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Research

Natural Elemental Concentrations and Fluxes: Their Use as Indicators of Repository Safety

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SKI and SSI Perspective

Background

The safety of nuclear waste disposal must be assessed into the far future. For long-lived waste, including spent nuclear fuel, the necessary time-frames span over hundreds of thousands of years. In fact, similar assessments are required for disposal of all long-lived or stable toxic materials. Regardless of the type of long-term risks involved, the acceptability of disposal of hazardous waste must be judged against established criteria. In the case of nuclear waste disposal, expected radiation doses and radiological risk to humans have since long been applied as indicators of safety. Corresponding criteria in terms of dose or risk limits have been decided or proposed by competent authorities in many countries. However, the long timeframes make the calculation of these safety indicators difficult. This is mainly due to the unavoidable uncertainties in predicting human behaviour and biosphere evolution. On the other hand, the confidence in calculated values of radionuclide flux from a repository and the resulting biosphere concentrations is considerably greater. As a consequence, environmental concentrations and fluxes of radionuclides released from a repository have been discussed as safety indicators complementary to dose and risk. SKI and SSI have participated in these discussions and in the development of complementary safety indicators for about 15 years.

The criteria, or target values, for concentrations or fluxes could be based on model calculations for a suitable set of standard biospheres. The most obvious choice of target values, however, would be based on natural concentrations and fluxes of radionuclides. An international research programme with the aim of providing background data for this purpose is presently conducted by IAEA, and it is expected to be concluded in 2003. SKI and SSI are jointly contributing to this programme with a compilation and analysis of Swedish data.

SKI has indicated the possibility to use concentrations and fluxes of radionuclides as complementary safety indicators in its guides for disposal of nuclear wastes. Presently, SSI is preparing guides to their regulations for disposal, and complementary safety indictors are discussed in this work.

SKI and SSI Objectives

To explore the feasibility of compiling data on environmental abundances of natural radio-elements and calculation of elemental fluxes for use as references when concentrations and fluxes are employed as safety indicators.

Results

The study has demonstrated that it is possible to compile from the published literature a substantial database of elemental abundance in natural materials, and, using this data, to calculate a range of elemental and activity fluxes arising due to different processes at different spatial scales. *(From the Summary.)*

Continued work

The results will be employed together with the results of the on-going IAEA research programme (see above) in order to establish a set of background data for further work with development of complementary safety indicators.

Project information

Responsible staff: Stig Wingefors (for SKI) and Maria Nordén (for SSI).

SKI Project number: 99054
SSI Project number: P 1111:98

See also SKI Report 97:29 – *Natural Elemental Mass Movement in the Vicinity of the Äspö Hard Rock Laboratory (W.M. Miller, G.M. Smith, P.A. Towler, and D. Savage)*

Comments added in proof

- ***The handling of short-lived daughter nuclides in decay chains as discussed in Section 1.2 is further elaborated in Appendix A.2 of SKI Report 97:29 (see above).***
- ***It should be observed that the equations given for the activity of the U and Th decay-chains on p. 11 and 12 only consider the long-lived radionuclides. The omission of the short-lived radionuclides may not be relevant for all applications.***
- ***In Table 1.1 on p.12, the specific activities are quoted as Bq/kg – this should read as Bq/g.***
- ***In Table 1.1 on p. 12, the numbers given in parentheses for certain nuclides denote the number of decays of short-lived daughter nuclides included in the specific activity. (See Appendix A.2 of SKI Report 97:29.)***

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Contents

Summary

The calculated post-closure performance of a radioactive waste repository is generally quantified in terms of radiological dose or risk to humans, with safety being determined by whether the calculated exposure values are consistent with predetermined target criteria which are deemed to represent acceptable radiological hazards. Radiological exposure based target criteria are used widely by licensing authorities, and dose and risk have been universally adopted as end-points in all recent PAs. Despite their general acceptance, however, dose and risk are not perfect measures of repository safety because, in order to calculate them, gross assumptions must be made for future human behaviour patterns. Such predictions clearly become increasingly uncertain as forecasts are made further into the future. As a consequence, there has been a growing interest in developing other ways of assessing repository safety which do not require assumptions to be made for future human behaviour.

One proposed assessment method is to use the distributions of naturally-occurring chemical species in the environment, expressed either as concentrations or fluxes of elements, radionuclides or radioactivity, as *natural safety indicators* which may be compared with the PA predictions of repository releases. Numerous comparisons are possible between the repository and natural systems (e.g. a comparison between natural and repository derived radioactivity fluxes in groundwater discharges). The primary objective is to use the natural system to provide context to the hazard presented by the repository releases. Put simply, if it can be demonstrated that the flux to the biosphere from the repository is not significant compared with the natural flux from the geosphere, then its radiological significance should not be of great or priority concern.

Natural safety indicators may be quantified on a site specific basis, using information derived from a repository site characterisation programme, and can be compared to the outputs from the associated site specific PAs. Such calculations and comparisons may be very detailed and might examine, for example, the spatial and temporal variations in the distributions and fluxes of naturally-occurring chemical species arising from individual processes, such as groundwater discharge, river flow and erosion at specific locations. The approach can also be of value at the generic level of repository development, before site characterisation programmes have been undertaken. They could be used, for example, as a component in comparative evaluations of alternative generic disposal concepts. The objective at the generic level would be to define typical or average natural elemental concentrations and fluxes in geological systems representative of the environments which might host a repository, and to compare these with the outputs from the associated generic PAs.

To define average elemental concentrations and fluxes requires that sufficient information is available on natural elemental distributions in the different rocks, sediments and waters which comprise typical disposal environments, as well as the rates of processes which drive the elemental fluxes in these systems. Much of this information is available but is widely scattered across a broad spectrum of the earth science literature (including geology, geochemistry and physical geography). Thus, to facilitate the use of the natural safety indicators methodology at

the generic level, this study has undertaken to bring together and to compile much of the required information.

This information has been used to quantify average elemental mass fluxes at the global scale for a range of processes, including groundwater discharge, erosion and sediment transport. The point of these calculations is that they provide a baseline against which site or geological environment specific natural fluxes, from anywhere in the world, can be compared on an equal basis to evaluate if they are higher or lower than the global average and, thus, are useful for providing a broad natural context for predicted repository releases.

In separate calculations, elemental mass fluxes were quantified for a number of *reference environments* which are chosen to be representative of the types of sites and geological systems which may host a deep repository. The reference environments were an inland pluton, basement under sedimentary cover and a sedimentary basin. The fluxes for these environments were calculated for systems with spatial scales of a few hundred square kilometres and, as such, approximate closely to the repository systems modelled in PAs because a reference environment represents the same system, with the same rock, groundwater and surface conditions as those controlling the release and transport of contaminants from the repository.

In further calculations, the elemental mass fluxes of U, Th, K and Rb were used to calculate total alpha and non-alpha radioactive fluxes. For U and Th, activity fluxes were calculated for the radioelements alone (in normal isotopic proportions) as well as for their respective decay chains, assuming secular equilibrium in the chains and considering only the longer-lived nuclides with half-lives longer than one day. For K and Rb, activity fluxes were calculated for the non-series nuclides ^{40}K and ^{87}Rb. These natural activity fluxes are considered to be particularly useful safety indicators because they can be readily compared with the results from PAs, because the calculated repository releases normally expressed as dose can be recast in terms of equivalent activity fluxes.

Lastly, orebodies and hydrothermal systems were considered briefly because they provide the potential for maximum concentrations and maximum fluxes, respectively, in geological systems. Although it would be unlikely that a repository would ever be located in these geological systems, they are useful to consider here because they provide further context to the broadest variability in natural systems for comparison with the repository releases.

This study has demonstrated that it is possible to compile from the published literature a substantial database of elemental abundances in natural materials and, using this data, to calculate a range of elemental and activity fluxes arising due to different processes at different spatial scales. Although it was not attempted in this work, these fluxes should be comparable to standard PA results, with some modification to the PA calculations explicitly to output the concentrations and activities associated with the repository releases (usually only dose or risk are explicitly given as output).

Sammanfattning

Säkerheten hos ett slutförvar för radioaktivt avfall efter förslutning anges oftast i termer av beräknade doser eller risker för människor från joniserande strålning. Hur säkert ett slutförvar är avgörs därvid av hur de beräknade doserna förhåller sig till referensvärden som bedöms svara mot en acceptabel risk. Sådana dos- eller riskkriterier används allmänt av tillståndsgivande myndigheter, och dos och/eller risk har använts som bedömningskriterier i de flesta säkerhetsanalyser. Trots att användningen av beräknade framtida doser är allmänt accepterad så har denna metod en inneboende svaghet i och med att de framräknade doserna är behäftade med mycket stora osäkerheter. Visserligen kan man försöka att konsekvent välja beräkningsförutsättningar så att doserna inte underskattas, men detta leder till ett felaktigt eller förvrängt beslutsunderlag. Osäkerheterna beror främst på det omöjliga i att kunna förutsäga människors vanor och samhällets utveckling i mycket långa tidsperspektiv (tusentals – hundratusentals år). Till följd av dessa svårigheter har man försökt att utveckla andra metoder att bedöma säkerhet, utan att behöva förutsätta något om mänskliga vanor långt in i framtiden.

En av dessa föreslagna bedömningsmetoder går ut på att använda beräknade halter av radionuklider i marken runt ett slutförvar och/eller beräknade flöden av radionuklider från slutförvaret som mått, indikatorer, på riskerna med verksamheten. Dessa beräknade halter och flöden skulle sedan kunna jämföras med beräknade eller uppmätta halter och flöden av naturligt förekommande radioaktiva ämnen. Man kan på detta sätt använda halter och flöden som *säkerhetsindikatorer* med motsvarande naturliga värden som *referensvärden*[1]. Om det t.ex. går att visa att flödet till biosfären från ett slutförvar är obetydligt i förhållande till jämförbara naturliga flöden så borde det innebära att den radiologiska risken från slutförvaret är acceptabel.

Naturliga referensvärden till säkerhetsindikatorer, såsom halter och flöden, kan kvantifieras för platser som valts ut för slutförvaring, varvid de lämpligen tas fram i samband med respektive platsundersökningar. Dessa värden kan sedan jämföras med resultaten från platsspecifika säkerhetsanalyser. Sådana beräkningar och jämförelser kan göras med olika detaljeringsgrad och ta hänsyn till rumslig och tidsmässig variation hos en rad olika processer såsom utflöde av grundvatten, ytvattenhydrologi och erosion. Metodiken kan också användas generiskt, före platsundersökningar, för att utvärdera olika slutförvarskoncept.

För att ta fram data på globala medelvärden för halter och flöden av olika grundämnen behövs tillräckligt med information om fördelning av halter av grundämnena i bergarter, sediment och vattendrag. Dessutom behövs information om hastigheten hos de processer som styr flödena av grundämnen i dessa system. Det mesta av denna

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[1] Dessa definitioner överensstämmer inte med de som används i rapporten (inklusive rubriken). Där anges att det är referensvärdena som är ”safety indicators”. Någon full enighet om nomenklaturen på detta område har ännu inte utbildats, varken i Sverige eller utomlands. Här har begreppen använts i enlighet med SKI:s och SSI:s uppfattning. (SKI och SSI har haft begränsat inflytande på rapportens utformning eftersom den bekostats av flera organisationer.)

information finns framtagen men är spridd i den geovetenskapliga litteraturen (t.ex. geologi, geokemi, naturgeografi). Detta arbete har utförts för att underlätta generiska studier av användning av halter och flöden som säkerhetsindikatorer genom att kompilera och sammanställa mycket av den information som behövs.

Denna information har använts för att beräkna flöden av grundämnen på global nivå för en rad processer såsom utflöde av grundvatten, erosion och transport av sediment. Tanken bakom dessa beräkningar är att resultaten skall kunna användas som utgångsvärden vid bedömning av motsvarande platsspecifika (lokala) data. En sådan global jämförelse kan användas för att fastställa i vad mån platsspecifika data ligger inom ett rimligt intervall.

I särskilda beräkningar har massflöden av grundämnen tagits fram för ett antal geologiska referensformationer. Dessa har valts som representativa exempel på platser och geologiska system som är tänkbara för lokalisering av slutförvar: ett bergsmassiv i inlandet, urberg under sedimenttäcke och en sedimentär formation. Flödena för beräknades för dess system på en skala av ett par hundra kvadratkilometer.

I andra beräkningar har flöden av U, Th, K och Rb tagits fram, varifrån sedan beräknats flödena av alfa- och icke-alfaaktivitet. För U och Th beräknades aktivitetsflödena för dessa radioelement enbart (med den naturliga isotopsammansättningen för uran) och för respektive sönderfallskedjor. I de senare fallen antas radioaktiv jämvikt gälla och endast ”långlivade” nuklider (med halveringstider längre än ett dygn) har medtagits[2]. För K och Rb beräknades aktivitetsflödena för isotoperna ^{40}K och ^{87}Rb. De naturliga aktivitetsflödena kan anses särskilt lämpade för användning som referensvärden eftersom de på relativt enkelt sätt kan jämföras med data som tas fram vid dosberäkningar i en säkerhetsanalys.

Slutligen har malmer och hydrotermala system diskuterats eftersom dessa har potential att ge de högsta halterna och de största flödena i naturliga geologiska system. Även om det är osannolikt att slutförvar lokaliseras i sådana system kan de vara värda att ta upp som exempel på största tänkbara variationer i naturliga halter och flöden.

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[2] Detta uteslutande av kortlivade nuklider kan diskuteras. I vad mån det är relevant beror på hur framtagna data skall användas. Se även kommentarer under ”SKI and SSI Perspective”.

1 Introduction

The generally accepted best practicable option for dealing with long-lived radioactive wastes is final disposal in engineered repositories located deep underground in suitable geological environments.

The safety of any proposed radioactive waste repository is evaluated in a performance assessment (PA) which models in a simplified but adequate fashion, the many processes which may lead to the release and transport of radionuclides from the repository, through the host rock to the surface environment and eventual uptake by humans. Post-closure repository performance is generally quantified in terms of radiological dose or risk to humans, with safety being determined by whether the calculated exposure values are consistent with predetermined target criteria which are deemed to represent acceptable radiological hazards.

Radiological exposure based target criteria have been widely adopted by licensing authorities, and dose and risk have been universally calculated in all recent PAs. Despite their general acceptance dose and risk are not, however, ideal measures of repository safety and recently there has been some discussion concerning the use of other, complementary safety indicators in PA (e.g. IAEA, 1994).

The single largest problem associated with dose and risk as a safety indicator is that gross assumptions need to be made for future human behaviour (i.e. the human exposure pathway). While it is true that some degree of uncertainty affects all aspects of the repository system, it is, at least, possible to attempt to predict subsurface radionuclide behaviour on the basis of the application of known physical and chemical laws. Future human behaviour will, however, be determined not only by people's reactions to evolving environmental (e.g. climate) conditions but also by the changing socio-political situation. So, for example, to allow dose and risk to be calculated, assumptions need to be made for changes to the size, location, diet, agricultural practices, housing and recreational patterns of future generations. Such changes obviously become progressively more difficult to predict with any degree of certainty as forecasts are made further into the future. As a consequence, it could be argued that it is not scientifically valid to base licensing criteria on predicted exposures to humans for times in excess of a few hundred or thousand years into the future.

A partial resolution of this problem is to describe a series of so-called 'reference biospheres' (BIOMOVS, 1996a) that represent future biosphere environments that, it is thought, probably or possibly may occur in the future, and to calculate exposures for the human population for each scenario. There are, however, no guarantees that the real future environments will actually be included in the list of scenarios, regardless of how long that list is and how inventive the scenario developers are. Nonetheless, using this approach, it is possible to investigate the radiological consequences if the predicted releases were to occur today, using present-day conditions, at a chosen repository site or in other locations, as a reference.

Given these problems, there has been a growing interest in developing other ways of assessing repository safety which do not require assumptions to be made for future human behaviour. A favourable alternative methodology is to compare PA predictions of repository releases with the distribution of naturally-occurring chemical species in the environment. Comparisons between the distribution of both the repository and natural species may be expressed either in terms of concentrations or fluxes, and units of mass or radioactivity can be used as appropriate.

Put simply, this means that it should be possible (provided relevant data are available) to compare the predicted total repository-derived radioactive flux (e.g. in Bq/yr) crossing the geosphere-biosphere interface in the vicinity of the repository with the natural equivalent. The fundamental logic behind this comparison is that, if the flux to the biosphere from the repository is not significant compared with the natural flux from the geosphere, then its radiological significance should not be of great or priority concern. Numerous comparisons between repository and natural species concentrations and fluxes are possible, and decisions will need to be made to determine the most appropriate comparison(s) to meet the objectives of the safety assessment in hand, e.g. generic, site-specific etc.

This method has previously been proposed as a mechanism for defining maximum allowable releases from a repository. Such an approach has been considered seriously in the Nordic countries, and specific proposals were included in the first and second editions of the Nordic Flagbook which state that:

> *"The radionuclides released from the repository shall not lead to any significant changes in the radiation environment. This implies that the inflows of the disposed radionuclides into the biosphere, averaged over long time-periods, shall be low in comparison with the respective inflows of natural alpha emitters."* (Nordic Radiation Protection and Nuclear Safety Authorities, 1989; 1993)

Likewise, in the UK, a criterion of this type was expressed explicitly in the Guidance on Requirements for Authorisation document [known as the GRA] which states in Requirement R4 that:

> *"It shall be shown to be unlikely that radionuclides released from the disposal facility would lead at any time to significant increases in the levels of radioactivity in the accessible environment."* (Environment Agency et al., 1997)

The basic philosophy behind using this method to define maximum allowable repository releases to the biosphere is simply to restrict these releases to some (small) fraction of the natural radioactive flux or field. Unfortunately, developing and applying a quantitative release criterion of this nature is non-trivial. Considerable discussion would be required to define concepts such as a 'significant change' and, indeed, to determine what the background fluxes of naturally-occurring elements and radionuclides actually are. Furthermore, the implication of restricting allowable releases to a small fraction of the natural radiation field at the repository site would be that repositories planned to be sited in locations with relatively low levels of natural radiation would be subject to much more restrictive (quantitatively lower) release limits than those planned for locations with above average levels of natural radiation.

As a consequence of these considerations, more recently there has been a move to consider natural fluxes and concentrations as a way, not of defining release limits, but of evaluating repository releases in a natural context, i.e. to use concentrations and fluxes as *natural safety indicators*. In other words, to use them for qualitative evaluation of safety rather than for quantitative definition of safety limits. An important factor here is that natural safety indicators are used as *complementary* indicators of safety to dose and risk, rather than as an *alternative* or replacement for them. This is in accordance with the general view that repository safety has to be demonstrated using multiple and independent lines of evidence.

That this should be possible is evident once it is realised that natural processes, such as weathering, erosion, river flow and sedimentation are busily moving elements and radionuclides around within the same system that hosts the repository, but independently of it, and which is being modelled in PA. This is shown illustratively in Figure 1.1.

