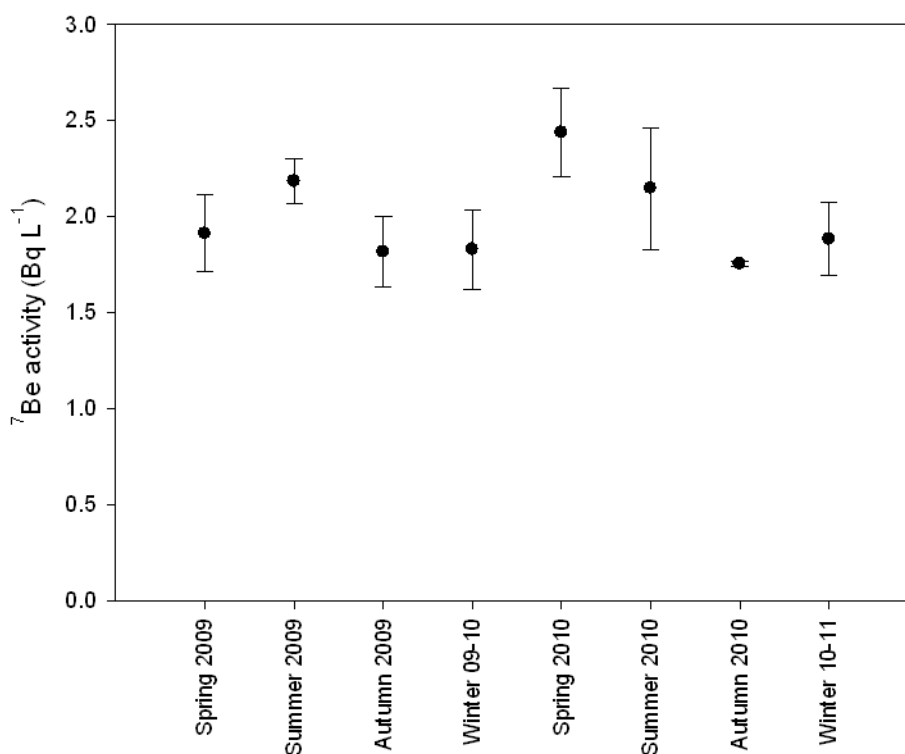
Figure 2.2: Mean seasonal [7]Be activity in rainfall (Bq L^{-1}) derived from monthly values. Spring values derived from monthly values of March, April and May, summer: June, July and August, autumn: September, October, November and winter: December, January and February. Standard deviation between monthly values shown

2.3.2. Spatial variability of ^{7}Be activity in rainfall

Monthly ^{7}Be rainfall activities for 2009 have been reported for Chilton, England (51° 34' 02" N, 1° 17' 43" W, 114 m a.m.s.l.) and Aberporth, Wales (52° 07' 49" N, 4° 32' 22" W, 55 m a.m.s.l.) (Mitchell, 2009). Analyses were undertaken on the raw data provided by Mitchell (2009) to provide comparison for Plymouth data. Data show spatial variation between the sites (Figure 2.3) with annual means of 0.75 (± 0.09) Bq L^{-1}, 1.27 (± 0.09) Bq L^{-1} and 1.95 (± 0.21) Bq L^{-1} for Chilton, Aberporth and Plymouth respectively. Kruskal Wallice test (a non-parametric test since data failed to meet assumptions for normality and equal variance) showed a significant (95 % confidence level) difference in monthly concentrations between locations (H (2) = 14.68, $p < 0.01$). The complexity surrounding the atmospheric processes which control ^{7}Be fallout concentrations mean that it is difficult to identify reasons for spatial variability with limited data. However, Baskaran et al. (1993) suggested that higher ^{7}Be activity at coastal sites may relate to the greater abundance of aerosols in surface air which could explain the higher activities for Aberporth and Plymouth in comparison to Chilton. There was no significant correlation between ^{7}Be activity and monthly rainfall for Chilton or Aberporth (r_s = -0.116, $p > 0.05$; r_s = -0.385, $p > 0.05$ respectively).

Although concentrations are significantly different between the sites, temporal patterns are closely correlated ($p < 0.05$) (Table 2.1) suggesting the influence of the same controlling factors. The rise in concentration for February at all sites is noteworthy (Figure 2.3) although it is difficult to determine a potential controlling factor here. Low rainfall for this month at Aberporth and Plymouth (23 mm and 11 mm respectively) may provide an explanation but this is not reflected in the rainfall received at Chilton (48 mm) which is comparable to January (49 mm)

and in excess of that received in March (24 mm). These data suggest that characterising [7]Be activity in rainfall should not only consider temporal variability but sampling should also be site-specific.
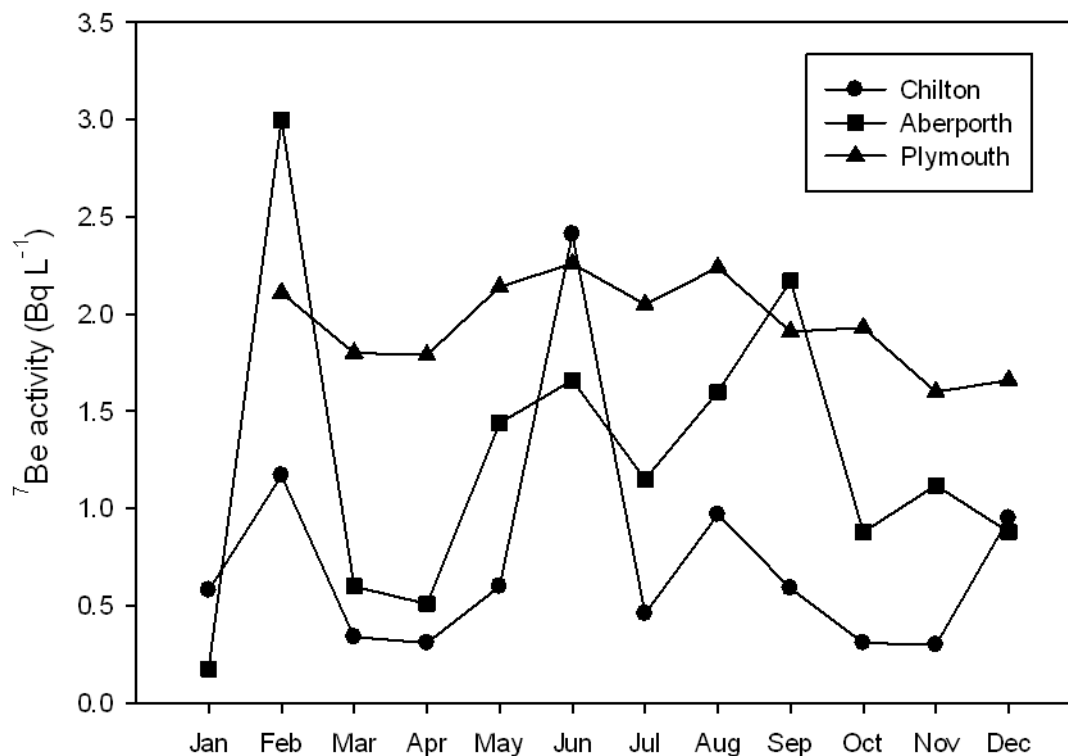
Figure 2.3: Monthly [7]Be activity in rainfall at UK sites for 2009. No value available for January in Plymouth. Chilton and Aberporth data obtained from Mitchell (2009).

	Chilton	**Aberporth**
Plymouth	$r_s = 0.70$ $p = 0.01$	$r_s = 0.67$ $p = 0.02$
Aberporth	$r_s = 0.66$ $p = 0.01$	

Table 2.1: Spearman correlation coefficient (r_s) values for monthly [7]Be activity in rainfall at three UK sites in 2009. Spearman test used owing to failure to meet the assumption of normality for all data sets.

2.3.3. Temporal variability of ^{7}Be deposition

Total rainfall for the study period was 1789 mm with rainfall in 2010 below the 30 year average (1971 - 2000, 1000 mm (Met Office)) at 841 mm. Total deposition for the study period was 3376 (± 323) Bq m^{-2} with annual deposition in 2010 reaching 1594 (± 138) Bq m^{-2}. The average monthly deposition for the study period was 135 (± 12) Bq m^{-2}, with a range of 22 (± 2.2) Bq m^{-2} (February, 2009) to 294 (± 27) Bq m^{-2} (July, 2009). Deposition is reported as being well correlated with rainfall, for example, Ayub et al. (2009) and Ioannidou & Papastefanou (2006) reported coefficient (r) values of 0.92 and 0.83 respectively. It is not surprising, therefore, that the annual deposition in this study exceeds those reported for semi-arid regions (e.g. Gonzalez-gomez et al., 2006 reported 285-592 Bq m^{-2} yr^{-1} for Grenada, Spain) although is comparable to the deposition reported for locations with similar rainfall (e.g. Caillet et al., 2001, 2087 Bq m^{-2} yr^{-1} for Geneva, Switzerland).

In agreement with wider research, ^{7}Be deposition (Bq m^{-2}) in this study was significantly (95 % confidence level) correlated with rainfall (mm) (r = 0.95, p < 0.001) (Figure 2.4) suggesting around 90 % (r^2 = 0.9) of the variability in deposition can be explained by rainfall at this site. This dependence upon rainfall appears to be higher than that for other locations, for example Caillet et al. (2001) reported r^2 0.66 for Geneva and Doering and Akber (2008b) reported r^2 0.72 for Brisbane. Similarly, data for Aberporth (Mitchell, 2009) returned r^2 0.58 (r = 0.76, p < 0.01) which suggests greater importance of other atmospheric processes (affecting rainfall activity) upon ^{7}Be deposition. Following Doering and Akber (2008b), by using the y intercept (in Figure 2.4), estimations of the contribution of dry fallout to the deposition can be calculated. Dry fallout contributed approximately 9 % of the average monthly deposition

(135 Bq m^{-2}) (i.e. 11.65/135) which agrees with general findings of < 10 %

contribution of dry fallout to total deposition (Ioannidou & Papastefanou, 2006;

Wallbrink & Murray, 1994).
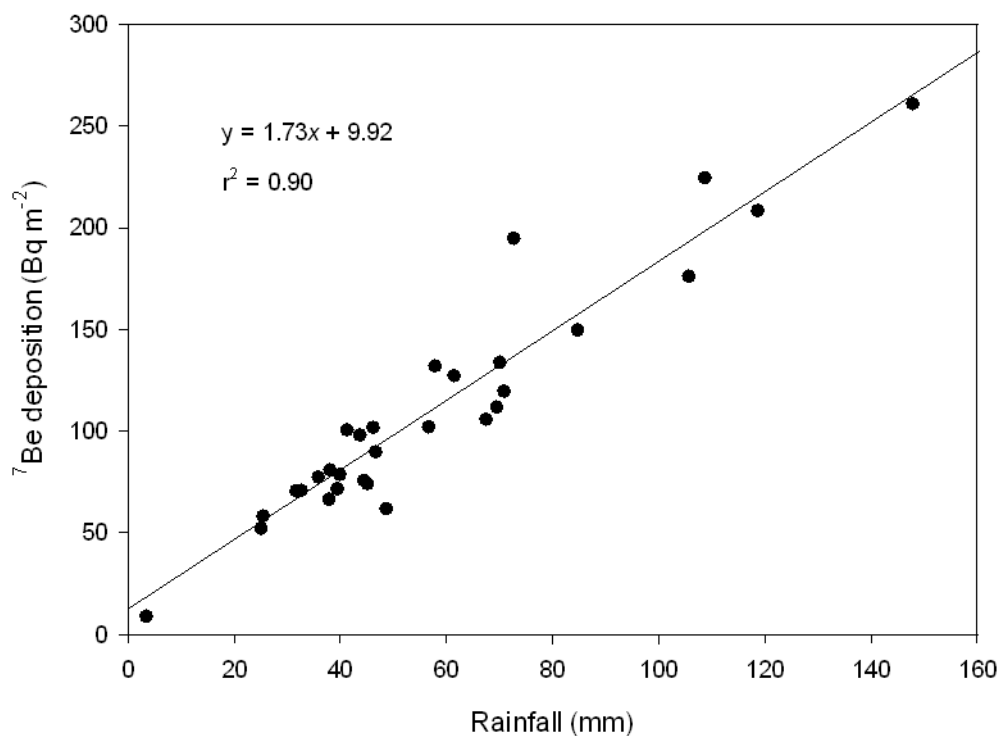
Figure 2.4: Correlation between rainfall and ^{7}Be deposition at Plymouth based upon 30 sample activities

To demonstrate temporal variability in the relationship between deposition flux

and rainfall, data were transformed into proportions of the total deposition and

proportions of total rainfall for the study period (Figure 2.5). The ratio of the

proportion of deposition to the proportion of rainfall (Figure 2.6) provides an

indication of points where variability in deposition is less dependent upon rainfall,

i.e. where deposition exceeds rainfall the ratio is > 1 (Baskaran, 1995).

Changes in the ratio reflect the temporal variation in the ^{7}Be activity in rainfall

and this can be associated with the atmospheric processes described in section

2.3.1.

For example, Figure 2.5 shows a higher deposition proportion in comparison to the rainfall proportion for spring, 2010. The ratios for March, April and May of that year were 1.17, 1.41 and 1.28 respectively and are likely to correspond to STE and vertical circulation within the troposphere increasing the activity of [7]Be in rainfall (Baskaran, 1995) (Figure 2.1). Lower ratios for summer-autumn, 2010 (0.97, 0.83 and 0.92 for July, August and September respectively) are likely to reflect washout owing to high rainfall magnitude. Total rainfall for these months was 87 mm, 98 mm and 89 mm respectively, showing an increase when compared to August and September, 2009 (52 mm and 26 mm). However, rainfall for July, 2009 (144 mm) exceeded that of July 2010, although the ratio for 2009 remained close to 1 (1.08). This highlights the effect of using an average value of [7]Be activity in rainfall upon deposition estimates as described below.

The [7]Be activity in rainfall shown for July 2009 (Figure 2.1) was a mean value from 3 samples and the slight decrease in activity for this month resulted from a lower value obtained for one sample owing to prolonged and heavy rainfall. The ratio for the low activity sample was 0.93, thus, reflecting washout. The ratios for the other two samples (which contribute to the mean) were 1.13 and 1.16, reflecting high fallout activity which can be expected in warmer months. Therefore, using an average monthly value in this case has masked the effects of changing rainfall activity upon deposition estimates. This indicates some potential for distorting event deposition when using average or constant values of [7]Be activity in rainfall across an extended time period. The effect of using a constant activity value upon [7]Be inventory estimation is discussed in Chapter 5 in the context of soil erosion estimates.
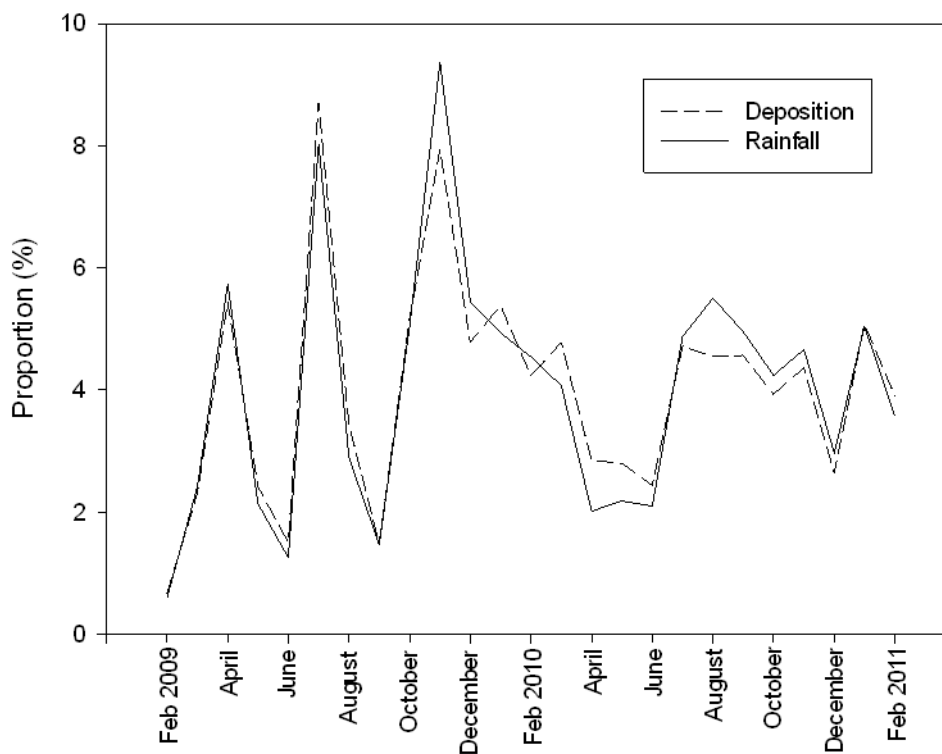
Figure 2.5: Proportion of total [7]Be deposition and proportion of total rainfall based upon monthly values
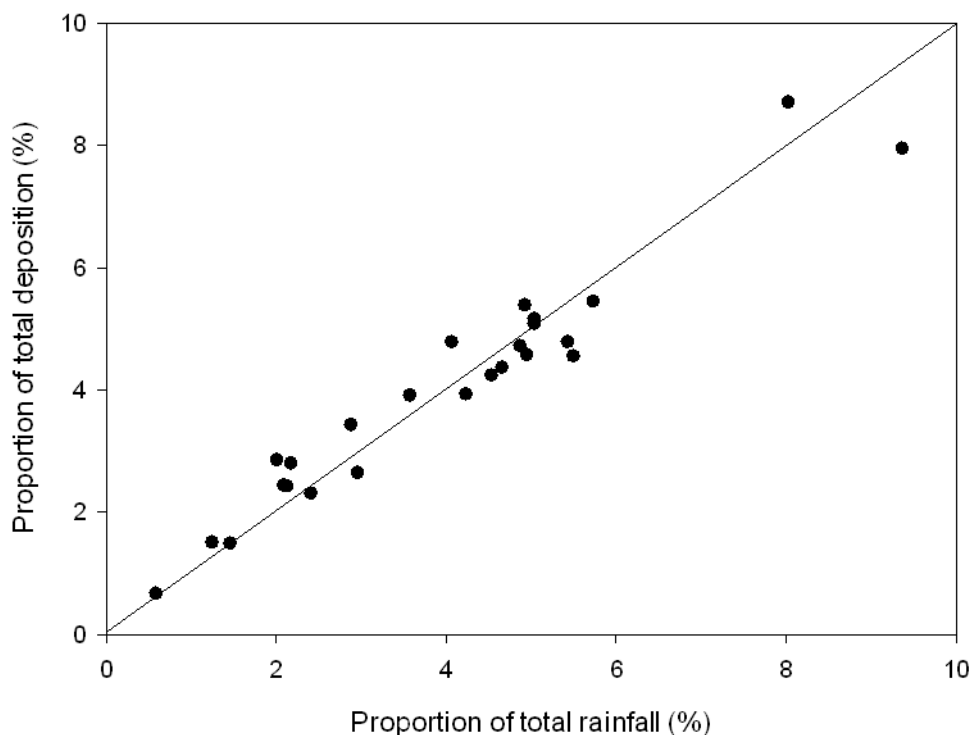
Figure 2.6: Proportion of total [7]Be deposition against proportion of total rainfall for the study period. Points which fall above and below the line indicate a ratio of > 1 and < 1 respectively. Ratios > 1 represent points where deposition exceeds the proportion of rainfall and are likely to reflect higher [7]Be rainfall activity (Bq L[-1]). Ratios < 1 may reflect the effect of washout (c.f. Baskaran et al., 1995).

2.3.4. Estimating a ^{7}Be cumulative inventory

The previous section discussed temporal variability of event deposition, here, a method of estimating the cumulative ^{7}Be inventory in soil based upon event deposition is explored. Estimations of cumulative inventory are important in the context of soil erosion studies since estimations provide a comparison to reference values derived from soil cores (e.g. Blake et al., 1999). A ^{7}Be cumulative inventory can be estimated following the method of Doering and Akber (2008b) whereby increases in daily inventory from fallout input are considered in conjunction with on-going decay of already established inventory.

A cumulative inventory for the study period was estimated using sample fallout values (Figure 2.7). The maximum inventory achieved during the period was 498 (± 50) Bq m^{-2} in Spring, 2009 which is comparable to the inventory of 533 (Bq m^{-2}) reported by Blake et al. (1999) for a winter period in east Devon (~ 84 km from the Plymouth study site). Inventory estimations were compared to soil samples taken from trays which had been exposed to fallout for the same duration and at the same location as the rainwater sampling. ^{7}Be inventories in the soil samples were ~ 40 % lower than the estimated inventory implying that the rainfall method had returned an overestimation. Doering and Akber (2008b) also reported the potential for overestimating cumulative inventories using values of ^{7}Be rainfall activity (from monthly integrated samples) and rainfall volume and suggested this could be because of soil loss from the coring site or a general tendency for the method to overestimate. The maximum discrepancy between soil and estimated inventories found by Doering and Akber was of the same order of this study at 30 %. Loss of soil from the trays used in this study is unlikely although there was potential for the location of the trays to be

shadowed from some rainfall events compared to the location of the weather station.

To explore the latter issue, an independent check was carried out to determine the potential for rainfall shadowing by placing a rain gauge at the soil tray location. A comparison of 10 rainfall events showed there was no significant difference between the volume received at the soil tray location and the weather station (t (14) = -0.166, p > 0.05). However, data did reveal a 25 % discrepancy (lower volume at the soil location) for one major event, suggesting some potential for the data from the weather station to overestimate the volume of rainfall received by the soil trays. It may, however, also be possible that the use of integrated rainfall samples does not truly represent event deposition since these samples will provide an average ^{7}Be activity from the total contributions during the sample period. The use of an integrated value may, therefore, distort the estimated cumulative inventory. Studies which report close agreement between cumulative inventory estimations and independent soil cores are based upon event fallout samples (Blake *et al.*, 1999; Wallbrink & Murray, 1994). This suggests that estimations of cumulative ^{7}Be inventory should be validated by the use of independent soil samples and, where possible, rainfall should be sampled at regular intervals.
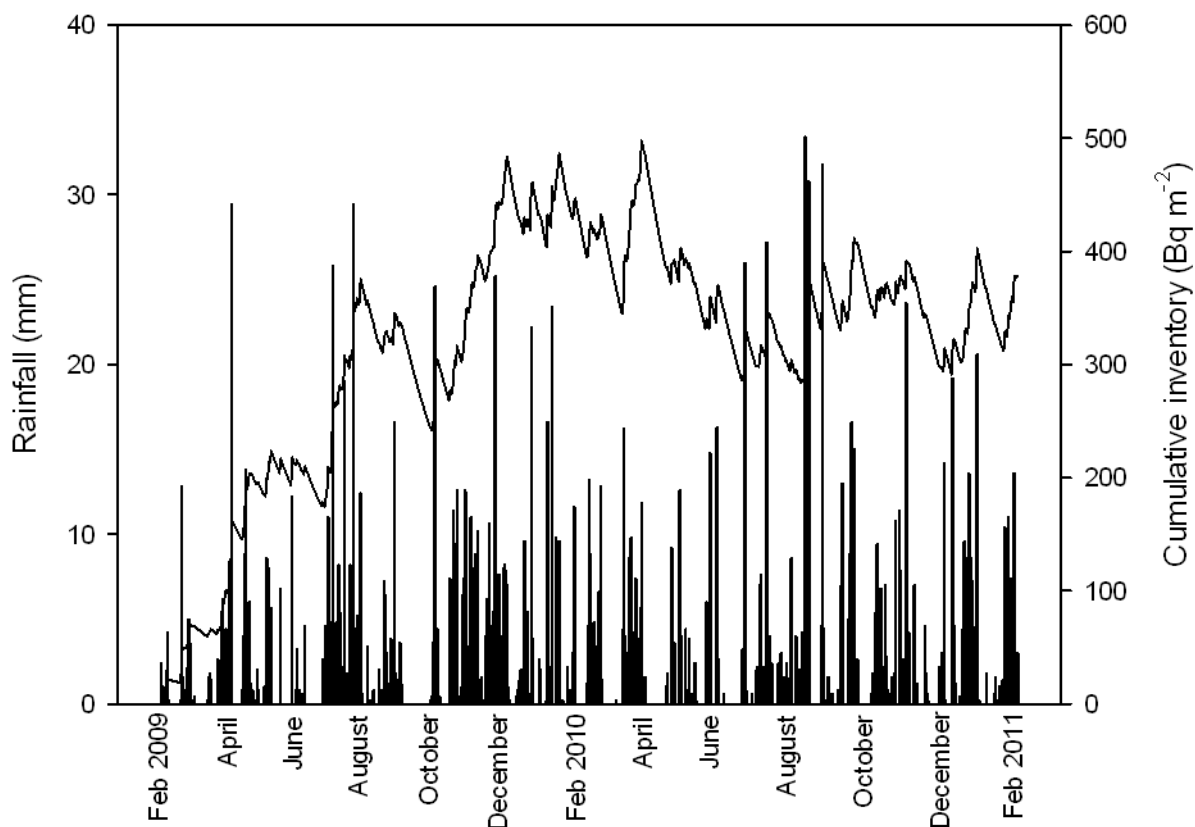
Figure 2.7: Estimated [7]Be cumulative inventory for the study period using sample activities

2.4. Conclusions

No significant difference was found between monthly [7]Be activity in rainfall at the study site although data demonstrated temporal variability, with a general trend for higher activity during the warmer months and this was likely to be influenced by STE and convective circulation within the troposphere. Multiple regression analysis showed no significant relationship between [7]Be activity in rainwater and rainfall magnitude, rainfall intensity, temperature and number of dry days in the sample period. Though statistically insignificant, weak negative correlations were found between [7]Be activity and rainfall magnitude and intensity. Given that the use of integrated samples is less likely to isolate the effects explanatory variables, these negative correlations imply a potential effect

of washout upon [7]Be activity in rainfall. Comparison with wider UK sites demonstrated significant spatial variation in [7]Be rainwater activity. Temporal trends, however, remained similar suggesting the influence of the same controlling factors. These temporal trends suggest that applying an average value of [7]Be activity in rainfall to a period of a few months in soil erosion studies is unlikely to be representative. In addition, spatial variability highlights the need for rainwater sampling to be site-specific.

[7]Be deposition at the study site was strongly correlated with rainfall suggesting that around 90 % of variability in deposition can be explained by rainfall dynamics. While this generally agrees with wider studies, regression values reported for other areas suggest that atmospheric processes (affecting [7]Be activity in rainwater) may have a greater influence upon deposition at these locations. The use of a deposition proportion : rainfall proportion ratio identified months where [7]Be deposition in Plymouth was influenced by variation in rainfall activity, linked to atmospheric processes. Data also suggested that using average values of [7]Be activity in rainfall can mask the effects of temporal variability within a particular month, thus, distorting estimates of event deposition. This has implications for the use of average values of [7]Be activity in rainfall when estimating deposition in erosion studies.

A cumulative inventory estimated for the study site over the sample period was ~ 40 % lower than the [7]Be inventory in soil trays adjacent to the rain gauge. Some difference may be attributed to rainfall shadowing although the potential for the use of integrated rainfall samples to overestimate cumulative inventory should also be considered. Determination of cumulative inventory during erosion studies is required to provide a comparative baseline for reference inventories derived from soil cores. Reliable estimation of [7]Be event deposition

and cumulative inventory during erosion studies will require rainfall sampling at regular intervals. Estimates of cumulative inventory should be validated by comparison with independent soil cores. Event-based sampling is likely to be beyond the scope of many research projects and, therefore, sampling programmes are likely to involve a careful compromise between the efficiency of integrated sampling and the sampling interval, with due attention paid to subsequent uncertainty.

Chapter 3. Optimisation of ^{7}Be gamma analysis following BCR sequential extraction

3.1. Introduction

Increased knowledge of the off-site impacts of soil erosion has highlighted the need for robust quantification of soil loss (Boardman, 2002; Brazier, 2004). Fallout radionuclide (FRN) tracing techniques provide valuable high-resolution data with regard to soil redistribution and, as such, are a useful tool for informing catchment management schemes (Schuller et al., 2010; Wallbrink, 2004; Walling & Collins, 2008; Wilson et al., 2008). The use of FRN tracers assumes rapid and irreversible adsorption to soil particles upon fallout. Currently, data regarding the adsorption behaviour of ^{7}Be is limited and, therefore, investigations are required to determine the geochemical behaviour of ^{7}Be in a range of soils types to underpin its use as a soil erosion tracer at the catchment-scale (Mabit *et al.*, 2008a).