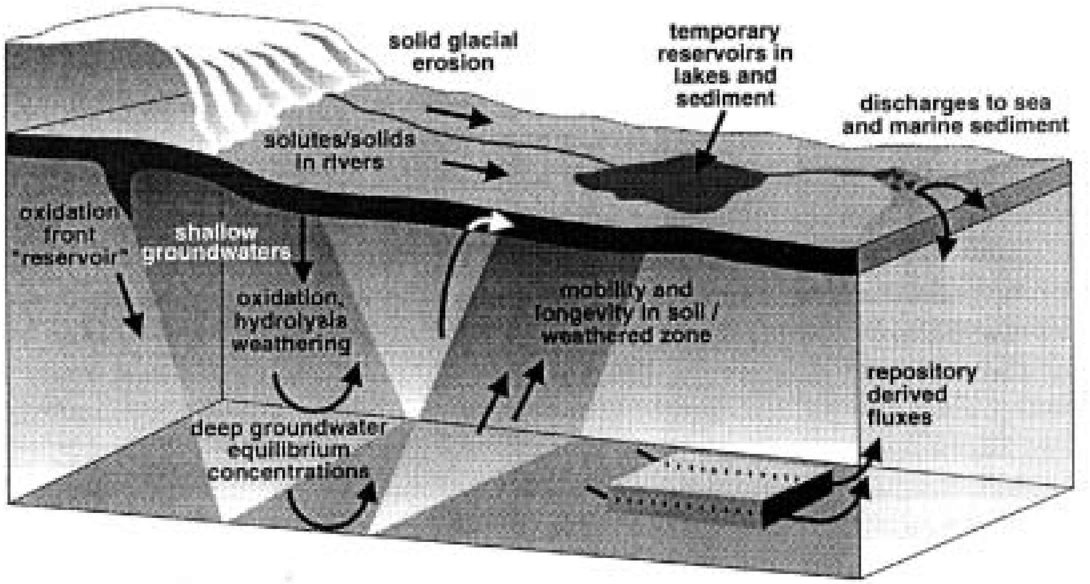

Figure 1.1: Natural geochemical fluxes occurring on the same timescale and in the same system as the repository provide useful contextual information for evaluating assessment results and thus can be considered as complementary natural safety indicators.

A further advantage of the fluxes methodology, beyond the avoidance of assumptions for future human behaviour, is that demonstrations of safety can be expressed in a natural context which may be more readily understandable by non-technical stakeholder groups (such as the public) than safety couched in units of radiological dose or risk. Lastly, investigation of how naturally-occurring elements move from the geosphere to the biosphere may enhance modelling of repository-derived radionuclides at the geosphere-biosphere interface. This interface was noted as a poorly modelled part of the system some time ago (SKI-SSI-SKB, 1989) and is still regarded as deserving greater attention (BIOMOVS, 1996b).

There is now growing international interest in the natural safety indicators approach. This interest is partly driven by recent recommendations from the NEA that PAs should demonstrate repository safety using ‘multiple lines of reasoning’ and should also include a number of additional non-dose/risk indicators to provide further context to the PA results (NEA, 1997, 1999a,b). This interest is reflected in the fact that two large-scale research projects have recently been launched to investigate the subject. The first study, run under the auspices of the

IAEA is a co-ordinated research project (CRP) which began in 1999 and is expected to finish in 2003. It involves 9 countries (Argentina, Brazil, China, Cuba, Czech Republic, Finland, Japan, Sweden and the United Kingdom) which are working together to build a database of measured concentrations and fluxes for a number of naturally-occurring elements and radionuclides in rocks, soils and waters. It is hoped these may be used to compare with intermediate outputs from PA calculations (Miller, 2001). The IAEA is further promoting international interest in natural safety indicators and is due to publish a report providing suggestions for their possible application to PA (IAEA, 2002). The second study, known as Safety and Performance INdicators (SPIN), is run under the auspices of the European Commission and involves a number of organisations across Europe. This study is complementary to the IAEA project in that it aims to define a suite of safety indicators which may be calculated in PAs, including the concentrations of repository derived contaminants in the geosphere and biosphere, and their fluxes across the geosphere-biosphere interface.

National programmes have also begun to consider ways to apply natural safety indicators in PA and in licensing issues. In Finland this idea has been put into practice and the Radiation and Nuclear Safety Authority (STUK) has recently issued a guide for the long-term safety of spent fuel disposal which includes constraints based on effective dose for the first few thousands of years and constraints based on activity releases to the environment for time periods further in the future, when probable climate changes make assessments for human exposures uncertain (STUK, 2001). These activity release constraints are expressed as nuclide specific activity fluxes across the geosphere-biosphere interface and are defined such that (i) at their maximum, the radiation impacts arising from disposal can be comparable to those arising from natural radioactive substances and (ii) on a large scale, the radiation impacts will remain insignificantly low. The repository flux from the geosphere to the biosphere is suggested in the Finnish guide as a suitable long-term safety indicator to avoid large uncertainties related to the evolution of the biosphere.

In Japan, natural safety indicators were used as supporting material in the recent H12 PA (JNC, 2000). In this PA, the calculated activity concentrations for repository derived radionuclides were compared to those of naturally occurring radionuclides in a number of geosphere and biosphere compartments, notably some Japanese rivers. The comparison indicated that the concentration of radionuclides released from the repository would be several orders of magnitude lower than that of natural radionuclides. This represents the first considered attempt to include natural safety indicators in a PA to complement the usual dose and risk end-points.

These ongoing projects have all indicated that a limitation of the natural safety indicators approach is the availability of reliable information on the concentrations and fluxes of relevant naturally occurring chemical species. Investigations of the natural concentrations and fluxes of certain elements have previously been made, notably for the major nutrient elements (e.g. C, N, O, P and S). These investigations were, however, primarily concerned with the movement of these elements within the biosphere, and their availability and uptake by the flora and fauna (for review, see Butcher et al., 1992) and not with the transfer of elements from the geosphere to the biosphere. A number of studies have examined geochemical fluxes of certain trace elements but these studies are usually concerned with assessing the effects of anthropogenic pollution on the biosphere (e.g. Benjamin and Honeyman, 1992) rather than focussing on the natural system. As a consequence, one of the objectives of the present study is to compile sufficient information on trace element distributions in natural materials to allow relevant fluxes to be determined for use in the evaluation of repository safety. This should be enhanced by the results of the IAEA CRP which intends to publish a database of additional concentration and flux information.

1.1 Applying the natural safety indicators methodology

As was suggested earlier, there are many different comparisons which possibly could be made between repository-derived contaminants and naturally-occurring chemical species in the geosphere or at the Earth's surface. The greatest benefit from the natural safety indicators methodology comes about, however, from considering only the most appropriate and relevant comparisons. The two most important considerations for relevance are the comparisons between chemical species and the comparisons between flux pathways. These are discussed separately below.

1.1.1 Comparisons between natural and repository chemical species

The chemical species of interest to the natural safety indicator methodology are elements and radionuclides, rather than compounds. In other words, it is the mass of a particular element or radionuclide which is of interest, rather than its chemical speciation. Such a view may be challenged because the chemotoxic hazard presented by some elements is partly controlled by speciation. In the absence of detailed information on elemental speciation and changes throughout the geosphere-biosphere system, however, it is not possible accurately to take speciation into account. This could possibly be improved in future work.

When considering elements, it is possible directly to compare elemental concentrations (e.g. in µg/l or mg/kg) for both the repository and natural species. Likewise, it is possible to compare elemental mass fluxes (e.g. in kg/km^2/yr). Such comparisons are sensible for stable elements which may represent a chemical (chemotoxic) hazard because the degree of hazard relates partly to elemental abundance, although chemical speciation is also important as mentioned above. Chemotoxic elements are interesting to consider here because some of the contaminants released from a repository will be poisonous and some concern is now being expressed about the non-radiological risks associated with repository releases (e.g. Persson, 1988; CEC, 1991).

Furthermore, the natural safety indicators methodology can be transposed directly from the arena of radioactive waste disposal to that of toxic waste disposal. Toxic wastes are now beginning to be considered with the same level of concern and detail as radioactive wastes and similar methods for geological disposal may be developed. For example, these concerns are expressed in the second edition of the Nordic Flagbook which states:

> *"Universally applicable hazard coefficients for both radioactive and non-radioactive wastes would be very valuable. However, too little is known about the genotoxic properties of*

> *various substances to allow such hazard indexes to be defined for each substance. In addition, the risk assessment methodologies for genotoxic chemicals are generally not so developed as those for radioactive substances. Further exchange of information between the fields of nuclear and non-radioactive waste management would be desirable to harmonise safety principles and management practices."* (Nordic Radiation Protection and Nuclear Safety Authorities, 1993)

Calculations of the fluxes and risks associated with the natural movement of chemotoxic elements (particularly the heavy metals) through the geosphere, and between the geosphere and the biosphere is a first step in applying the safety standards from the radioactive waste industry to the toxic waste industry, as well as a necessary step in quantifying the absolute risk associated with releases into the biosphere from a radioactive waste repository. As a consequence a number of chemotoxic elements are considered in this study (see Section 2.1.4).

Elemental concentration or mass flux comparisons between the natural and repository systems can also be made for radioelements but, to do so, does not provide a complete picture of the associated radiological hazard because this is dependent, not only on the elemental concentration, but also on the isotopic abundance and this is often non-natural in the case of the repository-derived contaminants. For example, the enriched ^{235}U content in the waste means that the activity associated with a given mass of elemental uranium from the repository is greater than for the same mass of natural elemental uranium. Furthermore, a number of radioelements in the waste do not occur in nature in concentrations above normal detection limits (e.g. Pu). It is useful, therefore, in some cases, to convert from units of mass flux (e.g. kg/m^2/yr) to units of activity flux (e.g. Bq/km^2/yr) when considering the distribution of repository-derived and natural radioelements. A natural radioactive flux can then be compared directly with the PA predictions of releases. A number of assumptions have to be made, however, when making the conversion from mass to activity and these are discussed in Section 1.2.

1.1.2 Comparisons between natural and repository flux pathways

Natural fluxes of elements and radionuclides can be broadly classified into two types, *endogenic* and *exogenic*. Figure 1.2 provides a graphical comparison of various types of endogenic and exogenic process and the range in their process rates.

Endogenic fluxes occur over long time periods and at some depth within the Earth's crust and in the mantle. They are responsible for the creation and modification of the igneous and metamorphic rocks which form the basement rocks within the crust, as indicated in Figure 1.3. Endogenic fluxes, therefore, operate without any significant input or influence from surface processes. Since the depths and timescales over which these processes occur is beyond those of relevance to PA, elemental fluxes associated with endogenic processes are not considered to be of interest to this work.

Exogenic fluxes occur at the Earth's surface or at some relatively shallow depth within the crust (generally within the top few kilometres). In all cases, exogenic fluxes are driven, at least in part, by surface processes, as indicated in Figure 1.4. These exogenic fluxes are characterised by erosional, transportational and depositional processes which are responsible for the creation and modification of soils, sediments and sedimentary rocks at the Earth's surface, and for the movement of both ground and surface waters. Examples are erosion of upland areas, river flow and transport of sediments. Exogenic processes operate in the same regions of the continents and over times periods similar to those considered in PA and are, therefore, important to consider for natural safety indicators.

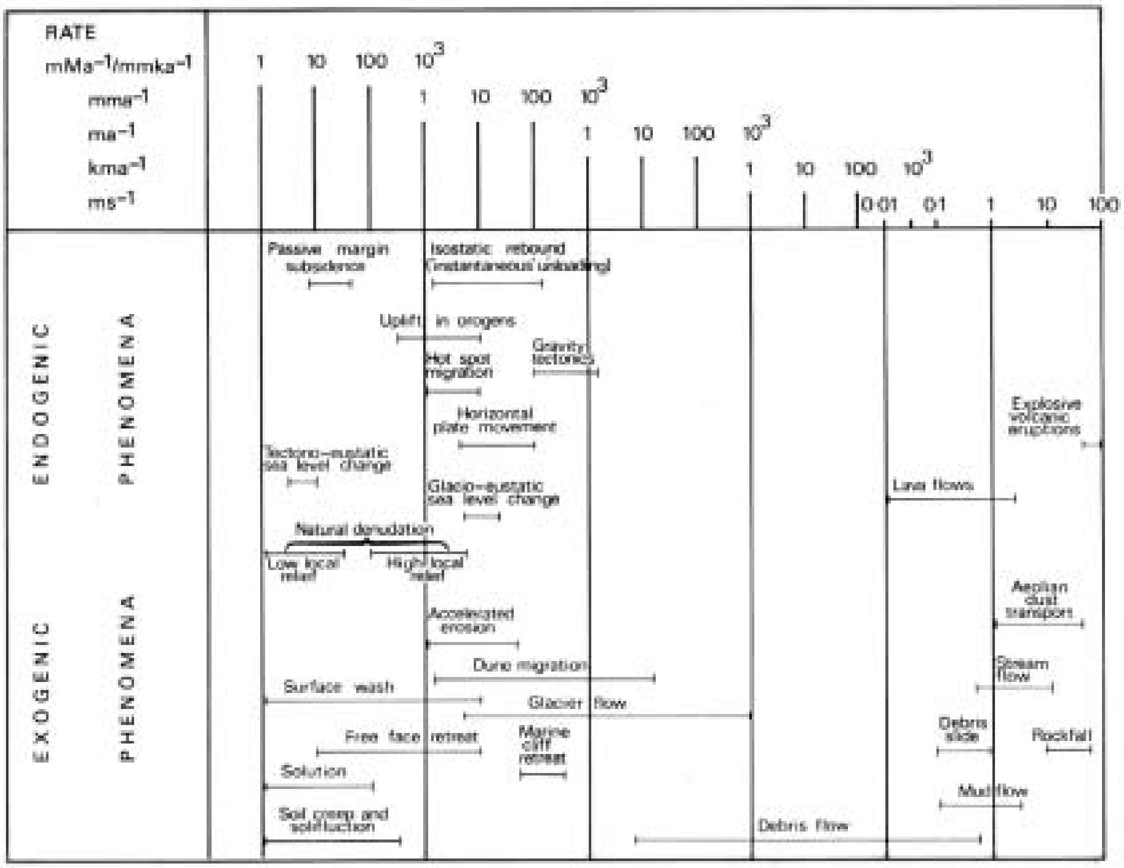

Figure 1.2: Comparison between the rates of various endogenic and exogenic processes. From Summerfield (1991).

Naturally-occurring elements and radionuclides are constantly moving at or close to the Earth's surface on the land, in the oceans, groundwaters and rivers, and in the atmosphere due to exogenic processes. However, not all of these movements can be compared directly with repository releases. To focus the natural safety indicators method on to relevant fluxes, Miller et al. (1996) defined four guidelines to help identify flux pathways which are most significant when assessing repository safety, these are:

1) *The pathway passes through the same material and across the same boundaries as the repository derived species.* This generally implies fluxes associated with groundwater transport because most assessments suggest that groundwaters are likely to be the primary vector for repository derived radionuclides to pass from the deep geosphere to the biosphere. It follows that natural fluxes associated with groundwaters rising upwards from depth are the most significant according to this guideline.

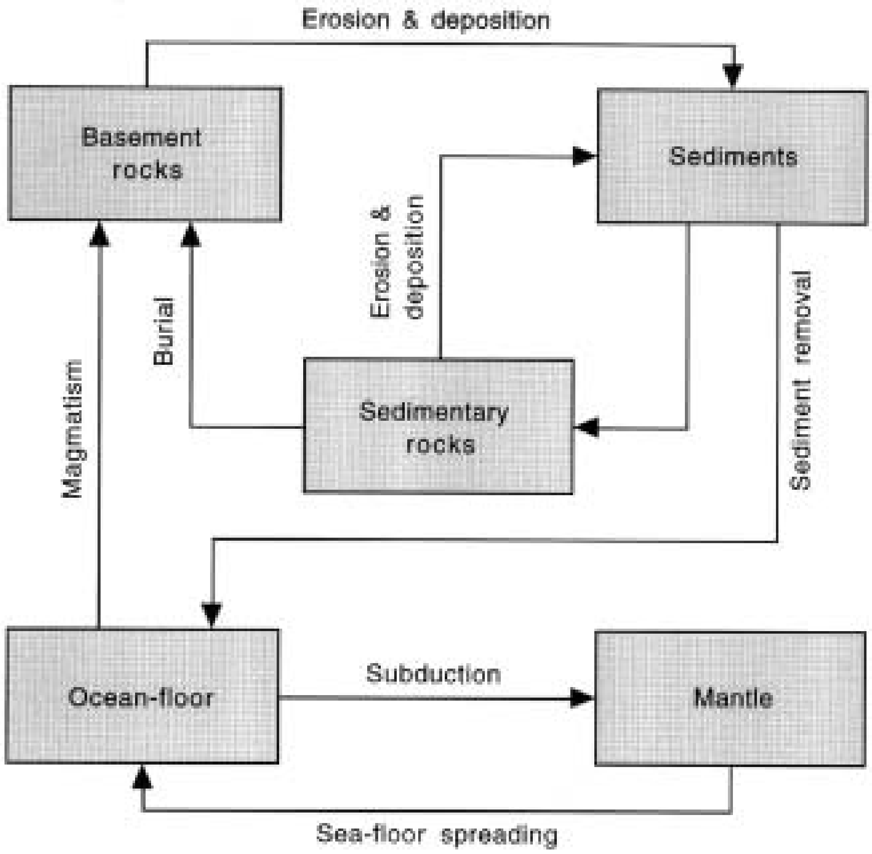

Figure 1.3: Long-term mass movements in the Earth, showing that many flux processes are endogenic, occurring in the mantle and the deep crustal rocks, and are therefore not relevant to this study.

2) *The pathway has a large natural flux.* It may be sensible to compare repository releases to a range of natural fluxes, including the largest, to define the natural context in its broadest range. In this case, care should be taken to identify those pathways carrying the largest natural fluxes. In its simplest form, this means that the nature of the flux is not important, only its magnitude.

3) *The pathway has material passing along it in a form that can be readily taken-up by the human body.* It may be sensible to consider fluxes of material which present the greatest chemotoxic or radiological hazard and this generally is controlled by accessibility to humans and by the potential for up-take (bioavailability) by the human body. In this case, the magnitude of the natural flux is less significant. The important fluxes would be those in the form of solute or fine suspended particles which may be ingested, rather than larger solid material.

4) *The pathway operates on a long time scale.* Due to the constantly changing nature of the natural environment, some pathways operate for short durations (e.g. some small rivers) while others are longer term or continuous (e.g. many erosional processes). The fluxes

associated with some short-term processes become integrated into the long-term averages over the long time scales of a PA or other safety analyses, and are not considered independently. However, it should be noted that certain transient events may produce a high natural elemental flux of a short duration. An example of this might be a 'pulse' release of radionuclides in groundwaters when permafrost melts. Such releases may not be significant when integrated into the long-term averages but they might present a significant but localised hazard at their time of operation.

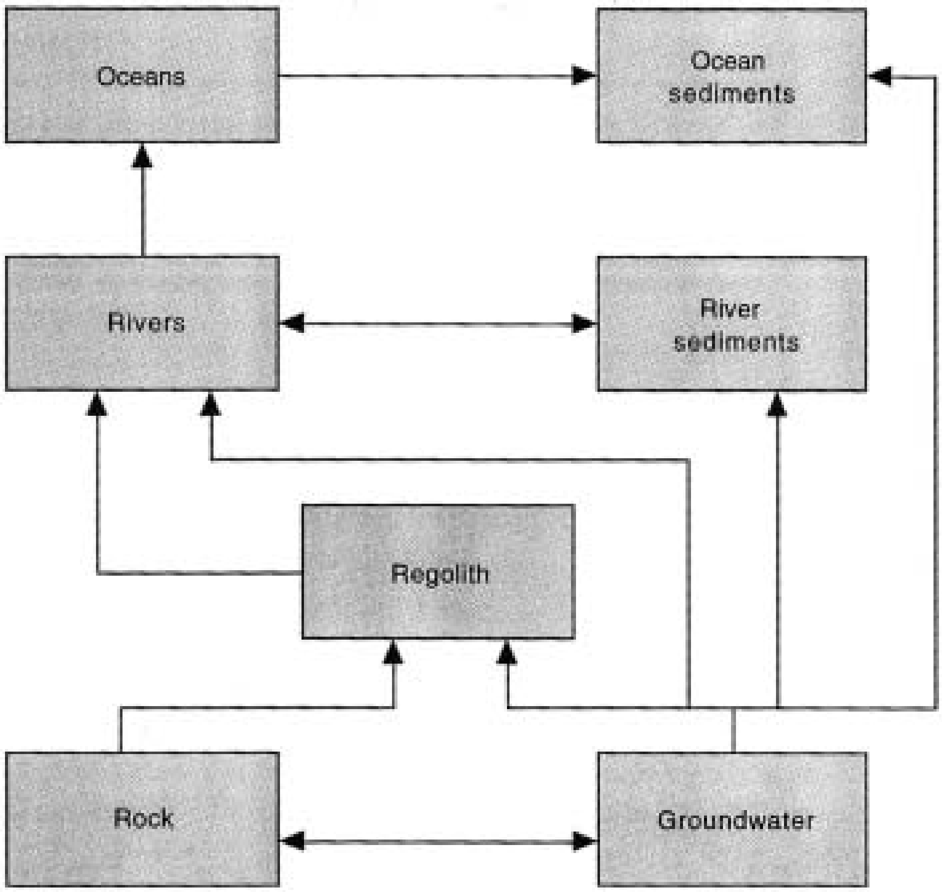

Figure 1.4: Short to medium-term mass movements in the Earth, showing that many of the important flux processes are exogenic, occurring at or close to the Earth's surface, and are therefore relevant to this study.

In general terms, these guidelines suggest that the most relevant fluxes are exogenic fluxes which operate between the upper crustal rocks and the Earth's surface (i.e. transfer between the geosphere and the biosphere). Types of processes of potential importance are, therefore, weathering and erosion, rock-groundwater interactions, groundwater discharge to surface water bodies (lakes, rivers etc.) and, in certain cases, gaseous discharge from the geosphere to the atmosphere.

No natural flux is likely to meet all four guidelines. For example, the most important repository relevant pathway (groundwater transport) would probably represent only a small magnitude natural flux compared to erosion. On the other hand, although groundwaters may carry only a small flux, this flux is readily available for uptake and, thus, may present a proportionately higher bioavailable radiological or chemical hazard than, say, large solid material released by erosion. These guidelines thus need to be considered in the context of the safety assessment objectives, which might be to compare a range of generic geological environments as potential repository host locations or to evaluate a specific candidate site.

Certain flux pathways may be more important for some elements than for others because the differences in the chemistry of the elements causes them to respond differently to some processes. Take, for example, copper and mercury which behave very differently in the biosphere. The movement of copper at the Earth's surface is dominated by river transport (Nriagu, 1979) and, in water, dissolved copper is usually associated with humic or fulvic acids (Benjamin and Honeyman, 1992). By contrast, the natural cycle of mercury is dominated by atmospheric transport (Schroeder et al., 1989) although, of the potentially interesting trace elements, mercury is the only metal to demonstrate this characteristic. Therefore, identification of the most important flux pathways should, ideally, be done on an element-by-element basis.

So far, the word ‘flux’ has been used quite loosely. Strictly, a flux refers to the amount of material crossing a surface of unit area in unit time. In terms of the natural safety indicators methodology, such a rigid definition cannot always be adhered to. The reason for this is demonstrated by reference to groundwater flow, although the same concept applies to most processes causing elemental movement in natural systems. Typically, groundwater carries with it a load of dissolved elements. In some parts of a flow system, the groundwater may infiltrate throughout the entire rock mass (porous medium) but, in other parts, may be channelled (fractured medium).

Using the strict definition, the *flux* of dissolved elements would be said to be changing if the groundwater moves from a porous to a fractured rock because the groundwater is being concentrated into a smaller flowing volume and is, thus, crossing a smaller cross-sectional area. The *mass* of dissolved elements moving in the system is, however, unchanged. Therefore, in some cases in this report, fluxes are given in *mass per unit time* (e.g. kg/yr) and not mass per unit time per unit cross-sectional area (e.g. kg/km^2/yr). This simplification is consistent with much of the literature on chemical fluxes.

1.2 Calculation of activity

As discussed earlier, it is sometimes useful to convert a natural elemental mass flux to an activity flux for comparison with predicted repository releases because PAs generally are phrased in terms of activity and dose (or risk).

The naturally-occurring radionuclides of relevance to the calculation of activity fluxes are the longer lived radionuclides present in the geosphere, which can become mobilised and released into the biosphere in groundwater, or which may be released in solid material by erosion of the near-surface rocks and sediments. Various reviews (e.g. Hughes and O'Riordan, 1993; UNSCEAR, 1993) show that the major contributions to natural terrestrial radiation come from the natural series decay chains (headed by U and Th), ^{40}K and ^{87}Rb. This means that U, Th, K and Rb are the radioelements of prime interest to natural activity fluxes. These radioelements occur naturally in the geosphere but they will also be present in the radioactive waste and will, therefore, be present in both the natural and repository fluxes. This factor makes them useful candidates for comparison.

In this work, activity fluxes associated with the U and Th decay chains are calculated considering only the longer-lived nuclides in the natural series decay chains (those with half-lives longer than 1 day) on the assumption that the decay chains are in secular equilibrium. This assumption will not be correct for all cases because some of the daughter nuclides in the chains can be in a state of disequilibrium with respect to their parent nuclides in the near-surface environment. This is particularly likely to be true for ^{222}Rn which is a major contributor to radiation fields in the human environment (UNSCEAR, 1993). This is a short-lived radioactive gas and a daughter of ^{226}Ra, in the ^{238}U decay series.

The radiation exposure associated with ^{222}Rn arises primarily due to releases as a gas into buildings via foundations. As such, the level of radiation is very dependent upon the pneumatic connection with the geosphere through building foundations and the rate of air change in the buildings. These factors are controlled by human behaviour and building design. In the natural environment (i.e. in the open air) ^{222}Rn does not accumulate because it is a gas and is rapidly dispersed in the atmosphere. In either case, ^{222}Rn and its daughters are unlikely to be in equilibrium with the parent ^{226}Ra and the other nuclides in the chain.

Nonetheless, despite the possible errors involved, the assumption of secular equilibrium provides the best possible estimate of activity fluxes in the absence of any detailed (measured, site-specific) information on the actual abundance of each individual nuclide in the decay chains. It should be noted that the assumption of secular equilibrium is also commonly made in some PAs.

The calculation of activity associated with the three isotopes of uranium uses the following equations:

- ^{234}U activity = mass of elemental U × isotopic abundance of ^{234}U × specific activity of ^{234}U
- ^{235}U activity = mass of elemental U × isotopic abundance of ^{235}U × specific activity of ^{235}U
- ^{238}U activity = mass of elemental U × isotopic abundance of ^{238}U × specific activity of ^{238}U

The specification of secular equilibrium means that 1 Bq of activity from a parent radionuclide produces 1 Bq of activity from each of the daughter nuclides of interest in the decay chain. The various radionuclides considered in the U and Th decay chains (with half-lives longer than 1 day) are given in Table 1.1, together with information on isotopic abundance and specific activity. From this table, it can be seen that ^{238}U has one immediate longer-lived daughter in the chain (^{234}Th), ^{234}U has six longer-lived daughters and ^{235}U has five. Thus the total activity associated with uranium is calculated as:

- U chain activity = (^{234}U activity × 7) + (^{235}U activity × 6) + (^{238}U activity × 2)

The calculation of activity associated with thorium is based on the assumption that elemental thorium is all ^{232}Th (isotopic abundance of ^{232}Th = 1) and that ^{232}Th has three longer-lived daughters (from Table 1.1). Thus the total activity associated with thorium is calculated from:

- ^{232}Th activity = mass of elemental Th × specific activity of ^{232}Th
- Th chain activity = ^{232}Th activity × 4

In addition to the U and Th decay chains, the activities associated with ^{40}K and ^{87}Rb are also considered in the calculation of the total activity fluxes because these provided the largest contribution to the non-alpha terrestrial flux (and are shown in Table 1.1). These nuclides are not members of decay chains and thus their associated activities are calculated simply from:

- K activity = mass of elemental K × isotopic abundance of ^{40}K × specific activity of ^{40}K
- Rb activity = mass of elemental Rb × isotopic abundance of ^{87}Rb × specific activity of ^{87}Rb

Other natural radionuclides, such as ^{14}C, contribute to natural background radiation but are produced in the biosphere by cosmic radiation and their release from the geosphere is very minor. Consequently, they are not considered here as a useful comparator to repository releases.

*Table 1.1: Natural terrestrial radionuclides with half-lives longer than 1 day. *Reflects shorter lived daughters in U and Th decay chains not included in the calculation of activity fluxes, with the number of omitted daughters given in parentheses. §All Th is assumed to be ^{232}Th in the activity calculations.*

Radionuclide	**Half-life**	**Isotopic abundance**	**Specific activity (Bq/kg)**
^{238}U	4.5×10^{9} years	0.9927	1.24×10^{4}
^{234}Th*(2)	24.0 days	-	2.57×10^{15}
^{234}U	2.4×10^{5} years	0.000056	2.30×10^{8}
^{230}Th	7.7×10^{4} years	-	7.63×10^{8}
^{226}Ra	1.6×10^{3} years	-	3.66×10^{10}
^{222}Rn*(5)	3.8 days	-	2.80×10^{16}
^{210}Pb	22 years	-	2.82×10^{12}
^{210}Bi	5 days	-	4.59×10^{15}
^{210}Po	140 days	-	1.66×10^{14}
^{235}U	7.0×10^{8} years	0.0072	7.11×10^{4}
^{231}Th	25 hours	-	1.97×10^{16}
^{231}Pa	3.3×10^{4} years	-	1.75×10^{9}
^{227}Ac	22 years	-	2.68×10^{12}
^{227}Th	19 days	-	1.14×10^{15}
^{223}Ra*(6)	11 days	-	1.18×10^{16}
^{232}Th	1.4×10^{10} years	$1^{§}$	4.1×10^{3}
^{228}Ra*(1)	5.8 years	-	1.9×10^{13}
^{228}Th	1.9 years	-	2.9×10^{13}
^{224}Ra*(6)	3.7 days	-	3.5×10^{16}
^{40}K	1.3×10^{9} years	0.000118	2.09×10^{5}
^{87}Rb	4.8×10^{10} years	0.2785	3.20×10^{3}

If the possible radiological doses to humans associated with natural fluxes are also to be considered then the potential should be taken into account for individual radionuclides to give rise to different levels of radiation dose per unit activity released into the biosphere. Some radionuclides can give rise to individual doses which are orders of magnitude larger than the dose from others, per unit of activity released (Charles and Smith, 1991).

It is not recommended, however, that radiological doses be calculated for the natural activity fluxes because this would require assumptions to be made for ingestion and exposure pathways for humans, and this is incompatible with the philosophy of the natural safety indicators methodology (i.e. that it is independent of assumptions for future human behaviour). For this reason, the end-points for the calculations presented in this report are either elemental mass fluxes or concentrations, or activity fluxes, as appropriate to the calculation, and not dose or risk. In this regard, the comparison with PA predictions requires that the some intermediate PA calculation of activity would need to be compared with the natural flux calculations because most PA end-points are either dose or risk.

1.3 Spatial scales, sensitivity and accuracy

An important consideration for the natural safety indicators methodology is the spatial scale over which fluxes are calculated. In theory, it would be possible to calculate natural elemental or activity fluxes at a range of scales from, say, a 1 m^3 block of rock, through local and region scales to the entire global system. Useful information may be derived from each of these scales but care needs to be exercised in the interpretation of the values. In this report, global scale average fluxes are calculated in Section 4 because they provide the best datum against which site specific fluxes can be compared to evaluate whether they are higher or lower than average. This is useful to know because such information can help with the broad objective of placing the repository releases into a natural context. A global average flux value (for example, the global average activity flux due to groundwater discharge) masks considerable variation in the fluxes which occur at different sites, and in different geological and climatic environments. A global average flux value alone is, therefore, inadequate as a natural safety indicator. To appreciate the full spatial variation in the fluxes, it is necessary to determine the fluxes which occur at different sites over smaller scales, such as the scale of an individual region, area or site.

In practical terms, a useful scale to consider is that of an river catchment or watershed because these generally define the limits of the groundwater flow system, and the erosional and depositional processes. The catchment scale essential defines the extent of the system in which natural fluxes are moving about and which would similarly control the movement of repository releases, if a repository were to be located in the catchment. Therefore, the catchment scale is often the most appropriate one for the direct comparison of repository and natural fluxes while, at the same time, using the global average flux values to set the catchment fluxes into an overall natural context. For these reasons, both global average fluxes and fluxes from a range geological/climatic environments at the catchment scale are calculated here.

There are, however, systems for which catchment scale flux calculations would be inappropriate. This is the case in central Canada, for example, where the groundwater flow systems and river catchments are very large and essentially take place on a continental scale. In such a large system, it might not be sensible to look at the natural fluxes over the entire catchment area. As an alternative, it may be more practical to define an area local to any proposed repository and calculate the natural fluxes for just this area. As an example of this approach, Miller et al. (1996) proposed the Repository Equivalent Rock Volume (RERV) as a method for defining an appropriate scale for the direct comparison of natural and repository fluxes. The RERV is defined as the volume of rock which may contain a repository, at repository depth (typically a volume with dimensions of the order of 2.5 km × 2.5 km × 30 m, although this will be repository specific). Natural fluxes can be calculated for processes which cause material to leave or enter this volume, and migrate to the land surface. In this way the calculated natural fluxes are representative of the processes which would cause releases from a repository located in the same geometrical and geological configuration. A RERV is not necessarily a closed system to natural fluxes in the way that a river catchment is. For this reason, the catchment scale remains the preferred choice for the natural flux calculations.

Although there are sound scientific reasons for considering natural fluxes on different spatial scales, there are also inherent problems in trying to calculate these fluxes. In the first instance, there is a requirement for input data at an appropriate level of detail (e.g. a sufficient number of measurements in the system to provide representative concentrations or process rates). So, as the natural safety indicators methodology focusses on the smaller scales representative of a particular geological environment or site, then it is necessary to be able to obtain more comprehensive data which reflect this. In practical terms, this means that the calculation of groundwater fluxes in a granite pluton, for example, requires sufficient geochemical data to define a ‘granitic’ groundwater, as opposed to a more general or average groundwater composition. The applicability of the natural safety indicators methodology is, thus, inherently restricted by the availability of this input data. Similarly, the sensitivity of the method (i.e. its ability to quantify differences in fluxes arising in different systems and at different scales) is also dependent on the availability of sufficient and appropriate representative data from the different systems under examination.

The uncertainty in the calculated flux values is also affected by the accuracy of the input data. Some of these data are of a high precision, such as the measured rock and groundwater elemental concentrations, but other data (typically process rate values, e.g. erosion rates) have somewhat lower precision. The accuracy and sensitivity of the calculated fluxes are subject to all these limitations. It follows, therefore, that the fluxes presented in this report should not be considered as absolute but rather as order of magnitude approximations. This does not, however, limit their use as comparators to repository releases because an equivalent or even greater level of uncertainty will be associated with the PA calculations with which the natural fluxes may be compared. This is because the PA calculations themselves similarly use proxy or generic data. In reality, if the natural safety indicators methodology were to be applied to a proposed repository at a specified location, then it should be possible to obtain all the necessary high quality input data from the site characterisation programme. At the generic level of safety assessment, natural fluxes must be calculated using proxy data obtainable from the published literature.

2 Elemental concentrations in natural materials

This chapter presents a compilation of elemental concentrations (abundances) measured in a variety of natural materials, such as rocks, soils, ground and surface waters. This information has been extracted from published literature and, where possible, from previous geochemical reviews which have identified most appropriate ‘average’ or ‘typical’ elemental abundances or ranges for different natural materials. The elements considered for this review are identified in the following sections, together with the reasoning for their choice.

All natural systems display some variation in chemistry and, therefore, it is sometimes problematic to define a meaningful ‘average’ composition. This is generally a greater problem for waters and, in particular, groundwaters. The abundances of trace elements in groundwaters are controlled by a range of factors, including the composition of the mineral surfaces in contact with the groundwater, the overall physico-chemical environment (e.g. P, T, Eh and pH) and the duration of rock-water interactions. As a consequence, trace element concentrations in groundwater are significantly spatially variable. This fact, combined with the relatively few published groundwater analyses for trace elements (compared with rocks), makes estimation of average trace element concentrations difficult. Generally, though, (and by definition), these elements have low solubilities and occur in groundwaters at around the ppb (µg/l) level. Probably, the groundwater elemental abundances are subject to the greatest uncertainties in this study. However, if the natural safety indicators method were to be applied to a candidate (real) repository site, then accurate elemental abundances for groundwaters could be obtained from the site characterisation study.

2.1 Elements considered in the study

The concentrations (abundances) of elements in natural materials (e.g. rocks, sediments, soils and waters) is one of the fundamental information requirements for the calculation of natural fluxes. The distribution of elements in various natural materials is discussed in the following sections, and their abundances (ranges and averages) quantified. A number of different ‘types’ of elements are considered:

- naturally-occurring radioelements,
- PA relevant radioelements,
- chemical analogue elements, and
- chemotoxic elements.

These groups are not mutually exclusive and several elements can be considered to fall into two or more groups. For example, U can be considered as a member of all four groups: it is a naturally-occurring radioelement, it is of primary importance in PA, it can be used as a chemical analogue for other radioelements, such as Pu, and it is chemically toxic to humans.

Knowledge of the distributions of trace elements at or close to the surface is based, to a large extent, on measurements of their concentrations within various materials, such as rivers and lake waters, rocks, soils etc. Due to the generally low concentrations of trace elements, accurate measurements have only been possible in the past two to three decades since the sensitivity of analytical equipment has improved. Unfortunately, this time frame corresponds to the period of greatest pollution of the environment by human activity. It follows that it is sometimes very difficult to distinguish between natural and anthropogenic trace element abundances in the surface environment, at least for some trace-elements, e.g. lead. As far as possible, the elemental concentrations reported in this compilation represent natural conditions, and data obviously reflecting anthropogenic contamination have been omitted.

2.1.1 Naturally-occurring radioelements

A primary use of the natural safety indicators methodology is to compare repository hazards to the natural hazards. The most obvious comparison to make is between the PA predictions of repository radioactive releases and the natural radioactivity and, for this, it is necessary to know the abundances of the naturally-occurring radioelements in rocks, waters etc.

In this work, we are concerned only with naturally-occurring radioelements with a terrestrial origin: therefore, cosmogenic radionuclides are beyond the scope of this work, as are the anthropogenic radionuclides released to the human environment from nuclear power and nuclear weapons technology. Nonetheless, it may be useful to consider them in further work to establish the ‘total’ radioactive environment.

Cosmogenic radionuclides are generated when cosmic rays impinge on atoms in the atmosphere and in surface materials causing spallation and neutron activation. There are many cosmogenic radionuclides formed this way, mostly in the atmosphere, but their concentrations are highly dependent on atmospheric and surface conditions and, hence, are highly variable in space and time. Four cosmogenic radionuclides contribute to measurable doses to humans: ^{14}C, ^{3}H, ^{22}Na and ^{7}Be. One important cosmogenic radionuclide is formed substantially in crustal materials: ^{36}Cl which is formed from neutron capture by the stable nuclide ^{35}Cl. Approximately 70% of the Earth’s inventory of ^{36}Cl is formed in this way.

Terrestrial radionuclides occur in three forms: natural series radionuclides, non-series radionuclides and those formed by spontaneous fission.