Sequential extraction techniques provide a means of assessing element-solid phase interaction in soils, an understanding of which provides an important platform from which to assess the potential for tracer mobility in the natural environment (Bacon & Davidson, 2008). Extraction schemes have been widely applied to assess potential mobility and bioavailability from a contaminant perspective (e.g. Davidson et al., 2006; Pueyo et al., 2008), although data comparability has been hampered owing to variations in the type of extraction scheme applied. Many extraction procedures have been based upon an early method developed by Tessier et al. (1979). More recently, the Bureau of Community Reference (BCR) developed a modified version of a three-step

scheme and provided a Certified Reference Material (CRM) in an attempt to harmonise procedures (Pueyo et al., 2001).

Numerous studies document the use of sequential extraction techniques to assess the fractionation of natural radionuclides in soils (Kanai, 2011; Leopold et al., 2009; Strok & Smodis, 2010). While these techniques offer a means of assessing the interaction of ^{7}Be with operationally-defined soil and sediment phases, the short half-life and often low activity concentrations of ^{7}Be in soil present analytical challenges. It is, therefore, important that these methods are tested and optimised to generate relevant data for ^{7}Be.

Analysis of extractions requires high resolution gamma spectrometry which offers a means of detecting low levels of natural radioactivity by employing high purity germanium (HpGe) crystal detectors. Software conversions allow the number of detected decay events to be plotted as a peak with a Poisson distribution. Statistical uncertainties, are, therefore closely related to the number of decay observations $(\sqrt{N})$. Further sources of uncertainty are derived from background interference within the peak and poor peak resolution due to low counts. Software functions can account for such interference by using peak fitting applications to determine net peak area, uncertainty and activity quantification. Where gamma signals are weak (i.e. in low activity samples) it becomes more difficult to distinguish these background effects, and, combined with lower count numbers, higher statistical uncertainties can be expected (Wallbrink et al., 2002).

The application of sequential extraction procedures to assess the fractionation of natural ^{7}Be fallout in soils is, therefore, problematic owing to i) commonly low levels of natural ^{7}Be activity in soils, ii) rapid decay of activity owing to the short

half-life and iii) removal of proportions of the total activity following each extraction step, thus, further reducing sample activity. These factors combine to present the challenge of maximising gamma counts to reduce analytical uncertainties as far as possible. Maximising counts to improve statistics requires careful consideration of counting times and sample geometry. Since it is often impractical to run samples for extended time periods, improvements in sample mass and geometry should be considered. Increasing sample mass will increase the number of photons emitted and, therefore, potential detection. However, attenuation effects from the resulting mass increase could reduce absolute efficiency (the number of impulses detected compared to the number of photons emitted). The geometry of the sample can also influence efficiency by determining the proportion of the sample which is in close proximity to the detector head (Wallbrink *et al.*, 2002). Although the effects of changes in efficiency are corrected for during calibration, obtaining optimal counts to reduce uncertainty remains a key challenge for the researcher.

The research reported here details the use of the optimised BCR three-step sequential extraction procedure with soils which had been exposed to natural [7]Be fallout. The aim of this investigation was to determine a method to reduce analytical uncertainties in [7]Be sequential extraction data by investigating three approaches to analysing sample extracts. These were (i) analysis of the solid soil material following extraction, (ii) analysis of preconcentrated extract solution using coprecipitation with metal oxyhydroxides and (iii) analysis of combined and preconcentrated (metal oxyhydroxide coprecipitation) extract solutions from triplicate samples, while using stable Be to assess procedural uncertainties.

3.2. Methodology

3.2.1. Characterisation of soils and exposure to [7]Be fallout

Methods for soil sampling, characterisation and exposure to fallout are detailed in Chapter 4 which is focussed upon [7]Be behaviour in each soil type. For the purpose of this analytical chapter, characterisation and exposure techniques are introduced only as a brief overview. Four soils, representative of arable agricultural land in Devon, UK, were selected for the investigation. A sandy silt loam soil (Soil C) was used to determine the most effective method and was, thus, used in each of objectives (i) to (iii) above. Once the most effective method had been established, this method was then applied to the remaining experimental soils to provide a comparison across all soil types.

Soil pH was determined using a Meterlab PHM201 Radiometer with 10 g of moist soil in ultra-pure (Milli-Q) water at a soil:solution ratio of 1:2.5. Total Organic Carbon (TOC) and Inorganic Carbon (IC) were calculated from Total Carbon (TC) measurements carried out using a Skalar Primacs SLC Analyser (Skalar UK Ltd). Cation Exchange Capacity (CEC) was determined by leaching 5 g of soil with ammonium acetate (1M) as outlined in Rowell (1994). Particle size analysis for > 63 µm and < 63 µm was carried out using a Mastersizer 2000 (Malvern, UK) with Hydro-G in compliance with ISO 13320. Clay soil fractions were calculated using settling columns following BS 1377 (BSI, 1990). Major elements were determined using ICP-OES (Varian 725-ES, Varian, Australia). Tables of characteristics are given in Chapter 4.

3.2.2. Exposure of soils to [7]Be fallout and sampling for sequential extraction investigations

Soil samples were homogenised manually and then compacted to their field bulk densities in trays for exposure to natural [7]Be fallout for an 8 month period (Chapter 4). This allowed the soils to acquire an inventory of [7]Be representative of field conditions. Sampling times were selected according to inventory estimations determined from [7]Be activity in rainfall (Bq L^{-1}) and rainfall volume (mm) data. A baseline inventory of 400 Bq m^{-2} was deemed appropriate for obtaining suitable [7]Be counts since this is a representative wet season inventory in the study area (Blake et al., 1999). Surface soil samples (0-2 mm layer) were used for the sequential extractions since these uppermost layers of the soil profile are likely to have higher [7]Be activity. Owing to the short half-life of [7]Be, samples were exposed for as long as possible before the experiments began to maintain the inventory. Samples for each experiment were, therefore, taken at different times meaning that the activity of the soil for each extraction varied.

3.2.3. Gamma spectrometry

All [7]Be analyses were carried out using a high purity germanium (HPGe) Gamma detector (GEM-FX8530-S Planar, Ortec, UK) in the Plymouth University Consolidated Radioisotope Facility (CORiF) which operates within ISO 9001:2008-certification. Sample calibration was carried out using a standard of the same geometry as the extract samples. Standards were prepared using QCY58b mixed standard solution (G E Healthcare, Amersham, UK) distributed in a mineral matrix or as a thin-source filter paper (0.45 µm

cellulose nitrate). Energy emission of [7]Be (477.6 keV) was interpolated between emission values of [137]Cs (661.7 keV) and [113]Sn (391.7 keV). All sample counts were corrected for background emission, geometry efficiency and decay using Gammavision-32 software. Sample values were reported as activity (Bq kg^{-1}).

Laboratory analytical quality control procedures were carried out in accordance with Wallbrink et al. (2002). Detector performance was monitored using internal Analytical Quality Control (AQC) procedures whereby an independent standard matrix was analysed on a monthly basis and data output logged to ascertain uniformity in performance. External AQC practice was also undertaken by participation in an inter-laboratory comparison (IAEA-CU-2009-03 World-Wide Open Proficiency Test) using standards of unknown composition and concentration provided by the International Atomic Energy Agency (IAEA). The results were in close agreement to the certified activities provided by the IAEA which indicated that the laboratory was performing at an 'acceptable' standard.

3.2.4. The optimised BCR three-step sequential extraction procedure

Table 3.1 outlines the optimised BCR three-step sequential extraction procedure (Pueyo et al., 2001). In step 1 (readily exchangeable, carbonate-bound target phase), 40 mL of acetic acid (0.11 M) was added to 1 g of soil and shaken for 16 hours on a reciprocal shaker. The extract was then separated from the solid by centrifugation at 3000 g for 20 minutes. The supernatant was retained for analysis. The soil was rinsed in 20 mL ultra-pure water by shaking for 15 minutes. Following centrifugation the rinse solution was discarded. The process was repeated for step 2 with the use of hydroxylammonium chloride (0.5 M) (Fe/Mn oxide target fraction). The pH of the reagent was adjusted (pH

1.5) by the addition of 25 mL HNO_3 (2 M). In step 3 (organic/sulphide target fraction), 10 mL of hydrogen peroxide (8.8 mol L^{-1}) was added to the residue and the vessel covered loosely and left to stand for one hour. The digestion was continued by heating the uncovered vessel in a water bath at 85 ± 2 °C, reducing the volume to approximately 3 mL. A further 10 mL of the reagent was then added and the heating continued until the volume was reduced to approximately 1 mL. Following this, 50 mL of ammonium acetate (1.0 mol L^{-1}) buffered to pH 2 ± 0.1 with concentrated HNO_3 was then added to the residue and treated as in steps 1 and 2. The method recommends carrying out an aqua regia digest under reflux on the remaining soil residue and on a separate soil sample which has not been subjected to the sequential extraction procedure. A summation of steps 1 to 3 and the residual can then be compared to the total element concentration in the single digest.

All glassware used for the above was acid washed using 10 % v/v HCl. Ultra-pure water was obtained from a Millipore Milli Q Plus 185 system. All reagents were of analytical grade. A reciprocating shaker was used owing to the size of vessels employed (750 mL), thus, the method was validated using 1 g sub samples of the BCR 701 Certified Reference Material, in triplicate. The CRM aqua regia digest was carried out using microwave assisted digestion following Hssan et al. (2007). Recovery values were generally between 90 and 108 % for all elements in each step and, therefore, in close agreement with mean values and uncertainties given in Pueyo et al. (2001). An exception was the low recovery (67 %) of Pb in step 3, however, Pueyo et al. (2001) also stated the occurrence of low Pb recoveries in this step which contributed to high uncertainties associated with the certified mean (RSD 33 %). The summation of

step and residual digest values were within uncertainty of the total digest concentration for each element suggesting good overall recovery.

	Reagent	Procedure	Fraction/phase
Step 1	Acetic acid (0.11 M)	Shake for 16 hours. Centrifuge at 3000 g for 20 minutes	Weak acid-soluble, exchangeable/Readily exchangeable, carbonate-bound
Step 2	Hydroxylammonium chloride (0.5 M)	Shake for 16 hours. Centrifuge at 3000 g for 20 minutes	Reducible/Fe/Mn oxyhydroxides
Step 3	Hydrogen peroxide (8.8 M) / Ammonium acetate (1 M)	Digest with hydrogen peroxide at 85 ± 2 °C. Add ammonium acetate and shake for 16 hours as above	Oxidisable/Organics and sulphides
Residual	Aqua regia	Digestion under reflux	Residual

Table 3.1: Overview of the optimised BCR three-step sequential extraction procedure

3.2.5. Sequential extraction with experimental soils

Different approaches to gamma analysis of the sequential extractions were assessed using a 24 ± 2 hour count time. Optimal analysis time considers the balance between improved counting statistics for one sample and the on-going radioactive decay of ^{7}Be in the overall batch of samples, given the short half-life of ^{7}Be. Therefore, it can be challenging to carry out extractions and analyses in triplicate within an appropriate time scale unless a significant number of gamma detectors are available.

3.2.5.1. BCR three-step sequential extraction; counting the solid soil sample

Soil C was used to assess data quality obtained when soil was gamma counted following each extraction step i.e. a 'subtraction' approach. Extractions were carried out using 14 g of air dried soil (< 2 mm fraction) in a 750 mL centrifuge vessel. Prior to extraction, the vessel and soil were placed directly on a gamma detector (GEM-FX8530-S Planar, Ortec, UK) to determine the total activity (Bq kg^{-1}). The spectrum was calibrated with a partially-full 90 mm Petri dish standard geometry representative of the geometry of the soil as distributed across the base of the centrifuge vessel (also 90 mm diameter). The [7]Be remaining in the soil was then quantified after each extraction step, using the same solid sample geometry. The extracted [7]Be was calculated by subtracting the remaining activity from the initial total activity. This is the simplest method for processing samples in a sequential extraction scheme.

To investigate the effect of soil mass on the counting statistics, 20 g of a second sample was also taken through the extraction procedure. The weight restrictions on the centrifuge (Sorvall Legend RT, Sorvall, UK) meant that the solid:solution ratio suggested by BCR had to be adjusted from 1:40 to 1:20 in the first two steps and from 1:50 to 1:25 in the ammonium acetate extraction of the third step. The effect of these changes on Be extraction were assessed using both the original and adapted methods on soil that had been equilibrated with stable Be ([9]Be) (section 3.2.3.4).

3.2.5.2. Analysing the extract solution of individual samples

Further extractions were used to characterise the counting statistics obtained when the phase extracts in solution were preconcentrated by MnO_2 precipitation

(Short et al., 2007) and gamma counted. The preconcentration was carried out to improve counting statistics by providing a concentrated thin-source geometry. In this experiment, duplicate 20 g soil samples with the modified soil:solution ratio were used. To obtain the MnO_2 precipitate, 400 µL of $KMnO_4$ (0.2 M) was added to the extract solution (adjusted to 500 µL for step three extractant) and the solution buffered to pH 8-10 using concentrated NH_4OH. 400 µL of $MnCl_2$ (0.3 M) (500 µL in step 3) was then added and the precipitate allowed to flocculate and settle for 24 hours. The precipitate was collected by filtration under vacuum and the filter papers (cellulose nitrate 0.45 µm) were then placed in a 50 mm Petri dish, air dried and then fixed with cellophane prior to analysis by gamma spectrometry. When the pH of the step 2 reagent was adjusted, a red precipitate formed due to precipitation of Fe released in this step rather than MnO_2 from the addition of carrier solutions. The recovery of ^{7}Be was determined by comparison of the summation of step activities to the total activity in the solid material prior to extraction.

An aqua regia extraction was not necessary when the soil was counted (section 3.2.3.1.), since any residual radioactivity could be detected in the solid sample. However, for completeness in this approach, 200 mL of aqua regia was added to each sample in a 2 L beaker, and the soil was digested on a hot plate under reflux by gently boiling for 2 hours. Following this, the aqua regia was evaporated off until nearly dry. Samples were then diluted with 200 mL ultra-pure water and the pH was checked to ensure it was < 2. The solution was centrifuged as in previous steps and the supernatant preconcentrated as described above.

3.2.5.3. Counting the extract solution; combining triplicate samples

The final analytical approach involved carrying out the sequential extraction procedure using 20 g of soil as above, but here triplicate samples were used and these were sub-sampled (5 mL) for stable Be analysis before being combined for MnO_2 co-precipitation and gamma analysis. This allowed the reproducibility between triplicates to be determined using stable Be extracted from the soil, while maximising the activity presented to the detector for gamma analysis.

3.2.5.4. Determining the effects of modifying the soil:solution ratio

Sub-samples of soil were equilibrated with a 1 mg L^{-1} Be solution ($BeCl_2$; adjusted to pH 5.6 with NaOH) over a 120 hour period on a reciprocating shaker and then subjected to the BCR three-step sequential extraction procedure using both the modified and method-stipulated soil:solution ratios. Preliminary sorption investigations (Chapter 4) informed the equilibration time and the concentration of 1 mg L^{-1} allowed clear detection of equilibrated Be above natural background concentrations in extract solutions while remaining within the soil CEC. Following equilibration, samples were centrifuged at 3000 g for 20 minutes and the supernatant decanted. Moist samples were then aged for 53 days by incubating at a constant temperature of 20°C, to allow post-sorption changes to occur over the equivalent of one half-life of [7]Be. Samples were kept moist during the incubation period by maintaining the post-centrifuged sample mass with the addition of ultra-pure water.

Samples were taken through the two sequential extraction procedures in triplicate. Control extractions of soil that had not been equilibrated with Be were

also performed to correct for the distribution of the natural background Be. All analyses were carried out using ICP-OES (Varian 725-ES, Varian, Australia).

3.3. Results and discussion

3.3.1. Counting the solid soil sample

Figure 3.1 shows the ^{7}Be activities and counting statistics obtained using direct gamma analysis of samples following each sequential extraction step. The total activities were relatively low (30.7 and 26.9 Bq kg^{-1} respectively) when compared to literature values obtained following prolonged periods of fallout (relating to higher rainfall) where approximately 60 Bq kg^{-1} can be achieved in surface layers in the study region (Blake et al., 1999). Relative Standard Deviation (% RSD (2σ)) analytical uncertainties of the initial activity are, therefore, in excess of 20 %. Following step 1, activity concentrations in samples 1 (14 g) and 2 (20 g) fell to 67 % and 65 % of the respective total activities. Owing to the further decrease in activity, the analytical uncertainties increased to around 50 % and, thus, the sample activity after the first step was within uncertainty of the total activity. Analyses of the soil following step 2 demonstrated a further decline in ^{7}Be activity to below the Minimum Detectable Activity (MDA). It was, therefore, not necessary to take the remaining samples through the complete extraction procedure.

Although analytical uncertainties were high for both samples, the benefit of using a greater mass in Sample 2 is apparent, as the counting uncertainties were reduced despite the lower ^{7}Be activity. Low-moderate levels of recent rainfall (and, thus, fallout) contributed to the low total sample activities shown here. With greater total activity (from higher recent rainfall and fallout), analytical

uncertainties could be expected to be lower. However, the samples used here remain representative of a winter period and given the short half-life of ^{7}Be, alternative methods to improve counting statistics should be considered. Maintaining sample geometry for analysis following extractions is also problematic using this approach.
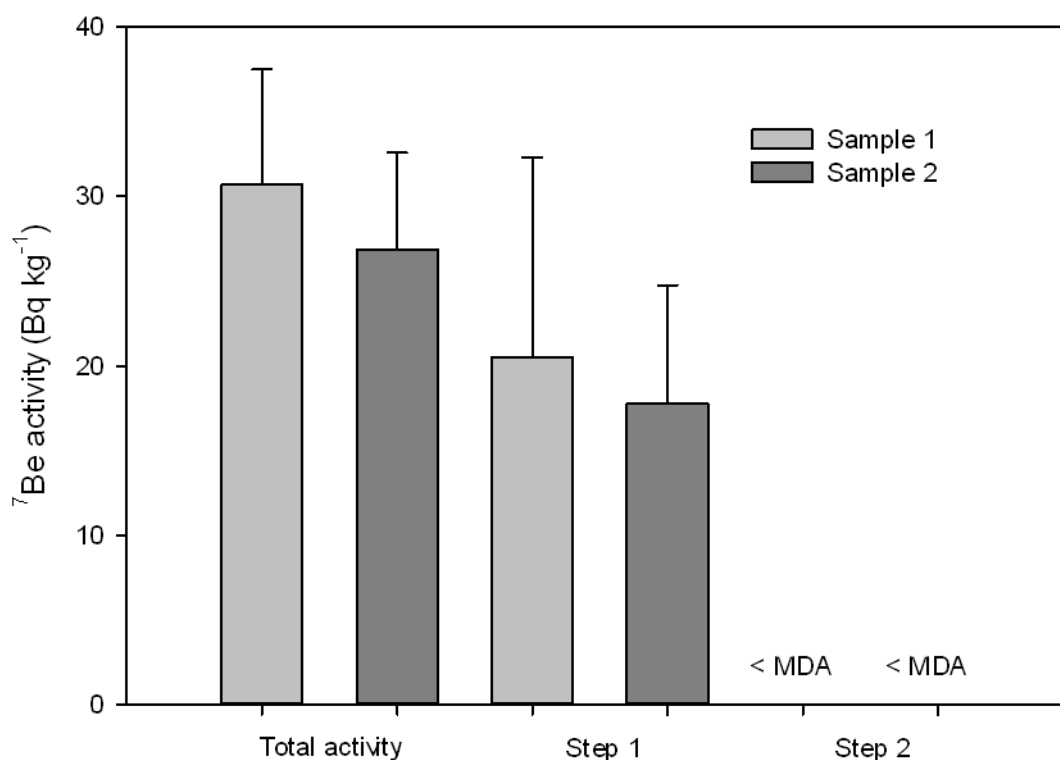
Figure 3.1: ^{7}Be activity in individual solid soil samples following sequential extractions steps. Analytical uncertainties are given as 2σ

3.3.2. Counting the extract solution

3.3.2.1. Analyses of ^{7}Be activity within individual extractions

Preconcentrating the liquid extract of duplicate samples individually resulted in uncertainties of > 30 % in step 1 and > 15 % in step 2 (Figure 3.2), despite the higher activity concentrations in these samples compared to those in section 3.1. Therefore, the ^{7}Be activity in step 1 and step 2 sample extracts were within

uncertainty. The activity in step 3 and the residual fraction remained below the Minimum Detectable Activity (MDA) for both samples. Comparison of summation values and the total activity for Sample 1 showed that these values were not within uncertainty (RSD 2σ) at 95.4 Bq kg^{-1} (± 16.6 %) and 67.6 Bq kg^{-1} (± 16.1 %) respectively. Recoveries for sample 2 were also in excess of the total activity with a summation of 84.2 Bq kg^{-1} (± 21.3 %) and a total activity of 70.21 Bq kg^{-1} (± 13.9 %) (Table 3.2).
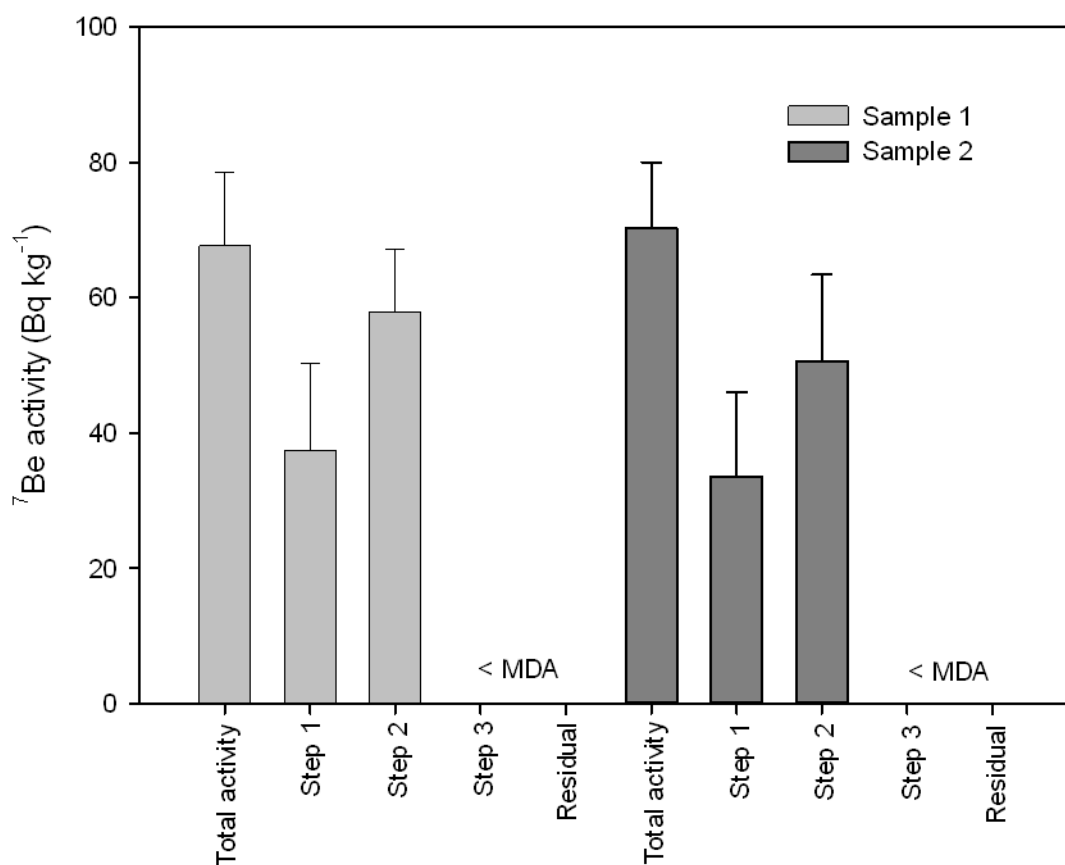
Figure 3.2: [7]Be activity in liquid extracts of duplicate samples. Analytical uncertainties given as 2σ

	Sample 1	Sample 2
Total activity	67.64	70.21
RSD	*16.13*	*13.94*
Step 1	37.48	33.56
RSD	*34.00*	*37.22*
Step 2	57.86	50.60
RSD	*16.10*	*25.28*
Step 3	<MDA	<MDA
Residual	<MDA	<MDA
Σsteps + residual	95.34	84.16
*RSD	*16.55*	*21.24*

Table 3.2: ^{7}Be total activities and preconcentrated individual sample extract activities (Bq kg^{-1}). Analytical uncertainties are given as % RSD (2σ). *RSD of $\sqrt{\Sigma 2\sigma^2}$

3.3.2.2. Analyses of ^{7}Be activity within combined extractions from triplicate samples

Triplicate extracts were combined to assess the effect upon counting statistics. Figure 3.3 shows the improvement in analytical uncertainties in comparison to the data obtained from the individual extracts (Figure 3.2). Combining triplicate extracts reduced the uncertainties from > 33 % to 21 % and > 16 % to 11 % in steps 1 and 2 respectively. It is noteworthy that these improvements were obtained despite the total activity of the samples being lower (~ 15 % lower) at the time of sampling. This approach enabled the detection of ^{7}Be in the third step, which was not achieved in the previous analyses. The recovery of ^{7}Be through the extraction procedure was within uncertainty of the total activity derived from analysis of the soil samples prior to extraction (Table 3.3).