The natural series radionuclides belong to three different decay chains headed respectively by the nuclides ^{238}U, ^{235}U and ^{232}Th. Each chain contains numerous nuclide members with various half lives. The longer-lived nuclides in the chains, with half-lives longer than one day, were listed in Table 1.1. As discussed in Section 1.2, in geological systems it is sometimes assumed that the decay chains are in secular equilibrium (i.e. the number of atoms of each nuclide is in the same proportion to the number of atoms of the nuclide at the head of the series as its half life is to the half life of the head of the series). Therefore, if the elemental abundances of U and Th are known, then the abundance of each daughter nuclide in the series can be calculated, as can the radioactivity generated by the entire chains. However, at the surface and in the biosphere, secular equilibrium is generally not established because the behaviour of many of the short lived and gaseous radionuclides in the chain (e.g. ^{222}Rn) is governed by atmospheric and surface conditions rather than by the flux of these daughters from the geosphere. Given that this study is not concerned with atmospheric processes, calculations of radioactivity are made assuming secular equilibrium and, thus, only the natural abundances of the radioelements U and Th are of direct interest, since then total activity for the entire chain can be calculated.

There are 17 naturally-occurring non-series terrestrial radionuclides which decay to stable nuclides (Table 2.1, after Eisenbud and Gesell, 1997). Fifteen of these have such a combination of half-life, isotopic abundance and elemental abundance that they have negligibly small specific activities and are not significant dosimetrically. The remaining 2 nuclides, ^{40}K and ^{87}Rb, are significant sources of radiation and are, therefore, included in this study.

Table 2.1: Non-series terrestrial radionuclides. After Eisenbud and Gesell (1997).

Radionuclide	Half-life (years)	Isotopic abundance (%)	Elemental abundance in crustal rock (ppm)	Specific activity in crustal rock (Bq/kg)
^{40}K	1.26×10^{9}	0.01	2.09×10^{4}	630.00
^{50}V	6.00×10^{15}	0.25	135.00	2.00×10^{-5}
^{87}Rb	4.80×10^{10}	27.85	90.00	70.00
^{113}Cd	1.30×10^{15}	12.26	0.20	2.00×10^{-6}
^{115}In	6.00×10^{14}	95.77	0.10	2.00×10^{-5}
^{123}Te	1.20×10^{13}	0.87	2.00×10^{-3}	2.00×10^{-7}
^{138}La	1.12×10^{11}	0.09	30.00	0.02
^{142}Ce	5.00×10^{16}	11.07	60.00	1.00×10^{-5}
^{144}Nd	2.40×10^{15}	23.87	28.00	3.00×10^{-4}
^{147}Sm	1.05×10^{11}	15.07	6.00	0.70
^{152}Gd	1.10×10^{14}	0.20	5.40	7.00×10^{-6}
^{174}Hf	2.00×10^{15}	0.16	3.00	2.00×10^{-7}
^{176}Lu	2.20×10^{10}	2.60	0.50	0.04
^{187}Re	4.30×10^{10}	62.93	1.00×10^{-3}	1.00×10^{-3}
^{190}Pt	6.90×10^{11}	0.01	5.00×10^{-3}	7.00×10^{-8}
^{192}Pt	1.00×10^{15}	0.78	5.00×10^{-3}	3.00×10^{-6}
^{209}Bi	2.00×10^{18}	100.00	0.17	4.00×10^{-9}

The majority of the naturally-occurring isotopes of U, Th and Pa undergo spontaneous fission as an alternative to the principal mode of radioactive decay (NCRP, 1987). In all cases, the radioactivity due to fission and the decay of the fission products is insignificant. Consequently, no radionuclides derived from spontaneous fission are considered in this study.

In addition to the radionuclides so far mentioned, some transuranic nuclides and fission products were formed within the natural fission reactors at Oklo, Gabon (see Miller et al., 2000), although many of these have since decayed to very low levels. Oklo is the only known natural fission reactor and, because of the limited occurrence of these radionuclides, they are not considered further.

2.1.2 PA relevant radioelements

Although high-level radioactive wastes contain a very large number of nuclides of many different elements, only a small number of these are problematic in the sense that they can generate high doses in PA calculations for certain scenarios. For this to occur, these nuclides must be capable of comparatively rapid transport away from the waste to the surface environment.

The actual nuclides which are problematic are both waste and concept specific and, thus, a nuclide which dominates repository releases for one repository design may not be an issue in a different system. However, as a rule of thumb, the radioelements I and Cl are of particular concern because, when they occur in anionic form, they are conservative in solution, and can migrate relatively rapidly through the geosphere. Many other radioelements have also been found to be important in some PAs, and can dominate releases in certain time intervals after repository closure, such as C, Ni, Tc, Se, Sn, Zr, Pd, Ra, Np, Th , U, Am and Pu.

These PA relevant elements also occur in nature (excepting the transuranic elements), although often in very low concentrations and with isotopic abundances which may be very different to the waste-derived element. Some of these PA relevant elements were chosen for consideration in this study, they are C, Cl, Ni, Se, Sn, I, Th and U.

A secondary benefit of the natural indicators methodology is the potential to gain improved understanding of the behaviour of these problematic elements and radionuclides in natural systems. For example, to learn about the behaviour of redox sensitive species (e.g. U) at the geosphere-biosphere boundary. In this sense, information on the concentrations and behaviour of naturally-occurring elements may be used to help predict the behaviour of equivalent repository species. This is essentially using information on natural elemental distributions as a natural analogue. It should be noted, however, that it is not the prime objective of this study to focus in detail on the specifics of the geochemical and transport behaviour of these PA relevant radioelements.

2.1.3 Chemical analogue elements

As was indicated earlier, there are a number of radioelements which are important or problematic in PA but which have no naturally-occurring counterpart. Thus, it is not possible to use their distributions in natural systems to predict their behaviour in repository systems. An approach to circumvent this problem is to identify naturally-occurring elements which are likely to exhibit similar chemical behaviour to the repository species; i.e. to identify *chemical analogues*. The concept of chemical analogues was first discussed in detail by Chapman et al. (1984) who demonstrated how chemical analogues might be selected on the basis of the well established chemical periodicities of the elements.

It is now realised (e.g. Miller et al., 2000) that a single chemical analogue cannot be ascribed to every non-natural repository nuclide which would be appropriate under all conditions. That is to say, chemical analogues must be determined on a case-by-case basis. However, using the chemical periodicities methodology from Chapman et al. (1984), it is possible to indicate potential chemical analogues for some of the non-natural radioelements which are problematic in PA.

In general terms, the PA relevant radioelements which have no abundant natural counterparts are the transuranic actinides, especially Np, Pu and Am. In the simplest case, using chemical periodicities as a guide, the most appropriate chemical analogues for these actinides would be the lanthanides (rare earth elements). Chemical analogues can also be identified for PA relevant radioelements which do exist in nature but in very low concentrations (e.g. Tc, Ac and Pa), due to which they are difficult to measure and examine in natural systems. For this study, the lanthanides Nd and Sm are considered as representative chemical analogues, as are U, Th which have already been mentioned.

As discussed in the previous section, the use of chemical analogues is adopting a natural analogue approach to the natural safety indicators methodology. Again, it is not the prime objective of this study to focus in detail on the specifics of the geochemical and transport behaviour of these elements.

2.1.4 Chemotoxic elements

The last group of elements to be considered in this study are the chemotoxic elements. As mentioned in Chapter 1, certain elements in radioactive wastes present a chemotoxic hazard instead of (or, in some cases, as well as) a radiotoxic hazard, e.g. cadmium. For this reason, it was considered a sensible approach to include a small number of chemotoxic elements in this study to allow some evaluation of chemical risks from natural systems to be compared both to the radiological risks from the same natural systems and to the repository system. The chemotoxic elements chosen for the study are Cd, Cu, Zn and Pb.

2.2 Elemental abundances

Given the discussions above, the elements considered in this study are (in order of increasing atomic number): C, Cl, K, Ni, Cu, Zn, Se, Rb, Cd, Sn, I, Nd, Sm, Pb, Th and U. The distribution and abundances of these elements in different natural materials is discussed below on an element-by-element basis.

Other elements could be included because they have relevance to one or more disposal programmes. These elements could be considered at a later date, following the approach defined in this study.

2.2.1 Carbon (C)

Carbon has an atomic number of 6. It is a non-metal and member of the Group IV elements in the periodic table. Carbon is of interest here because the radionuclide ^{14}C can be problematic in some repository designs, especially in L/ILW designs where large volumes of gas can be generated by degradation of organic material. The ^{14}C can be incorporated into gases (e.g. as

$^{14}CO_2$ and $^{14}CH_4$) and, since these are mobile, they can provide a rapid release mechanism to the surface.

Carbon is not a primary element for most silicate minerals and thus is not generally abundant in crystalline rocks, where it usually occurs in trace amounts in elemental form, in fluid inclusions, as minor carbonate or as a gas. However, C is abundant in many sedimentary rocks either as carbonate (CO_3^{2-}), usually associated with calcium in limestones, or as dispersed organic C in rocks such as mudstones and shales. Coal is, perhaps, the best known example of a C-rich geological material. Soils and many sediments also contain high organic C contents. Carbon is also an essential component of hydrocarbons, in gaseous, liquid and solid states, and as a methane hydrate. Crystallised organic C compounds are rare in nature.

Other metals are frequently found in association (co-precipitates or sorption) with carbon in sediments and sedimentary rocks, most notably Co, Cd, Cu, Fe, Mn, Ni, Pb, Sr, U and Zn (Pendias and Pendias, 1984). They can associate either with organic C or with carbonate.

Carbon is found free in nature in three allotropic forms: amorphous, graphite, and diamond. Graphite is one of the softest known materials while diamond is one of the hardest. Carbon, as microscopic diamonds, is found in some meteorites and associated impact rocks. Natural diamonds are found in kimberlites at the sites of ancient volcanic ‘pipes’ such as those found in South Africa.

The carbon content in waters is also primarily of organic origin, as indicated by its isotopic signature. In groundwater, carbon commonly occurs as HCO_3^- in concentrations of up to several hundred ppm (mg/l). Wedepohl (1978) quotes an average HCO_3^- content in freshwater (lakes and rivers) of 58.4. mg/l. However, this is highly variable due to the carbonate content of surface rocks and sediments. Wedepohl (1978) also quotes an average HCO_3^- concentration for seawater of 145 mg/l and a total mass in the world’s oceans of 190×10^{15} kg. The elemental carbon concentration in seawater is 28 mg/l (inorganic) and 0.5 mg/l (organic).

Table 2.2: Carbon concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	1990	mg/kg	Wedepohl (1995)
Crustal average	480	mg/kg	Bowen (1979)
Upper crust	3240	mg/kg	Wedepohl (1995)
Lower crust	588	mg/kg	Wedepohl (1995)
Granite	220-500	mg/kg	Wedepohl (1978)
Granite	360	mg/kg	Bowen (1979)
Granodiorite	180-510	mg/kg	Wedepohl (1978)
Rhyolites/obsidian	300-490	mg/kg	Wedepohl (1978)
Basalt	610	mg/kg	Bowen (1979)
Basalt	85-390	mg/kg	Wedepohl (1978)
Gabbro	40-170	mg/kg	Wedepohl (1978)
Peridotite, dunite	20-160	mg/kg	Wedepohl (1978)
Schist/gneiss	40-490	mg/kg	Wedepohl (1978)
Clay, shales	67000	mg/kg	Wedepohl (1978)

Natural material	Elemental concentration	Concentration units	Reference
Shale	116000	mg/kg	Bowen (1979)
Sandstone	16000	mg/kg	Bowen (1979)
Sand, sandstone	24000	mg/kg	Wedepohl (1978)
Lime mud, limestones	23000	mg/kg	Wedepohl (1978)
Average sediment	29400	mg/kg	Bowen (1979)
Soil	[20] 7-500	g/kg	Bowen (1979)
Marine clay	4500	mg/kg	Chester & Aston (1976)
Marine carbonate	66000	mg/kg	Chester & Aston (1976)
Freshwater	[11] 6-19	mg/l	Bowen (1979)
Groundwater (crystalline)	58-63	mg/l	Pearson & Scholtis (1993)
Groundwater (clay)	52-215	mg/l	Pearson & Scholtis (1993)
Seawater	28	mg/l	Li (1991)
Seawater (inorganic C)	28	mg/l	Wedepohl (1978)
Seawater (organic C)	0.5	mg/l	Wedepohl (1978)
Seawater	28	mg/l	Bowen (1979)

2.2.2 Chlorine (Cl)

Chlorine has an atomic number of 17. It is a non-metal and member of the Group VII (halogen) elements in the periodic table. Chlorine is of interest because the radionuclide ^{36}Cl can be problematic in some repository designs, when the Cl occurs in anionic form which is conservative in solution, and can migrate relatively rapidly through the geosphere.

In the geosphere, there is often a very close relationship between Cl and Br, and most Br compounds are similar to their corresponding Cl compounds. The Br/Cl ratio is an important factor for defining various geological units (Wedepohl, 1978). The Cl content in most rocks ranges from 10 to 15000 mg/kg but is highest in evaporite deposits.

Chlorine is a volatile element, with complete non-metallic behaviour and, hence, is mobile and reactive in the geosphere. This, together with the fact that its salts such as halite (NaCl) and sylvite (KCl) are readily soluble, means that its geochemistry is closely related to water chemistry and to evaporite deposits.

Chlorine is found in minerals in the form of chlorides, borates, sulphates, phosphates and some silicates. Wedepohl (1978) lists over 170 chlorine naturally occurring minerals and compounds. It is often found substituting for OH^- in hydrous minerals such as amphiboles and, particularly, micas.

The chlorine found in natural rocks and sediments often has a marine origin and many of the high chlorine contents quoted for some natural materials probably reflects saline waters trapped in pore spaces. As a consequence, it is sometimes difficult to be certain that chlorine contents quoted for rocks, minerals and sediments actually represent primary Cl contents.

The chlorine content in rivers, up to 12 mg/l (Wedepohl, 1978), is mostly due to precipitation derived from the oceans, and is not due to rock weathering. In the same way, many chlorine contents in groundwaters from crystalline and argillaceous rocks are believed to have a marine origin, although some saline waters can be derived by long-term rock-water interactions, such as the saline groundwaters encountered in the crystalline Canadian shield.

Table 2.3: Chlorine concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	472	mg/kg	Wedepohl (1995)
Crustal average	130	mg/kg	Bowen (1979)
Upper crust	640	mg/kg	Wedepohl (1995)
Lower crust	278	mg/kg	Wedepohl (1995)
Granite, granodiorite	23-1180	mg/kg	Wedepohl (1978)
Granite	200	mg/kg	Bowen (1979)
Syenites	10-2000	mg/kg	Wedepohl (1978)
Basalt	30-2180	mg/kg	Wedepohl (1978)
Basalt	60	mg/kg	Bowen (1979)
Andesite, dacite	20-3900	mg/kg	Wedepohl (1978)
Gabbro, diorite	80-700	mg/kg	Wedepohl (1978)
Dunite, peridotite	7-1000	mg/kg	Wedepohl (1978)
Schist, gneiss	10-1000	mg/kg	Wedepohl (1978)
Shale, mudstone	30-1100	mg/kg	Wedepohl (1978)
Shale	160	mg/kg	Bowen (1979)
Limestone	76	mg/kg	Bowen (1979)
Limestone, dolomite	10-2000	mg/kg	Wedepohl (1978)
Sandstone	510	mg/kg	Bowen (1979)
Sandstone	10-14900	mg/kg	Wedepohl (1978)
Average sediment	190	mg/kg	Bowen (1979)
Soil	[100] 8-1800	mg/kg	Bowen (1979)
Peat	130-650	mg/kg	Wedepohl (1978)
Marine clay	22000	mg/kg	Chester & Aston (1976)
Riverwater	8-12	mg/l	Wedepohl (1978)
Freshwater	[7] 1-35	mg/l	Bowen (1979)
Thermal water	2-27400	mg/l	Wedepohl (1978)
Groundwater (crystalline)	0.7-193	mg/l	Wedepohl (1978)
Groundwater (shale)	2-1710	mg/l	Wedepohl (1978)
Groundwater (sandstone)	1.5-442	mg/l	Wedepohl (1978)
Groundwater (limestone)	1-112	mg/l	Wedepohl (1978)
Groundwater (crystalline)	26-128	mg/l	Pearson & Scholtis (1993)
Groundwater (clay)	10-16775	mg/l	Pearson & Scholtis (1993)
Seawater	18.8	g/l	Li (1991)
Seawater	19.4	g/l	Wedepohl (1978)
Seawater	19.4	g/l	Bowen (1979)

2.2.3 Potassium (K)

Potassium has an atomic number of 19. It is a member of the Group I (alkali metals) elements in the periodic table. Potassium is of interest here because the radionuclide ^{40}K is a significant contributor to the total natural background radiation of terrestrial origin. In fact, it is the most significant natural non-alpha emitter.

Potassium is a ‘major element’ which means that it is one of the ten elements which, together, comprise (as oxides) over 90 % of the mass of common rocks in the continental crust. Potassium is an essential constituent of many minerals, including feldspars, micas and clay minerals. Wedepohl (1978) lists the following types of more common K-bearing minerals: around 60 silicates, 10 phosphates, 14 halides and 35 sulphates and carbonates. However, there are many more less common ones.

As a consequence of being a major element, K is essentially ubiquitous in high concentrations in all crustal rock types. The abundance of K in crustal rocks averages around 20 g/kg but can reach up to 40 g/kg in some granitic rocks. However, K contents of feldspar poor rocks, such as limestones and sandstones, can be an order of magnitude lower than the crustal average.

The K-bearing feldspar minerals are prone to weathering and thus the K content of ground and surface waters can be quite high, ranging up to a few tens or hundreds of mg/l. Martin and Meybeck (1979) quote average K abundances in rivers of 1350 µg/l for the dissolved and 20000 mg/kg for the suspended component. Groundwaters contain K contents of up to 100 mg/l but are generally < 10 mg/l. Seawater contains around 390 mg/l of potassium.

Table 2.4: Potassium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	21400	mg/kg	Wedepohl (1995)
Crustal average	21000	mg/kg	Taylor & McLennan (1995)
Crustal average	9100	mg/kg	Bowen (1979)
Upper crust	28650	mg/kg	Wedepohl (1995)
Upper crust	28000	mg/kg	Taylor & McLennan (1995)
Lower crust	13140	mg/kg	Wedepohl (1995)
Granite	33400	mg/kg	Bowen (1979)
Granite, granodiorite	25500-45300	mg/kg	Wedepohl (1978)
Basalt	8300	mg/kg	Bowen (1979)
Basalt	1700-10000	mg/kg	Wedepohl (1978)
Gabbro	3000-7000	mg/kg	Wedepohl (1978)
Peridotite, dunite	4-643	mg/kg	Wedepohl (1978)
Shale	24500	mg/kg	Wedepohl (1978)
Shale	24500	mg/kg	Bowen (1979)
Limestone	3100	mg/kg	Wedepohl (1978)
Limestone	3100	mg/kg	Bowen (1979)
Sandstone	15000	mg/kg	Wedepohl (1978)
Sandstone	15000	mg/kg	Bowen (1979)
Average sediment	20000	mg/kg	Bowen (1979)
Soil	[14] 80-37	g/kg	Bowen (1979)
Marine clay	27000	mg/kg	Chester & Aston (1976)
Marine carbonate	12000	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	1500	µg/l	Martin & Whitfield (1983)

Natural material	Elemental concentration	Concentration units	Reference
Riverwater (suspended)	20000	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	1350	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	20000	mg/kg	Martin & Meybeck (1979)
Riverwater (dissolved)	0.1-238	mg/l	Wedepohl (1978)
Lakewater	0.2-7560	mg/l	Wedepohl (1978)
Freshwater	[2.2] 0.5-10	mg/l	Bowen (1979)
Groundwater	0.1-98	mg/l	Wedepohl (1978)
Groundwater (crystalline)	4.2-8.5	mg/l	Pearson & Scholtis (1993)
Groundwater (clay)	2-28	mg/l	Pearson & Scholtis (1993)
Hydrothermal water	1-2325	mg/l	Wedepohl (1978)
Seawater	390	mg/l	Li (1991)
Seawater	392	mg/l	Wedepohl (1978)
Seawater	399	mg/l	Bowen (1979)

2.2.4 Nickel (Ni)

Nickel has an atomic number of 28. It is a metal and a member of the transition elements in the periodic table. Nickel is of interest here because ^{59}Ni is a PA relevant nuclide formed by activation of stainless steel in fuel assemblies and can be an important nuclide in some PAs.