All soil types were therefore analysed using this approach. Over all sample types, the 2σ counting uncertainties were close to 10 % when the extract activity was > 40 % of the total activity (Table 3.3), and all step summations were within uncertainty of the respective total activities. These data, therefore, provide confidence in the co-precipitation method, as applied to the different extraction solutions. The procedural uncertainties were quantified by the analysis of stable Be in the 5 mL aliquots of the individual samples, and these demonstrated reproducibility in all steps (1-3), with RSD values < 1 % and residual phase RSD values < 10 % (Table 3.4). This provided confidence that the gamma counting statistics dominate the uncertainty assessment using this approach.
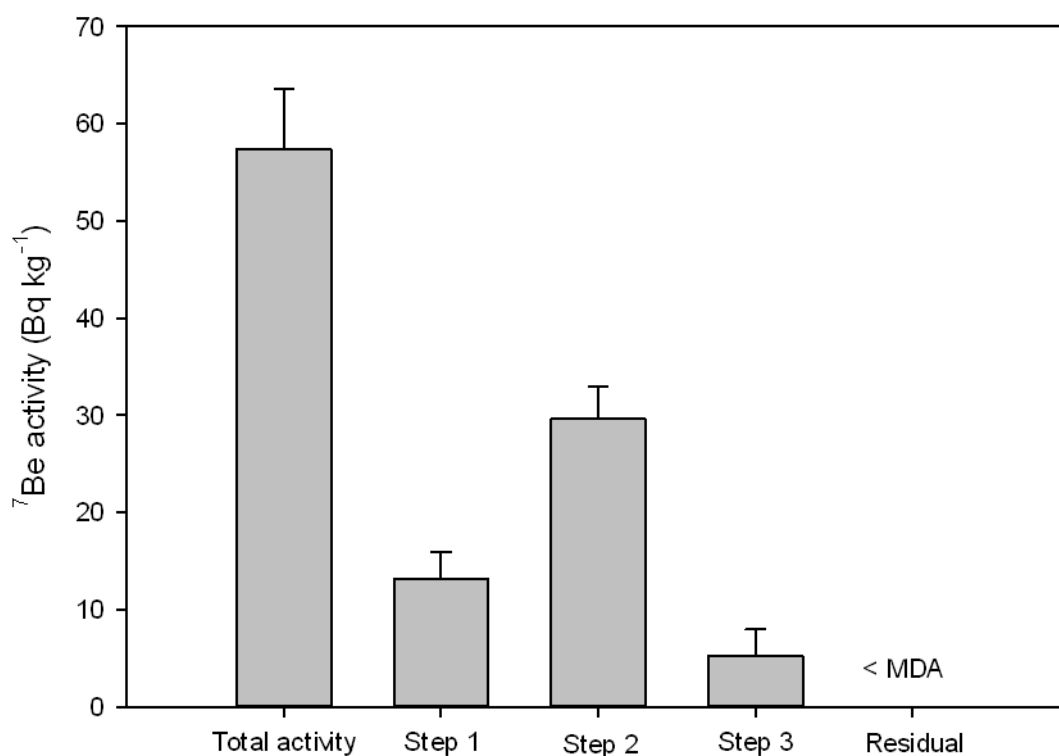
Figure 3.3: [7]Be activity concentration in preconcentrated combined triplicate extracts. Uncertainties given as 2σ

	Soil A	Soil B	Soil C	Soil D
Total activity	45.94	108.83	57.42	79.04
RSD	*9.17*	*7.22*	*10.73*	*7.67*
Step 1 extraction	12.76	45.18	13.12	24.34
RSD	*24.22*	*10.31*	*21.34*	*13.93*
Step 2 extraction	23.37	50.50	29.55	44.59
RSD	*12.58*	*9.88*	*11.37*	*9.17*
Step 3 extraction	5.35	25.76	5.30	5.25
RSD	*38.51*	*16.46*	*51.13*	*45.33*
Residual	<MDA	<MDA	<MDA	<MDA
Σsteps + residual	41.48	121.44	47.97	74.18
*RSD	*11.43*	*6.62*	*10.74*	*7.85*

Table 3.3: ^{7}Be activity (Bq kg^{-1}) in combined triplicate extracts of all experimental soils. Analytical uncertainties given as % RSD (2σ) *RSD of $\sqrt{\Sigma 2\sigma^2}$

	Soil A	Soil B	Soil C	Soil D
Step 1	0.02	0.04	0.02	0.02
RSD	*0.04*	*0.07*	*0.20*	*0.11*
Step 2	0.08	0.12	0.06	0.10
RSD	*0.04*	*0.10*	*0.20*	*0.11*
Step 3	0.05	0.21	0.03	0.06
RSD	*0.04*	*0.10*	*0.20*	*0.10*
Residual	0.15	0.45	0.15	1.45
RSD	*0.23*	*2.82*	*9.35*	*1.16*

Table 3.4: Mean stable Be concentrations (mg kg^{-1} dry weight) and standard deviations (% RSD) from triplicate aliquots

3.3.3. Sequential extraction with soil equilibrated with stable Be

3.3.3.1. Determining the effects of the modified soil:solution ratio

Table 3.5 shows the concentration of Be extracted from soils equilibrated with stable Be. Data are for extractions carried out using the modified soil:solution ratio applied in this study (C1) and extractions using the soil:solution ratio stipulated in the optimised BCR three-step procedure (C2). All values are corrected for background Be to allow comparison with ^{7}Be data, although this background was typically < 10 % of the Be extracted in steps 1 to 3. Residual extractions were within uncertainty of the control extraction for this step demonstrating the extraction of background Be only. The step summations for C1 and C2 are in very close agreement and both of these values are also within uncertainty of the total digest. This, therefore, enables step concentrations to be compared between the two samples and provides confidence in the recovery of equilibrated Be.

The different solid:solution ratios, however, did result in differences in the recovery of Be in each step. C2 resulted in greater extraction in step 1 than C1 and, therefore, lower Be yields in steps 2 and 3. When shown as a percentage of total Be extracted (Table 3.6), approximately 12 % less Be is detected in the first step extraction for C1 in comparison to C2. This is counterbalanced by an 11 % increase in Be concentration for the second step extraction for C1. It is possible that a proportion of Be mobilised during the first step in the C1 sample had redistributed to subsequent soil phases and this has been observed for some metals in wider studies (Ho & Evans, 2000). Analysis of Fe and Mn concentrations in extract solutions of the two samples were in close agreement suggesting reagent selectivity could not account for the observed difference in

Be extraction. It is, therefore, likely that data returned using the modified soil:solution ratio in this study will not be directly comparable to data using the ratios stipulated in the BCR 3-step procedure (Pueyo *et al.*, 2001).

	Soil C 1	Soil C 2
Step 1 extraction	4.60	6.02
RSD	*1.19*	*2.64*
Step 2 extraction	4.94	3.96
RSD	*7.10*	*0.71*
Step 3 extraction	0.37	0.31
RSD	*10.60*	*8.49*
Residual extraction	<LoD	<LoD
RSD		
Summation	9.91	10.29
*RSD	*3.61*	*1.59*
Total digest	10.20	
RSD	*9.75*	

Table 3.5: Extraction of equilibrated Be (mg kg^{-1} dry weight) using modified (C 1) and method stipulated (C 2) soil : solution ratios. Mean and RSD (%) from triplicate samples shown. *RSD of $\sqrt{\Sigma\sigma^{2}}$

	Soil C 1	Soil C 2
Step 1 extraction	46.42	58.50
RSD	*1.19*	*2.64*
Step 2 extraction	49.85	38.49
RSD	*7.10*	*0.71*
Step 3 extraction	3.73	3.01
RSD	*10.60*	*8.49*
Residual extraction	0	0

Table 3.6: Total Be extracted (%) using modified (C 1) and method stipulated (C 2) soil:solution ratios. Mean and RSD (%) from triplicate samples shown

3.3.3.2. The use of stable beryllium as a proxy for [7]Be in sequential extraction investigations

The challenges of investigating the behaviour of natural [7]Be fallout in soils mean that it would be convenient to be able to use stable Be as a proxy for [7]Be in laboratory experiments. The sequential extraction data obtained for soils equilibrated with stable Be and [7]Be fallout offers an opportunity to assess whether this could be a meaningful approach. Chemically, both isotopes will behave in the same manner, but the concentrations used here were many orders of magnitude different which may affect their sorption behaviour owing to the effects of concentration on speciation and the relative availability of binding sites. Table 3.3 demonstrates the extraction of approximately 27 % of the total extracted [7]Be in step 1 for soil C. This is in contrast to stable Be data, where 46.4 % of the Be was extracted in this step for the same soil (Table 3.6). Given that equilibrated soils were aged for the equivalent of one [7]Be half-life,

differences in extraction values were likely to be the result of the high concentration used (1 mg L^{-1}). These initial data show the potential to overestimate ^{7}Be association with the exchangeable fraction when using stable Be as a proxy at relatively high concentrations.

3.4. Conclusion and recommendations

Investigating the geochemical behaviour of natural ^{7}Be fallout using sequential extractions is challenging owing to often low soil inventories and a short half-life, which combine to increase analytical uncertainties for gamma spectrometry. Given the need for typical count times of 24 hours, a method for pre-treating samples prior to gamma detection is required to maximise counts and produce robust data with regard to ^{7}Be phase association.

Directly analysing solid samples following extraction steps returned high analytical uncertainties when used with soils with a low-mid activity concentration (i.e. 30 Bq kg^{-1}). Maintaining sample geometry in-keeping with the calibration standard geometry following centrifugation was also problematic and may have further influenced analytical uncertainties. Coprecipitation of ^{7}Be from extract solutions using metal oxyhydroxides provided a method by which to preconcentrate ^{7}Be from large volumes of solution producing a thin source geometry for gamma detection. Preconcentration of ^{7}Be in extract solution from individual samples returned analytical uncertainties in the region of 30 %, thus, hindering comparison of step extraction values. By preconcentrating ^{7}Be from combined triplicate extracts uncertainties were sufficiently reduced (RSD (2σ) ~10 % where extract activity > 40 % of total activity) to allow distinction between step concentrations and detection of ^{7}Be in the third step extract.

Preconcentration of ^{7}Be extracted from large sample masses during sequential extraction experiments is, therefore, recommended. Check summations undertaken within this study provided activities that were within uncertainty of total activities providing confidence in ^{7}Be recovery throughout the procedure. Data obtained from background Be analyses showed good reproducibility within step extract triplicates (RSD < 1 %).

Sequential extraction with equilibrated Be demonstrated that by modifying the soil:solution ratio, data were not directly comparable to those obtained using standard BCR extraction ratios which may have been the result of redistribution of Be mobilised in the first step to subsequent soil phases. Soils equilibrated with stable Be at a solution concentration of 1 mg L^{-1} exhibited greater Be association with the exchangeable phase than soils exposed to ^{7}Be fallout. This was likely to reflect the difference in Be concentration used in comparison to natural fallout ^{7}Be. Stable Be as a proxy for ^{7}Be in sorption investigations concerning geochemical association should, therefore, be used with caution.

Chapter 4. Physicochemical behaviour of ^{7}Be in agricultural soils

4.1. Introduction

Recent concerns regarding erosion estimates determined from the use of ^{137}Cs have been put forward by Parsons and Foster (2011) owing to a lack of data to support the major assumptions surrounding fallout radionuclide (FRN) use in tracing studies. In particular, the use of FRNs tracers assumes that upon fallout, adsorption to soil particles is rapid and irreversible. Parsons and Foster (2011) have raised important questions surrounding this assumption regarding the use of ^{137}Cs under some environmental conditions. In comparison to the use of ^{137}Cs as a tracer, ^{7}Be is in the early stages of development with regard to its employment across a broad range of applications. ^{7}Be offers a complimentary means to estimate hillslope soil redistribution at the event-scale (Blake et al., 1999; Sepulveda et al., 2008) or across wet seasons (Schuller et al., 2010; Walling et al., 2009) and can also be used in combination with ^{137}Cs and ^{210}Pb to determine sediment sources (Burch et al., 1988; Wallbrink & Murray, 1993; Yang et al., 2006) , floodplain storage (Blake et al., 2002) and transport distances and residence times (Matisoff et al., 2005; Whiting et al., 2005). The continuous natural production and delivery of ^{7}Be also offers a distinct advantage.

^{7}Be could, therefore, be used as a decision support tool at the catchment-scale by contributing to the construction of sediment budgets which in turn can be used to inform management plans by predicting responses to mitigating strategies (Walling & Collins, 2008). Thus, the potential economic benefits associated with the use of ^{7}Be as a catchment-scale tracer are highlighted.

To achieve the full potential of ^{7}Be as a catchment-scale sediment tracer, greater knowledge of its geochemical behaviour is required to satisfy the key assumption for its use (Mabit *et al.*, 2008a). Currently, detailed investigation into ^{7}Be geochemical behaviour in a range of soils is lacking.

Rapid adsorption upon fallout is, largely, assumed from the occurrence of shallow depth profiles displayed in soils (Blake *et al.*, 1999; Wallbrink & Murray, 1996) and high partition coefficient values (K_d) (Hawley et al., 1986) but limited data exists with regard to adsorption rates at fine temporal scales. Also, knowledge of the vertical distribution of ^{7}Be in soils is crucial to enable erosion estimation although the factors controlling distributions have been, largely, unexplored. Studies investigating vertical distributions in conjunction with geochemical behaviour under semi-controlled conditions are required to elucidate physical and chemical controls upon depth profile behaviour.

To underpin the use of ^{7}Be at the catchment-scale requires data to demonstrate that the tracer will remain adsorbed to soil particles during transport and storage under varying environmental conditions from the field to the wider catchment. Knowledge of ^{7}Be partitioning within soil particles can provide an indication of the potential for ^{7}Be mobility. Although there is some indication of ^{7}Be affinity with organic and Fe/Mn phases (Bai et al., 1997; Blake et al., 2009), knowledge of ^{7}Be partitioning behaviour, both in terms of temporal dynamics and geochemical associations in a range of soil types, is generally poor.

Against this background, this research aimed to investigate the adsorption behaviour of ^{7}Be in four agricultural soils and the implications of this behaviour upon the use of ^{7}Be as a tracer at field and catchment scales. This has been achieved via the following research objectives:

i)   Quantifying adsorption rates following fallout using stable Be in batch experiments

ii)   Assessing variation in the vertical distribution of [7]Be between soil types by sampling fine depth increments of soils exposed to natural [7]Be fallout

iii)   Investigating the potential for soil-adsorbed [7]Be to become mobile in an artificial rainwater solution using batch experiments i.e. considering tracer stability under common, oxic field conditions

iv)   Investigating the association of [7]Be to operationally-defined soil fractions using the optimised BCR three-step sequential extraction scheme to consider tracer stability under conditions of changing salinity, oxidation status and pH

v)   Assessing the potential effects of residence time on adsorption and tracer stability.

4.2. Methodology

4.2.1. Experimental soil sampling and characterisation

4.2.1.1. Field sampling

Soil samples were taken from four cultivated agricultural field sites in Devon, UK (soils A – D). Soil associations were Yeollandpark (Soil A) (0.05 % of England and Wales landmass), Hallsworth (soil B) (0.2 % of England and Wales landmass), Denbigh (soil C) (~ 3 % of England and Wales landmass) and Bridgnorth (soil D) (0.44 % of England and Wales landmass) (NSRI, 2008). Surface samples (< 20 mm depth) of bare, cultivated soil at each location were taken systematically in a grid to achieve representative along and cross-profile

selection from an undulating slope following sampling protocols described by Pennock and Appleby (2002b). Samples were bulked in 10 L buckets (3 x 10 L for each site) prior to being homogenised in the laboratory. At each sample location, soil compaction (to a depth of 50 mm) was assessed using a cone penetrometer and 9 soil cores (UK-style Pitman Corer) were taken for bulk density measurements (Rowell, 1994) to ensure experimental soil profiles reconstructed in the laboratory were packed to equivalent field density (Section 4.2.3.1).

4.2.1.2. Soil preparation

The bulk soil samples were partially air-dried prior to homogenising to aid the mixing process. For each field location, the contents of the 10 L buckets were placed into a separate large plastic container and mixed by hand. Three sub-samples (approximately one third of the bucket sample) were then taken from each of the mixing containers and bulked and further homogenised by hand. This step was repeated three times until the entire soil sample for that particular site had been homogenised. During the mixing process larger gravels (> 10 mm) and organic debris were removed. A sub-sample of 200 g of each soil type was removed following homogenisation and sealed in a plastic bag and refrigerated (< 5 °C). These sub samples were used to characterise the soils for pH, Total Organic Carbon (TOC) and Inorganic Carbon (IC), Cation Exchange Capacity (CEC) and particle size.

4.2.1.3. Soil characterisation

Soil pH was determined using a Meterlab PHM201 Radiometer with 10 g of soil dispersed in ultra-pure water at a soil-solution ratio of 1:2.5. Total Organic Carbon (TOC) was calculated from Total Carbon (TC) and Inorganic Carbon (IC) measurements carried out using a Skalar Primacs SLC Analyser (Skalar UK Ltd). Cation Exchange Capacity (CEC) was determined by leaching 5 g of soil with ammonium acetate (1M) as outlined in Rowell (1994). Background metal concentrations for each soil type were characterised using ICP-OES (Varian 725-ES, Varian, Australia) following microwave assisted digestion (MARS 5 microwave accelerated reaction system, CEM (microwave technology) Ltd, UK) of triplicate soil samples (Hassan et al., 2007).

Prior to particle size analysis by laser granulometry, wet oxidation was carried out to remove organic matter based on methods outlined in Pieri et al. (2006). Particle size analysis for > 63 μm and < 63 μm fractions was determined using a Malvern Mastersizer 2000 (Malvern, UK) with Hydro-G in compliance with ISO 13320. Optimal particle dispersion was achieved using sodium hexametaphosphate (0.2 %) in solution and 90 seconds of ultrasonication during analysis. Pump and stirrer speeds were 2250 and 800 rpm respectively. Each sub-sample was analysed for 30 seconds using red and blue laser and this was repeated to produce five data sets for each sub-sample. Software used an enhanced general model for non-spherical particles with an assumed refractive index of 1.53 and initial light adsorption value of 0.01.

In addition to laser granulometry, clay soil fractions were calculated using settling columns following BS 1377. Soil samples (18 g of < 63 μm fraction) were added to 500 mL columns containing distilled water and 25 mL dispersing

agent (33 g sodium hexametaphosphate and 7 g sodium carbonate per litre). Analysis was undertaken in triplicate for each soil sample. Columns were placed in a water bath and left to stand for 24 hours to allow soils to settle (Figure 4.1). Solution was kept at a constant 23 (± 0.2) °C throughout the investigation. After 24 hours each column was inverted several times to thoroughly mix the sample and then allowed to settle. After 7 hours 26 minutes (corresponding to the settling time of > 2 µm fractions) 5 mL was extracted from each column using a calibrated pipette and placed into vials of known mass. Vials were placed in an oven at 105 °C for drying before being reweighed to calculate mass of remaining solid. Mass of clay in each 500 mL column was calculated as:

$$M_1 \times (500 \, / \, V_1) \hspace{4cm} (4.1)$$

Where M_1 is the mass of oven dried solid (g) and V_1 is the volume of the calibrated pipette (mL).

The percentage clay in each sample could then be calculated as:

$$\left(M_2 - M_3\right) \, / \, \left(M_4\right) \times 100 \hspace{3cm} (4.2)$$

Where M_2 is the mass of clay in 500 mL (g), M_3 is the mass of dispersant in 500 mL (g) and M_4 is the total sample mass (g).

The percentage silt in each experimental soil could then be calculated by subtracting the percentage of clay (column) from the percentage of < 63 µm determined using the Mastersizer.

Figure 4.1: Settling columns for determination of clay fractions

4.2.2. Equilibration of soil with stable Be for determination of adsorption rates

To quantify adsorption rates following fallout, samples of soil C were equilibrated with a solution of stable Be at a concentration of 1mg L^{-1} using a soil:solution ratio of 1:10. This concentration enabled quantification of Be sorption above natural background levels and is within the CEC of all soils used. $BeCl_2$ salt (99 %) (Sigma-Aldrich, UK) was dissolved in ultra-pure water to obtain the desired concentration. The pH of the solution was buffered to 5.6 (natural rainwater pH) using NaOH. To determine equilibration time, sorption experiments were carried out in triplicate over the following times: 0.1, 0.5, 1, 4, 12, 24, 48, 72, 120, 168 and 240 hours. At the given time the pH of the solution was checked and the sample centrifuged at 4000 g for 20 minutes. The supernatant was then analysed using ICP-OES to determine the Be concentration remaining in solution. The concentration in the solution was then

compared to the initial Be concentration of the solution to determine adsorption. Finally, the vessels were rinsed of soil and solution and acid washed with a known volume of 3 % HCl by shaking overnight on an end-over-end shaker. Analysis of the rinse solution was carried out to permit any adsorption to vessel walls to be accounted for (adsorption to vessel was < 1 %). Partition coefficient values (K_d) were determined from filtered (< 0.22 μm) sub-samples of the supernatant from the 240 hour equilibration and were calculated as:

$$\frac{[Be]_P}{[Be]_S \, [SPM]} \qquad (4.3)$$

Where $[Be]_P = [Be]_{Total} - [Be]_S$, (mg L^{-1}), $[Be]_{Total}$ and $[Be]_S$ are the measured dissolved Be concentrations (mg L^{-1}) and $[SPM]$ is the concentration of suspended particulate matter (kg L^{-1}).

4.2.3. Investigating [7]Be depth distribution in experimental soils

4.2.3.1. Exposure of soil to [7]Be fallout

Soils A, B C and D were packed into trays (365 × 265 × 70 mm) at densities representative of those found in the field. Because dry bulk density was determined from the cores, the gravimetric soil moisture in the air-dried samples was calculated from oven drying sub-samples at 105 °C until a constant mass was achieved (Rowell, 1994). The trays could then be packed with representative densities by accounting for the moisture in air dried samples. Densities were representative of cultivated areas which had been allowed to settle for a period of 3-5 months. Twelve soil trays were prepared, three for each soil type. Once packed into trays, soils were left to settle for 48 hours prior to being exposed to natural rainfall. The exposure site was located on a flat

roofing area, four storeys above ground level where little rain shadow from buildings was likely to occur. A purpose-built dexion stand was used to hold the sample trays and rainfall sampling equipment (Figure 4.2). Total (wet and dry) fallout was determined by precipitation sampling following methods outlined in Wallbrink and Murray (1994). Rainfall was collected in two 3 L polypropylene bottles using 0.05 m^2 funnels which were placed above the surface of the soils to avoid surface splash contamination. Prior to deployment 2 mL HCl was added to the bottle to prevent loss of [7]Be by adsorption to container walls.

Figure 4.2: Soil trays and rainfall sampler in place on the flat roof

[7]Be activity concentration in rainwater was determined following the method of Short et al. (2007). Rainfall was analysed for [7]Be after each major event or several small events and a cumulative soil inventory was developed. The full method is detailed in Chapter 2.

4.2.3.2. Incremental depth sampling of exposed soils

A purpose-built depth increment sampler (Figure 4.3) enabled soil profile increments of approximately 2 mm to be sampled. Once a sufficient [7]Be

inventory was estimated to be in place, soil blocks were cut to the size of the sampler *in situ* and then frozen. The sample area was deliberately less than the total tray area to avoid the tray boundaries being sampled, thus, eliminating any edge effects. Frozen soil blocks were transferred to the soil sampler and allowed to thaw and dry before sampling. The screws visible in Figure 4.3 control the movement of a base plate and the screws were calibrated so that a given number of turns raised the base plate by 2 mm. The soil increment could then be removed by running a scraper along the level edges of the sampler as shown.

Figure 4.3: Depth increment sampler

4.2.3.3. Soil sample processing for gamma spectrometry

Soils were processed following the methods of Pennock and Appleby (2002a). Upon sampling, samples were air-dried (< 40 °C) and ground by hand using a pestle and mortar. Samples were then sieved to remove the material > 2 mm. Retaining organic material was not necessary for the purpose of this study since

any plant growth was regularly removed during soil exposure to avoid ^{7}Be interception. Both the > 2 mm and < 2 mm fractions were weighed. A sub-sample of the < 2 mm fraction was then oven dried at 105 °C to provide a dry-weight correction value. The remaining air-dried < 2 mm soil was then packed and sealed into either 50 mm or 90 mm Petri dishes for gamma counting.

4.2.3.4. Gamma Spectrometry

Analysis was carried out using a high purity germanium (HPGe) gamma detector (GEM-FX8530-S Planar, Ortec, UK) under ISO 9001:2008-certification in the Plymouth University Consolidated Radioisotope Facility (CORiF). Sample calibration was carried out using a standard of the same geometry. Standards were prepared using QCY58b mixed standard solution (G E Healthcare, Amersham, UK) which was distributed in a mineral matrix (or as a thin-source Gelman 0.45 μm filter paper for filtered samples). Detector efficiency for ^{7}Be (477.6 keV) was determined by interpolation between the efficiency values of ^{137}Cs (661.7 keV) and ^{113}Sn (391.7 keV). Sample counts were corrected for background emission, geometry efficiency and decay. All values were decay corrected to the day of sampling and reported as activity (Bq kg^{-1}). Laboratory analytical quality control procedures were carried out in accordance with Wallbrink et al. (2002).

4.2.4. Investigating stability of adsorbed ^{7}Be in artificial rainwater solution

^{7}Be in experimental soils was subjected to extraction using an artificial rainwater (ultra-pure water) solution following the method applied in Chapter 3. Samples

of 20 g were extracted in 400 mL ultra-pure water for 16 hours on a reciprocating shaker. Following centrifugation (Sorvall Legend RT, Sorvall, UK) at 3000 g for 20 minutes, ^{7}Be in the supernatant was preconcentrated using MnO$_2$ (Short *et al.*, 2007). Extracted ^{7}Be was then analysed as a thin source. The remaining solid residue was placed on the gamma detector to determine a mass balance with regard to the total activity in the sample prior to extraction. To assess adsorption to vessel walls, vessels were rinsed of soil and washed in 3 % HCl by shaking overnight. The rinse solution was then preconcentrated as above and the thin source analysed for ^{7}Be. For all laboratory studies, vessels were cleaned using 10 % v/v HCl prior to use. Ultra-pure water was obtained from a Milli pore Mill Q Plus 185 system. All reagents were of analytical grade.

4.2.5. Investigating the association of ^{7}Be to operationally-defined soil fractions

The optimised BCR three-step sequential extraction procedure (Pueyo et al., 2001) was employed to investigate the partitioning of ^{7}Be between the operationally-defined exchangeable/carbonate-bound, reducible, oxidisable and residual soil fractions. The full method for carrying out sequential extractions with experimental soils is detailed in Chapter 3. The results reported in this chapter are those obtained using the adjusted method whereby triplicate extracts are combined and preconcentrated prior to analysis.

4.2.6. Investigating the effect of residence time upon Be partitioning in soil

Samples of soil C were equilibrated with 1 mg L^{-1} stable Be for an equilibration time established from the procedure outlined in section 4.2.2. Following

centrifugation samples were taken through the BCR three-step sequential extraction procedure. Separate triplicate sets were aged for 53 days following centrifugation by incubating at a constant temperature of 20 °C. Samples were kept moist during the incubation period by maintaining the post-centrifuged sample mass with the addition of ultra-pure water. Following the aging process sequential extractions were carried out as above. To correct for the extraction of background soil Be, samples which had not been equilibrated with Be were also taken through the extraction steps. Sequential extractions were undertaken using both control soil:solution ratios (those stipulated in the BCR procedure) and experimental ratios (those applied in this study). Details of the effect of modifying the ratio are given in Chapter 3. The results reported in this chapter focus upon those obtained using the modified ratio to enable comparison to extractions with natural [7]Be fallout.

4.3. Results

4.3.1. Experimental soil characteristics

Characteristics of the experimental soils are given in Tables 4.1 and 4.2. pH values are similar for Soils A, B and D at around 6.5, commonly found at agricultural sites owing to this being a favourable pH for CEC (Sparks, 1995; White, 2006). CEC values for soil B are low at 4.85. This soil type has the highest percentage of clay and, therefore, may be expected to have a higher CEC owing to the contribution of clay particles to the negative charge at soil particle surfaces. However, it is perhaps a high kaolinite content which contributes to a low surface charge at this pH owing to limited isomorphous substitution within the mineral lattice structure (White, 2006). Kaolinite will

display a pH dependent negative surface charge at high pH (> 9), thus, CEC will increase when this pH has been achieved (White, 2006). This is unlikely given the pH buffering capacity of most agricultural soils owing to the release of H^+ from hydroxyl groups serving to buffer a rise in pH (Sparks, 1995). Organic matter can also contribute to CEC owing to negative surface charges resulting from the dissociation of carboxyl groups in humic and fulvic acids. The low TOC in Soil B is, therefore, likely to be another factor contributing to low CEC. The higher CEC value obtained for soil A is likely to be a reflection of the type of clay minerals present in this soil given that TOC values between soils A, C and D are similar. Experimental soil textures (Figure 4.4) correspond to clay loam (soil B), sandy silt loam (soils A and C) and loamy sand (soil D) classes.
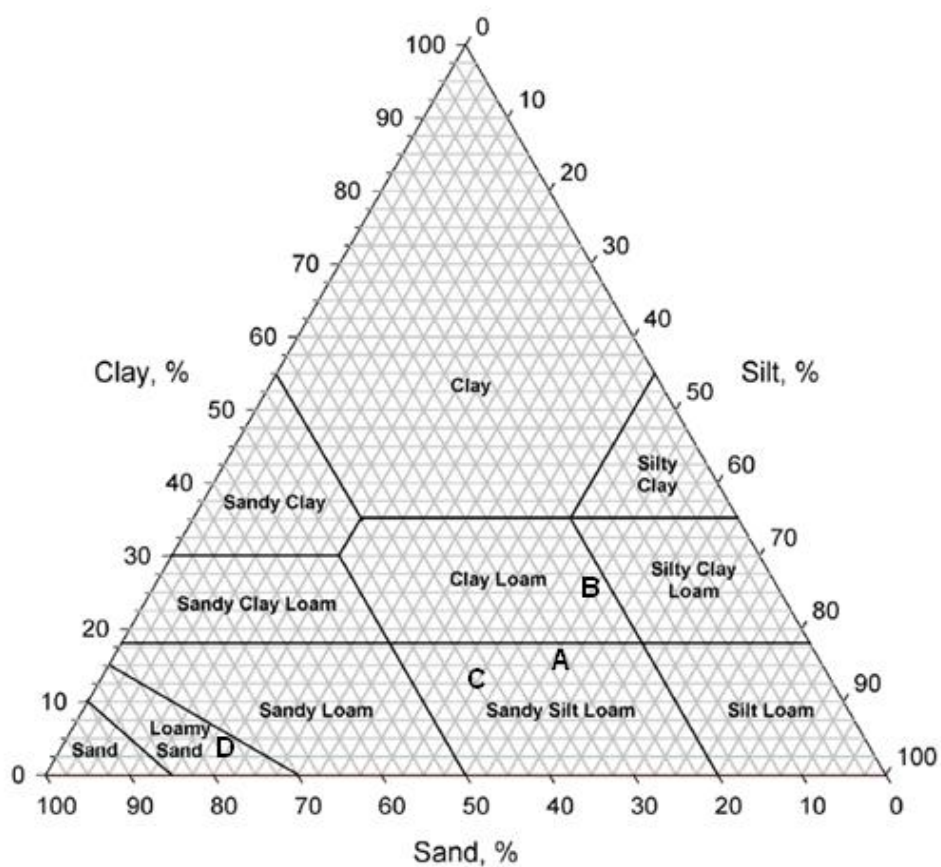
Figure 4.4: Experimental soil textures according to the Soil Survey of England and Wales (White, 2006)

	pH	CEC (cmol$_c$ kg^{-1})	Sand (%)	Silt (%)	Clay (%)	TOC (%)	IC (%)
Soil A	6.62	10.50	30.20	50.80	19.00	3.02	<LoD
s	*0.18*	*0.12*	*1.00*	*1.20*	*1.08*	*0.01*	
Soil B	6.52	4.85	23.70	51.20	25.10	1.49	<LoD
s	*0.12*	*0.04*	*1.00*	*1.80*	*0.40*	*0.04*	
Soil C	5.68	6.82	43.00	40.90	16.10	2.32	<LoD
s	*0.10*	*0.09*	*1.00*	*1.74*	*0.89*	*0.02*	
Soil D	6.55	8.06	76.30	18.70	5.00	2.78	<LoD
s	*0.11*	*0.08*	*1.11*	*1.56*	*0.19*	*0.26*	

Table 4.1: Key characteristics of experimental soils. Mean and standard deviation from triplicate samples shown

	Be	Ca	Fe	K	Mg	Mn
Soil A	0.673	2142	38400	2670	1300	2160
s	*0.002*	*129*	*1800*	*547*	*94*	*232*
Soil B	0.785	828	55300	2380	1000	863
s	*0.104*	*10*	*953*	*916*	*141*	*233*
Soil C	0.687	1243	32000	3930	1230	1400
s	*0.009*	*43*	*3000*	*199*	*60*	*56*
Soil D	1.34	1432	13100	4520	1460	220
s	*0.05*	*177*	*1170*	*99*	*112*	*22*

Table 4.2: Background elements in experimental soils (mg kg^{-1} dry weight). Mean and standard deviation from triplicate samples shown

4.3.2. Determination of Be adsorption time in experimental soil

Figure 4.5 shows adsorption of Be over experimental time intervals at a solution concentration of 1 mg L^{-1}. Equilibrium was achieved after 120 hours for all concentrations. Data show rapid adsorption of Be with > 93 % of solution Be sorbed to soil particles after 0.1 hours of contact. Partition coefficient values (K_d) calculated after 240 hours were 1.6 x 10^3 L kg^{-1}.

4.3.3. [7]Be Depth profiles in experimental soil profiles

[7]Be depth profiles in the experimental soils (Figures 4.6a - 4.6d) demonstrate concentration of [7]Be in the uppermost surface layers (< 20 mm) with greatest activity found within the top 2 mm of the soil profile. Activity rapidly decreases with depth agreeing with profile forms reported elsewhere (Blake *et al.*, 1999; Schuller *et al.*, 2010; Wallbrink & Murray, 1996). Values of the relaxation mass depth (h_0) are variable between the soils ranging from 1.75 kg m^{-2} (negative) in soil B (Figure 4.6b) to 3.97 kg m^{-2} (negative) in soil C (Figure 4.6c).
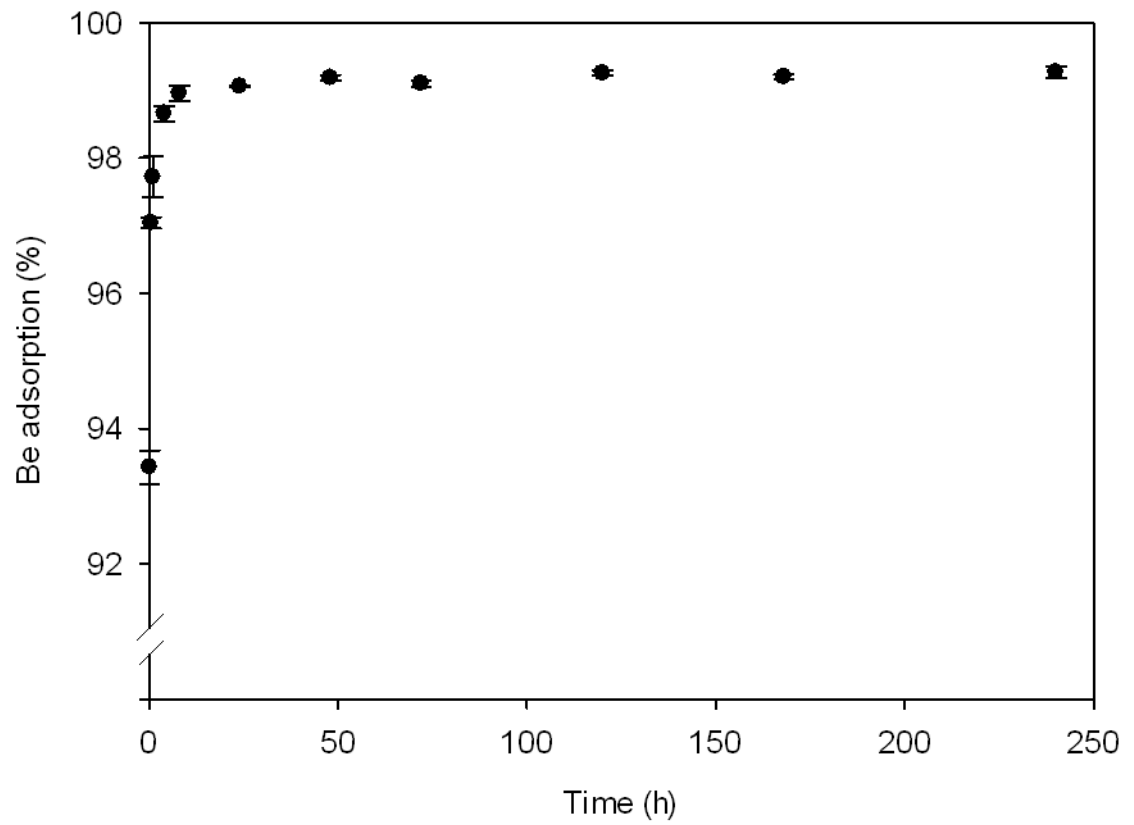
Figure 4.5: Be adsorption rates at experimental time intervals. Mean and RSD (%) from triplicate samples shown
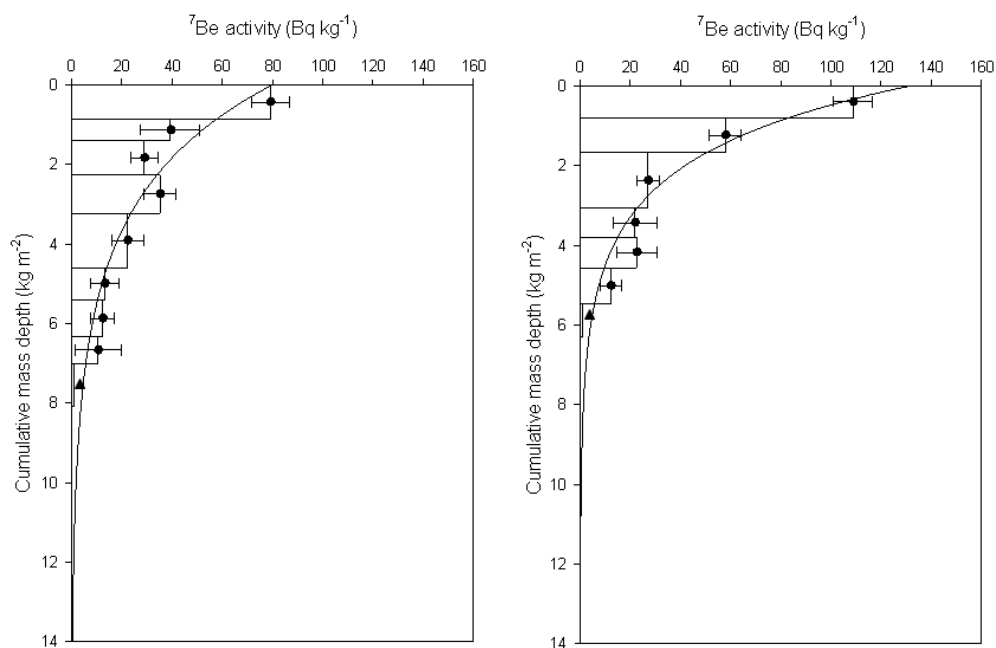
Figures 4.6a and 4.6b
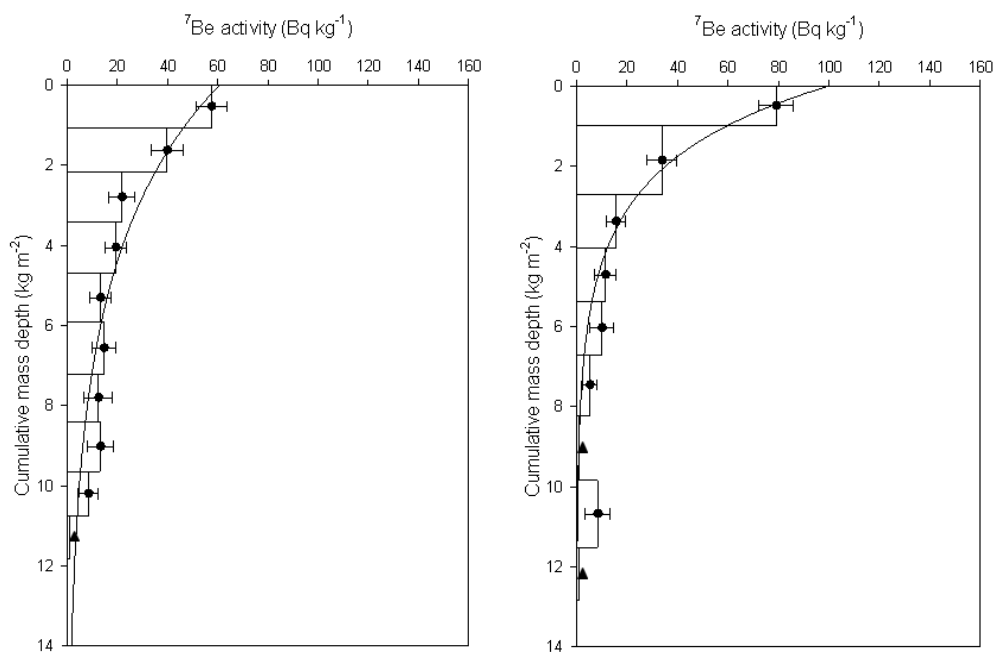
Figures 4.6c and 4.6d

Figure 4.6a: Soil A depth distribution. h_0 = 2.65 kg m^{-2} (negative)
Figure 4.6b: Soil B depth distribution. h_0 = 1.75 kg m^{-2} (negative)
Figure 4.6c: Soil C depth distribution. h_0 = 3.97 kg m^{-2} (negative)
Figure 4.6d: Soil D depth distribution. h_0 = 1.92 kg m^{-2} (negative)
Analytical uncertainties shown as 2σ
▲ indicates depth of Minimum Detectable Activity (MDA)

4.3.4. Stability of adsorbed ^{7}Be in artificial rainwater solution

Extractions for all soils using artificial rainwater were below Minimum Detectable Activity (MDA) (MDA range < 1.89 - < 2.4 Bq kg^{-1}). The concentrations in the soils prior to extraction were between 45 (± 6) Bq kg^{-1} and 68 (± 7) Bq kg^{-1}. Therefore, > 3.5 - 4.3 % of the sample ^{7}Be activities would have to have been extracted to reach the MDA. Results, therefore, demonstrate that < 4.3 % of sample ^{7}Be was extracted from these soils. Analyses of the acid wash solutions were also below detectable levels. ^{7}Be activity in the solid material following extraction was within uncertainty of the total activity. During extraction solution pH values decreased (from those given in Table 4.1) to around 4.5 for each soil, demonstrating ^{7}Be stability in weak acid solution.

	Soil A	Soil B	Soil C	Soil D
Total activity Bq kg^{-1}	67.49	56.24	54.02	44.56
2σ	*7.40*	*7.37*	*7.30*	*5.49*
Extract activity Bq kg^{-1}	< 2.43	< 2.10	< 2.28	< 1.89
Solid post-extraction Bq kg^{-1}	63.33	62.81	50.80	45.90
2σ	*5.52*	*6.56*	*6.79*	*6.01*
Vessel adsorption Bq kg^{-1}	< 3.00	< 2.79	< 3.09	< 2.80

Table 4.3: ^{7}Be extractions in an artificial rainwater solution. Analytical uncertainties shown as 2σ

4.3.5. Association of ^{7}Be to operationally-defined soil fractions

All extractable ^{7}Be is confined to steps 1-3 of the optimised BCR three-step sequential extraction procedure (Table 4.4) identifying association with the exchangeable, reducible and oxidisable fractions. Across all experimental soils 27-37% of ^{7}Be is associated with the exchangeable fraction with 42-62% of extracted ^{7}Be associated with the reducible fraction (Figure 4.7). The majority of ^{7}Be is, therefore, associated with the exchangeable and reducible fractions whereby 87%, 79%, 89% and 93% of total extracted ^{7}Be is associated with these two fractions in soils A-D respectively.

	Soil A	Soil B	Soil C	Soil D
Total Activity Bq kg^{-1}	45.94	108.83	57.42	79.04
2σ	*4.21*	*7.87*	*6.16*	*6.06*
Total extracted Bq kg^{-1}	41.48	121.44	47.97	74.18
$\sqrt{\Sigma 2\sigma^2}$	*4.74*	*8.04*	*5.15*	*5.82*
Step 1 Extraction Bq kg^{-1}	12.76	45.18	13.12	24.34
2σ	*3.09*	*4.66*	*2.80*	*3.39*
% of total extracted	30.76	37.20	27.35	32.81
Step 2 Extraction Bq kg^{-1}	23.37	50.50	29.55	44.59
2σ	*2.94*	*4.99*	*3.36*	*4.09*
% of total extracted	56.34	41.59	61.60	60.11
Step 3 Extraction Bq kg^{-1}	5.35	25.76	5.30	5.25
2σ	*2.06*	*4.24*	*2.71*	*2.38*
% of total extracted	12.90	21.21	11.05	7.07
Step 4 Extraction Bq kg^{-1}	< 3.01	< 3.81	< 2.87	< 3.16

Table 4.4: Sequential extractions of ^{7}Be fallout. Total activity refers to the initial activity of the sample prior to extractions. Total extracted ^{7}Be is the summation of all extraction steps + residual. Analytical uncertainties shown as 2σ. Summation uncertainties calculated from $\sqrt{\Sigma 2\sigma^2}$
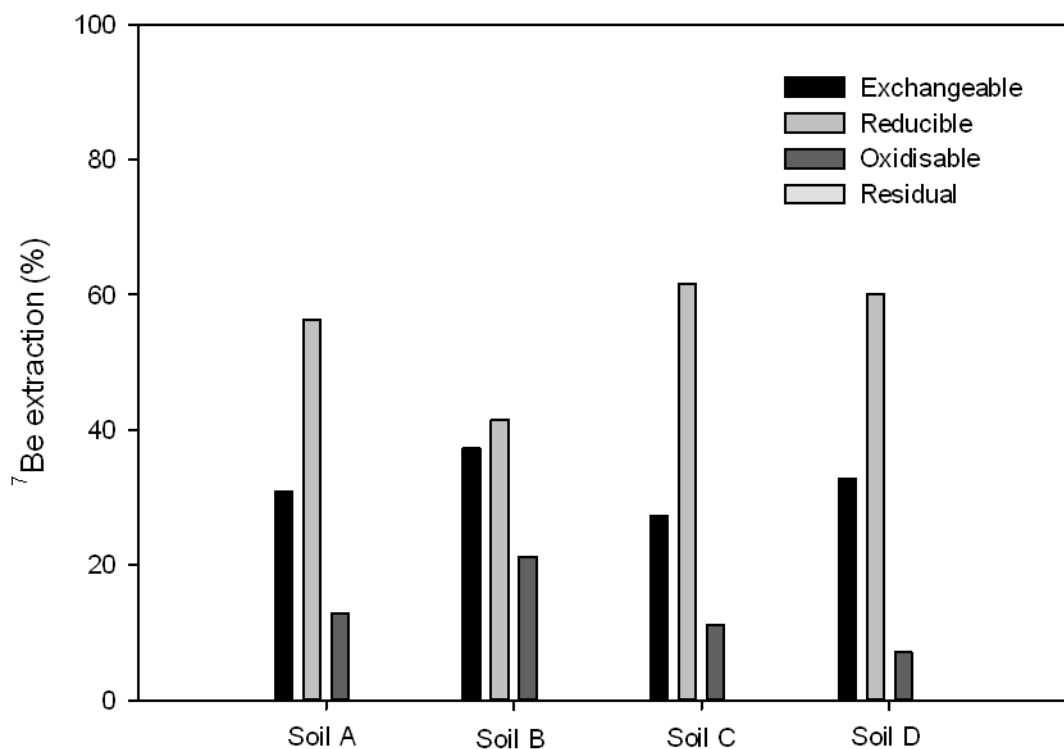
Figure 4.7: [7]Be sequential extractions as % of total [7]Be extracted

4.3.6. The effect of residence time upon Be partitioning in soil

Data obtained from stable Be extractions in both recently equilibrated (5 day) soil and soil aged for 53 days, are given in Table 4.5. As outlined in Chapter 3, extraction data are not directly comparable to those obtained using [7]Be fallout owing to the high concentrations of Be used in the investigation. However, these equilibrations can be used to begin to explore the effect of residence time upon Be partitioning. A greater proportion of extracted Be was associated with the weak acid soluble, exchangeable and carbonate-bound phase (step 1) in the 5 day sample compared to the aged sample. This corresponded to a greater association of Be with the reducible (step 2) fraction in the aged sample although it should be noted that 5 day and 53 day extractions for this step are within uncertainty.

	5 day	53 day
Step 1 extraction %	54.32	46.42
RSD	3.87	1.19
Step 2 extraction %	42.78	49.85
RSD	7.07	7.10
Step 3 extraction %	2.90	3.73
RSD	8.59	10.60
Residual extraction %	0	0

Table 4.5: Effect of residence time upon sequential extraction of Be. Mean and RSD (%) from triplicate samples shown

4.4. Discussion

The above results provide a basis from which to determine adsorption behaviour from the time of fallout and with increasing residence time in soils. Discussion will focus upon the implications of this behaviour for use of [7]Be as a tracer at the slope-scale to the catchment-scale.

4.4.1. [7]Be adsorption in cultivated soils

4.4.1.1. Adsorption rate

The rapid adsorption rate found using 1 mg L^{-1} Be supports the widely accepted adsorption behaviour of [7]Be based upon the occurrence of shallow depth profiles (Blake *et al.*, 1999; Schuller *et al.*, 2010; Wallbrink & Murray, 1996) and it is consistent with the assumption that [7]Be becomes rapidly adsorbed upon contact with soil particles following fallout. The K_d value of 1.6 x 10^3 L kg^{-1} is,

however, lower than those reported in literature which may reflect the high concentration of Be used in this study. This may also be attributed to variation in the methods and soil:solution ratios used in this study in comparison to those cited elsewhere, since choice of method can influence K_d estimation (U.S.EPA, 1999). For example, Olsen et al. (1986) reported field K_d values of 10^4 - 10^5 for freshwater systems at low suspended sediment concentrations (< 0.002 kg L^{-1}) and similarly, Dibb and Rice (1989) reported experimental K_d values of 10^5 at suspended sediment concentrations < 0.005 kg L^{-1} at pH > 6. An increase in suspended sediment concentrations has been shown to decrease K_d (Hawley *et al.*, 1986; You et al., 1989) although the use of a high solid:solution ratio in this investigation provided a closer representation of hillslope conditions where fallout ^{7}Be adsorption is likely to occur. Therefore, the adsorption rate of Be under these conditions strongly supports the fundamental requirement of rapid ^{7}Be adsorption upon fallout.

4.4.1.2. ^{7}Be depth distributions

The vertical distributions of ^{7}Be fallout in all experimental soils in this study are complimented by the adsorption rates demonstrated in soil C with greatest activity concentrations found in the uppermost 2 mm with no detectable activity at depths > 20 mm. Values of the relaxation mass depth (h_0) determined from the current profiles are in close agreement to those reported by Sepulveda et al. (2008), (3.4 kg m^{-2}), Schuller et al. (2006), (2.14 kg m^{-2}) and Schuller et al. (2010), (1.28-3.04 kg m^{-2}). Profiles exhibit some variation between soil types and given that ^{7}Be is not readily mobile in representative solutions of the experimental soils (section 4.3.4), variations in vertical distribution are likely to

be driven by physical processes. The profiles in Figures 4.6a - 4.6d have been developed under semi-controlled conditions with no plant growth or bioturbation and samples were taken in a laboratory setting, thus, reducing the influence of disturbance and sampling errors upon [7]Be vertical behaviour. Hydrological processes influenced by soil textural characteristics are, therefore, likely to contribute to the difference in values of h_0 between soil types. Direct assessment of infiltration behaviour was not undertaken here to avoid disturbance to soil profiles. Instead, discussion of profiles is supported by observation and knowledge of the Hydrology of Soil Type (HOST) classes (Boorman et al., 1995, cited in NSRI (2008)).

The shallow profile displayed in Soil B, the clay loam, implies a drainage control on the resulting depth profile which is supported by the general low permeability of these soils (NSRI., 2008) and observed ponding at the soil surface following events. This behaviour is reflected in the high concentration of [7]Be in the upper layer and steep decline to around 12 mm depth producing the lowest h_0 value of 1.75 kg m^{-2} (negative) (Figure 4.6b). This is in contrast to the Soil C distribution, which, being a free draining soil type (NSRI., 2008), displays greater depth penetration and is characterised by a longer and less abrupt profile with a distinct 'tail' producing an h_0 value of 3.97 kg m^{-2} (negative) (Figure 4.6c). It is possible that the greater depth distribution is associated with the rapid transport of rainwater and, thus, [7]Be through preferential flow pathways such as macropores. This may have been facilitated by the higher proportion of > 2mm material in this soil (22 % of bulk mass) in comparison to soils A and B (9 % and 2 % respectively). Desiccation cracks were also evident in soils (particularly Soil A) following dry periods which may have influenced [7]Be transport.

Schimmack et al. (1994) demonstrated an increased depth distribution of ^{137}Cs in a sandy podsol with increased rainfall intensity which was likely to be the result of increased macroporous flow reducing radionuclide sorption in uppermost surface layers. This is supported by the findings of Bundt et al. (2000) where the activities of fallout ^{210}Pb and ^{137}Cs were found to be higher in the soil matrix associated with preferential flow pathways of forest soil. Other studies have demonstrated the effect of preferential flow upon rapid migration of adsorbing tracers through soil profiles (Kung et al., 2000) and the role of macropore continuity upon solute distributions (Allaire-Leung et al., 2000).

Soils A and D also demonstrate the potential influence of macroporous flow with Soil A showing steep decline in ^{7}Be activity followed by an increase in concentration at around 8 mm depth (3.2 kg m^{-2} mass depth) (Figure 4.6a). Similarly, Soil D shows recurring ^{7}Be activity at a depth of approximately 16 mm (11.5 kg m^{-2} mass depth) (Figure 4.6d) which may be the result of migration through preferential flow pathways facilitated by the coarse texture of this soil (37 % of bulk mass > 2 mm). Aside from preferential flow influencing ^{7}Be transport by reducing contact with the adsorbing particle surface, the transport and accumulation of fine fractions should also be considered since ^{7}Be is more likely to be associated with fine fractions, particularly in the < 20 μm range (Blake *et al.*, 2009, ; Chapter 5). However, particle size analysis of profile sections did not support this, therefore, suggesting migration in solution via preferential flow.

Given the potential for variability within a single profile owing to preferential flow, spatial variation of soil hydraulic properties within a field site should be considered when assessing radionuclide depth distributions (Alletto & Coquet, 2009; Strudley et al., 2008) and this is of particular importance when

characterising h_0 during erosion studies. For accurate determination in the field, therefore, a series of profiles should be taken over a spatially representative scale. The variation in profiles between soil types places further emphasis on the importance of on-site field sampling to determine values of h_0. Variation in h_0 over temporal scales has not been considered in this study and such knowledge is of value when considering the application of ^{7}Be as a tracer over an extended time period (Schuller et al., 2010; Walling et al., 2009).

4.4.2. Evaluating the conservative behaviour of ^{7}Be; implications for its use as a catchment-scale tracer

4.4.2.1. The potential for ^{7}Be mobility under common, oxic field conditions

No detectable ^{7}Be was found to be extracted by the artificial rainwater solution (pH 5.6) in all experimental soils (Table 4.3). ^{7}Be mobility in representative field solutions of the experimental soils is, therefore, minimal providing confidence in the use of ^{7}Be as a tracer under common, oxic field conditions. On the basis of this behaviour there is potential for robust estimation of soil erosion at the slope-scale using ^{7}Be (Blake *et al.*, 1999; Schuller *et al.*, 2006; Sepulveda *et al.*, 2008; Wilson et al., 2003). However, one area of uncertainty lies in the adsorption dynamics after runoff initiation. Rainfall simulation experiments carried out by Dalgleish and Foster (1996) showed that under saturated conditions, ^{137}Cs was not bound to soil at the point of raindrop impact and it is likely that the same issue could occur for ^{7}Be under certain conditions. Critically, a significant proportion of the pre-event inventory needs to be in place prior to surface runoff initiation and experimentation is required (c.f. Dalgleish & Foster, 1996) to explore the potential impact of this on erosion estimates.

4.4.2.2. The potential for ^{7}Be mobility beyond the slope boundary

To provide confidence in the application of ^{7}Be as a tracer at wider spatial scales, investigation into the conservative behaviour of the tracer beyond the slope boundary is required. Walling and Collins (2008) identify the importance of quantifying sediment sinks (in-field, field to channel, floodplain and channel bed deposition zones) as a crucial component of a sediment budget with radionuclide tracers enabling high resolution estimates of storage. Owing to the possibility of changing physical and chemical parameters in storage zones it, therefore, becomes necessary to assess the adsorption behaviour of ^{7}Be under varying conditions.

Sequential extractions using the optimised BCR three-step procedure were carried out to determine the potential for ^{7}Be to remain adsorbed to soil particles under changing environmental parameters. The extractions identified that the majority of ^{7}Be in experimental soils was associated with the exchangeable and reducible fractions with a greater affinity for the latter (Table 4.4). This indicates the potential for ^{7}Be mobility with changing environmental conditions and, therefore, discussion should focus upon the implications of these phase associations in the context of using ^{7}Be as a tracer at the catchment-scale. Numerous investigations have employed ^{7}Be as a tracer at a wider spatial scale, demonstrating its use to estimate bed sediment transport and remobilisation (Blake *et al.*, 2002; Salant et al., 2007) deposition rates (Blake *et al.*, 2002; Neubauer et al., 2002) and sediment transport distances and residence times within a catchment (Matisoff *et al.*, 2005; Whiting *et al.*, 2005) but to date, the post depositional mobility of ^{7}Be has not been considered. To further improve the use of ^{7}Be at this scale requires attention to conditions which may influence ^{7}Be adsorption both at the sampling location and at preceding storage zones. A

summary of the potential parameter changes which may influence the use of ^{7}Be as a tracer within catchment sediment budgets is provided in Table 4.6 and accompanies the following discussion which considers i) potential mobility of weakly adsorbed ^{7}Be, ii) potential mobility of metal oxide-adsorbed ^{7}Be and iii) mobility as a function of residence time.

i. *Potential mobility of 'weakly' adsorbed ^{7}Be*

The target phases of the step 1 reagent are the weak acid-soluble, exchangeable and carbonate-bound cations which may be mobilised by decreasing pH and increases in the ionic strength of the contact solution. The effects of increasing salinity should, therefore, be considered since desorption of exchangeable metals from sediment has been reported upon increasing salinity owing to competition from Ca^{2+} and Mg^{2+} and complexation by Cl^{-} (Millward & Liu, 2003). This is perhaps reflected in the findings of You et al. (1989) where the rate of adsorption of ^{7}Be to sediment was reduced in the presence of seawater. Similarly, Hawley et al. (1986) found lower K_d values in saline conditions compared to freshwater areas. This may have implications for the use of ^{7}Be as a tracer at the freshwater-marine interface causing a reduced ^{7}Be signature in sediments, thus, hampering source fingerprinting and transport time estimations. However, Olsen et al. (1986) found no correlation between sediment ^{7}Be concentration and salinity in estuarine and coastal waters and, similarly, the findings of Casey et al. (1986) would suggest that varying levels of salinity has little effect upon ^{7}Be sorption behaviour. The same study, however, highlighted the role of decreasing pH as one of increasing ^{7}Be mobility. This is supported by the findings of You et al. (1989) where ^{7}Be partitioning between sediment and solution was reduced at pH < 6.