There is general similarity between the distribution of Ni, Co and Fe in crustal rocks (Pendias and Pendias, 1984). Thus, Ni is concentrated in ultramafic and mafic rocks, with maximum abundances in these rock types of up to 20000 mg/kg, (Pendias and Pendias, 1984; Krauskopf and Bird, 1995), with concentrations decreasing with increasing acidity of igneous rocks. Sedimentary rocks contain Ni in the range of 1 to 90 mg/kg, with the highest range being for argillaceous rocks and the lowest for sandstones and limestones. Organic matter reveals a strong ability to absorb Ni. Therefore, Ni is likely to be concentrated in coal and oil.

With its divalent charge and ionic radius (in octahedral coordination) of 0.69 Å, Ni readily substitutes for Mg^{2+} (ionic radius 0.66 Å), Mn^{2+} (0.80 Å), Fe^{2+} (0.74 Å), Cu^{2+} (0.72 Å) and Co^{2+} (0.72 Å) in crystal structures. Ni has the highest crystal field octahedral site preference energy of all the +2 transition metal cations (Wedepohl, 1978).

Geochemically, Ni is siderophile and will join metallic Fe wherever such a phase occurs. Thus, Ni tends to partition into ferromagnesian minerals such as olivine, pyroxene, amphibole and spinel, whereas at lower temperatures it will be incorporated into a variety of silicates and hydroxides, such as smectite clay, sepiolite, talc and brucite (Decarreau, 1985; Velde, 1988). Ni forms rare carbonate minerals and is the least stable of the M^{2+} ions in $Ca^{2+}M^{2+}(CO_3)_2$ (dolomite) compounds.

Ni has appreciable chalcophilic behaviour and in the presence of HS^- will form sulphides, either substituting for Fe^{2+} in pyrite, FeS_2 (there is almost complete solid solution in the FeS_2-NiS_2 system), co-precipitating with Fe^{2+} in pentlandite ($[Fe, Ni]_9S_8$), with Fe^{2+} and Cu^{2+} in chalcopyrite ($CuFeS_2$), or as discrete Ni-sulphides, such as the pyrite-structured vaesite (NiS_2) or millerite (NiS).

Nickel is enriched up to a factor of 4 during lateritic weathering of ultramafic rocks, so that such soils may be commercially-mined deposits of Ni (Golightly, 1981). Si and Mg are preferentially removed in weathering solutions, but Ni is concentrated in solid products such as (Ni end-member in parenthesis):

- sepiolite ('falcandoite' $Ni_4Si_6O_{15}(OH)_2 \cdot 6H_2O$),
- talc ('kerolite' $Ni_3Si_4O_{10}(OH)_2$),
- serpentine ('nepouite' $Ni_3Si_2O_5(OH)_4$), and
- saponite ('pimelite' $Ni_3Si_4O_{10}(OH)_2$).

The solubilities of the Ni end-member minerals are considerably less than those of other metals except Al (Golightly, 1981). Although Ni may be sorbed strongly by goethite, there is no apparent incorporation of Ni into this mineral.

The Ni abundance in soils is highly dependent on the Ni content of parent rocks. However, the concentration of Ni in surface soils also reflects soil-forming processes and pollution. The highest Ni contents are always in clay and loamy soils, in soils over basic and volcanic rocks, and in organic-rich soils. Especially peaty serpentine soils are known for high Ni levels existing in easily soluble organic complexes. Also soils of arid and semi-arid regions are likely to have a high Ni content.

Soils throughout the world contain Ni within the broad range of from 2 - 750 mg/kg, while the range for soils of the U.S. is from 5 - 200 mg/kg (Pendias and Pendias, 1984). In soils, Ni is either strongly associated with Mn and Fe oxides, or appears to occur mainly in organically bound forms. Thus the Ni distribution in soil profiles is related either to organic matter or to amorphous oxides and clay fractions, depending on soil types.

Concentrations of Ni in natural solutions in different soils vary from around 3 to 25 µg/l. Generally, the solubility of soil Ni is inversely related to the soil pH. In aqueous media, nickel is dominated by its +2 oxidation state, such that its speciation in natural waters is relatively insensitive to redox conditions. Nickel generally has a low mobility relative to Ca, Mn, Fe, Zn, Cu in natural systems and this is shown by its low concentrations in groundwaters.

Webster (1994) measured concentrations of 0.73 and 0.58 µg/kg Ni respectively for river water and a saline lake in Antarctica. Bruno et al. (1992) measured Ni concentrations in the range 2×10^{-9} to 1×10^{-7} M in groundwaters in alkalic rocks at Poços de Caldas, Brazil.

Hamilton et al. (1988) measured the concentrations of a variety of trace elements in spring waters they classified as 'non-precipitating springs', 'iron precipitating springs', 'springs in granite terrain' and 'high discharge cold springs' in the Nahanni National Park Reserve, Canada. Nickel concentrations were <2 to 16, <2 to 273, <2 to 101 and <2 to 8 µg/l, respectively in these spring types.

Reimann et al. (1996) measured a median concentration of 0.74 µg/l Ni in 145 samples of groundwater from fractured hard rock in Norway. Banks et al. (1995a) report nickel concentrations in the range 0.2 to 1.6 µg/l also in groundwaters in fractured hard rocks of Norway.

In the presence of iron and manganese (hydr)oxides or clays, Ni will be scavenged from aqueous solution by sorption processes (e.g. Barrett et al., 1987). However, with time, ageing of iron oxides may result in the release of Ni to aqueous solution (Walker, 1989). The sorption of Ni on clay and silica substrates has been interpreted as a precipitation process, resulting in the formation of a Ni-hydrous silicate (Charlet and Manceau, 1994).

Ni recently has become a serious pollutant which is released in the emissions from metal processing operations and from the increasing combustion of coal and oil. The application of sludges and certain phosphate fertilisers also may be important sources of Ni. Anthropogenic sources of Ni, from industrial activity in particular, have resulted in a significant increase in the Ni content of soils. In particular, Ni in sewage sludge that is present mainly in organic chelated forms is readily available to plants and therefore may be highly phytotoxic. Soil treatments, such as additions of lime, phosphate, or organic matter, are known to decrease Ni availability to plants.

Table 2.5: Nickel concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	56	mg/kg	Wedepohl (1995)
Crustal average	80	mg/kg	Bowen (1979)
Crustal average	105	mg/kg	Taylor & McLennan (1995)
Upper crust	18.6	mg/kg	Wedepohl (1995)
Upper crust	20	mg/kg	Taylor & McLennan (1995)
Lower crust	99	mg/kg	Wedepohl (1995)
Granite	0.5	mg/kg	Bowen (1979)
Granite, rhyolite	4.5-16	mg/kg	Wedepohl (1978)
Basalt	150	mg/kg	Bowen (1979)
Basalt	25-530	mg/kg	Wedepohl (1978)
Gabbro	130-160	mg/kg	Pendias & Pendias (1984)
Gabbro	14-491	mg/kg	Wedepohl (1978)
Gneiss	5-15	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	20	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	5-55	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	1400-20000	mg/kg	Pendias & Pendias (1984)
Tonalite	19	mg/kg	Wedepohl (1978)
Greywacke	24	mg/kg	Wedepohl (1978)
Shale	20-90	mg/kg	Wedepohl (1978)
Shale	68	mg/kg	Bowen (1979)
Argillaceous rocks	40-90	mg/kg	Pendias & Pendias (1984)
Limestone	1-24	mg/kg	Wedepohl (1978)
Limestone	7	mg/kg	Bowen (1979)
Limestone, dolomite	2-20	mg/kg	Pendias & Pendias (1984)
Sandstone	20	mg/kg	Wedepohl (1978)
Sandstone	9	mg/kg	Bowen (1979)
Average sediment	52	mg/kg	Bowen (1979)
Soil	[50] 2-750	mg/kg	Bowen (1979)
Marine clay	225	mg/kg	Chester & Aston (1976)

Natural material	Elemental concentration	Concentration units	Reference
Marine carbonate	30	mg/kg	Chester & Aston (1976)
Marine clay	16-320	mg/kg	Wedepohl (1978)
Riverwater (dissolved)	0.5	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	90	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	2.2	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	90	mg/kg	Martin & Meybeck (1979)
Freshwater	[0.5] 0.02-27	µg/l	Bowen (1979)
Spring water	2-273	µg/l	Hamilton et al. (1988)
Groundwater (crystalline)	0.4-10	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	0.74	µg/l	Reimann et al. (1996)
Groundwater (crystalline)	0.2-1.6	µg/l	Banks et al. (1995a)
Groundwater (clay)	10	µg/l	Pearson & Scholtis (1993)
Seawater	0.53	µg/l	Li (1991)
Seawater	6.6	µg/l	Wedepohl (1978)
Seawater	[0.56] 0.13-43	µg/l	Bowen (1979)

2.2.5 Copper (Cu)

Copper has an atomic number of 29. It is a metal and a member of the transition elements in the periodic table. Copper is of interest here because it is one of the more abundant chemotoxic elements.

Copper is most abundant in mafic and intermediate rocks and has a tendency to be excluded from carbonate rocks. This element occurs in native metal form and as metallic alloys. However, it is also a component of many other minerals, including around 100 sulphides and arsenides, 20 halides, 12 oxides and hydroxides, 10 carbonates, 30 sulphides, 15 phosphates and nitrates, and 10 silicates (Wedepohl, 1978).

Many of these minerals are readily soluble during weathering processes and release Cu ions, especially in acid environments. Therefore, Cu is considered among the more mobile of the heavy metals in hypergenic processes. However, Cu is a very versatile trace cation and in soils or depositional material exhibits a great ability to chemically interact with mineral and organic components of soil. The Cu ions can also readily precipitate with various anions such as sulphide, carbonate, and hydroxide. Thus, Cu is a rather immobile element in soils and shows soil abundances from 2 - 250 mg/kg with the highest values for the ferralitic soil group and lowest for sandy soils and organic soils.

The regularity of large-scale Cu occurrence in soils indicates that two main factors, parent material and soil formation processes, govern the initial Cu status in soils. The common characteristic of Cu distribution in soil profiles is its accumulation in the top horizons. This phenomenon is an effect of various factors, but above all, Cu concentration in surface soils reflects the bioaccumulation of the metal and also recent anthropogenic sources of the element.

Many common soil minerals are capable of absorbing Cu ions from solution and these properties depend on the surface charge carried by the adsorbents. The surface charge is strongly controlled by pH, therefore, the adsorption of Cu ion species can be presented as a function of pH.

The concentration of Cu in ground and surface waters is variable but generally low. Webster (1994) measured concentrations of 1.9 and 0.771 µg/kg Cu respectively for river water and a saline lake in Antarctica. Banks et al. (1995a) reported copper concentrations in groundwaters in fractured hard rocks of Norway in the range 1 to 8 µg/l.

Hamilton et al. (1988) measured the concentrations of a variety of trace elements in spring waters they classified as 'non-precipitating springs', 'iron precipitating springs', 'springs in granite terrain' and 'high discharge cold springs' in the Nahanni National Park Reserve, Canada. Copper concentrations were <2 to 16, <2 to 25, <2 to 13 and <2 to 8 µg/l, respectively in these spring types.

Reimann et al. (1996) measured a median concentration of 11.75 µg/l Cu in 145 samples of groundwater from fractured hard rock in Norway. Ledin et al. (1989) determined copper concentrations in groundwaters in crystalline rocks in Sweden in the range 0.3 to 4 µg/l.

Table 2.6: Copper concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	25	mg/kg	Wedepohl (1995)
Crustal average	50	mg/kg	Bowen (1979)
Crustal average	75	mg/kg	Taylor & McLennan (1995)
Upper crust	14.3	mg/kg	Wedepohl (1995)
Upper crust	25	mg/kg	Taylor & McLennan (1995)
Lower crust	37.4	mg/kg	Wedepohl (1995)
Granite	13	mg/kg	Bowen (1979)
Granite	1-73	mg/kg	Wedepohl (1978)
Basalt	90	mg/kg	Bowen (1979)
Basalt	10-380	mg/kg	Wedepohl (1978)
Gabbro	10-400	mg/kg	Wedepohl (1978)
Basalt, gabbro	60-120	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	10-30	mg/kg	Pendias & Pendias (1984)
Schist, gneiss	1-200	mg/kg	Wedepohl (1978)
Rhyolite, trachyte, dacite	5-20	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	15-80	mg/kg	Pendias & Pendias (1984)
Diorite, andesite	3-345	mg/kg	Wedepohl (1978)
Peridotite, dunite	10-40	mg/kg	Pendias & Pendias (1984)
Tonalite	19	mg/kg	Wedepohl (1978)
Greywacke, sandstone	0-150	mg/kg	Wedepohl (1978)
Shale, clay	3-300	mg/kg	Wedepohl (1978)
Shale	39	mg/kg	Bowen (1979)
Shale	40	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	40-60	mg/kg	Pendias & Pendias (1984)
Limestone	1-500	mg/kg	Wedepohl (1978)
Limestone	5.5	mg/kg	Bowen (1979)
Limestone, dolomite	2-20	mg/kg	Pendias & Pendias (1984)

Natural material	Elemental concentration	Concentration units	Reference
Sandstone	30	mg/kg	Wedepohl (1978)
Sandstone	30	mg/kg	Bowen (1979)
Sandstone	5-30	mg/kg	Pendias & Pendias (1984)
Coal	1-400	mg/kg	Wedepohl (1978)
Average sediment	33	mg/kg	Bowen (1979)
Soil	[30] 2-250	mg/kg	Bowen (1979)
Sandy soils	[14] 1-70	mg/kg	Pendias & Pendias (1984)
Clay soils	[29] 7-70	mg/kg	Pendias & Pendias (1984)
Soil over crystalline rock	[24] 7-70	mg/kg	Pendias & Pendias (1984)
Soil over volcanic rock	[41] 10-150	mg/kg	Pendias & Pendias (1984)
Desert soils	[24] 5-100	mg/kg	Pendias & Pendias (1984)
Marine clay	25	mg/kg	Chester & Aston (1976)
Marine carbonate	30	mg/kg	Chester & Aston (1976)
Marine clay	9-7500	mg/kg	Wedepohl (1978)
Riverwater (dissolved)	1.5	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	100	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	10	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	100	mg/kg	Martin & Meybeck (1979)
Riverwater (dissolved)	0.07-105	µg/l	Wedepohl (1978)
Lakewater	0.5-5	µg/l	Wedepohl (1978)
Freshwater	[3] 0.2-30	µg/l	Bowen (1979)
Spring water	2-25	µg/l	Hamilton et al. (1988)
Groundwater (crystalline)	2-10	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	11.75	µg/l	Reimann et al. (1996)
Groundwater (crystalline)	1-8	µg/l	Banks et al. (1995a)
Groundwater (crystalline)	0.3-4	µg/l	Ledin et al. (1989)
Groundwater (clay)	5	µg/l	Pearson & Scholtis (1993)
Groundwater	0-210	µg/l	Wedepohl (1978)
Seawater	0.21	µg/l	Li (1991)
Seawater	0.9	µg/l	Wedepohl (1978)
Seawater	[0.25] 0.05-12	µg/l	Bowen (1979)

2.2.6 Zinc (Zn)

Zinc has an atomic number of 30. It is a metal and a member of the transition elements in the periodic table. Zinc is of interest here because it is one of the more abundant chemotoxic elements.

Zinc seems to be distributed rather uniformly in igneous rocks, showing a slight concentration increase in the more basic rocks (Pendias and Pendias, 1984). The Zn concentration in argillaceous sediments and shales is enhanced, ranging up to 130 mg/kg, while in sandstones and carbonates, concentrations of this metal range up to 100 mg/kg.

Wedepohl (1978) lists around 200 minerals that contain zinc as a component, including around 30 silicates where it substitutes for Mg^{2+}. However, Zn occurs chiefly as single sulphides (ZnS).

The dissolution of Zn minerals during weathering produces mobile Zn^{2+}, especially in acid, oxidising environments. Zinc is, however, also easily adsorbed by mineral and organic components which means it tends to accumulate in surface sediment horizons.

Average soil concentrations are in the range 1 - 900 mg/kg, being highest in alluvial soils and lowest in light mineral and light organic soils.

The Zn balance in different ecosystems shows that the atmospheric input of this metal exceeds its output due to both leaching and the production of biomass. Only in non-polluted forest regions of Sweden is the discharge of Zn by water flux higher than its atmospheric input.

The most common and mobile Zn in soil is believed to be Zn^{2+}, but several other ionic species may occur in soils. The important factors controlling the mobility of Zn in soils are very similar to those listed for Cu, but Zn appears to occur in more readily soluble forms. Many studies of Zn adsorption and retention in soils have shown that clays and soil organic matter are capable of holding Zn quite strongly.

The greater solubility of Zn means that its concentration in ground and surface waters is higher than some other metals. Webster (1974) measured concentrations of 1.6 and 2.9 µg/kg Zn respectively for river water and a saline lake in Antarctica.

Hamilton et al. (1988) measured the concentrations of a variety of trace elements in spring waters they classified as ‘non-precipitating springs’, ‘iron precipitating springs’, ‘springs in granite terrain’ and ‘high discharge cold springs’ in the Nahanni National Park Reserve, Canada. Zinc concentrations were <5 to 44, <5 to 1488, <5 to 3936 and <2 to 8 µg/l, respectively in these spring types.

Bruno et al. (1992) measured Zn concentrations in the range 1×10^{-6} to 9×10^{-6} M in groundwaters in alkaline rocks at Poços de Caldas, Brazil.

Reimann et al. (1996) measured a median concentration of 23.4 µg/l Zn in 145 samples of groundwater from fractured hard rock in Norway. Banks et al. (1995a) report zinc concentrations in the range 4 to 58 µg/l also in groundwaters in fractured hard rocks of Norway. Ledin et al. (1989) determined zinc concentrations in groundwaters in crystalline rocks in Sweden in the range 2 to 40 µg/l.