Within the catchment environment, decreases in pH can occur by, for example, sulphide oxidation following sediment resuspension or lowering of the water table (Du Laing et al., 2009b). In partition studies, decreasing pH tends to reduce K_d values. From the perspective of using ^{7}Be as a tracer, attention should focus upon the potential for desorption of ^{7}Be from deposited material. Extractions using artificial rainwater solutions in this study demonstrate stability of ^{7}Be in weak acid solutions of the experimental soils (~ pH 4.5). Further research is required to demonstrate the potential for ^{7}Be desorption in a range of soil solutions of representative pH and salinity, the latter being particularly important with regard to the use of ^{7}Be for sediment fingerprinting at the freshwater-marine interface.

ii. *Potential mobility of metal oxide-adsorbed ^{7}Be*

The large proportion of ^{7}Be associated with the reducible fraction suggests an affinity with Fe and Mn oxides. ^{7}Be mobility will, therefore, be largely dependent upon the occurrence of suitable reducing conditions in the natural environment which is likely to be highly site-specific. Reducing conditions can occur in floodplain soils during periods of saturation. Vaughan et al. (2009) reported that reducing conditions can develop in floodplain soils after 2 days at temperatures > 9 °C at depths in excess of 20 cm. Increased concentration of dissolved Mn and Fe in pore waters can be used as an indicator of reduction of Mn and Fe oxides. Du Laing et al. (2009a) demonstrated that the concentration of Mn in soil pore waters at depths of 10 cm was dependent upon saturation regime. After a month of waterlogged conditions (waterlogged to soil surface) increased concentration of dissolved Mn in three soil types provided evidence of reducing

conditions. Slower rates of reduction were found to occur in a soil with a more permeable texture possibly owing to greater penetration of oxygen into the soil profile, further highlighting the importance of site-specific factors.

Du Laing et al. (2007) investigated temporal effects upon Mn oxide reduction in relation to fluctuations in hydrological conditions. Mn oxides are reduced at higher redox potentials than Fe oxides and this was reflected in a faster response of dissolved Mn in pore waters to changing redox conditions. Pore waters were sampled at 5 cm below the soil surface with waterlogging induced by raising water levels 5 cm above the surface of the soil. A significant positive correlation was found between dissolved Mn in pore waters and hydrological regimes involving both constant waterlogging and in soils where fluctuations of 2 days waterlogging and 2 days emergence occurred. A positive response of Mn to regimes involving 2 weeks of waterlogging followed by 1 week of emergence was also found. Where soils were waterlogged for 2 days followed by 8 days emergence there was little response of Mn in pore waters demonstrating the predominance of oxidised conditions and, thus, increased metal stability. The latter is perhaps more representative of catchments showing a flash response to rainfall events. Low oxygen conditions can also be found in channel bed sediment, with evidence of lower redox potential being observed with increased sediment depth from of 5-10 cm, particularly where finer sediment fractions are deposited (Geist & Auerswald, 2007).

The more rapid response of Mn oxides to the onset of reducing conditions is noteworthy given the potential for [7]Be to be associated with discrete Mn oxides under the pH range of most agricultural soils. Mn oxides display a pH-dependent surface charge with the point of zero charge (PZC) commonly found between pH 2-8. Resulting negative surface charges, therefore, encourage the

adsorption of cations (Ackermann et al., 2010; White, 2006). Under reducing conditions metals sorbed to Mn oxides can be released according to:

$$MnO_2 + 2e^- + 4H^+ \leftrightarrow Mn^{2+} + 2H_2O \qquad (4.4)$$
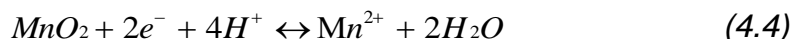
Furthermore, metal mobility may be enhanced by subsequent complexation with organic ligands (Du Laing *et al.*, 2009b).

Where reducing conditions occur the potential for sediment ^{7}Be signatures to become depleted owing to metal oxide dissolution should be considered. The extent to which conditions will promote ^{7}Be mobility is clearly site-specific and dependent upon a number of factors including temperature, soil type, accretion depths and hydrological regime (Du Laing *et al.*, 2007, 2009b). Where shallow deposition occurs following events, such as that detailed by Blake et al. (2002) (0.24 g cm^{-2} mean deposition) and Walling et al. (1996) (0.09-0.8 g cm^{-2} for the River Culm and 0.01- 0.66 g cm^{-2} for the River Stour) adsorption behaviour is unlikely to be affected particularly where waterlogging is short lived (Du Laing *et al.*, 2007). In riparian areas where accretion rates are considerably higher and frequent and prolonged inundation of occurs, there is potential for reducing conditions to promote tracer mobility. Similarly, the possibility of reducing conditions in channel bed sediment should also be considered particularly where high accretion rates have occurred over short time scales as a result of flash events.

iii. ^{7}Be mobility as a function of residence time

 The extent to which ^{7}Be is influenced by changing environmental conditions may also be a product of the age of adsorbed ^{7}Be. Batch experiments with stable Be showed a higher proportion of Be was extracted in the exchangeable fraction after 5 days equilibration in comparison to aged soil. This finding

corresponds to an increase in Be associated with the reducible and oxidisable phases with time. This is consistent with respect to other metals where aging soils results in the migration of metals from the exchangeable to Fe/Mn and organic target phases (Lu et al., 2005). This would suggest that the sequential extractions using natural ^{7}Be fallout in this investigation are representative of aged soils with soils experiencing only recent fallout likely to have an increased association with the exchangeable fraction and, thus, mobility is more likely to be affected by factors such as pH and ionic strength of solution as outlined above. This is of greatest relevance to studies in climatic zones where a large proportion of ^{7}Be inventory which could be used to assess soil erosion and sediment redistribution rates is delivered within a short time frame (Ayub et al., 2009; Othman et al., 1998).

Sediment budget component	^{7}Be application	Potential for changing environmental parameters	Implications for ^{7}Be application	Examples of ^{7}Be application
Hillslope transfer	Soil redistribution quantification	Unlikely at the hillslope-scale	^{7}Be remains adsorbed to particles under oxic field conditions	Blake et al., 1999; Schuller et al., 2006; 2010; Sepulveda., 2008
Slope to channel deposition i.e. wet riparian zones	Accretion estimates	Lower pH and redox change in saturated zones	Increased ^{7}Be mobility, therefore, reducing or displacing inventory. Overestimation of delivery ratio	Blake et al., 2008
Suspended sediment source identification	Fingerprinting surface material	Lower pH and changing redox conditions in preceding storage zones	Reduced ^{7}Be fingerprint affects estimates of surface contributions to suspended sediment	Whiting et al., 2005
Overbank deposition i.e. floodplains	Accretion rates	Lower pH and redox change but unlikely in units with low deposition rates	Potential for lowering of ^{7}Be inventory owing to increased mobility of tracer. May lead to underestimation of recent accretion	Blake et al., 2002 Neubauer et al., 2002
In-channel storage and remobilisation	Combined radionuclide signature ratios	Lower pH and change in redox conditions in preceding and channel storage zones	Reduced ^{7}Be/^{210}Pb ratio. Overestimation of storage times and underestimation of recent material in suspension	Blake et al., 2002; Salant et al., 2007
Suspended sediment age/transport distance	Combined radionuclide signature ratios	Lower pH and redox change in preceding storage zones and influence of increased salinity in estuarine areas	Reduced ^{7}Be/^{210}Pb ratio. Overestimation of sediment age and underestimation of transport distance of recent material	Matisoff et al., 2002; 2005, Whiting et al., 2005

Table 4.6: Summary of potential effects of environmental parameters upon ^{7}Be mobility at the catchment-scale

4.4.3. Perspective

While sequential extraction data cannot provide detailed knowledge of metal speciation, the phase association data provided gives a clear indication of the potential for mobility within specific catchment environments. The extent to which changing conditions will affect adsorption behaviour needs to be considered in sediment budget and residence time studies and necessary experiments undertaken to provide some quantification of uncertainties surrounding the use of ^{7}Be as a tracer under specific conditions. Careful consideration needs to be given to the likelihood of such conditions occurring within the timescale of use of ^{7}Be as a tracer and these considerations are very much site-specific. For example in smaller catchments where connectivity is high, reducing conditions may be less likely to affect tracer adsorption owing to rapid transport of sediment through the system. Where large-scale transport and deposition occurs periodically, consideration should be given to the potential for ^{7}Be adsorption to be influenced by changing conditions particularly where the hydrological regime is favourable.

4.5. Conclusions and recommendations

Batch experiments undertaken with stable Be support the key assumption that upon fallout ^{7}Be rapidly adsorbs to soil particles. Vertical distributions in experimental soils and the literature are consistent with this finding showing concentration of ^{7}Be in uppermost surface layers. Variability in vertical distributions is likely to be controlled by physical processes, particularly preferential flow via macropores and cracks and this is an important consideration for erosion studies given the need to accurately characterise h_0.

[7]Be fallout remained adsorbed in representative solutions of soil and rainwater (pH 5.6) providing confidence in its use as a tracer at the slope-scale. Sequential extractions using the optimised BCR three-step procedure demonstrated a 27-37 % association of fallout [7]Be with the weak acid-soluble, exchangeable and carbonate-bound phase. This suggests potential for [7]Be to become mobile from sediment in saline conditions at the freshwater-marine interface and areas of decreasing pH. It is unlikely that such factors will affect adsorption at the point of fallout at the field-scale but attention should be placed upon the potential effect of these parameters on the desorption of [7]Be from deposited or entrained sediment. Extractions also showed 42-62 % of fallout was associated with the reducible soil fraction and consequently, there is potential for [7]Be mobility in deposition zones under suitable redox conditions. Soils equilibrated with stable Be suggest some migration of [7]Be to the reducible fraction over time with recent fallout more likely to increase the proportion associated with the weak acid soluble, exchangeable and carbonate-bound phase. Recently adsorbed fallout may, therefore, be more susceptible to the influence of salinity and pH.

The extent to which reducing conditions will occur in the natural environment is site-specific and [7]Be adsorption behaviour is unlikely to be affected by reduction in systems with high connectivity where sediment residence times are low. In this respect, the effect of changing environmental parameters upon the use of [7]Be as a tracer at the wider catchment scale is a function of the timescale for tracer use in conjunction with specific system dynamics.

It is recommended that further laboratory investigations are undertaken to investigate the mobility of [7]Be in solutions of increasing salinity, decreasing pH and in conditions of changing redox potential. These investigations should be

coupled with *in situ* sampling across a range of field locations and at various temporal scales to determine the likelihood of conditions becoming favourable for tracer mobility in the natural environment.

Chapter 5. Field-scale erosion estimates using [7]Be inventories: Model validation and practical considerations

5.1. Introduction

The wider impacts of agricultural intensification in the UK became apparent in the 1980s with recognition of the potential economic and environmental threats posed by increasing rates of soil loss (Evans, 2010). To date, the off-site impacts of Diffuse Water Pollution from Agriculture (DWPA) are well documented (e.g. Biot & Lu, 1995; Camargo & Alonso, 2006; Clark, 1985; Pretty et al., 2000; Ulen & Kalisky, 2005; Weijters et al., 2009). In the UK, efforts to reduce DWPA have been driven by the Water Framework Directive (2000/60/EC) with sustainable soil use promoted by targeted liaison with stakeholders. In England this is largely undertaken through the England Catchment Sensitive Farming Delivery Initiative (ECSFDI). Landowners are provided with Best Management Practice (BMP) guidelines (Defra, 2005) for reducing soil loss with the implementation of mitigation measures encouraged through economic incentives (Capital grants within ECSFDI or funding within the Environmental Stewardship scheme). Included in BMP guidelines is the consideration of the type and time of machinery application to a particular site, highlighted as an important factor for reducing soil compaction, particularly with regard to wheelings (Defra, 2005). Wheelings can be significant pathways for sediment transport (Chambers & Garwood, 2000; Withers et al., 2006) and have recently been the focus of research which aimed to reduce wheeling compaction by developing mitigating measures such as the use of low-pressure tyre designs (Jackson et al., 2010). It is essential to continue field-

based research regarding soil loss to supply data which will enable the effectiveness of mitigating schemes to be monitored and to ultimately inform policy decisions within an integrated approach to catchment management (Evans, 2010).

As a monitoring tool, ^{7}Be tracing offers the potential for robust quantification of the impacts of land use change at the field-scale (Schuller et al., 2010) providing distinct advantages over traditional techniques with regard to spatial and temporal resolution (Mabit et al., 2008a). Approaches to estimating soil redistribution using ^{7}Be rely upon determining changes in ^{7}Be inventories at a sampling site by either i) assessing change at the sampling site between successive events (Wilson et al., 2003) or ii) comparing sample site inventories to those of a stable reference location experiencing no soil movement (Blake et al., 1999; Schuller et al., 2006; Schuller *et al.*, 2010; Sepulveda et al., 2008; Walling et al., 1999; Walling et al., 2009). The latter is the most widely used approach since it has the advantage of avoiding the need for repeat sampling at the eroding site. To convert changes in the ^{7}Be inventory into quantitative estimates of soil loss or gain, a simple conversion model is used which considers the ^{7}Be depth distribution.

Crucial for the successful application of this model is the accurate determination of the shape of the ^{7}Be distribution in the soil profile. Careful characterisation is, therefore, required to account for any spatial variation influenced by changes in hydrological processes across a field site (c.f. Alletto & Coquet, 2009; Strudley et al., 2008). Another important consideration is the association of ^{7}Be with grain size fractions. A correction factor is often required to avoid overestimating erosion rates by failing to account for preferential adsorption to fine fractions.

More recently, extending the timescale for ^{7}Be tracing requires knowledge of fallout input, erosivity and decay (Walling *et al.*, 2009).

Although the profile distribution approach has been widely used, little attention has been given to the validation of soil redistribution estimates. Comparison of model estimates to observations made using erosion pins has been carried out at the field-scale (Schuller *et al.*, 2006; Shi et al., 2011; Walling *et al.*, 2009), although it is difficult to directly compare data owing to the low spatial resolution obtained using pin estimates. More recently, Liu et al (2011) found close agreement between estimates of deposition rate and the mass of soil deposited at the exit of a small plot and Shi et al. (2011) found a discrepancy of 14 % between erosion estimates using ^{7}Be and a captured mass of eroded soil. To the best of the author's knowledge, the latter study is the only published literature regarding direct validation of the profile distribution model at the event-scale and no attempt has been made to validate profile distribution model estimates of erosion over an extended timescale. Against this background and in the context of erosion along tractor wheelings, the research reported here aimed to:

1) Carry out event-scale validation of the profile distribution soil erosion model to assess erosion from wheelings at the plot-scale.

2) Validate the approach at the field-scale to assess wheeling erosion over an extended time period.

Moreover, this research provided an opportunity for detailed scrutiny of the key model components and the practical implications associated with establishing these components.

The wheeling erosion scenario was selected for the study since the research was initially intended to provide comparative data to assess the mitigating methods developed by Jackson et al. (2010). Wheelings also offer a challenging environment in terms of characterising the ^{7}Be depth distribution.

The research aims were achieved via the following research objectives:

i) Determining ^{7}Be depth distributions in tractor wheelings

ii) Determining ^{7}Be particle size enrichment factors in field soils using stable Be in laboratory batch experiments

iii) Plot-scale rainfall simulation to compare model estimates of event-scale erosion to a soil mass captured at the plot exit

iv) Field-scale sampling to estimate a sediment budget for two wheelings over an autumn-winter period using the profile distribution model for extended timescales (Walling *et al.*, 2009)

v) Comparing model estimates of erosion over the autumn-winter period to a known mass of exported soil and assessing model sensitivity by adjusting key model controls

Elements of this research were initially carried out in collaboration with Environment Group ADAS UK Ltd in conjunction with a project which aimed to assess methods for minimising compaction in field wheelings (Jackson et al., 2010). Although some field sampling at the ADAS site was permitted to achieve objectives i and iv, owing to unforeseen company restrictions, permission to undertake objective iii was withdrawn at short notice and, therefore, an alternative field location was used for this purpose.

5.2. Methodology

5.2.1. Study sites

5.2.1.1 Experimental plot for event-scale validation

The study site for objective iii (also including objectives i and ii) was located in an arable field near Okehampton, Devon (50° 45' 3" N, 3° 54' 40" W) (site 1). The area is 160 m a.m.s.l. receiving approximately 1200 mm of rainfall annually (Phillips & McGregor, 2002). Soils are Denbigh association with a sandy silt loam texture (Soil Survey of England and Wales, (White, 2006)) and represent around 3 % of the landmass of England and Wales. Denbigh soils are largely confined to southwest England and Wales and are commonly used for the production of fodder crops in lowland areas (NSRI, 2008); at the time of study the field had been sown with maize. The experimental plot was a length of wheeling located on a uniform section of slope with an angle of approximately 5° (Figure 5.1). The plot was divided into two 5 m sections with the upper 5 m section used for determining the [7]Be depth distribution and the reference baseline inventory and the lower 5 m section used for the rainfall simulation experiment.

Figure 5.1: Experimental plot in Devon used for rainfall simulation (site 1)

Figure 5.2: Experimental plots and sediment traps used by ADAS UK Ltd (site 2)

5.2.1.2. Experimental field site for extended time-scale validation

Site 2 (Figure 5.2) was used for objectives iv and v (also including objectives i and ii). This was an experimental arable field site (53° 38' 51" N, 2° 10' 23" W) used by ADAS UK Ltd to assess the effectiveness of strategies for reducing wheeling compaction associated with the autumn spraying of cereal crops (Jackson *et al.*, 2010). The site is 124 m a.m.s.l. receiving annual rainfall of approximately 700 mm (Met Office). Slopes are uniform with an average gradient of 3.7 ° with Clifton soils of a sandy loam texture. These soils represent around 1.6 % of the landmass of England and Wales and are generally confined to the west Midlands and northwest England (NSRI, 2008).

Cereal cultivation and pasture are land uses commonly associated with these soils. The site had been cultivated and sown with winter wheat in September, 2010 and was divided into sets of wheelings which had received different treatments. Three treatments were trialled with each treatment having a triplicate set of tramlines. The research reported here focussed upon (i) a wheeling which had been produced using a tyre manufactured to reduce pressure and, thus, compaction and (ii) a wheeling produced using a conventional tyre. At the footslope of each treatment, sediment traps were installed by ADAS to monitor sediment export throughout the autumn/winter period.

The experimental plots used in this research consisted of the two wheelings (low pressure tyre and conventional tyre) each covering 160 m from the footslope to the break of slope. Each wheeling was subdivided into five 30 m sections and three of these sections were selected to represent lower, middle and upper slope plots. The two wheelings were in close proximity enabling

subsections in each to be uniformly spaced to aid comparison. A topographic survey was carried out using a Total Station (Geodimeter 610 with an ACU controller running Trimble Survey Controller software v11.40) to demonstrate slope uniformity (Figure 5.3).
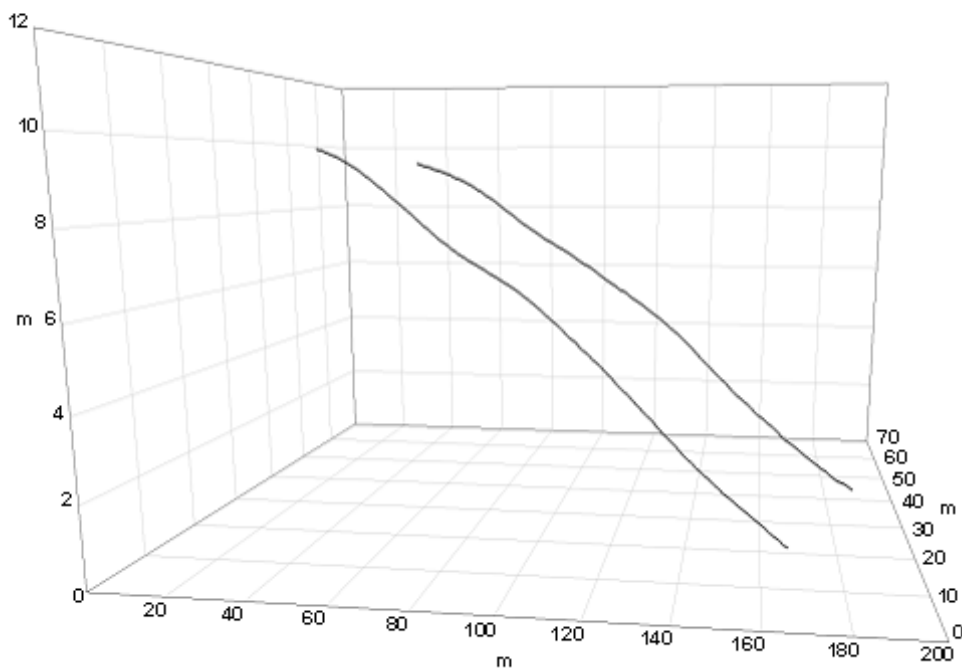
Figure 5.3: Wheeling profiles determined using topographic survey data

5.2.2. Determining [7]Be depth distributions in study soils

[7]Be depth distributions were determined at both study locations using a purpose built, steel depth increment sampler (Figures 5.4a and 5.4b). At site 1, the depth profile was determined by taking 2 cores from the upper 5 m plot. Cores of 270 mm diameter were taken across the width of the wheeling at opposite ends of the plot. The cores were then placed upon the depth increment sampler (similar to that described by Mabit et al., 2008b) which enabled sections of approximately 2 mm to be sampled through the soil profile. The specific depth

increments from the cores were bulked prior to analysis to provide a total sample area of ~0.1 m^{-2}. At site 2, depth distributions were determined for each wheeling using the method described above although for this site three cores were taken (owing to larger available sampling area) and bulked from level areas of the wheeling beyond the slope break. These areas were assumed to be stable with regard to soil redistribution. A depth distribution was also determined for a neighbouring bed area (between wheelings) using the same approach, for comparison.
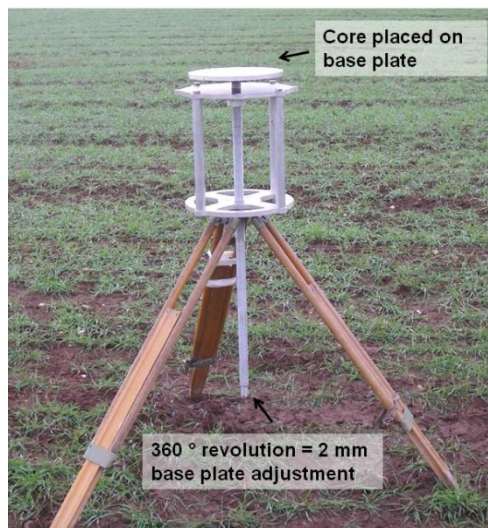
Figure 5.4a: Increment sampler frame showing the base plate and screw which enables the core to be raised at 2 mm increments

Figure 5.4b: Core cylinder placed upon the base plate with depth increments removed using a hand-held scraper

5.2.3. Determining Be association with particle size fractions

To determine site-specific particle size enrichment factors, triplicate subsamples of soil (100 g < 2 mm fraction) from both sites were equilibrated with 200 mL of stable Be solution (5 mg L^{-1} obtained from $BeCl_2$ salt, pH 5.6 (NaOH)) for 48 hours on a reciprocal shaker. The samples were air dried, bulked and homogenised by hand prior to being soaked in ultra-pure water and placed in an ultrasonic bath to achieve particle dispersion. Samples were then placed in a column, mixed and allowed to settle for a desired time following Stokes' Law to enable samples of < 63 μm, < 20 μm and < 2 μm fractions to be obtained.

Triplicate samples of the total bulk soil and the settled fractions were air dried and microwave digested (MARS 5 microwave accelerated reaction system, CEM (microwave technology) Ltd, UK) following Hassan et al. (2007), prior to analysis using ICP-OES (Varian 725-ES, Varian, Australia). Control samples (not equilibrated with Be) were also digested to enable correction for background Be. Separate subsamples were oven dried at 105 °C to determine moisture content. Acidified (pH 2 HCl) vacuum filtered samples of the column water were also analysed to determine desorption of Be during settling. Enrichment factors were calculated by dividing the settled fraction Be concentrations by the Be concentration in the total bulk sample.

5.2.4. Validating the use of the profile distribution model at the event-scale

5.2.4.1. Rainfall simulation and sampling at site 1

For the purpose of this investigation which used simulated rainfall on a slope plot, the pre-experiment reference inventory also needed to be established from

the same slope section i.e. it could not be assumed that zero soil loss had occurred prior to simulation, thus, comparison to a stable site inventory would not be reliable. The pre-simulation inventory across the entire experimental plot (10 m) was assumed to be uniform given the uniformity in topography. The upper 5 m section of the plot could, therefore, be used to determine a reference inventory and any soil loss following simulation in the lower 5 m section would be reflected by a lower inventory in comparison to the reference baseline.

Because cores had been taken from both ends of the upper 5 m plot to determine the depth distribution (section 5.2.2), the remaining undisturbed 4 m length was used for the reference inventory cores. Within each 1 m subsection, 6 cores with a diameter of 105 mm were taken to depths of 30 mm. The sampling was standardised to ensure that 3 cores were taken from the centre of the wheeling and 3 from the edge of the wheeling. Each core included an equal proportion of the wheeling imprint to account for the effect of microtopography upon soil transport. To achieve satisfactory spatial representativeness against analysis constraints, the 6 samples were bulked to form a composite sample, with 4 composite samples being taken in total. Including the inventory from the section cores, 5 reference values were obtained over the 5m section (covering a total of ~30 % of the section area).

The lower 5 m section of wheeling was subjected to simulated rainfall to generate soil transport. The rainfall simulator consisted of a lightweight metal frame with 5 sections of hose each with a nozzle (Delevan BNM6) evenly spaced along a cross bar which was located over the centre of the wheeling (Figure 5.5a). Water was supplied from a 200 L tank placed at the slope break with constant pressure generated using a mechanical pump. A pressure gauge was fitted to a bracket above each nozzle and the pressure adjusted using a

valve to ensure that each nozzle received equal pressure (0.2 bar). This produced a rainfall intensity of approximately 30 mm h^{-1}. Intensity and drop size naturally vary between each nozzle and, therefore, laboratory pilot studies were carried out to select nozzles with a similar output. Simulation was undertaken for a period of 20 minutes, during which, runoff from the plot was captured in pre-weighed bottles through a funnelled collector at the plot exit (Figure 5b). During simulation the plot area (2 m^2) received approximately 20 L (10 mm m^{-2}) of rainfall with 15 L of runoff captured at the plot exit. This suggests 5 L of infiltration (2.5 mm m^{-2}) and hence an average infiltration rate of around 7.5 mm hr^{-1}. Although it was important to achieve representative simulation i.e. realistic rainfall intensities, it must be noted that the study was primarily concerned with generating soil transport *per se* rather than rates representative of the local system. The above experimental conditions were deemed appropriate for this purpose.

Figure 5.5a: Rainfall simulator erected on the lower 5 m plot

Following rainfall simulation, 5 composite sample cores were taken using the method outlined above. This enabled changes in the [7]Be inventory across the plot to be assessed. Runoff sample bottles were weighed and allowed to settle for 48 hours before decanting and retaining the overlying water. The remaining solid material was air dried at 40 °C before re-weighing. The decanted water was vacuum filtered through pre-weighed 0.45 µm cellulose nitrate filter papers. The filter papers were then air dried and weighed. The filtered solution was acidified (~ pH 2) using HCl and a 2 L subsample was retained. To determine potential desorption of [7]Be in the simulation water, a subsample of filtrate was analysed following the procedure outlined in Short et al. (2007) to preconcentrate any [7]Be in solution. The dried runoff sediment was bulked and homogenised by hand and subsamples taken for particle size analysis using a Malvern Mastersizer 2000 with Hydro-G (Malvern, UK) in compliance with ISO 13320. To correct for moisture content a further set of triplicate samples were oven dried at 105 °C until at constant mass. The remaining runoff sediment was retained for gamma spectrometry.
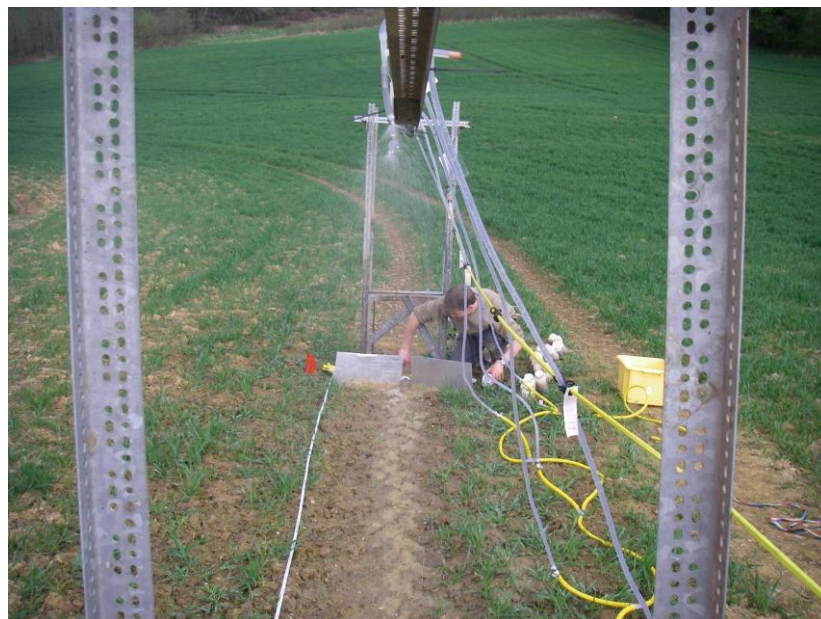
Figure 5.5b: Sampling of sediment exported from the plot during rainfall simulation

All field samples were air dried, lightly ground by hand and sieved (< 2 mm) prior to packing into Marinelli beakers (core samples) and 90 mm Petri dishes (section core and runoff samples). Analysis was carried out using high purity germanium (HPGe) gamma detectors (GM50-83-LB-C-SMN-S Planar and GEM-FX8530-S Planar, Ortec, UK) in the Plymouth University Consolidated Radioisotope Facility (CORiF) which operates under ISO 9001:2008-certification. Sample calibration was carried out using a standard of the same geometry. Standards were prepared using QCY58b mixed standard solution (G E Healthcare, Amersham, UK) which was distributed in a mineral matrix. Detector efficiency for ^{7}Be (477.6 keV) was determined by interpolation between the efficiency values of ^{137}Cs (661.7 keV) and ^{113}Sn (391.7 keV). Sample counts were corrected for background emission, geometry efficiency and decay. All values were reported as activity concentration (Bq kg^{-1}). Laboratory analytical quality control procedures were carried out in accordance with Wallbrink et al. (2002).

5.2.4.2. Determining erosion rates from ^{7}Be inventories

The profile distribution model applied in this study is detailed in Blake et al. (1999) and Walling et al. (2009).

The exponential depth distribution of ^{7}Be in the soil profile can be described as:

$$C(x) = c\,e^{-x/h_0} \tag{5.1}$$

Where C_x (Bq kg^{-1}) is the ^{7}Be activity at mass depth x (kg m^{-2}), c is a constant value and h_0 is the relaxation mass depth, the depth at above which 63.2 % of

the ^{7}Be inventory can be found. The value of the relaxation mass depth describes the shape of the ^{7}Be distribution.

Erosion rates (kg m^{-2}) can be estimated by comparing the ^{7}Be inventories at the sample site, A (Bq m^{-2}), to the reference inventory, A_{ref} (Bq m^{-2}). Where a mass of soil has been lost (h) (kg m^{-2}) changes in the sample site inventories can be represented as:

$$A = \int_{-h}^{\infty} C(x)\, dx = A_{ref}\, e^{h/h0} \tag{5.2}$$

Erosion rate, h (kg m^{-2}, negative), can, therefore, be calculated as:

$$h = h_0 \ln\left(A / A_{ref}\right) \tag{5.3}$$

Deposition of material is reflected in an excess of ^{7}Be inventory at the sample site with respect to the reference site. The depth of deposition, h' (kg m^{-2}, positive), can be calculated as:

$$h' = \left(A - A_{ref}\right) / C_d \tag{5.4}$$

Where C_d (Bq kg^{-1}) is the mean activity concentration of ^{7}Be in the deposited sediment.

The ^{7}Be activity concentration in the eroding sediment at each upslope point, C_e (Bq kg^{-1}), can be calculated from the loss of inventory divided by the mass of soil loss:

$$C_e = \left(A_{ref} - A\right) / h \tag{5.5}$$

The mean activity concentration of soil mobilised from the study area, S (m^2), can then be calculated as:

$$C_d = \int_s h\ C_e\ dS\ /\int_s h\ dS \qquad\qquad (5.6)$$

At site 1, estimates of soil loss (kg) from the plot were obtained by areal adjustment of the calculated erosion rate, h, (kg m^{-2}) derived from the five composite samples. Each composite sample was representative of a 0.4 m^{-2} area (1 m length × 0.4 m width) and, therefore, areal loss (kg) can be given by:

$$h \times 0.4 \qquad\qquad (5.7)$$

Estimates of erosion from each composite area were summed to give total erosion along the 5 m plot.

5.2.5. Application of ^{7}Be as a tracer to assess wheeling erosion at the field-scale

5.2.5.1 Estimating soil redistribution over an extended time period using ^{7}Be inventories

The profile distribution approach described in Section 5.2.4.2 is used to estimate soil redistribution on an event-scale basis. For the method to be applied over longer time periods considering several events, modifications to the existing approach are required to account for inventory flux (Bq m^{-2}), decay and the erosivity of events. Failure to account for these factors has been shown to lead to underestimation of redistribution rates (Walling *et al.*, 2009). In this approach the cumulative change in inventory at the sample site is considered rather than direct comparison to a stable reference value for each day. A

reference inventory for the field site is required, however, to provide an indication of erosion or deposition at each individual sample location. The model applied in this research follows Walling et al. (2009) and is described below with regard to i) calculating relative erosivity of rainfall, ii) estimating soil loss and iii) estimating deposition.

i. *Calculating relative erosivity of rainfall*

Values of relative rainfall erosivity, E_r, were calculated following Schuller et al. (2010) and are based on calculations used in the Revised Universal Soil Loss Equation (RUSLE) derived from:

$$E \times I_{30} \tag{5.8}$$

Where E is a value of storm kinetic energy (J m^{-2}) and I_{30} is the maximum 30 minute rainfall intensity (mm hr^{-1}). Calculations of E in this research followed the approach described by Yin et al. (2007) whereby each storm was divided into 'k' parts according to logging intervals (r). Rainfall intensity, i_r (mm hr^{-1}), for each interval t_r (hr) was calculated as:

$$v_r / t_r \tag{5.9}$$

Where v_r represents rainfall depth (mm).

With e_r representing rainfall kinetic energy (J m^{-2} mm^{-1}) at interval, r, total storm energy (J m^{-2}) could then be described as:

$$E = [\sum_{r=1}^{k} e_r v_r] \tag{5.10}$$

To calculate kinetic energy (e_r) an equation suitable for northwest Europe (from Morgan, 2001) was applied to give:

$$e_r = 8.95 + (8.44 \log_{10} i_r) \qquad (5.11)$$

I_{30} (mm hr^{-1}) was derived from:

$$P_{30} / 0.5 \qquad (5.12)$$

Where P_{30} is the maximum 30 minute rainfall depth.

Values of relative erosivity (E_r) were then assigned to each rainfall day by dividing the erosivity value (EI_{30}) for that day by the total erosivity of the study period.

ii. *Estimating rates of soil loss at a sampling point*

The inventory (Bq m^{-2}) existing at a sampling point at the end of each day, $A(t)$, can be defined as:

$$A(t) = A(t-1)\,\mathrm{e}^{(-\lambda)} + F(t) - A_{loss}(t) \qquad (5.13)$$

Where $A(t-1)$ is the sample area inventory at the end of the previous day (Bq m^{-2}), λ is radioactive decay, $F(t)$ is the ^{7}Be fallout input (Bq m^{-2}) and $A_{loss}(t)$ is inventory loss (Bq m^{-2}) associated with erosion.

Inventory loss (Bq m^{-2}) is dependent upon the mass of soil eroded, $R(t)$ (kg m^{-2}), and the ^{7}Be depth distribution in the soil (h_0). $R(t)$ is assumed to be proportional to a value of relative erosivity (E_r) for that day and can be calculated as:

$$R(t) = E_r(t) \times C \qquad (5.14)$$

Where C represents a constant value.

Inventory loss at a sampling point on day t can then be described as:

$$A_{loss}(t) = \left[A(t-1) e^{(-\lambda)} + F(t) \right] \times \left[1 - e^{-R(t)/h_0(t)} \right] \qquad (5.15)$$

iii. *Estimating rates of deposition at a sampling point*

Where deposition has occurred, the inventory (Bq m^{-2}) in place at the end of each day, $A'(t)$, can be described as:

$$A'(t) = A(t-1) e^{(-\lambda)} + F(t) + A_{gain}(t) \qquad (5.16)$$

The increase in inventory at a sample point on day t ($A_{gain}(t)$) (Bq m^{-2}) will reflect the depth of deposition $R'(t)$ and the activity concentration (Bq kg^{-1}) of the deposited sediment $C_d(t)$:

$$A_{gain}(t) = C \times E_r(t) \times C_d(t) \qquad (5.17)$$

Where $R'(t)$ is again assumed to be proportional to relative erosivity.

$C_d(t)$ is calculated as the weighted mean concentration of soil eroded from upslope points on a given day; $C_e(t)$. $C_e(t)$ can be calculated as:

$$C_e(t) = A_{loss}(t) / R(t) \qquad (5.18)$$

Consequently, C_d (t) can be represented as:

$$C_d(t) = \sum_{n=1}^{p} C_e(t)R(t) / \sum_{n=1}^{p} R(t) \qquad (5.19)$$

For both erosion and deposition calculations, particle size correction factors were applied to account for preferential adsorption of ^{7}Be to fine fractions. For the erosion calculations, particle size correction factors were applied to values of $R(t)$ and for the deposition estimates, correction factors were applied to values of $C_e(t)$.

5.2.5.2. Validating the use of ^{7}Be as a tracer over an extended time period: Field monitoring and sampling at site 2

The field sampling components necessary for achieving quantitative estimates of soil redistribution over an extended time period are detailed in points i and ii below.

i. *Determination of event ^{7}Be fallout input (F) during the study period*

The monitoring period for this research extended from mid-October, 2010 to mid-February, 2011.

Reference inventories (Bq m^{-2}) can be used as benchmarks to determine daily ^{7}Be fallout input (Bq m^{-2}) following the method outlined by Schuller et al. (2010). To determine a ^{7}Be reference inventory, a level area of permanent pasture in close proximity ($\sim$ 400 m) to the experimental field site (Figure 5.6) was selected for coring. The reference location was assumed to be stable with regard to soil

redistribution and assumed to receive the same [7]Be event fallout input (Bq m^{-2}) as the sample site. Two sets of reference cores were taken, one at the beginning of the monitoring period (mid-October) and one at the end of the period (mid-February). Each set consisted of 11 composite samples with each sample comprising 5 cores (105 mm x 300 mm) taken within a 500 mm x 500 mm area. The composite samples were taken systematically at grid intersects with 30 m intervals to be spatially representative following guidelines provided in Loughran et al. (2002). All cores were processed and analysed following the method outlined in section 5.2.4.1 with vegetation retained for analysis.

Figure 5.6: Reference location with the experimental field site visible in the far background

To determine [7]Be fallout input (Bq m^{-2}), rainfall data (mm) (0.2 mm resolution, 15 minute logging interval) were obtained from an Environment Agency station in close proximity (~ 3 km) to the sample site. [7]Be rainfall activity (Bq L^{-1}) was

estimated based on the approach used by Schuller et al.(2010) and is described below.

The mean inventory (Bq m^{-2}) obtained from the October reference cores was used as a starting point in conjunction with daily rainfall inputs (mm) to estimate rainfall activity (Bq L^{-1}). By considering radioactive decay, the daily fallout input (Bq m^{-2}) was manipulated (by changing the value of [7]Be activity in rainfall (Bq L^{-1}) using an iterative fitting process until the calculated reference value at the end of the study period was equal to the value obtained from the February cores (and the adjusted value, see below). The time of tillage at the experimental field site was mid-September and at this point the field inventory was assumed to be reset (Blake *et al.*, 1999).

It was necessary to calculate the reference inventory at the time of tillage to be able to account for excess residual inventory in the reference cores at the end of the monitoring period (i.e. it could not be assumed that the reference inventory in place at the time of tillage would have decayed to zero by the end of the monitoring period). This was determined by using backward steps from the October inventory (determined *in situ*) accounting for inventory flux to the point of tillage. This value was then decay corrected to the end of the monitoring period in February to determine any excess residual reference inventory. This component was then subtracted from the February reference inventory (obtained *in situ*) to give an adjusted reference value specific to the field surface. A daily reference value could then be calculated for the experimental sample site considering the inventory flux and decay from the point of zero inventory at the time of tillage to the end of the monitoring period, with the final baseline value being equal to the adjusted reference value. Sample inventories could then be compared to this baseline to indicate erosion or deposition.

ii. *Field sampling to determine soil redistribution rates*

Composite samples were taken from each wheeling (conventional tyre treatment and low pressure tyre treatment) in mid-February on the same day as the reference core samples. These were taken within 30 m sections of the wheeling from 0-30 m (from the point of the sediment traps 10 m above the footslope), 60-90 m and 120-150 m (to the slope break). Representative sections of lower, middle and upper slope areas were, therefore, sampled. Sections from each wheeling were evenly spaced to enable comparisons to be made and this was supported by uniformity across the slope profile (Figure 5.3). Each 30 m section was subdivided into 6 m sections within which one composite sample was taken (to provide five samples per 30 m section). Each composite sample comprised 10 cores (105 mm x 200 mm) taken at 600 mm intervals along the centre of the wheeling. The centre of the wheeling was sampled as this was considered the most susceptible area to soil movement, therefore, optimising detection. Each core consisted of equivalent areas of the surface imprint produced by the tyre to account for the influence of micro topography upon soil transport.

All samples were processed and analysed following the method described in section 5.2.4.1. A wheeling sediment budget was calculated for the total slope length by apportioning the erosion and deposition rates determined from the composite samples to the study area. Each redistribution rate (kg m^{-2}) estimated for the 6 m sections was assigned to a 10 m section multiplied by the sample width (0.1 m) to provide estimates of redistribution (kg) across the 150 m slope length (15 composite sample inventories applied to 10 m sections). The budget estimations were then compared to the mass of soil captured in the

sediment traps erected by ADAS UK Ltd (an approximate value obtained by verbal communication).

5.3. Results

5.3.1. [7]Be depth distributions in study soils

The depth distributions of [7]Be determined from the section cores taken from sites 1 and 2 are shown in Figures 5.8a-d. The wheeling distributions (Figures 5.8a-c) demonstrate a confused pattern owing to the challenge of sampling depth increments through a profile with a wheeling imprint. For practical reasons, the section cores were taken across the entire width of the wheeling, thus, including a complete surface imprint. When sampling increments through a wheeling profile, the raised area of the imprint was sampled first and, therefore, these upper sections can be taken as representative of the uppermost surface layers of the soil.

There became a point deeper in the profile where the lower area of imprint became included in the sample increments. This added 'fresh' surface material to the sample and, thus, confused the depth distribution from this point downwards (Figure 5.7). This is shown in Figures 5.8a to 5.8c where the dashed line indicates the point at which the mixing of fresh material occurred (i.e. the approximate depth of the imprint). For site 1, the upper four points in the graph were taken as representative of the surface distribution since these points were sampled prior to the introduction of surface material below 6.5 kg m^{-2} mass depth. An exponential fit was, therefore, placed through these upper data points to derive an h_0 value of 1.93 kg m^{-2} (negative) for use in the profile distribution model.

The depth distributions for site 2 also displayed a confused pattern, particularly the conventional tyre wheeling (Figures 5.8b and 5.8c). An exponential fit was placed through the upper 2 data points on both distributions returning h_0 values of 3.19 kg m^{-2} (negative) and 4.15 kg m^{-2} (negative) for the conventional tyre and low pressure tyre wheelings respectively. The depth distribution for a neighbouring cultivated bed (h_0 = 4.74 kg m^{-2}) area is shown for comparison (Figure 5.8d) to demonstrate a decrease in activity with depth, further highlighting the effect of the wheeling imprint.
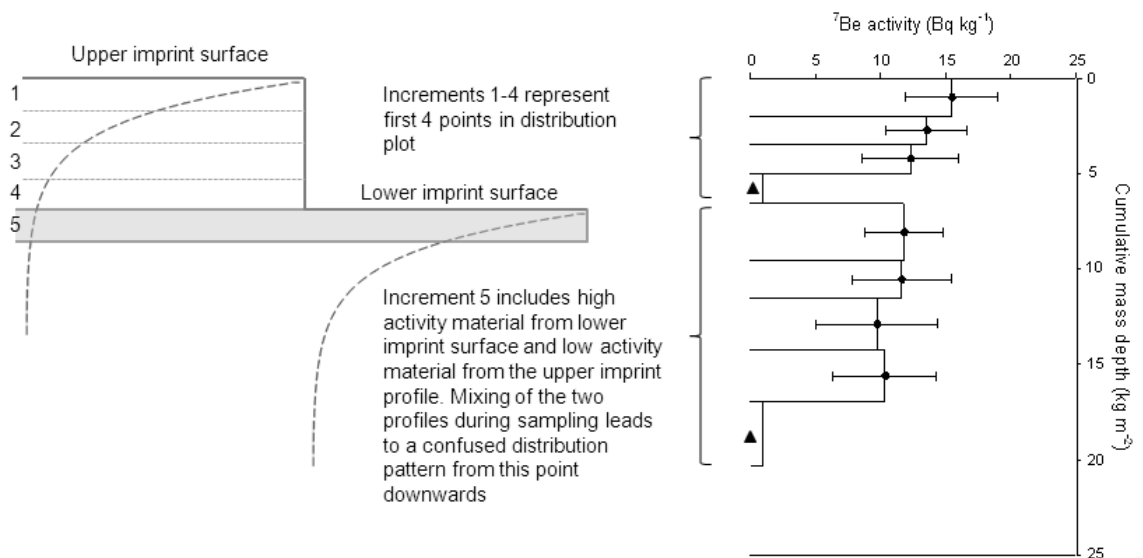
Figure 5.7: Conceptual diagram of [7]Be depth distribution in the wheeling imprint at site 1. The distribution is assumed to be the same for both the upper and lower sections of the wheeling imprint. The [7]Be activity decreases with depth through increments 1-4 and this is reflected in the upper 4 points in the distribution plot. Increment 5 includes both fresh material from the lower imprint surface which would have a greater activity and low activity material from the upper imprint profile, thus, leading to a confused distribution from this point downwards. ▲ indicates Minimum Detectable Activity (MDA).
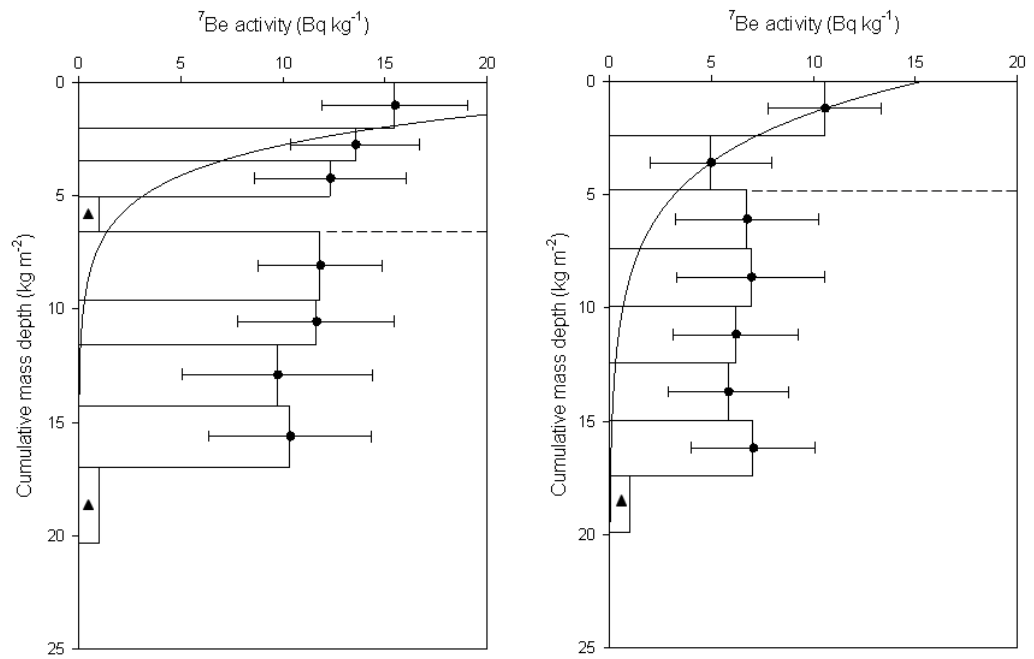
Figures 5.8a and 5.8b
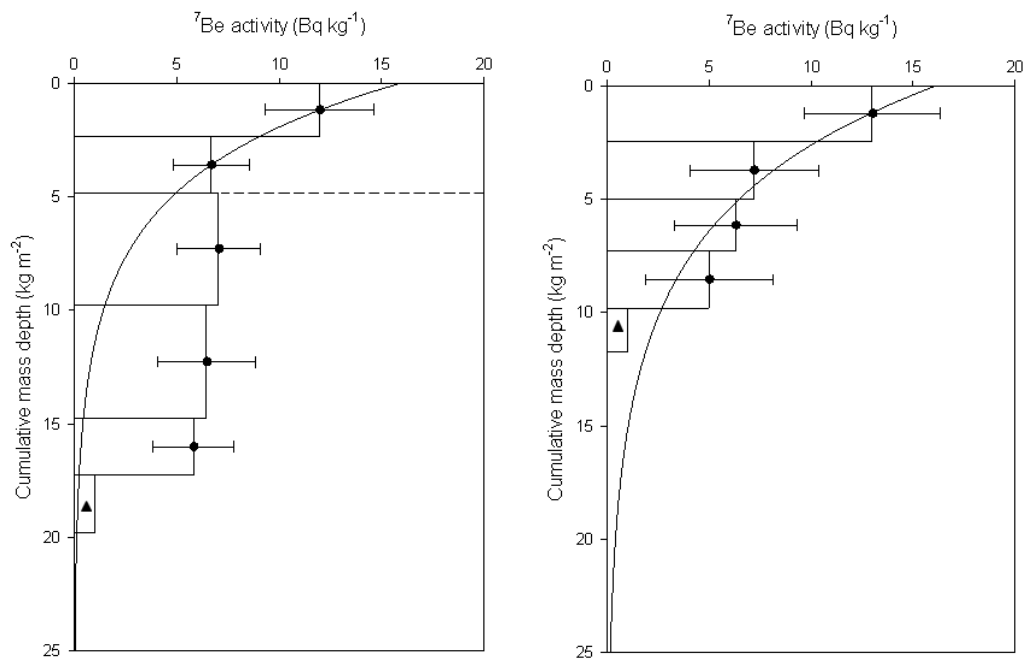
Figures 5.8c and 5.8d

Figure 5.8a: [7]Be depth distribution at site 1
Figure 5.8b: [7]Be depth distribution in the conventional tyre wheeling at site 2
Figure 5.8c: [7]Be depth distribution in the low pressure tyre wheeling at site 2
Figure 5.8 d: [7]Be depth distribution in a cultivated bed at site 2
Analytical uncertainties are shown as 2σ
Dashed line indicates the depth of the wheel imprint below which fresh surface material becomes included in the distribution causing a confused pattern below this point
▲ indicates Minimum Detectable Activity (MDA).

5.3.2. Be association with particle size fractions

The laboratory batch experiments identified preferential adsorption of stable Be to fine soil fractions (< 63 μm) in both soil types (Table 5.1) with enrichment factors increasing with decreasing grain size. When comparing the two soil types, larger enrichment factors were obtained for the sandy loam (site 2) soil for all settled fractions with > 50 % greater enrichment factors for < 20 μm and < 2 μm fractions. The difference in enrichment factors within each soil type is also noteworthy; the sandy silt loam soil displayed an increase in enrichment of approximately 22 % between the < 63 μm fraction and the < 2 μm fraction whereas an increase of > 70 % was found in the sandy loam between these fractions.

	Bulk mg kg^{-1}	> 63 μm mg kg^{-1}	< 63 μm mg kg^{-1}	< 20 μm mg kg^{-1}	< 2 μm mg kg^{-1}
Sandy silt loam (site 1)	8.47 ± 0.75	1.99 ± 0.08	14.30 ± 0.50 **1.69**	16.49 ± 0.60 **1.95**	18.33 ± 0.67 **2.16**
Sandy loam (Site 2)	9.29 ± 1.02	1.36 ± 0.09	17.34 ± 0.46 **1.87**	40.76 ± 0.64 **4.39**	61.49 ± 3.82 **6.62**

Table 5.1: Background corrected concentrations of stable Be (mg kg^{-1} dry weight) in bulk and settled soil fractions with enrichment factors shown in bold type. Mean and standard deviation from triplicate samples shown

5.3.3. Validating the profile distribution model at the event-scale

The mean reference value calculated from the composite cores in the upper 5 m plot (at site 1) was 186 (± 44 (2σ analytical uncertainty)) Bq m^{-2} with < 5 % relative standard deviation (RSD) between individual values. [7]Be inventories in the eroded plot and the erosion model estimates are shown in Table 2. Given that the largest proportion (~ 70 %) of the exported soil was < 20 μm in size, (Figure 5.9) an enrichment correction factor of 1.95 (Table 5.1) was applied to the erosion rate estimates for each sampling point.
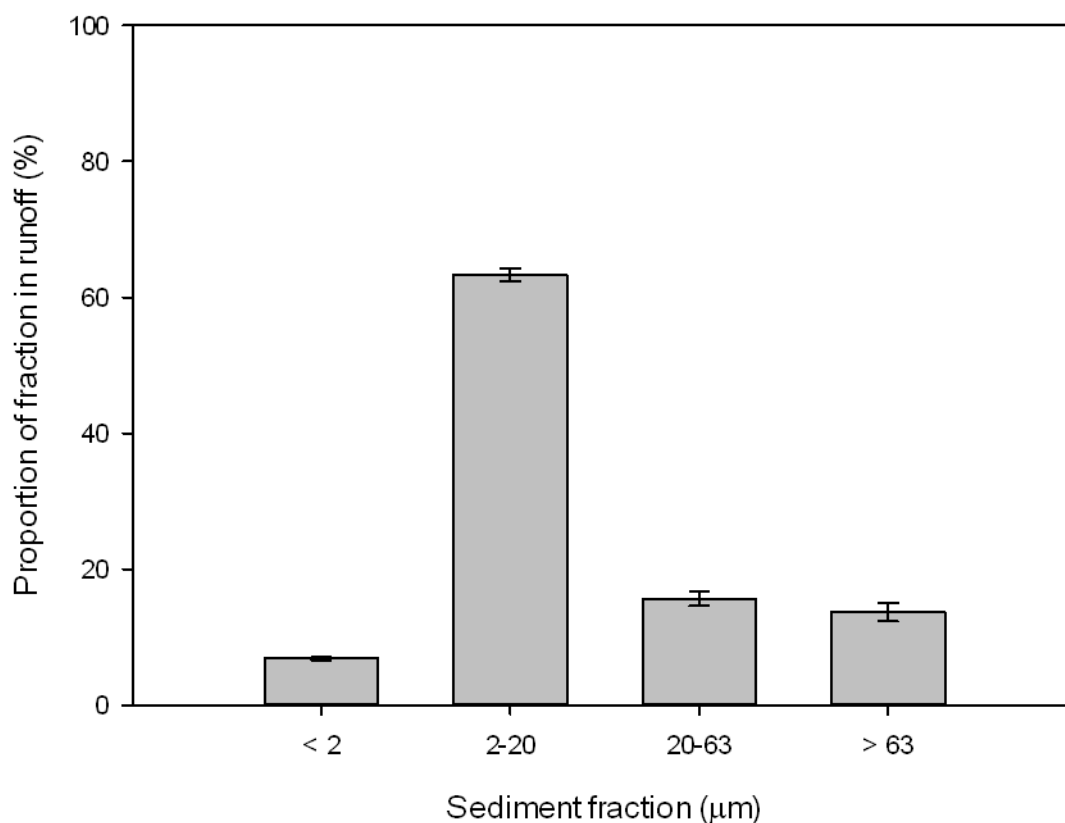
Figure 5.9: Distribution of grain size fractions in sediment exported from the plot. Mean and standard deviation from triplicate analyses shown

The estimate of total export, derived from the summation of the areal erosion rates was 0.36 kg (± 0.09). This is an overestimate of 44 % of the mass of soil captured directly from the plot which was 0.25 kg. The mean activity of the eroded sediment was 21.7 (± 4.79 (2σ analytical uncertainty)) Bq kg^{-1}. Applying a correction factor (of 1.95) to account for enrichment suggested that the bulk material in the eroding layer had an activity of 11.1 (± 2.45 (22 % analytical uncertainty)) Bq kg^{-1}. This activity is comparable to the activity shown in the upper data point of Figure 5.8a but does not support the estimated surface activity given by the exponential fit, i.e. the exponential fit estimates activity at the surface to be around 45 Bq kg^{-1}.