Table 2.7: Zinc concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	65	mg/kg	Wedepohl (1995)
Crustal average	75	mg/kg	Bowen (1979)
Crustal average	80	mg/kg	Taylor & McLennan (1995)
Upper crust	52	mg/kg	Wedepohl (1995)
Upper crust	71	mg/kg	Taylor & McLennan (1995)
Lower crust	79	mg/kg	Wedepohl (1995)
Granite	10-210	mg/kg	Wedepohl (1978)
Granite	52	mg/kg	Bowen (1979)
Granodiorite	5-141	mg/kg	Wedepohl (1978)
Basalt	40-420	mg/kg	Wedepohl (1978)

Natural material	Elemental concentration	Concentration units	Reference
Basalt	100	mg/kg	Bowen (1979)
Basalt, gabbro	80-120	mg/kg	Pendias & Pendias (1984)
Gabbro	73-135	mg/kg	Wedepohl (1978)
Syenite	14-326	mg/kg	Wedepohl (1978)
Schist	30-230	mg/kg	Wedepohl (1978)
Gneiss	15-150	mg/kg	Wedepohl (1978)
Granite, gneiss	40-60	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	40-100	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	40-100	mg/kg	Pendias & Pendias (1984)
Diorite, andesite	5-127	mg/kg	Wedepohl (1978)
Peridotite, dunite	40-60	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	25-91	mg/kg	Wedepohl (1978)
Tonalite	61	mg/kg	Wedepohl (1978)
Greywacke	37-198	mg/kg	Wedepohl (1978)
Shale	50-130	mg/kg	Wedepohl (1978)
Shale	120	mg/kg	Bowen (1979)
Shale	80-120	mg/kg	Pendias & Pendias (1984)
Black shale	15-1500	mg/kg	Wedepohl (1978)
Coal	50-150	mg/kg	Wedepohl (1978)
Argillaceous rocks	80-120	mg/kg	Pendias & Pendias (1984)
Limestone	4-100	mg/kg	Wedepohl (1978)
Limestone	20	mg/kg	Bowen (1979)
Limestone, dolomite	10-25	mg/kg	Pendias & Pendias (1984)
Sandstone	30	mg/kg	Wedepohl (1978)
Sandstone	30	mg/kg	Bowen (1979)
Sandstone	15-30	mg/kg	Pendias & Pendias (1984)
Average sediment	95	mg/kg	Bowen (1979)
Soil	[90] 1-900	mg/kg	Bowen (1979)
Marine clay	165	mg/kg	Chester & Aston (1976)
Marine carbonate	35	mg/kg	Chester & Aston (1976)
Marine clay	7-350	mg/kg	Wedepohl (1978)
Riverwater (dissolved)	30	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	250	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	30	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	350	mg/kg	Martin & Meybeck (1979)
Riverwater (dissolved)	0.1-145	µg/l	Wedepohl (1978)
Lakewater	0.3-100	µg/l	Wedepohl (1978)
Freshwater	[15] 0.2-100	µg/l	Bowen (1979)
Spring water	5-3936	µg/l	Hamilton et al. (1988)
Groundwater (crystalline)	4-30	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	23.4	µg/l	Reimann et al. (1996)
Groundwater (crystalline)	4-58	µg/l	Banks et al. (1995a)
Groundwater (crystalline)	2-40	µg/l	Ledin et al. (1989)
Groundwater (clay)	50	µg/l	Pearson & Scholtis (1993)
Groundwater	20-40	µg/l	Wedepohl (1978)
Hydrothermal water	10-10000	µg/l	Wedepohl (1978)

Natural material	Elemental concentration	Concentration units	Reference
Seawater	0.32	µg/l	Li (1991)
Seawater	5	µg/l	Wedepohl (1978)
Seawater	[4.9] 0.2-48	µg/l	Bowen (1979)

2.2.7 Selenium (Se)

Selenium has an atomic number of 34. It is a non-metal and a member of the Group VI elements in the periodic table. Selenium is of interest here because ^{79}Se is an important fission product which is problematic in some PAs and because Se is chemotoxic.

Selenium occurs in most natural materials but rarely at concentrations exceeding 0.05 mg/kg. Although, in rocks, selenium may be present at an order of magnitude higher concentration in shales than in igneous rocks such as granite or basalt (Krauskopf and Bird, 1995). An estimate of the ratio of sulphur to selenium in igneous rocks is 6000 to 1. In sedimentary rocks, Se is associated with the clay fraction and thus the smallest quantities of Se are in sandstones and limestones.

The electronegativity, ionic potential and ionic radius of Se are similar to those of sulphur and tellurium and thus its geochemical behaviour is intermediate between these elements but probably closer to sulphur. Selenium shows similar behaviour to sulphur in reduced chemical systems, but these elements behave quite differently under oxidising conditions. This is because sulphur is easily oxidised to sulphate, whereas selenium requires strongly oxidising conditions to form selenates (Berrow and Ure, 1989). Consequently, solid sulphates tend to contain no selenium.

Because of the similarity of ionic radius between sulphur (S^{2-} = 1.84 Å) and selenium (Se^{2-} = 1.91 Å), selenium will substitute readily for sulphur in solid sulphides and occurs in varying proportions in pyrite, chalcopyrite, pyrrhotite, galena, sphalerite, cinnabar, stibnite, molybdenite, arsenopyrite and others. Native Se occurs in nature only rarely. Selenium is a major component of 40 minerals and a minor constituent of 37 others (Elkin, 1982). Some selenium-bearing minerals are: ferroselite ($FeSe_2$); clausthalite (PbSe), stilleite (ZnSe), cadmoselite (CdSe), berzelianite (Cu_2Se) and eucairite (AgCuSe). Galena (PbS) and clausthalite (the most abundant Se-mineral) form an isomorphous series. Se also occurs as selenites (compared with sulphites, which do not occur in nature). Selenates are very rare minerals. Many selenates are isostructural with their corresponding sulphates (e.g. $PbSO_4$ is isostructural with $PbSeO_4$, kerstenite). Silicates of Se are not known.

Typical Se contents in minerals are (Wedepohl, 1978): galena, 0 to 20 %; molybdenite, 0 to 1000 ppm; pyrite, 0 to 3 %; pyrrhotite, 1 to 60 ppm; pentlandite, 27 to 67 ppm; sphalerite, 1 to 120 ppm; millerite, 5 to 10 ppm; marcasite, 3 to 80 ppm.

The geochemical behaviour of selenium has been reviewed by Howard (1977) who concluded that selenium behaviour was dominated by that of iron:

- under oxidising conditions, Se oxyanions, $HSeO_3^-$ and SeO_3^{2-} are strongly adsorbed by hydrated ferric oxide surfaces over the pH range 2 to 8. Selenium is thus enriched in sedimentary iron formations. Above pH 8, desorption occurs which is complete at pH 11.
- under reducing conditions, Se is either incorporated into pyrite (FeS_2) or forms the mineral ferroselite ($FeSe_2$).

Ferroselite occurs in roll front-type uranium deposits in sandstones and occurs at the interface between oxidised sandstone (containing goethite, limonite and hematite) and reduced pyritic uranium ore (Howard, 1977). This implies that selenium and ferrous iron in aqueous solution produced by the oxidation of seleniferous pyrite have combined to form ferroselite. Therefore, ferroselite is stable under conditions more oxidising than those required for pyrite.

During chemical weathering of rocks Se is easily oxidised and the state of its oxidation, as well as its solubility, are controlled by the oxidation-reduction regime and by pH of the environment. Also the biological methylation of Se, yielding volatile Se compounds, is common and plays a significant role in the geochemical cycle of Se. Selenite ions resulting from oxidation processes are stable and able to migrate until they are adsorbed on mineral or organic particles. In consequence, the Se level is increased in several coals, as well as in clay sediments. Concentrations of selenium in coal range from 0.47 to 8.1 mg/kg and in petroleum fuel oil from 2.4 to 7.5 mg/kg (Siu and Berman, 1989). The combustion of fossil fuels mobilises around 4.5×10^8 g of selenium annually.

The Se content of soils has received much attention in certain countries, mainly those where the role of Se in animal health has been widely recognised. Surface soil on a world-wide scale contains an average of 0.4 mg/kg Se. Elevated concentrations of Se are observed in some ferralsols, organic soils, and other soils derived from Se-rich parent materials. Also in salt-affected soil the total as well as the water-soluble Se is likely to be elevated. There is great concern about enriched water-soluble Se levels in soils because increased bioavailability of Se is a direct health risk to livestock.

In aqueous systems, selenium may occur as one of three oxidation states (II, IV, VI). Se^{IV} exists as selenite, $HSeO_3^-$ or SeO_3^{2-}. Se^{VI} occurs as selenate, SeO_4^{2-}. Se^{II} is found as hydrogen selenide, H_2Se or selenide, HSe^-. Selenate should be stable in oxygenated fresh waters at pH 6 - 9, whereas hydrogen selenide or selenium should be found in anoxic waters. Only two oxidation states of selenium are thought to be important in seawater, 4+ and 6+.

The selenium content of rivers worldwide is 0.2 - 9 nmol/kg, whereas that for lakes and reservoirs worldwide is 0.63 to 5044 nmol/kg (Cutter, 1989). Its abundance in seawater is 0.16 µg/l (Li, 1991), with concentrations tending to increase with depth (Siu and Berman, 1989).

Siu and Berman (1989) quote a non-weighted average for the Se content of river waters in seven North American rivers plus the Rhone and the Amazon as 0.2 µg /l. Reimann et al. (1996) measured a median concentration of 0.295 µg/l Se in 145 samples of groundwater from fractured hard rock in Norway.

Table 2.8: Selenium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	0.12	mg/kg	Wedepohl (1995)
Crustal average	0.05	mg/kg	Bowen (1979)
Crustal average	0.05	mg/kg	Taylor & McLennan (1995)
Upper crust	0.083	mg/kg	Wedepohl (1995)
Upper crust	0.05	mg/kg	Taylor & McLennan (1995)
Lower crust	0.17	mg/kg	Wedepohl (1995)
Granite	0.05	mg/kg	Bowen (1979)
Granite	0.1	mg/kg	Wedepohl (1978)
Granite, gneiss	0.01-0.05	mg/kg	Pendias & Pendias (1984)
Gabbro	0.1	mg/kg	Wedepohl (1978)
Basalt	0.1-0.2	mg/kg	Wedepohl (1978)
Basalt	0.05	mg/kg	Bowen (1979)
Basalt, gabbro	0.01-0.05	mg/kg	Pendias & Pendias (1984)
Shale	0.1-0.5	mg/kg	Wedepohl (1978)
Shale	[0.60] 0.1-675	mg/kg	Adriano (1986)
Shale	0.5	mg/kg	Bowen (1979)
Shale	0.6	mg/kg	Pendias & Pendias (1984)
Igneous rocks	0.05	mg/kg	Adriano (1986)
Peridotite, dunite	0.02-0.05	mg/kg	Pendias & Pendias (1984)
Limestone	0.03	mg/kg	Wedepohl (1978)
Limestone	[0.08] 0.1-6	mg/kg	Adriano (1986)
Limestone	0.03	mg/kg	Bowen (1979)
Sandstone	0.01	mg/kg	Wedepohl (1978)
Sandstone	0.05	mg/kg	Adriano (1986)
Sandstone	0.01	mg/kg	Bowen (1979)
Sandstone	0.05-0.08	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	0.1-2.5	mg/kg	Wedepohl (1978)
Average sediment	0.42	mg/kg	Bowen (1979)
Soil	0.4	mg/kg	Bowen (1979)
Soil	0.1-2	mg/kg	Adriano (1986)
Marine clay	0.17	mg/kg	Chester & Aston (1976)
Marine carbonate	0.17	mg/kg	Chester & Aston (1976)
Freshwater	0.0001-4	µg/l	Adriano (1986)
Freshwater	[0.2] 0.02-1	µg/l	Bowen (1979)
Riverwater (dissolved)	0.06	µg/l	Nriagu (1989)
Riverwater (suspended)	0.8	mg/kg	Nriagu (1989)
Groundwater (crystalline)	100	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	0.295	µg/l	Reimann et al. (1996)
Groundwater (clay)	1	µg/l	Pearson & Scholtis (1993)
Seawater	0.16	µg/l	Li (1991)
Seawater	0.09	µg/l	Wedepohl (1978)
Seawater	0.0002	µg/l	Adriano (1986)
Seawater	[0.2] 0.052-0.2	µg/l	Bowen (1979)

2.2.8 Rubidium (Rb)

Rubidium has an atomic number of 37. It is a member of the Group I (alkali metals) elements in the periodic table. Rubidium is of interest here because the radionuclide ^{87}Rb is a significant contributor to the total natural background radiation of terrestrial origin. In fact, it is one of the most significant natural non-alpha emitters.

Rubidium abundance in the major rock types reveals its geochemical association with K, and, therefore, it has high concentrations in acidic igneous rocks and sedimentary aluminosilicates. In these rocks, rubidium does not form its own minerals but substitutes for other elements, particularly K.

During weathering, Rb behaviour is also closely linked to K; however, its bonding forces to silicates appear to be stronger than those of K; therefore the K/Rb ratio continually decreases in soil-forming processes.

The Rb content of soils is largely inherited from the parent rocks, as is indicated by the highest mean Rb contents, 100 to 120 mg/kg, in soils over granites and gneisses, and in alluvial soils. The lowest Rb concentrations (30 to 50 mg/kg) are reported for sandy soils.

The mean Rb content for soils of various countries range from 20 to 1000 mg/kg as given by Bowen (1979). Organic matter and micaceous clay minerals increase the sorption capacity of soils for Rb.

Rubidium-bearing feldspar minerals are prone to weathering and thus the Rb content of ground and surface waters can be quite high, ranging up to a few tens of mg/l. Martin and Meybeck (1979) quote average Rb abundances in rivers of 1.5 µg/l for the dissolved and 100 mg/kg for the suspended component.

Reimann et al. (1996) measured an average rubidium concentration of 2.255 µg/l in 145 samples of groundwater from fractured hard rock in Norway. Likewise, 20 Bulgarian saline deep groundwaters have Rb concentrations in the range 0 to 800 µg/l (Pentcheva, 1965).

Table 2.9: Rubidium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	78	mg/kg	Wedepohl (1995)
Crustal average	90	mg/kg	Bowen (1979)
Crustal average	32	mg/kg	Taylor & McLennan (1995)
Upper crust	110	mg/kg	Wedepohl (1995)
Upper crust	112	mg/kg	Taylor & McLennan (1995)
Lower crust	41	mg/kg	Wedepohl (1995)
Granite	150	mg/kg	Bowen (1979)
Basalt	37	mg/kg	Bowen (1979)
Basalt, gabbro	20-45	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	150	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	100-200	mg/kg	Pendias & Pendias (1984)

Natural material	Elemental concentration	Concentration units	Reference
Diorite, syenite	100	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0.1-2	mg/kg	Pendias & Pendias (1984)
Tonalite	64	mg/kg	Wedepohl (1978)
Greywacke	72	mg/kg	Wedepohl (1978)
Shale	20-650	mg/kg	Wedepohl (1978)
Shale	160	mg/kg	Bowen (1979)
Shale	140-160	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	120-200	mg/kg	Pendias & Pendias (1984)
Limestone	6-160	mg/kg	Wedepohl (1978)
Limestone, dolomite	5-30	mg/kg	Pendias & Pendias (1984)
Limestone	52	mg/kg	Bowen (1979)
Sandstone	9-100	mg/kg	Wedepohl (1978)
Sandstone	46	mg/kg	Bowen (1979)
Sandstone	45	mg/kg	Pendias & Pendias (1984)
Average sediment	135	mg/kg	Bowen (1979)
Soil	[150] 20-1000	mg/kg	Bowen (1979)
Soil	10-1000	mg/kg	Wedepohl (1978)
Sandy soils	[50] 20-120	mg/kg	Pendias & Pendias (1984)
Clay soils	[80] 45-120	mg/kg	Pendias & Pendias (1984)
Soil over crystalline rock	[120] 20-210	mg/kg	Pendias & Pendias (1984)
Soil over volcanic rock	[65] 20-115	mg/kg	Pendias & Pendias (1984)
Desert soils	[95] 70-120	mg/kg	Pendias & Pendias (1984)
Marine clay	110	mg/kg	Chester & Aston (1976)
Marine carbonate	10	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	1.5	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	100	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	1.5	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	100	mg/kg	Martin & Meybeck (1979)
Riverwater (dissolved)	0.2-7.4	µg/l	Wedepohl (1978)
Freshwater	[1.0] 0.6-9	µg/l	Bowen (1979)
Groundwater	0-800	µg/l	Pentcheva (1965)
Groundwater (crystalline)	50	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	2.3	µg/l	Reimann et al. (1996)
Groundwater (clay)	300	µg/l	Pearson & Scholtis (1993)
Groundwater	0.1	µg/l	Wedepohl (1978)
Hydrothermal water	0.01-7.7	µg/l	Wedepohl (1978)
Seawater	120	µg/l	Li (1991)
Seawater	120	µg/l	Wedepohl (1978)
Seawater	[120] 67-195	µg/l	Bowen (1979)

2.2.9 Cadmium (Cd)

Cadmium has an atomic number of 48. It is a metal and a member of the transition elements in the periodic table. Cadmium is of interest here because it is one of the more abundant chemotoxic elements.

The abundance of Cd in most rocks does not exceed around 0.3 mg/kg, and is most likely to be concentrated in argillaceous and shale deposits. Cadmium is strongly associated with Zn in its geochemistry, but seems to have a stronger affinity for S than Zn, and exhibits also a higher mobility than Zn in acidic environments.

During weathering Cd goes readily into solution and, though is known to occur as Cd^{2+}, it may also form several complex ions ($CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $CdCl_3^-$, $CdCl_4^{2-}$, $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$) and organic chelates. However, the most important valence state of Cd in the natural environment is +2, and the most important factors which control the Cd ion mobility are pH and oxidation potential. Under conditions of strong oxidation, Cd is likely to form minerals (CdO, $CdCO_3$) and is also likely to be accumulated in phosphate, and in organic rich sediments and sedimentary rocks.

The main factor determining the Cd content of soil is the chemical composition of the parent rock. The average contents of Cd in soils lie between 0.01 and 2 mg/kg. However, the background Cd levels in soils is usually below 0.5 mg/kg, and all higher values reflect the anthropogenic impact on the Cd status in topsoils. The sorption of Cd species by clays in soils is the predominant process in Cd bonding. Also, adsorption, rather than precipitation, controls Cd concentrations in soil solutions until a threshold pH value is exceeded. The pH-solubility diagram indicates that above pH 7.5 Cd sorbed in soils is not easily mobile, therefore, the solubility of $CdCO_3$ would control the Cd mobility in soils.

The solubility of Cd appears to be highly dependent on the pH; however, the nature of sorbent surfaces and of organic ligands are also of importance. Cadmium is most mobile in acidic soils within the range of pH 4.5 to 5.5, whereas in alkaline soils, Cd is rather immobile. However, as the pH is increased in the alkaline range, monovalent hydroxy ion species are likely to occur (e.g., $CdOH^+$), which could not easily occupy the sites on cationic exchange complexes.

Cadmium concentrations in the soil solution is relatively low and is reported generally to range from 0.2 to 6 µg/l. Higher values presumably indicates contaminated soils. In soils developed under the influence of humid climate, migration of Cd down the profile is more likely to occur than its accumulation in the surface horizon; thus, the enrichment in Cd content observed so commonly in topsoils could be related to contamination effects. Soil contamination with Cd is believed to be a most serious health risk. Even in the forest or rural regions in various countries, the atmospheric input of Cd exceeds the output of this metal from the soil profile. The present concentration of Cd in topsoils is reported to be very high in the vicinities of Pb and Zn mines and, in particular, smelting operations. Sewage sludges and phosphate fertilisers are also known as important sources of Cd, and there are several comprehensive reviews of this subject.

Reimann et al. (1996) measured a median concentration of 0.032 µg/l Cd in 145 samples of groundwater from fractured hard rock in Norway. Banks et al. (1995a) report cadmium concentrations in the range 0.01 to 0.1 µg/l also in groundwaters in fractured hard rocks of Norway. Ledin et al. (1989) determined cadmium concentrations in groundwaters in crystalline rocks in Sweden in the range 0.006 to 0.1 µg/l.

Hamilton et al. (1988) measured the concentrations of a variety of trace elements in spring waters they classified as 'non-precipitating springs', 'iron precipitating springs', 'springs in granite terrain' and 'high discharge cold springs' in the Nahanni National Park Reserve, Canada. Cadmium concentrations were <2 to 3, <2 to 39, <2 to 5 and <2 to 3 ppb, respectively in these spring types.