Sample inventories (Bq m^{-2})	Erosion estimate (kg m^{-2})	Uncertainty (kg m^{-2})	Mass eroded from plot area (kg)	Uncertainty (kg)
182 (*36.9*)	0.0229	0.00465	0.00916	0.00186
120 (*30.6*)	0.431	0.110	0.172	0.0440
137 (*33.5*)	0.303	0.0739	0.121	0.0296
178 (*34.2*)	0.0440	0.00845	0.0176	0.00338
168 (*30.5*)	0.0984	0.0178	0.0394	0.00712
		Total	**0.360**	**0.0859**

Table 5.2: ^{7}Be inventories at the eroded sample points and associated model erosion estimates. The eroded mass (kg) is derived from the area adjusted erosion rate e.g. 0.0229 kg m^{-2} × 0.4 m^{-2} = 0.00916 kg loss. Uncertainties are obtained by propagating the analytical uncertainty (2σ) associated with the sample inventories (shown in brackets) through the model

5.3.4. Validating the use of ^{7}Be inventories to assess wheeling erosion at the field-scale over an extended time period

5.3.4.1. Reference inventory values

Reference cores were taken (at site 2) at the beginning (October) and at the end of the study period (February) to provide benchmarks from which to estimate fallout input (*F*) (Bq m^{-2}) (section 5.2.5.2.). The mean inventory value obtained from the October cores was 221(± 57 (2σ analytical uncertainty)) Bq m^{-2} with < 10 % RSD between samples (Figure 5.10a). The mean value obtained from the February cores was 161 (± 36 (2σ analytical uncertainty)) Bq m^{-2} with 15 % RSD between samples (Figure 10b).
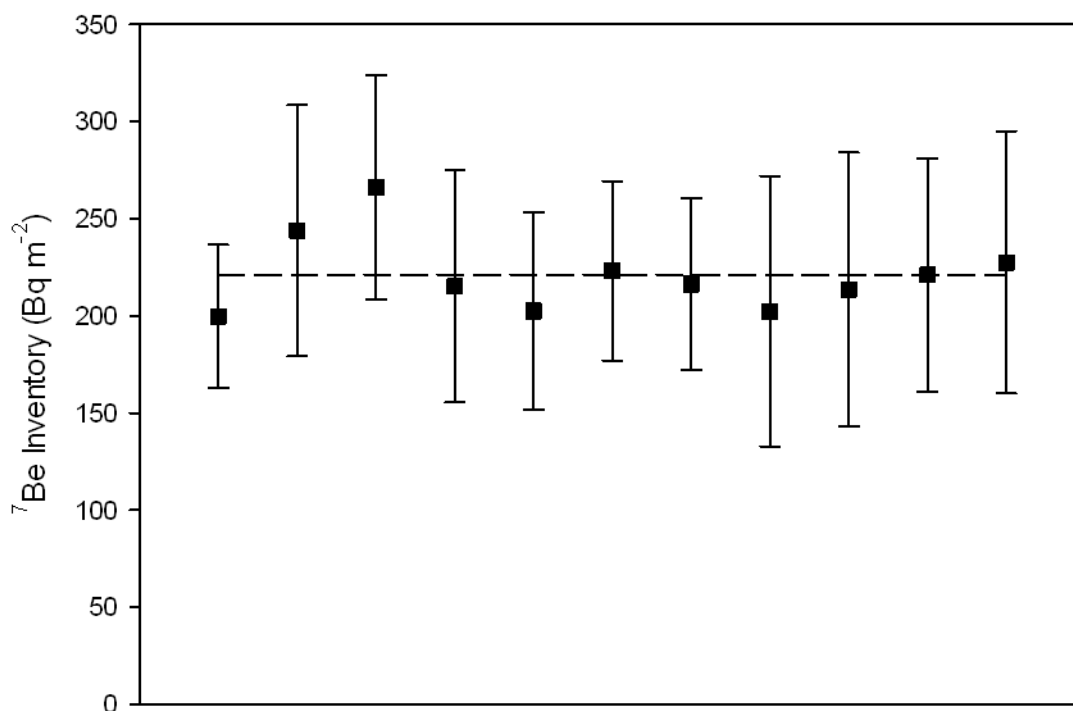
Figure 5.10a: October reference core inventories with analytical uncertainty given as 2σ. Dashed line denotes mean value
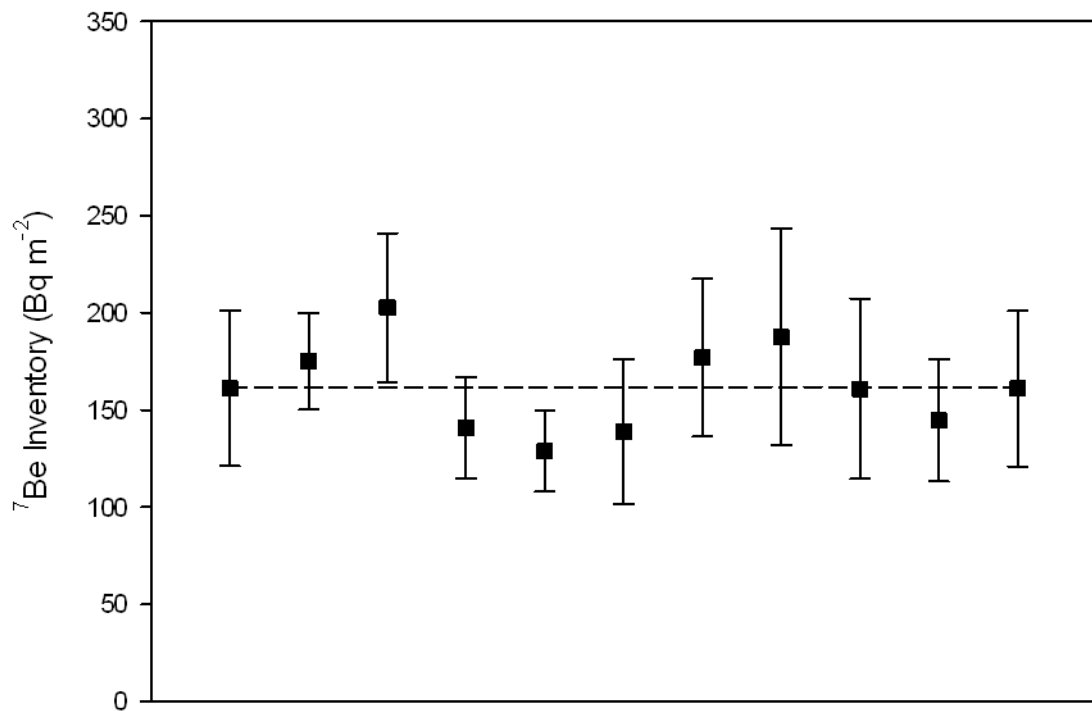
Figure 5.10b: February reference core inventories with analytical uncertainty given as 2σ. Dashed line denotes mean value

5.3.4.2. [7]Be fallout input (F)

Following the method described in section 5.2.5.2., the mean [7]Be activity in rainwater during the study period was estimated at 2 Bq L^{-1} with the exception of December where twice the mean value was applied owing to the predominance of snowfall (Ioannidou & Papastefanou, 2006). Considering rainfall (mm) and radioactive decay, a cumulative (reference) inventory was developed from the point of zero inventory (Bq m^{-2}) at the time of tillage to the sampling date in February, 2011 (Figure 5.11). The final reference value at the time of sampling was 138 Bq m^{-2} which was in close agreement with the mean inventory determined from the February reference cores (161 Bq m^{-2}) with the residual inventory (22 Bq m^{-2}) subtracted i.e. 139 Bq m^{-2}.
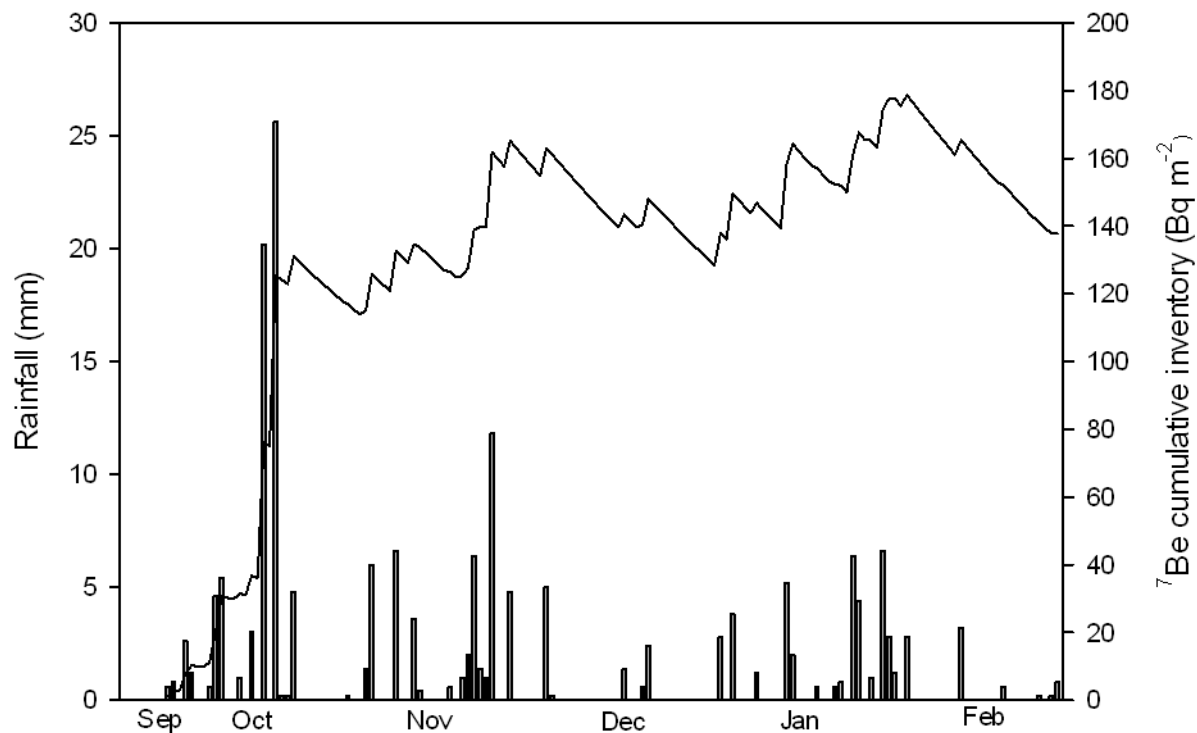
Figure 5.11: Daily rainfall and [7]Be cumulative inventory for the study period estimated using the October and February reference cores and the rainfall input

5.3.4.3. Relative erosivity of rainfall

The relative erosivity of each rainfall day was calculated using values of EI_{30} as described in section 5.2.5.1. The first half of the study period, running from the point of tillage to the end of November, 2010, contributed > 70 % of the total rainfall for the whole period. It is unsurprising, therefore, that this half of the study duration experienced the greatest erosivity (i.e. 90 % of the erosivity assigned to the whole study period) (Figure 5.12).
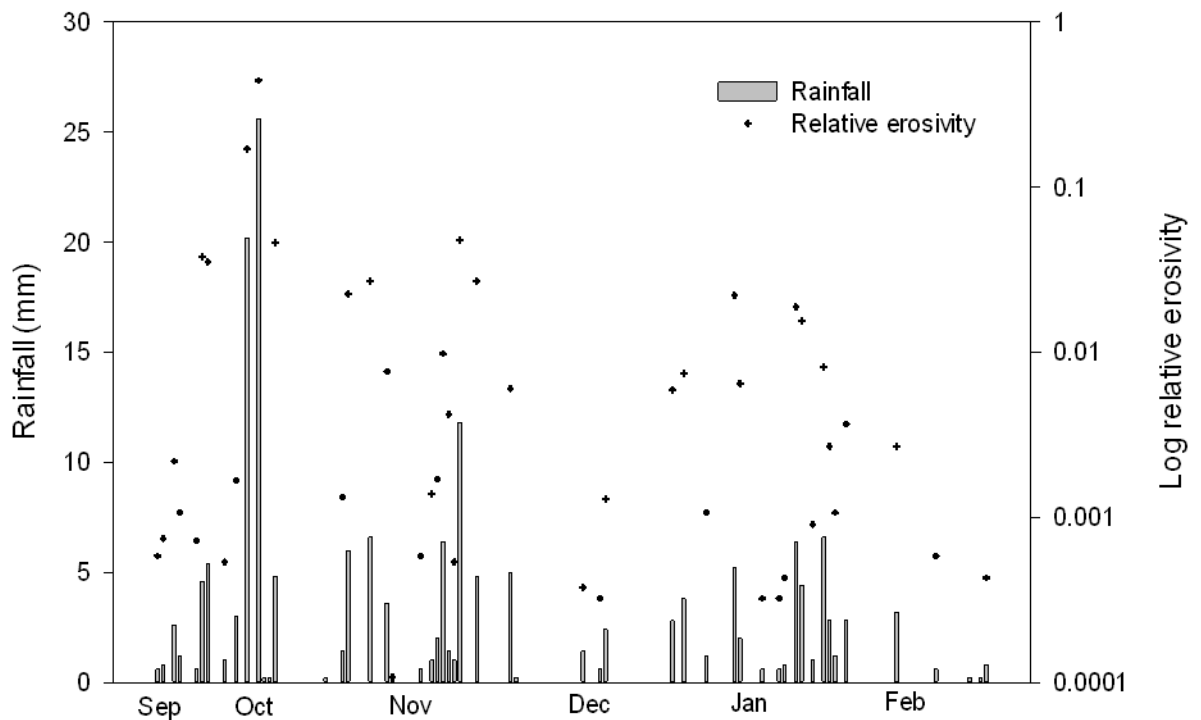
Figure 5.12: Daily rainfall and associated relative erosivity values for the study period

5.3.4.4. Composite sample inventories

Sample inventories determined from the composite core samples taken from the wheelings (section 5.2.5.2.) ranged from 77 to 132 Bq m^{-2} for the low pressure tyre wheeling and from 92 to 135 Bq m^{-2} for the wheeling produced by the conventional tyre. The reference baseline shown in Figure 5.13 is the estimated inventory for the sample day calculated using the method described in section 5.2.5.2. All sample inventories were below the reference baseline, therefore, indicating soil loss although it is noteworthy that the conventional wheeling experienced a lesser reduction in inventory.
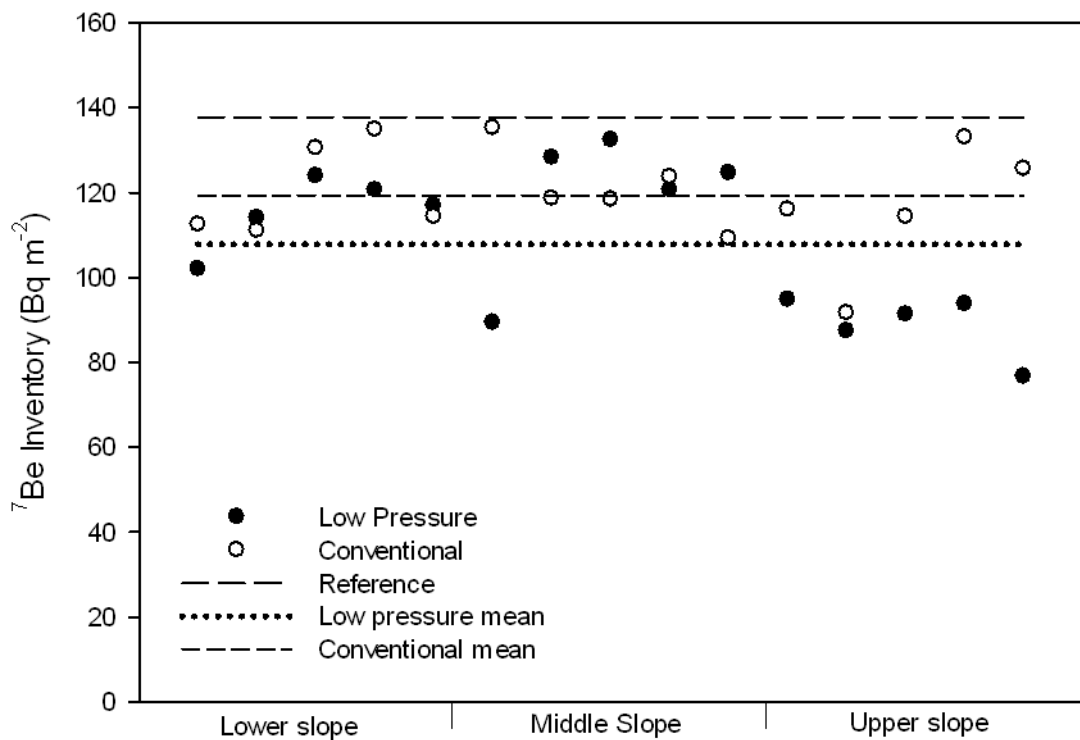
Figure 5.13: Composite sample inventories for both wheelings with the mean of 15 samples shown. The reference baseline shown is the field reference inventory at the time of sampling estimated using the method in section 5.2.5.2

5.3.4.5. Sediment budget estimates

Using the method described in section 5.2.5.1 estimates of soil redistribution (kg m^{-2}) for each 6 m section were determined for the autumn-winter period. A hill slope sediment budget was calculated for each wheeling by apportioning the redistribution rates estimated from the composite cores to the study area (section 5.2.5.2.). Model analyses were undertaken using a series of scenarios to test the sensitivity of model output to changes in key parameters. This involved adjustment to values of particle size enrichment, h_0 and fallout input and each scenario is detailed in turn below. Initial model analysis was undertaken using a particle enrichment factor for the < 63 µm fraction (commonly applied in erosion studies), the value of h_0 determined at the end of

the study period (section 5.3.1.) and the estimated fallout input (F) using the value of ^{7}Be activity in rainfall determined from the iterative fitting process (section 5.3.4.2.). Using these parameters, estimates of soil loss vastly exceeded the ca.1 kg mass of soil captured directly in the sediment traps (Table 5.3). It should be noted that erosion estimates were dominated by the events occurring on 1st and 3rd October, 2010 with ~60 % of the total erosion for the period occurring during these days. During the events, deposition approximately doubled the field inventory of the previous day. Subsequent analyses were undertaken to determine the sensitivity of model estimates to values of i) particle enrichment, ii) h_0 and iii) fallout input.

i *The effect of particle enrichment factors upon hill slope sediment budget estimates*

Subsequent model runs were undertaken where redistribution rates were estimated for erosion of different particle size fractions using the enrichment correction factors determined from the batch experiments (section 5.2.3). Here, the values of h_0 and fallout input were fixed to those described in section 5.3.4.5. The large range in enrichment factors across particle size classes in this soil type (Table 5.1) is reflected in the sediment budget calculations (Table 5.3). By applying the correction factor for < 63 µm fraction, estimates of soil loss are over 50 % greater than estimates using the correction factor for < 20 µm fraction for both wheelings. Using the correction factor for the < 2 µm fraction, estimates of erosion are < 30 % of those determined using the < 63 µm correction factor.

	< 63 μm	< 20 μm	< 2 μm
Low Pressure	59.3 *13.6*	25.2 *5.80*	16.7 *3.84*
Conventional	21.8 *4.81*	9.28 *2.05*	6.14 *1.36*

Table 5.3: Wheeling sediment loss (kg) derived using three particle size enrichment factors. Values of h_0 were set at 3.19 and 4.15 kg m^{-2} (negative) for conventional and low pressure tyre wheelings respectively. The applied values of fallout input (F) were determined using a value of 2 Bq L^{-1} for [7]Be rainfall activity. Uncertainties (italics) are calculated using RSD (2σ) analytical uncertainties associated with the sample inventories

ii. *The influence of relaxation mass depth (h_0) upon model estimates*

The soil redistribution model assumes a constant relaxation mass depth (h_0) throughout the study period. According to Walling et al. (2009), h_0 can display temporal variations, with a lower h_0 likely to occur at the start of the study period. In this study h_0 was determined at the end of the winter period at the time of sampling and, may not, therefore, be representative of the whole study period. If the relaxation mass depth was zero at the time of tillage and assuming a linear change to the point of sampling (Walling *et al.*, 2009), it can be considered to be more representative to apply an h_0 of half the value obtained *in situ* (section 5.3.1) across the study period (i.e. a mean h_0 for the study period). When calculated in this way, h_0 values of 1.6 kg m^{-2} (negative) and 2.1 kg m^{-2} (negative) were applied to the conventional and low pressure tyre wheelings respectively. Redistribution rates and corresponding budget estimates using the adjusted h_0 were reduced to 50 % of those shown in Table 5.3.

iii. *The sensitivity of model estimates to realistic changes in fallout input*

The estimated daily [7]Be inventory flux was calculated using reference inventories from cores taken in October and February (the beginning and end of study period) in conjunction with daily rainfall data (section 5.2.5.2.) based upon the method described by Schuller et al. (2010). An average rainfall activity of 2 Bq L^{-1} (4 Bq L^{-1} during December) was estimated for the study duration using this approach. Given the variability displayed between the February reference samples (15 %) (Figure 5.10b), for comparison, model estimates were recalculated using an average [7]Be activity from the directly measured Plymouth rainfall data for the same period (Chapter 2). This rainfall activity was slightly lower than the estimated value for the site at 1.82 Bq L^{-1} although the estimated cumulative inventory using this fallout value returned a sample day inventory of 152 (± 15 (2σ analytical uncertainty)) Bq m^{-2} which was within uncertainty of the mean inventory from the February cores (162 ± 24 Bq m^{-2}). By subtracting the residual [7]Be (section 5.2.5.2.) a new cumulative reference inventory was estimated with a final sample day value of 129 Bq m^{-2}.

Sediment budget estimates using this slightly adjusted inventory flux were reduced by ~ 28 % for the low pressure tyre wheeling and > 40 % for the conventional tyre wheeling (Table 5.4). The large reduction in the latter reflects the occurrence of deposition at 4 sample points owing to the lowering of the reference value on the sample day (from 138 Bq m^{-2} to 129 Bq m^{-2}) (see Figure 5.13), indicating the sensitivity of model outputs to the reference value when erosion rates are low.

	< 63 µm	< 20 µm	< 2 µm
Low Pressure	42.7	18.1	12.0
	10.0	*4.20*	*2.83*
Conventional	11.7	4.93	3.28
	2.68	*1.13*	*0.75*

Table 5.4: Wheeling sediment budgets (kg) derived with fallout input (*F*) estimated using an average [7]Be rainfall activity value (Bq L^{-1}) from Plymouth data for the same study period. Uncertainties (italics) are calculated using RSD (2σ) analytical uncertainties associated with the sample inventories

The approach used by Walling et al. (2009) and Schuller et al. (2010) assumes that values of rainfall activity are constant across the study period. However, the potential for rainfall activity variability is demonstrated in Chapter 2 and because fallout input (*F*) is a key component of equations 5.13 and 5.15, the effect of using a mean value of rainfall activity upon redistribution estimates was investigated.

To demonstrate the potential for variation in [7]Be rainfall activity (Bq L^{-1}) between events in the same month, data were taken from Caillet et al. (2001) and mean monthly values and standard deviations were determined. Large standard deviations (12-49 %) were evident, particularly in the warmer months. To further illustrate the effect of using an average [7]Be activity value to calculate [7]Be inventory, a cumulative inventory was derived using the event values given in Caillet et al. (2001) and compared to a cumulative inventory for the same period determined using a mean activity value estimated from an iterative fitting process (described in section 5.2.5.2.). The final inventory values are equal but the effect of the discrepancy (up to ~ 25 %) between the actual (event) and

estimated (mean) fallout input upon the cumulative inventory is notable (Figure 5.14).
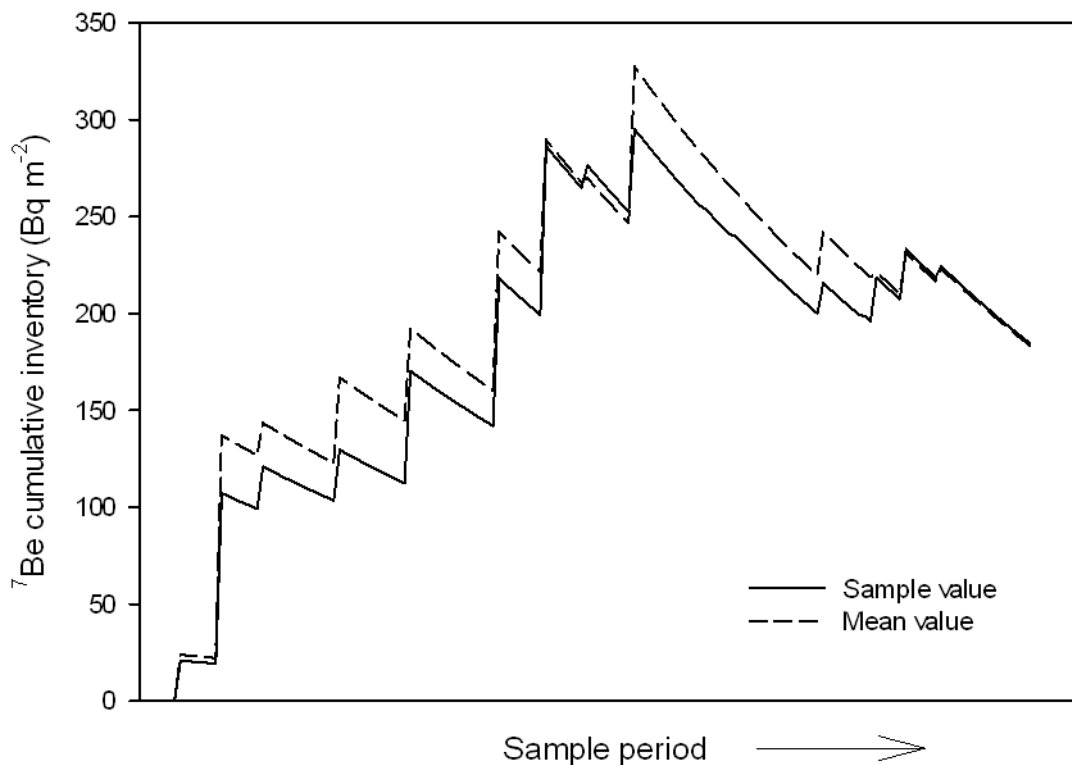
Figure 5.14: Cumulative inventories derived using [7]Be rainfall activity in event samples and a mean rainfall activity value for the sample period taken from Caillet et al. (2001). The final inventory values are equal although fallout input (Bq m^{-2}) has been overestimated during the sample period using a mean value.