Table 2.10: Cadmium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	0.10	mg/kg	Wedepohl (1995)
Crustal average	0.11	mg/kg	Bowen (1979)
Crustal average	0.098	mg/kg	Taylor & McLennan (1995)
Upper crust	0.102	mg/kg	Wedepohl (1995)
Upper crust	0.098	mg/kg	Taylor & McLennan (1995)
Lower crust	0.101	mg/kg	Wedepohl (1995)
Granite	0.003-0.6	mg/kg	Wedepohl (1978)
Granite	0.09	mg/kg	Bowen (1979)
Basalt	0.13	mg/kg	Bowen (1979)
Basalt	0.02-0.7	mg/kg	Wedepohl (1978)
Basalt, gabbro	0.13-0.22	mg/kg	Pendias & Pendias (1984)
Gabbro	0.03-0.28	mg/kg	Wedepohl (1978)
Andesite, syenite	0.04-2	mg/kg	Wedepohl (1978)
Granite, gneiss	0.09-0.20	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	0.05-0.20	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	0.13	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0.03-0.05	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0.001-2	mg/kg	Wedepohl (1978)
Shale	0.22	mg/kg	Wedepohl (1978)
Shale	0.22	mg/kg	Bowen (1979)
Shale	0.22-0.30	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	0.3	mg/kg	Pendias & Pendias (1984)
Limestone	0.028	mg/kg	Wedepohl (1978)
Limestone, dolomite	0.035	mg/kg	Pendias & Pendias (1984)
Limestone	0.028	mg/kg	Bowen (1979)
Sandstone	0.05	mg/kg	Wedepohl (1978)
Sandstone	0.05	mg/kg	Bowen (1979)
Sandstone	0.05	mg/kg	Pendias & Pendias (1984)
Average sediment	0.17	mg/kg	Bowen (1979)
Soil	[0.35] 0.01-2	mg/kg	Bowen (1979)
Marine clay	0.21	mg/kg	Chester & Aston (1976)
Marine carbonate	0.23	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	0.02	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	1	mg/kg	Martin & Whitfield (1983)
Riverwater (suspended)	1	mg/kg	Martin & Meybeck (1979)
Freshwater	[0.1] 0.01-3	µg/l	Bowen (1979)
Spring water	2-39	µg/l	Hamilton et al. (1988)
Groundwater (crystalline)	0.032	µg/l	Reimann et al. (1996)
Groundwater (crystalline)	0.01-0.1	µg/l	Banks et al. (1995a)
Groundwater (crystalline)	0.006-0.1	µg/l	Ledin et al. (1989)

Natural material	Elemental concentration	Concentration units	Reference
Groundwater (clay)	0.2	µg/l	Pearson & Scholtis (1993)
Seawater	0.08	µg/l	Li (1991)
Seawater	0.11	µg/l	Wedepohl (1978)
Seawater	[0.11] 0.01-9.4	µg/l	Bowen (1979)

2.2.10 Tin (Sn)

Tin has an atomic number of 50. It is a metal and a member of the Group IV elements in the periodic table. Tin is of interest here because ^{126}Sn is an important PA relevant fission product.

The abundance of Sn in common rocks shows an increased concentration in argillaceous sediments (6 to 10 mg/kg) and relatively lower amounts in ultramafic and calcareous rocks (0.35 to 0.5 mg/kg).

Tin can exhibit siderophilic, lithophilic and chalcophilic behaviour. Tin occurs both as the stannous (Sn^{2+}) and stannic (Sn^{4+}) valence states in nature, depending upon redox state and pH. Sn^{2+} has an ionic radius of 0.93 Å in octahedral coordination, whereas that for Sn^{4+} is 0.71 Å. Tin has 10 stable isotopes between mass numbers 112 and 124 which is the largest number for any element.

Tin tends to form only a few independent minerals. The principal economic source of tin is the oxide, cassiterite (SnO_2) which is associated with granitic magmatism. Sn will also form solid solutions with various ferromagnesian silicates such as pyroxenes, micas and amphiboles. This relates to the substitution of Sn (ionic radius 0.71 Å) for Ti (ionic radius 0.68 Å) and Fe^{3+} (ionic radius 0.64 Å). Sn in biotite and muscovite may be as high as 1250 ppm. Tin will also occur in sulphides such as stannite, Cu_2FeSnS_4, canfieldite, Ag_8SnS_6, and teallite, $PbSnS_2$. Tin minerals are comparatively few.

The mobility of Sn during weathering is highly pH dependent. Especially Sn^{2+}, a strong reducing agent, can be present only in acid and reducing environments. Soluble Sn follows the behaviour of Fe and Al and remains in the weathered residue along with hydroxides of these metals. The ability of Sn to form complexes with organic substances, both soluble and insoluble, has been reported, therefore, Sn is generally enriched in organic rich sediments and sedimentary rocks.

The occurrence of Sn in soil has not receive much study. Although Sn in soils is largely derived from Sn in the bedrock, all soil surface horizons contain fairly similar amounts of this element, ranging from 1 - 200 mg/kg.

Jackson and Helgeson (1985) have reviewed the speciation and solubility behaviour of tin. Although both Sn^{2+} and Sn^{4+} readily form complexes with Cl^-, OH^- and F^-, they concluded that the species $Sn(OH)_2^0$ and $Sn(OH)_4^0$ are the dominant tin species at temperatures up to 350 °C in acidic solutions, even with NaCl concentrations as high as 3 M. At temperatures < 250 °C, the solubility of tin is almost exclusively controlled by stannic species under all redox conditions.

Byrd and Andreae (1986) measured an arithmetic mean for dissolved tin in the world's rivers of 20.5 pM and estimated a dissolved flux of tin to the oceans of 0.76×10^6 mol/yr and 300×10^6 to 600×10^6 mol/yr for the particulate fraction.

Reimann et al. (1996) measured a median concentration of <0.005 µg/l Sn in 145 samples of groundwater from fractured hard rock in Norway. Edmunds et al. (1989) measured tin concentrations in groundwaters in various aquifers of the U.K. Concentrations in the range 0.3 to 1.0 µg/l were found in groundwaters in the Millstone Grit and Carboniferous Limestone of Derbyshire, the Old Red Sandstone of Moray, the Trias of Shropshire, the Wealden and Lower Greensand. In only one sample was tin above 1 µg/l. 20 Bulgarian saline deep groundwaters have Sn concentrations in the range 0 to 70 ppb (Pentcheva, 1965). The abundance of tin in hot springs (16-92 °C) in Japan was in the range <0.1 to 1 ppb (Ikeda, 1955).

Table 2.11: Tin concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	2.3	mg/kg	Wedepohl (1995)
Crustal average	2.2	mg/kg	Bowen (1979)
Crustal average	2.5	mg/kg	Taylor & McLennan (1995)
Upper crust	2.5	mg/kg	Wedepohl (1995)
Upper crust	5.5	mg/kg	Taylor & McLennan (1995)
Lower crust	2.1	mg/kg	Wedepohl (1995)
Granite	1-10	mg/kg	Wedepohl (1978)
Granite	3.5	mg/kg	Bowen (1979)
Basalt	1-6	mg/kg	Wedepohl (1978)
Basalt	1	mg/kg	Bowen (1979)
Basalt, gabbro	0.9-1.5	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	1.5-3.6	mg/kg	Pendias & Pendias (1984)
Schist, gneiss	0.1-20	mg/kg	Wedepohl (1978)
Andesite, diorite	0.1-5	mg/kg	Wedepohl (1978)
Rhyolite, trachyte, dacite	2-3	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	1.3-1.5	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0.35-0.50	mg/kg	Pendias & Pendias (1984)
Tonalite	2.4	mg/kg	Wedepohl (1978)
Shale	3-11	mg/kg	Wedepohl (1978)
Shale	6	mg/kg	Bowen (1979)
Shale	6	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	6-10	mg/kg	Pendias & Pendias (1984)
Limestone	0.5	mg/kg	Wedepohl (1978)
Limestone	0.5	mg/kg	Bowen (1979)
Limestone, dolomite	0.5	mg/kg	Pendias & Pendias (1984)
Sandstone	0.5	mg/kg	Wedepohl (1978)
Sandstone	0.5	mg/kg	Bowen (1979)
Sandstone	0.5	mg/kg	Pendias & Pendias (1984)
Average sediment	4.6	mg/kg	Bowen (1979)
Soil	[4] 1-200	mg/kg	Bowen (1979)
Sandy soils	[1.1] 0.1-7.7	mg/kg	Pendias & Pendias (1984)
Clay soils	[1.2] 0.3-3.1	mg/kg	Pendias & Pendias (1984)
Soil over crystalline rock	[1.2] 0.9-1.5	mg/kg	Pendias & Pendias (1984)
Soil over volcanic rock	[1.2] 0.8-1.7	mg/kg	Pendias & Pendias (1984)

Natural material	Elemental concentration	Concentration units	Reference
Desert soils	[1.2] 0.7-1.9	mg/kg	Pendias & Pendias (1984)
Marine clay	3.2	mg/kg	Chester & Aston (1976)
Marine carbonate	1.5	mg/kg	Chester & Aston (1976)
Freshwater	[0.009] 0.004-0.09	µg/l	Bowen (1979)
Groundwater (crystalline)	0.6	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	0.005	µg/l	Reimann et al. (1996)
Groundwater (sedimentary)	0.3-1.0	µg/l	Edmunds et al. (1989)
Seawater	0.006	µg/l	Li (1991)
Seawater	0.81	µg/l	Wedepohl (1978)
Seawater	[0.004] 0.002-0.81	µg/l	Bowen (1979)

2.2.11 Iodine (I)

Iodine has an atomic number of 53. It is a non-metal and member of the Group VII (halogen) elements in the periodic table. Iodine is of interest because the radionuclide ^{129}I is a problematic fission product in PA. Iodine is a volatile element and occurs in groundwaters in anionic form, therefore, can move rapidly through the rock mass with little involvement in rock-water interactions.

Geochemical characteristics of I resemble those of Br, however, its abundance in most rocks is less than that of Br. The I content of most rocks varies from 0.01 to 6 mg/kg, but is highest in evaporite deposits.

Iodine can form its own rare minerals such as CuI (marshite) and iodates (salesite: $Cu(OH)(IO_3)$) but is generally included in other minerals such as micas and amphiboles.

The high I content of some nitrate deposits, especially of Chile saltpeter (up to 400 mg/kg) has been the subject of much discussion. Apparently, the suggestion of an atmospheric origin seems to be most reasonable. All I compounds are readily soluble, therefore, weathering of rocks results in the release of much of their I content. Although I is known to be easily transported by waters to ocean basins, its great sorption by carbon, organic matter, and clays greatly influences I cycling.

The geochemistry of I, a biophile element, is strongly connected to its involvement in biological processes. The high I content of sediments and soils is mostly due to uptake of I by plankton or is due to fixation of I by organic matter. Like Br, the I content is reported to be closely correlated with organic carbon content of sediments. Sediments of reducing environments contain greater amounts of I than do oxidised sediments.

It is most unlikely that I occurs in soils in the form of I minerals. The association between I and organic matter, hydrous oxides of Fe and Al, and clay of the chlorite-illite group has been noted by several workers. However, organic matter is mostly responsible for I sorption in soil and therefore I is accumulated mainly in topsoil horizons.

The influence of soil reaction on the I status in soil is diverse. Soil acidity favours I sorption by soil components such as organic matter, hydrous oxides of Fe and Al, and illitic clays. The oxidation of iodide to iodate and further alteration to elemental I may occur in soils and also the exchange of volatile I compounds between soil and atmosphere is reported to be possible. Several ionic forms may occur in the soil porewaters.

The fact that soils contain several times as much I as do the parent rocks has been confirmed by numerous analyses. Also an accumulation of I in surface and/or subsurface soil horizons is usually reported. In gleyed water-rich soils, however, a higher I concentration in the lower soil horizons can be expected. The I concentrations in soils range from 0.1 - 25 mg/kg. Usually light soils of humid climatic regions are I poor, whereas high humus and clayed soils are I rich. This may vary greatly because the I level in soils is known to be dependent on atmospheric precipitation. Also the distance from the sea and recent glaciations influence the soil I status.

Since I released into the atmosphere from sea water seems to be a significant source of this element, soils from coastal districts are known to be enriched in this element where it is delivered as an aerosol. Soils derived from recent glacial (Pleistocene) deposits are usually I poor because this element has not yet been highly accumulated from atmospheric precipitation.

Reimann et al. (1996) measured a median concentration of 2.025 µg/l I in 145 samples of groundwater from fractured hard rock in Norway.

Table 2.12: Iodine concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	0.8	mg/kg	Wedepohl (1995)
Crustal average	0.14	mg/kg	Bowen (1979)
Upper crust	1.40	mg/kg	Wedepohl (1995)
Lower crust	0.14	mg/kg	Wedepohl (1995)
Granite	140-200	mg/kg	Wedepohl (1978)
Granite	0.2	mg/kg	Bowen (1979)
Basalt	0.08	mg/kg	Bowen (1979)
Basalt	18-130	mg/kg	Wedepohl (1978)
Andesite	30-270	mg/kg	Wedepohl (1978)
Peridotite, dunite	70-300	mg/kg	Wedepohl (1978)
Shale	0.2-17	mg/kg	Wedepohl (1978)
Shale	19	mg/kg	Bowen (1979)
Limestone	1-30	mg/kg	Wedepohl (1978)
Limestone	14	mg/kg	Bowen (1979)
Sandstone	0.02-1.5	mg/kg	Wedepohl (1978)
Sandstone	0.1	mg/kg	Bowen (1979)
Average sediment	16	mg/kg	Bowen (1979)
Soil	[5] 0.1-25	mg/kg	Bowen (1979)
Soil	1.5-18	mg/kg	Wedepohl (1978)
Marine clay	30	mg/kg	Chester & Aston (1976)
Marine carbonate	31	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	1-10	µg/l	Wedepohl (1978)
Groundwater	8-40	µg/l	Wedepohl (1978)
Hydrothermal water	30-330	µg/l	Wedepohl (1978)

Natural material	Elemental concentration	Concentration units	Reference
Freshwater	[2] 0.5-7	µg/l	Bowen (1979)
Groundwater (crystalline)	10	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	2.0	µg/l	Reimann et al. (1996)
Groundwater (clay)	1400	µg/l	Pearson & Scholtis (1993)
Seawater	64	µg/l	Wedepohl (1978)
Seawater	[60] 50-70	µg/l	Bowen (1979)

2.2.12 Neodymium (Nd)

Neodymium has an atomic number of 60. It is a metal and a member of the lanthanide (rare earth) elements in the periodic table. Neodymium is of interest here because it is a potential chemical analogue element for the actinides (e.g. Pu and Am) in the waste.

The terrestrial abundance of the lanthanides shows their contents decrease with the increase in their atomic weights, and the element with the even atomic number is more frequent than the next element with the odd atomic number.

Neodymium displays lithophilic geochemical behaviour and, because of similarities in ionic radius and valence, there is very similar behaviour across the group of lanthanide elements (elements 57 - 71, lanthanum-lutetium). Neodymium is generally grouped with the 'light' REE (lanthanum-samarium). The lanthanides are sensitive petrogenetic indicators and are routinely analysed in rocks. The aqueous behaviour of the lanthanides is less well understood.

The geochemical properties of the lanthanides are fairly similar, they occur mainly as +3 cations, show an affinity for oxygen, and are likely to be concentrated in phosphorites and in argillaceous sediments. Most often their lowest concentrations are reported for ultramafic and calcareous rocks. Neodymium concentrations in rocks range from 1 - 70 mg/kg, being most abundant in the silica rich igneous rocks.

Reimann et al. (1996) measured a median concentration of 0.155 µg/l Nd in 145 samples of groundwater from fractured hard rock in Norway. Smedley (1991) measured neodymium concentrations in shallow groundwaters in the Carnmenellis granite and surrounding metasedimentary rocks in the range 0.51 to 69 µg/l.

Table 2.13: Neodymium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	27	mg/kg	Wedepohl (1995)
Crustal average	38	mg/kg	Bowen (1979)
Crustal average	16	mg/kg	Taylor & McLennan (1995)
Upper crust	25.9	mg/kg	Wedepohl (1995)
Upper crust	26	mg/kg	Taylor & McLennan (1995)
Lower crust	28	mg/kg	Wedepohl (1995)
Granite	20-70	mg/kg	Wedepohl (1978)
Granite	44	mg/kg	Bowen (1979)

Natural material	Elemental concentration	Concentration units	Reference
Basalt	32	mg/kg	Bowen (1979)
Basalt, gabbro	3-30	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	33-47	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	18-80	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	30-65	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0-2.4	mg/kg	Pendias & Pendias (1984)
Tonalite	25	mg/kg	Wedepohl (1978)
Greywacke	25	mg/kg	Wedepohl (1978)
Shale	18-60	mg/kg	Wedepohl (1978)
Shale	41	mg/kg	Bowen (1979)
Shale	18-41	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	24-35	mg/kg	Pendias & Pendias (1984)
Limestone	2-9	mg/kg	Wedepohl (1978)
Limestone	9	mg/kg	Bowen (1979)
Limestone, dolomite	4.7-9.0	mg/kg	Pendias & Pendias (1984)
Sandstone	8-50	mg/kg	Wedepohl (1978)
Sandstone	38	mg/kg	Bowen (1979)
Sandstone	16-38	mg/kg	Pendias & Pendias (1984)
Average sediment	32	mg/kg	Bowen (1979)
Soil	[35] 4-63	mg/kg	Bowen (1979)
Soil	8.6-56.0	mg/kg	Pendias & Pendias (1984)
Marine clay	35	mg/kg	Chester & Aston (1976)
Marine carbonate	14	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	0.04	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	35	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	0.04	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	35	mg/kg	Martin & Meybeck (1979)
Freshwater	[0.15] 0.06-0.25	µg/l	Bowen (1979)
Groundwater	0.51-69.0	µg/l	Smedley (1991)
Groundwater (crystalline)	0.16	µg/l	Reimann et al. (1996)
Seawater	0.004	µg/l	Li (1991)
Seawater	0.0028	µg/l	Wedepohl (1978)
Seawater	0.0028	µg/l	Bowen (1979)

2.2.13 Samarium (Sm)

Samarium has an atomic number of 62. It is a metal and a member of the lanthanide (rare earth) elements in the periodic table. Samarium is of interest here because it is a potential chemical analogue element for the actinides (e.g. Pu and Am) in the waste.

Samarium displays lithophilic geochemical behaviour and, because of similarities in ionic radius and valence, there is very similar behaviour across the group of lanthanide elements (elements 57 - 71, lanthanum-lutetium). Samarium is generally grouped with the ‘light’ REE (lanthanum-samarium). Samarium concentrations in rocks range from 1 - 20 mg/kg, being most abundant in the silica rich igneous rocks.

The lanthanides are sensitive petrogenetic indicators and are routinely analysed in rocks. The aqueous behaviour of the lanthanides is less well understood. Sm can exist as 3+ (most common) and 2+. No ‘anomalies’ of behaviour (compared with europium) are reported in minerals and rocks. Transport in hydrothermal solutions is probably by carbonate, fluoride or sulphate complexes. Stability constants for lanthanide phosphate complexes have been estimated by Lee and Byrne (1992). They note that lanthanide phosphate complexes can be important relative to carbonate complexes in groundwaters of pH 7 to 9. Millero (1992) reports stability constants for inorganic rare-earth complexes as a function of ionic strength. He concludes that carbonate complexes dominate for all natural waters where the carbonate alkalinity is > 0.001 eq/l at pH ~ 8.

Around 200 minerals are known which contain up to 0.01 % lanthanides. Highest concentrations are in bastnaesite (around 64 wt %), monazite (around 60 wt %) and cerite (around 59 wt %). There are 3 fluorides, 10 oxides, 10 carbonates, 1 borate, 1 sulphate, 8 phosphates and 20 silicate minerals containing REE listed in Wedepohl (1978). REE contents of basalts and gabbros are concentrated in clinopyroxene rather than plagioclase. Biotites from granites contain more REE than feldspars and quartz.

Elderfield et al. (1990) report REE analyses of rivers and seawaters. Sm values in river waters are in the range 46 to 810 pmol/kg.