The average rainfall activity value for Plymouth applied above was derived from 7 individual samples with sample periods ranging from 5 to 30 days depending upon the magnitude of rainfall, with an activity concentration range of 1.74 to 2.06 Bq L^{-1}. To assess the potential effects of temporal variability of [7]Be activity in rainfall upon sediment budget estimates, the cumulative inventory using the average Plymouth value was recalculated based upon sample activities for the corresponding time period, with the final sample day value remaining equal to that estimated using an average activity. Discrepancies between both cumulative inventories across the study period were low (up to ~5 %) and

subsequently only minor differences between soil redistribution estimates were returned. By introducing temporal variability in [7]Be activity here, estimates of soil loss were reduced by ~4 % and ~8 % for the low pressure and conventional tyre wheelings respectively.

5.4. Discussion

5.4.1. Validating the use of the profile distribution model to estimate event-based soil redistribution

Using rainfall simulation, estimates of soil redistribution on an event-basis provided a value which was overestimated by 44 % relative to the mass of soil captured directly. Although minor loss to desiccation cracks was observed in the early stages of the simulation, it is unlikely that a sediment loss of the magnitude of the discrepancy occurred given the low infiltration rate (7.5 mm hr^{-1}) and the low susceptibility of these soils to bypass flow (Chapman et al., 2003). The discrepancy between the estimated and actual mass of soil exported is more likely to reflect the quantification of the key components of the model, these being i) the reference baseline, ii) the relaxation mass depth (h_0) and iii) the particle enrichment correction factor. Given the low variability between reference cores (< 5 %) and the detailed knowledge of the transported fraction together with laboratory determination of enrichment factors, it is more likely that h_0 is the key control here.

By using supporting data, the exponential fit applied to derive h_0 can be deemed inappropriate. With knowledge of the eroded fraction (predominantly < 20 μm) and the mean activity of this captured material (21.7 ± 4.79 Bq kg^{-1}), the activity in the bulk soil of the eroding layer can be estimated by applying a suitable

enrichment correction factor (1.95). This suggested that the eroding layer had an activity of around 11.1 (± 2.45) Bq kg^{-1} which is comparable to the data points in Figure 5.8a but less than the surface activity predicted from the exponential fit (~ 45 Bq kg^{-1}). It is likely, therefore, that field sampling failed to account for spatial variability of depth distributions within the plot at this site. The potential for [7]Be depth distributions to deviate from the smooth exponential decrease was discussed in Chapter 4 with reference to variability in hydrological processes (Strudley *et al.*, 2008; Wallbrink & Murray, 1996). It is possible that such variability may have been exaggerated here owing to differences in compaction across the wheeling caused by irregular load pressures at the soil surface (Way & Kishimoto, 2004).

To achieve erosion estimates in agreement with the captured soil mass, the value of h_0 would need to be reduced to from 1.93 to 1.35 kg m^{-2} (negative). Figure 5.8a shows only a slight decrease in activity in the upper three data points which contributed to estimates of a deeper profile. The influence of preferential flow upon these points cannot be dismissed and this highlights the need for studies to be able to suitably quantify spatial variability. In many studies, including this research, this is not achievable owing to the demand upon gamma counting facilities and researchers rely upon composite samples to account for variability. However, this can be misleading since one sample, which may not be representative, can influence the profile. Here, the distribution was characterised using a composite comprised of two (270 mm diameter) cores which was seen as a compromise owing to the need to assess reference core variability from the remainder of the small, uniform plot. If spatial variability is unable to be quantified, the research undertaken here demonstrates that

samples of eroded material together with knowledge of enrichment factors can provide a useful means of validating the estimated depth distribution.

Because of the disturbed depth distribution displayed in the wheeling profile, estimates of erosion using an alternative, proportional modelling approach following Wilson et al. (2003) were determined for comparison. This is a simple approach which does not rely upon characterising the ^{7}Be distribution in the profile and, therefore, may have been a suitable alternative in this situation. However, erosion estimates using this method were an order of magnitude greater (~ 2.5 kg) than the captured soil mass suggesting that the profile distribution model is likely to provide more reliable estimates, even in disturbed areas.

5.4.2. Validating the profile distribution model at the field-scale over an extended time period

Large overestimations were returned using the extended timescale approach with respect to the captured soil mass of ca.1 kg at site 2. Approximately 60 % of the estimated erosion for the study period occurred on 1st and 3rd October, 2010 during events of 20 mm and 26 mm magnitude respectively. These events delivered around 50 % of the total soil inventory for the given day. The model assumes that the ^{7}Be delivered during the event is adsorbed to soil particles upon fallout and, thus, inventory loss (A_{loss}) is attributed to soil erosion. However, it is possible that with the onset of overland flow, some inventory will be displaced independently of soil particles by being transported in solution. This is likely to be of particular relevance to compacted soils, such as those at the study site, where infiltration excess overland flow may inhibit adsorption.

Dalgleish and Foster (1996) demonstrated losses of ^{137}Cs in runoff with the proportion of loss (with respect to input) increasing with an increase in overland flow volume (r^2 = 0.86). It is possible, therefore, that a proportion of the overestimation of erosion at the study site may be related to this process i.e. the model is overestimating inventory loss. In the sediment budget here, however, it could be argued that the effect of this inventory displacement on erosion estimates will be counterbalanced by underestimating soil loss elsewhere in the wheeling. Further studies are required to quantify the potential for ^{7}Be loss in overland flow and the subsequent influence upon redistribution estimates.

Following the findings of the plot-scale study, it is likely that a large proportion of the model overestimation can be attributed to incorrect application of key model components. By using the approximate value of 1 kg mass of soil exported from each wheeling at site 2, factors contributing to overestimation of erosion rates can be explored by isolating the key model controls and adjusting these components to test model sensitivity. Indeed, Walling et al. (2009) highlighted that the extended timescale approach should be seen as a framework which can be refined with additional site-specific data. With initial testing of the model, Walling et al. reported uncertainty values of around 70 % of mean erosion values which were derived by propagating analytical uncertainties through the model. In the research reported here, rather than relying upon analytical uncertainty, realistic adjustments to key components were applied using supporting data, thus, reflecting variability in field processes.

For the extended timescale approach the key components remain particle enrichment correction and the relaxation mass depth with addition of fallout input (*F*) estimation. Arguably, the calculation of relative erosivity could be included as a key control should the daily inventory loss be wrongly apportioned

across the study period. However, in the absence of suitable-site specific data regarding erosivity, the approach applied was that proposed by Walling et al. (2009) and will not be scrutinised here.

5.4.2.1. The effect of particle enrichment factors upon hill slope sediment budget estimates

A large difference in enrichment factors between size classes was observed for the soil type at site 2, with enrichment of the < 2 µm fraction over three times greater than for the < 63 µm fraction. Greater enrichment of the clay fractions can be expected where the overall proportion of clay is low (He & Walling, 1996). The pronounced increase in enrichment suggests the need for knowledge of selective transport of particle size classes during events since redistribution estimates using the < 2 µm correction factor are over three times lower than those using the < 63 µm correction factor. The selective transport of size fractions during events is widely documented (Durnford & King, 1993; Fullen & Brandsma, 1995; Issa et al., 2006; Wan & El-Swaify, 1998) although the redistribution of these fractions can be affected by a number of factors including rainfall intensity, supply and microtopography.

Parsons and Stone (2006) studied the effect of rainfall intensity pattern across a range of soil types demonstrating differences in the selective transport of particles between soil types and the influence of rainfall pattern upon selective transport within the same soil type. Predicting selective transport is, therefore, challenging and the complexity of transport processes suggests that standard erodibility constants for different soil types may be insufficient (Durnford and King, 1993; Parsons and Stone, 2006). Because of the difficulty in estimating

selective transport of fractions and the importance of applying a suitable correction factor, an indication of the distribution of size fractions eroded under natural conditions should ideally be determined *in situ* from representative samples of mobilised material.

5.4.2.2. The influence of relaxation mass depth (h_0) upon model estimates

The importance of establishing an accurate and representative value of h_0 has been highlighted in section 5.4.1. The characterised distributions at site 2 provided more realistic surface concentrations and are, to some extent, supported by the distribution shown in the cultivated bed (Figures 5.8b-d). Using the extended timescale approach, the challenge of characterising h_0 becomes one of temporal as well as spatial importance. Walling et al. (2009) demonstrated the potential for h_0 to increase with time during the study period but also stressed that suitable knowledge regarding temporal changes in h_0 are lacking and, therefore, assumptions are not soundly underpinned. Temporal variations in [7]Be depth distributions are likely to be site-specific and, therefore, changes should be investigated by repeat sampling throughout the study period. For many research projects, including that reported here, this is not practically viable.

It is logical that, as suggested by Walling et al. (2009), the depth distribution of [7]Be was lower at the start of the study period and, assuming linear change, it is reasonable to apply half the value of h_0 sampled at the end of the study period, across the entire period. This is an important consideration for this study given that > 70 % of total rainfall (and a large proportion of relative erosivity (a factor of ~0.9)) fell in the first half of the study period. The adjusted value of h_0

reduced redistribution estimates by 50 %. Combined with the potential effects of selective transport and particle enrichment described in section 5.4.2.1, it becomes clear how large overestimations in soil redistribution rates can occur. It is, therefore, essential that further research be undertaken to document temporal changes in h_0 in a range of agricultural soil types to confirm that the change is linear and, hence, provide a sound platform upon which to base assumptions.

5.4.2.3. The influence of estimated fallout input (F)

The approach applied by Schuller et al. (2010) to estimate ^{7}Be rainfall activity (Bq L^{-1}) offers a practical means of establishing the fallout input (Bq m^{-2}) over the study period. However, owing to the potential for variability (> 10 %) between reference core inventories, (which provide the baseline for estimating fallout input across the study period), the effect of reference variability upon inventory flux estimates should be quantified.

In the research reported here, application of an average ^{7}Be rainfall concentration value derived from Plymouth data for the same study period provided a cumulative inventory which was within uncertainty of that predicted using the reference cores from the site. Therefore, the cumulative inventory estimated using this fallout value can be said to be a realistic scenario. The average rainfall activity of 1.82 Bq L^{-1} was only slightly less than the value predicted using the reference cores (2 Bq L^{-1}) although the reduction in soil redistribution estimates was substantial at > 40 % for the conventional wheeling. This magnitude of reduction in redistribution estimates reflected the transition of some sample point inventories to deposition zones owing to the lowering of the

reference baseline. A similar magnitude of sensitivity may not occur where erosion rates (and associated losses of inventory at the sample point) are higher. Nevertheless, considering the potential sensitivity of the model to slight changes in the daily inventory flux it is recommended that estimates are supported by direct analysis of ^{7}Be activity in rainfall (Bq L^{-1}).

In the approach suggested by Walling et al. (2009) the authors assume a constant value of ^{7}Be activity in rainfall with each event across the study period. However, seasonal variations in ^{7}Be fallout associated with atmospheric circulation are well documented (Ayub *et al.*, 2009; Caillet *et al.*, 2001; Doering & Akber, 2008a; Gonzalez-Gomez *et al.*, 2006; Ioannidou & Papastefanou, 2006; Short *et al.*, 2007; Wallbrink & Murray, 1994) and variation can also occur on an event basis within a given month owing to scavenging dynamics and the effects of washout (Caillet *et al.*, 2001; Ioannidou & Papastefanou, 2006). By estimating an average rainfall activity using the method described in section 5.2.5.2, there is potential for the 'true' fallout input to be distorted (Figure 5.14). Temporal variability in rainfall activity was, therefore, simulated by using sample activities from the Plymouth data rather than an average value for the study duration. This adjustment, however, led to only minor reductions in redistribution rates.

The Plymouth data used to estimate fallout input were not event-based but, rather, were samples collected over periods ranging from 5-30 days depending upon the frequency and magnitude of rainfall. These samples, therefore, represent an integrated fallout activity for the given sample period. Arguably, these sample activities may not truly represent the fallout input associated with each contributing event given the potential variability associated with rainfall rate and magnitude (Caillet *et al.*, 2001; Ioannidou & Papastefanou, 2006).

Using event fallout input, further reductions in redistribution estimates could be expected. However, it is unlikely that research programmes will be able to accommodate event-based sampling and analyses over an extended time period and, therefore, sampling at regular intervals depending upon the frequency of rainfall is likely to remain the most efficient method of estimating fallout input. Given the potential for discrepancy between estimated and 'true' fallout input (Figure 5.14), rainfall sampling is recommended and efforts should be made to reduce sample intervals as much as is practicable.

5.5. Conclusions

Plot-scale rainfall simulation demonstrated the importance of accurate determination of h_0 for reliable erosion estimates and the challenges surrounding characterisation of depth distributions in the field. Accounting for spatial variability in h_0 is of key importance and, at present, researchers rely upon composite section cores for this purpose although this method does not enable variability to be quantified. It is unlikely that quantification of variability will be achievable in most studies given the demand upon gamma detectors and it is crucial, therefore, that careful attention be given to effective spatial sampling. Where variability in h_0 cannot be determined directly, knowledge of the ^{7}Be activity and particle size distribution of eroded sediment together with enrichment factors could provide a useful validation of estimated profiles. Attempts should also be made to incorporate uncertainty surrounding h_0 variability into redistribution estimates using realistic scenario testing. Wider research is required to quantify depth distribution spatial variability in a range of environments to provide a useful baseline to support scenario testing and may

provide guidelines regarding the best practicable means of accounting for such variability.

Validation of the extended timescale approach using natural ^{7}Be fallout raised questions with regard to the potential for loss of ^{7}Be in overland flow. If inventory loss occurs independently of soil transport, overestimated erosion rates can be expected and this suggests the need for controlled studies (cf. Dalgleish and Foster, 1996) to determine the extent of ^{7}Be loss in solution with the onset of overland flow and subsequent effects upon redistribution and budget estimates.

The sensitivity of the extended timescale model to temporal variations of key components was identified by comparing model results for a range of data scenarios to a known target of soil (~ 1 kg) captured in sediment traps deployed by ADAS UK Ltd. Without knowledge of this baseline figure of actual soil mass exported from the wheelings, application of established methods from the literature (Walling et al., 2009) would have led to an overestimation of yield i.e. 21.8 kg and 60.6 kg for the conventional and low pressure tyre wheelings respectively. By making realistic adjustments to key model components, it was possible for erosion estimates to be in closer agreement with the known eroded mass, particularly if selective transport of fractions and a reduction in h_0 was considered.

A major advantage of radionuclide use a sediment tracers has traditionally been the low number of site visits (and, therefore, labour) required to provide high resolution estimates of soil redistribution (Mabit *et al.*, 2008a; Zapata, 2003). In light of the findings above, effective use of ^{7}Be over an extended timescale is likely to require greater labour and analytical hours. Table 5.5 provides a

conservative estimate of the quantity of labour and analyses hours required to provide effective determination of key model components over an extended time period in this study. It is clear that considerable labour hours are required (~64) and around 80 days use of a gamma detector to provide the minimum requirements for reliable redistribution estimates. It is also noteworthy that the values given in Table 5.5 are based upon the sampling required for one transect and do not include travel times. Although these values represent a minimum requirement for sound determination of a wheeling sediment budget in this study, it is likely that such expenditure will not be achievable within the scope of many projects, particularly given the cost of gamma analysis.

A compromise is, therefore, required to provide sufficient data to support the key model components while retaining the advantage of efficiency in the use of [7]Be as a retrospective tracer. Some aspects of Table 5.5 may be further reduced, for example, it may be sufficient to assess the temporal variability in h_0 by sampling at the beginning and end of the study period rather than monthly. Likewise the sampling of eroded sediment to determine transported fractions may also be reduced. However, the above findings suggest caution should be taken with regard to assumptions surrounding the key model components given the potential sensitivity of model outputs to minor adjustments in these parameters. If these components are unable to be quantified, sensitivity testing of the model output using realistic adjustments to key factors should be undertaken. Uncertainties in erosion estimates can then be reported which will reflect the variation of model components and processes rather than analytical uncertainty alone

Sample type	Sample numbers	Model component	Labour hours	Gamma analysis hours	Running total labour hours	Running total analysis hours (gamma)
Rainfall	[a]7	Fallout input	14 (2 hrs per sample not inc. settling time)	168 (24 hour analysis per sample)	14	168
Depth profiling	6 (composite, 1 per month)	h_0	18 (2 hours field, 1 hour processing per sample)	720 (6 samples of 5 increments)	32	888
Eroded sediment	6 (1 per month)	Validating profile estimate	6 (1 hr trap collection/ processing per sample)	144	38	1032
Batch experiments	1 (in triplicate)	Be enrichment	4	1 (ICP-OES)	42	1032
Eroded sediment particle size distribution	6 (1 per month)	Particle enrichment correction factor	6 (wet oxidation)	~6 (Mastersizer)	48	1032
Reference cores	22 (composite)	Reference inventory	10 (2 hrs sampling and 3 hrs processing per 11 composite)	528	58	1560
Slope samples	15 (composite)	Slope inventories	6 (3 hrs sampling and 3 hrs processing per 15 composite)	360	64	1920

Table 5.5: Estimated project hours required to effectively determine key components of the extended timescale model in this study. Estimations are for one transect and do not include travel times. Sample processing times are based upon the use of mechanical grinding. [a]value based upon Plymouth samples and is dependent upon the frequency of rainfall

Chapter 6. Conclusions and recommendations

6.1. Synthesis and conclusions

This thesis has explored questions surrounding key assumptions associated with the use of ^{7}Be as a sediment tracer. The broad knowledge gaps addressed in this research related to:

i) The spatial and temporal variability of ^{7}Be fallout which is important in the context of estimating inventory flux during erosion studies.

ii) The adsorption behaviour of ^{7}Be in agricultural soils encompassing adsorption rate upon fallout and geochemical association. Knowledge of adsorption rate is required to satisfy the fundamental principle of rapid ^{7}Be adsorption to agricultural soils upon fallout. Assessment of geochemical association is vital to underpin the use of ^{7}Be as a tracer at the catchment-scale.

iii) The reliability of ^{7}Be erosion model estimates with attention to key model controls which is of crucial importance given the current lack of research providing validation and clear indication of sources of uncertainty.

These knowledge gaps were addressed in chapters 2-5 of the thesis and a synthesis of each chapter is provided below.

6.1.1. Spatial and temporal variability of ^{7}Be fallout in southern UK

Chapter 2 aimed to address the question of fallout temporal variability by determining ^{7}Be activity in rainfall sampled in Plymouth, southwest UK at regular intervals over a two year period. Secondary data collected during the

same period were used to compare variability with wider UK sites and, to date, no published data consider intra-regional variability of fallout dynamics in the UK. These data permit assessment of the reliability of using a constant value of ^{7}Be activity in rainfall when applying the profile distribution soil erosion model over extended timescales.

Monthly values of ^{7}Be activity in rainfall demonstrated temporal variability with a general trend for higher activity in warmer months. This was likely to be influenced by enrichment of ^{7}Be in surface air linked to convective circulation. Results indicated that rainfall magnitude and intensity may also influence ^{7}Be activity in rainfall with lower activity occurring with higher magnitude and intensity. A significant difference in rainfall activity was found between southern UK sites although temporal variability was well correlated. In Plymouth, variability in ^{7}Be deposition was largely explained by precipitation whereas other locations demonstrated a greater role of additional atmospheric processes.

These findings suggested that the use of a constant value of ^{7}Be activity in rainfall across a period of a few months may lead to unreliable estimates of inventory flux. It is, therefore, recommended that fallout input is estimated using direct analysis of ^{7}Be activity in rainfall and given the finding of spatial variability, this should be on a site-specific basis. Samples should be taken at regular intervals and estimates of cumulative inventory compared to soil inventories for validation.

6.1.2. Optimisation of ^{7}Be gamma analysis following BCR sequential extraction

Chapter 3 provided development of an analytical method which was a necessary precursor to exploring the geochemical association of fallout ^{7}Be in

soils. This chapter discussed the difficulties associated with analysing low activity samples using gamma spectrometry with regard to high analytical uncertainties. A practical method for reducing uncertainties was proposed which maximised data quality during sequential extraction experiments. The chapter also explored the potential for using stable Be as a convenient proxy for natural ^{7}Be in adsorption investigations given the difficulty in sourcing ^{7}Be standard solutions.

Findings showed that gamma spectrometry counting statistics associated with ^{7}Be sequential extractions can be improved by preconcentrating the extract solution prior to analysis. The reduction in analytical uncertainty enabled distinction between step extractions and detection of low-level association with soil fractions. Extractions of natural ^{7}Be fallout were not directly comparable to extractions of adsorbed stable Be owing to the use of high concentrations of Be in solution. Therefore, where possible, sequential extraction of natural ^{7}Be fallout (or ^{7}Be equilibrated at representative activity) should be undertaken using the method developed here to maximise counting statistics. Where geochemical studies apply stable Be as a proxy at concentrations suitable for detection using ICP-OES, results should be treated with caution.

6.1.3. Physicochemical behaviour of ^{7}Be in agricultural soils

Chapter 4 aimed to determine the adsorption behaviour of ^{7}Be in agricultural soils by:

i)   Quantifying the adsorption rate of Be to soil using batch experiments to address the fundamental question of rapid adsorption upon fallout.

ii)   Determining the vertical distribution of ^{7}Be in experimental soils, developed under semi controlled conditions, to provide comparative data for adsorption rate. Coupled with knowledge of geochemical association, the distributions also enabled controls upon vertical behaviour to be explored and discussed in the context of field investigations.

iii)   Assessing the potential mobility of ^{7}Be in natural soil solutions at the slope-scale and under changing conditions at the catchment-scale to address the assumption of irreversible adsorption upon fallout.

Batch experiments showed adsorption of > 90 % stable Be from solution to soil after 0.1 h contact time, thus, supporting the fundamental tracer requirement of rapid adsorption upon contact with soil particles. This was reflected in the shallow depth distributions displayed in all experimental soils.

Fallout ^{7}Be depth distributions developed under semi-controlled conditions demonstrated the importance of textural characteristics and soil hydrology upon vertical profiles. Soil hydrological properties are likely to vary across a field site and this has practical implications for accurate determination of depth distributions which is a fundamental requirement of erosion models. To date, this source of variability has not been considered in erosion model estimates.

Sequential extractions identified that ^{7}Be was largely associated with exchangeable and reducible soil fractions in the experimental soils. This suggested potential for ^{7}Be to be mobilised independently of soil particles under conditions of increased salinity, reduced pH and low oxygen. These findings, therefore, have implications upon the use of ^{7}Be as a catchment-scale tracer. ^{7}Be did, however, remain adsorbed to all soils in artificial rainwater solutions, therefore, providing confidence in its use under common field conditions. In

future studies, it is recommended that preliminary sequential extractions are carried out following the methods described here, to determine potential for ^{7}Be mobility prior to application at the catchment-scale.

6.1.4. Field-scale erosion estimates using ^{7}Be inventories: Model validation and practical considerations

Chapter 5 aimed to validate estimates of erosion using the ^{7}Be profile distribution model by comparing model estimates to a known mass of exported soil. Investigations were undertaken to validate model estimates of erosion at the event-scale and the approach over an extended period of time. Key model controls were identified and the importance of accurate field characterisation of these components discussed. Here, the findings of chapters 2 and 4 were of relevance when considering the potential for fallout and depth distribution variability.

Comparison of estimates of event erosion using the profile distribution model to a known mass of soil eroded from an experimental plot showed a disparity of ~ 40 %. In this example the overestimation produced by the model was likely to be the consequence of inaccurate representation of the ^{7}Be depth distribution across the study site. Careful attention should, therefore, be given to characterisation of ^{7}Be depth profiles across a study site. Quantification of spatial variability is required although it is likely that this will be compounded in many studies by restriction to sample numbers owing to radioactive decay.

Large overestimations in erosion estimates were also returned when applying the approach over a period of a few months at the field scale. Sensitivity testing

of the model identified key model controls and highlighted the importance of direct determination of the following field components:

i) *^{7}Be depth distribution*. Characterising the depth distribution of ^{7}Be requires consideration of temporal as well as spatial variability and it is recommended that field studies account for this by repeat sampling.

ii) *Preferential adsorption to fine fractions.* Site-specific knowledge of ^{7}Be enrichment in fine fractions and the selective transport of these fractions is required to correct erosion estimates for preferential adsorption. This is particularly important for sandy soils where large increases in enrichment between fractions are likely to be found. It is recommended that site-specific enrichment factors are estimated using stable Be and some attempt is made to estimate the size of transported fractions in the field.

iii) *^{7}Be fallout input*. Where possible, it is recommended that ^{7}Be deposition is determined by direct sampling of rainfall at a field site given the potential sensitivity of model estimates to values of fallout input.

A combination of the factors listed above is likely to contribute to unreliable erosion estimates across an extended time period. Where factors cannot be measured directly, uncertainties should be reflected by reporting a range of erosion estimates based upon realistic sensitivity analysis of model components. In this manner, reported uncertainties will reflect field processes rather than propagated analytical uncertainty alone.

6.2. Recommendations for further research

Where sequential extraction experiments have identified the potential for tracer mobility, further research is required to quantify the mobility and potential effects upon tracer use. Given the large proportion of ^{7}Be associated with the exchangeable fraction in the experimental soils, further research should consider the potential for mobility under saline conditions at the freshwater-marine interface. Batch experiments similar to those carried out using artificial rainwater in this research would provide a useful indication of the potential for mobility in a range of salinities to support the use of ^{7}Be in estuarine and coastal environments.

Owing to the large association with the reducible soil fraction it is important to determine the extent of ^{7}Be mobility in low oxygen environments. Initially, studies are required which detail the proportion of total ^{7}Be mobilised under a range of reducing conditions and simple microcosm experiments may be suitable for this purpose. These studies should be coupled with field-based research to determine the likelihood for changing parameters to promote mobility in the natural environment. Sampling *in situ* would enable redox conditions to be monitored by, for example, use of Eh meters and determination of Fe/Mn concentration in pore waters. Should these combined studies indicate potential for mobility in representative field units, research could then consider the dynamics of mobility and effects upon tracer estimates. For example, it may be important to determine the effect of mobility upon ^{7}Be inventories in deposition zones. Column experiments in a low oxygen environment chamber may be suitable to quantify the effects of mobility upon the ^{7}Be depth distribution in soils. Studies could also be undertaken to investigate the effect of fluctuating saturation levels upon ^{7}Be inventories. These studies could then

provide an indication of the extent of inventory loss and/or recommend methods to account for increased mobility when sampling.

The potential for spatial variation in ^{7}Be depth distributions across a field site has been highlighted and unreliable erosion estimates have been returned where such variability has not been accounted for. Accurate characterisation of h_0 is vital for robust application of the profile distribution model and many studies will be unable to quantify spatial variability at a field location owing to limited capability to process a large number of samples. The use of composite samples does not provide a sound alternative since spatial variability is not quantified and cannot be accounted for using this method. For these reasons it would be useful if research were undertaken with the primary aim of quantifying spatial variability in a range of field locations. Data could then provide some indication of the extent of variability which researchers could incorporate into estimates of erosion by extending uncertainties accordingly. Such studies may also provide useful methodological development by suggesting sampling schemes to reduce uncertainty associated with spatial variability.

Further research is also required to address aspects of the use of ^{7}Be as a tracer which have not been considered in this thesis. Fallout uniformity at the field-scale is assumed and, to date, the potential for spatial variability has not been investigated. Although the research reported here has begun to explore the assumption of rapid adsorption upon fallout, there remains a question regarding the potential for displacement of inventory delivered during overland flow events and experimental studies should be undertaken to address this issue.

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