Sm concentrations in the range 0.09×10^{-10} to 2.39×10^{-10} mol/l are reported by Michard et al. (1987) in CO_2-rich groundwaters in granites from Vals-les Bains, France. The enrichment of heavy REE in these waters is ascribed to carbonate complexing. REE abundances in alkaline groundwaters in granites in southern Europe were associated with colloids (Alaux-Negrel et al., 1993). Smedley (1991) measured samarium concentrations in shallow groundwaters in the Carnmenellis granite and surrounding metasedimentary rocks in the range 0.05 to 10 µg/l. Reimann et al. (1996) measured a median concentration of 0.028 µg/l Sm in 145 samples of groundwater from fractured hard rock in Norway. Gosselin et al. (1992) investigated concentrations of REE in chloride-rich groundwater in the Palo Duro Basin, Texas. These authors noted Sm concentrations in the range 0.0053 to 7.30 µg/l. They concluded that chloride complexes dominated the REE speciation with only minor contributions from carbonate and sulphate species. Fresh groundwaters from wells in the schists of the Virginia Piedmont area of the U.S.A. have 60 ppb REE (Wedepohl, 1978).

Table 2.14: Samarium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	**Elemental concentration**	**Concentration units**	**Reference**
Crustal average	5.3	mg/kg	Wedepohl (1995)
Crustal average	7.9	mg/kg	Bowen (1979)
Crustal average	3.5	mg/kg	Taylor & McLennan (1995)
Upper crust	4.7	mg/kg	Wedepohl (1995)
Upper crust	4.5	mg/kg	Taylor & McLennan (1995)
Lower crust	6.0	mg/kg	Wedepohl (1995)
Granite	4-18	mg/kg	Wedepohl (1978)
Granite	8.5	mg/kg	Bowen (1979)

Natural material	Elemental concentration	Concentration units	Reference
Basalt	7.3	mg/kg	Bowen (1979)
Basalt, gabbro	0.9-7.0	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	8-9	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	6-11	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	6-18	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0-0.4	mg/kg	Pendias & Pendias (1984)
Tonalite	4.9	mg/kg	Wedepohl (1978)
Greywacke	4.6	mg/kg	Wedepohl (1978)
Shale	4-14	mg/kg	Wedepohl (1978)
Shale	7	mg/kg	Bowen (1979)
Shale	5-7	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	6-6.5	mg/kg	Pendias & Pendias (1984)
Limestone	0.5-2	mg/kg	Wedepohl (1978)
Limestone	2.1	mg/kg	Bowen (1979)
Limestone, dolomite	1.3-2.1	mg/kg	Pendias & Pendias (1984)
Sandstone	2-10	mg/kg	Wedepohl (1978)
Sandstone	8.4	mg/kg	Bowen (1979)
Sandstone	4-10	mg/kg	Pendias & Pendias (1984)
Average sediment	6.4	mg/kg	Bowen (1979)
Soil	[4.5] 0.6-23	mg/kg	Bowen (1979)
Soil	2.3-11.9	mg/kg	Pendias & Pendias (1984)
Marine clay	6.2	mg/kg	Chester & Aston (1976)
Marine carbonate	3.8	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	0.008	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	7	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	0.008	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	7	mg/kg	Martin & Meybeck (1979)
Freshwater	[0.06] 0.01-0.12	µg/l	Bowen (1979)
Groundwater	0.05-10	µg/l	Smedley (1991)
Groundwater (crystalline)	0.028	µg/l	Reimann et al. (1996)
Seawater	0.008	µg/l	Li (1991)
Seawater	0.00045	µg/l	Wedepohl (1978)
Seawater	0.00045	µg/l	Bowen (1979)

2.2.14 Lead (Pb)

Lead has an atomic number of 82. It is a metal and a member of the Group IV elements in the periodic table. Lead is of interest here because several isotopes of lead occur in radioactive waste and because the element is chemotoxic.

Lead tends to concentrate in silica rich igneous rocks and in argillaceous sediments which have Pb concentrations range from 20 to 100 mg/kg. Silica poor rocks, such as ultramafic rocks and calcareous sediments, have Pb concentrations range from 1 to 20 mg/kg.

Pb has highly chalcophilic properties and thus its primary form in the natural state is galena (PbS). Lead is comprised of four stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. ^{204}Pb is not of radioactive origin, whereas the others are derived from radioactive decay of ^{238}U, ^{235}U and ^{232}Th. There are 4 radioactive isotopes: ^{210}Pb and ^{204}Pb in the ^{238}U decay chain; ^{211}Pb in the ^{235}U chain and ^{212}Pb in the ^{232}Th chain. All except ^{210}Pb have half-lives less than 12 hours.

Pb occurs mainly as Pb^{2+}, although the +4 oxidation state, is also known. Pb^{2+} (1.20 Å) is similar in ionic size to K^+ (1.33 Å); Sr^{2+} (1.12-1.27 Å); and Ba^{2+} (1.34-1.43 Å). Because of its size Pb^{2+} will be incorporated into silicates as a large monovalent or divalent metal. It replaces K^+ in minerals (e.g. in feldspar). Mica usually contains less Pb than feldspar. Biotite typically contains 20 ppm Pb and muscovite contains 25 ppm. In K-feldspar, Pb may be greater than 50 ppm. Pb may also occur in plagioclase and amphibole. Around 240 Pb-bearing minerals are listed in Wedepohl (1978). More than one third of these are sulphides and sulphosalts. Sulphates and phosphates are almost as numerous. Lead halides are relatively rare. Metallic Pb is occasionally found in nature (e.g. at Oklo). Most Pb minerals are quite insoluble in natural waters.

During weathering Pb sulphides slowly oxidise and have the ability to form carbonates, and also to be incorporated in clay minerals, in Fe and Mn oxides, and in organic matter. The geochemical characteristics of Pb^{2+} somewhat resemble the divalent alkaline-earth group of metals, thus Pb has the ability to replace K, Ba, Sr, and even Ca, both in minerals and in sorption sites.

The natural Pb content of soil is inherited from parent rocks. However, due to widespread Pb pollution, most soils are likely to be artificially enriched in this metal, especially in the top horizon. There is much data available in the literature on soil Pb, but sometimes it is difficult to separate the data for background Pb levels in soils from those of anthropogenically influenced amounts in surface soils. Typical soil concentrations are 2 - 300 mg/kg, but suggestions are that an upper limit for the Pb content of a normal soil could be around 70 mg/kg.

The natural Pb content of soils is strongly related to the composition of the bedrock, and Pb is the least mobile among the other heavy metals. Although the Pb species can vary considerably from one soil type to another, it may be concluded that Pb is associated mainly with clay minerals, Mn oxides, Fe and Al hydroxides, and organic matter. However, in some soil Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations.

The characteristic localisation of Pb near the soil surface in most soil profiles is primarily related to the surficial accumulation of organic matter. The greatest Pb concentrations are also often found in the organically rich top horizons of uncultivated soils. Therefore, organic matter should be considered as the important sink of Pb in polluted soils.

In aqueous systems, Pb is soluble as a chloride complex ($PbCl_2^0$) at pH < 7 and moderately oxidising redox conditions, although fields of stability of $PbCO_3.PbCl_2$ (phosgenite) and $PbCO_3$ (cerussite) extend down to pH 7. Under reducing conditions, Pb is insoluble as galena.

Webster (1974) measured concentrations of 0.32 and 0.42 $\mu g\ kg^{-1}$ Pb respectively for river water and a saline lake in Antarctica. Chloride complexation of lead is important in deep groundwater environments. Complexation of lead with chloride has been investigated in the temperature range 25-300 °C by Seward (1984). At 25 °C, 5 species occur: Pb^{2+}, $PbCl^{+}$, $PbCl_2^{0}$, $PbCl_3^{-}$, $PbCl_4^{2-}$. Free Pb^{2+} predominates at $Cl^{-} < 0.05$ M. Acetate complexation of lead has been investigated by Yang et al. (1989). Strong $Pb(Ac)^{+}$, $Pb(Ac)_2$ and possibly $Pb(Ac)_3^{-}$ complexes were observed.

The solubility of galena (PbS) has been measured in 1 - 5 M NaCl solutions by Barrett and Anderson (1988) at temperatures up to 95 °C. The solubility of galena increases with temperature and increasing NaCl concentration. Galena is considerably less soluble than sphalerite (ZnS) under these conditions. The kinetics of dissolution of lead-barium sulphate solid solutions has been investigated by Paige et al. (1993). The solubility of lead sulphate in brines has been modelled by Paige et al. (1992).

Erel et al. (1991) report Pb concentrations in streamwaters of the Sierra Nevada, U.S.A. They observed that lead is taken up by particles (mostly iron oxides). Erel and Morgan (1992) concluded that lead both co-precipitates and is adsorbed on Fe-rich particles during early phases of the rock weathering cycle.

Bruno et al. (1992) measured Pb concentrations in groundwaters in alkaline crystalline rocks at Poços de Caldas in Brazil of up to 10^{-9} mol/dm^{3}. Edmunds et al. (1989) measured positive values for Pb in U.K. groundwaters only in aquifers in the Millstone Grit and Carboniferous Limestone of Derbyshire and these were all below 1 µg/l. Reimann et al. (1996) measured a median concentration of 0.3 µg/l Pb in 145 samples of groundwater from fractured hard rock in Norway. Banks et al. (1995a) report lead concentrations in the range 0.5 - 2 µg/l also in groundwaters in fractured hard rocks of Norway. Ledin et al. (1989) determined lead concentrations in groundwaters in crystalline rocks in Sweden in the range 0.02 - 0.3 µg/l.

Pb contents of oilfield brines may be as high as 17 mg/l due to complexing with chloride ions (Kharaka et al., 1980; Carpenter et al., 1974). Relatively high concentrations of Pb have been observed in Salton Sea brines (up to 111 µg/g) which was attributed to chloride complexation (Zukin et al., 1987).

Sorption of lead on goethite and hematite shows 90 % of Pb is sorbed from chloride solutions by iron oxyhydroxides at pH > 6.5. Sorption of lead onto chabazite, vermiculite, montmorillonite, hectorite and kaolinite was investigated by Liang and Sherriff (1993). These minerals contained 27, 16, 9, 9 and 0.4 wt % Pb respectively after equilibration with 0.01 M $Pb(NO_3)_2$ solutions. Ion exchange reached equilibrium after 24 hours for chabazite and vermiculite, but less than 5 minutes for montmorillonite and hectorite. Calcite impurities in the clay minerals effectively removed Pb from solution by the precipitation of cerussite, $PbCO_3$.

Table 2.15: Lead concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	14.8	mg/kg	Wedepohl (1995)
Crustal average	14	mg/kg	Bowen (1979)
Upper crust	17	mg/kg	Wedepohl (1995)
Lower crust	12.5	mg/kg	Wedepohl (1995)
Granite	2-150	mg/kg	Wedepohl (1978)

Natural material	Elemental concentration	Concentration units	Reference
Granite	24	mg/kg	Bowen (1979)
Basalt	1-38	mg/kg	Wedepohl (1978)
Basalt	3	mg/kg	Bowen (1979)
Basalt, gabbro	3-8	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	15-24	mg/kg	Pendias & Pendias (1984)
Schist, gneiss	5-65	mg/kg	Wedepohl (1978)
Rhyolite, trachyte, dacite	10-20	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	12-15	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0.1-1.0	mg/kg	Pendias & Pendias (1984)
Tonalite	14.2	mg/kg	Wedepohl (1978)
Greywacke	14.2	mg/kg	Wedepohl (1978)
Shale	10-60	mg/kg	Wedepohl (1978)
Shale	[20] 16-50	mg/kg	Adriano (1986)
Shale	23	mg/kg	Bowen (1979)
Shale	18-25	mg/kg	Pendias & Pendias (1984)
Igneous rocks	[15] 2-3	mg/kg	Adriano (1986)
Argillaceous rocks	20-40	mg/kg	Pendias & Pendias (1984)
Limestone	3-40	mg/kg	Wedepohl (1978)
Limestone	5.7	mg/kg	Bowen (1979)
Limestone, dolomite	3-10	mg/kg	Pendias & Pendias (1984)
Limestone	9	mg/kg	Adriano (1986)
Sandstone	1-50	mg/kg	Wedepohl (1978)
Sandstone	[7] 1-31	mg/kg	Adriano (1986)
Sandstone	10	mg/kg	Bowen (1979)
Sandstone	5-10	mg/kg	Pendias & Pendias (1984)
Average sediment	19	mg/kg	Bowen (1979)
Soil	[35] 2-300	mg/kg	Bowen (1979)
Soil (historic)	12	mg/kg	Bowen (1979)
Soil	[20] 2-200	mg/kg	Adriano (1986)
Sandy soils	[17] 10-70	mg/kg	Pendias & Pendias (1984)
Clay soils	[22] 10-70	mg/kg	Pendias & Pendias (1984)
Soil over crystalline rock	[21] 10-50	mg/kg	Pendias & Pendias (1984)
Soil over volcanic rock	[20] 10-70	mg/kg	Pendias & Pendias (1984)
Desert soils	[23] 10-70	mg/kg	Pendias & Pendias (1984)
Marine clay	80	mg/kg	Chester & Aston (1976)
Marine carbonate	17	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	0.1	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	100	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	1.0	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	150	mg/kg	Martin & Meybeck (1979)
Freshwater	3	µg/l	Adriano (1986)
Freshwater	[3] 0.06-120	µg/l	Bowen (1979)
Freshwater (historic)	0.5	µg/l	Bowen (1979)
Groundwater (crystalline)	0.25-5	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	0.3	µg/l	Reimann et al. (1996)
Groundwater (crystalline)	0.5-2	µg/l	Banks et al. (1995a)

Natural material	Elemental concentration	Concentration units	Reference
Groundwater (crystalline)	0.02-0.3	µg/l	Ledin et al. (1989)
Groundwater (sedimentary)	1	µg/l	Edmunds et al. (1989)
Groundwater (clay)	5	µg/l	Pearson & Scholtis (1993)
Seawater	0.003	µg/l	Li (1991)
Seawater	0.03	µg/l	Wedepohl (1978)
Seawater	0.03	µg/l	Adriano (1986)
Seawater	[0.03] 0.03-13	µg/l	Bowen (1979)

2.2.15 Thorium (Th)

Thorium has an atomic number of 90. It is a metal and a member of the actinide elements in the periodic table. Thorium is of interest here because several isotopes of thorium occur in radioactive waste and because it is a significant contributor to the total natural background radiation of terrestrial origin. It is an important naturally-occurring long-lived alpha emitter.

Among the actinide series, only Th and U occur in measurable abundances in crustal materials. Silica rich igneous rocks usually contain more Th than do mafic rocks, and in sediments Th is likely to be more concentrated in argillaceous deposits than in sandstones and limestones.

Similarities in ionic size and bond character link thorium, cerium, uranium and zirconium. ^{232}Th is the dominant isotope of thorium (approximately 100 % of natural abundance) and has a half-life of 1.4×10^{10} years. The stable product of the decay chain is ^{208}Pb. Thorium is found in natural systems as the tetravalent cation only.

Thorium occurs as a primary component only in rare phases such as thorianite (ThO_2) and thorite ($ThSiO_4$). The former mineral is isomorphous with uraninite, the latter with zircon. Consequently, a large part of naturally-occurring Th is in zircon. The chief source of Th is in monazite $(Ce,La,Y,Th)PO_4$ which usually contains 3 - 9 % and occasionally up to 20 % ThO_2. There are many examples of isostructural compounds of Th, Ce, U and Zr. However, there are only a few thorium silicates known as compared with the large number of zirconium silicates. A large number of Th-sulphides, selenides and tellurides is known. Thorium is a major cation in only a few minerals, none of which is common. Feldspars, biotites and amphiboles may contain only 0.5 - 50 ppm Th.

Most Th host minerals are resistant to weathering so that Th is generally considered a poorly soluble and immobile element. Th is usually fractionated from U during weathering because of the soluble U^{6+} ion. Th is strongly adsorbed by clays and oxyhydroxides so that relatively high concentrations of Th occur in bentonites, marine pelagic clays, manganese nodules and bauxites.

However, Th can be mobilised in forms of various complex inorganic cations and in organic compounds. The importance of microorganisms in the geochemical cycle of U is important. Also, several organic acids may increase the solubility of Th in soils. Comparatively little information seems to be available with respect to Th in soils. The world-wide mean of the Th content of soils is 1 - 35 mg/kg (Bowen, 1979).

The mobility of Th in natural waters has been reviewed by Langmuir and Herman (1980). Dissolved Th is almost always complexed in natural waters. The most common inorganic complexes are with OH^- and HPO_4^{2-}, although Th will also form strong complexes with H_2PO_4, SO_4^{2-}, F^-. Complexing with Cl^- and NO_3^- is insignificant. Organic ligands include oxalate, citrate and EDTA. Organic complexes must dominate inorganic complexes of Th in organic-rich waters. Th in fresh surface waters ranges from 0.01 to 1 ppb. Langmuir and Herman (1980) conclude that Th concentrations in natural waters are more likely to be limited by mineral dissolution kinetics and sorption than by true mineral-fluid equilibria.

Morland et al. (1997) measured thorium concentrations to be < 1 µg/l with a maximum concentration of 20 µg/l in fractured hard rocks of Norway. Banks et al. (1995b) report thorium concentrations in the range <0.01 - 2.2 µg/l also in groundwaters in fractured hard rocks of Norway.

Th in alkaline groundwaters in granites in southern Europe was found to be associated with particulate material and not contained in true solution (Alaux-Negrel et al., 1993). Bruno et al. (1992) measured Th concentrations up to 3×10^{-10} M and concluded that waters in alkaline rocks at Poços de Caldas, Brazil were in equilibrium with thorianite (ThO_2). Thorianite occurrence in the rocks was confirmed by mineralogical investigations. McKinley et al. (1988) measured a concentration of $<2\times10^{-10}$ M in hyperalkaline groundwaters in Oman. Th was significantly associated with colloids in groundwaters in contact with uranium ore bodies at Nabarlek and Koongarra in the Alligator Rivers region, Northern Territory, Australia (Short et al., 1988). Reimann et al. (1996) measured a median concentration of 0.013 µg/l Th in 145 samples of groundwater from fractured hard rock in Norway.

Copenhaver et al. (1993) investigated retardation of ^{232}Th decay chain radionuclides in aquifers in Long Island and Connecticut. They measured retardation coefficients of the order 10^4 - 10^5 for Th. Rock/brine concentration ratios of around $5x10^5$ were observed for ^{232}Th in high temperature (300 °C) brines of the Salton Sea geothermal field, indicating immobility of Th (Zukin et al., 1987).

Table 2.16: Thorium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	8.5	mg/kg	Wedepohl (1995)
Crustal average	12	mg/kg	Bowen (1979)
Crustal average	3.5	mg/kg	Taylor & McLennan (1995)
Upper crust	10.3	mg/kg	Wedepohl (1995)
Upper crust	10.7	mg/kg	Taylor & McLennan (1995)
Lower crust	6.6	mg/kg	Wedepohl (1995)
Granite	23	mg/kg	Bowen (1979)
Granite	8-56	mg/kg	Wedepohl (1978)
Basalt	1.6	mg/kg	Bowen (1979)
Basalt	0.2-5.4	mg/kg	Wedepohl (1978)
Basalt, gabbro	1-4	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	10-23	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	15	mg/kg	Pendias & Pendias (1984)

Natural material	Elemental concentration	Concentration units	Reference
Diorite, syenite	7-14	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0.005	mg/kg	Pendias & Pendias (1984)
Tonalite	6.4	mg/kg	Wedepohl (1978)
Greywacke	9	mg/kg	Wedepohl (1978)
Shale	12	mg/kg	Wedepohl (1978)
Shale	12	mg/kg	Bowen (1979)
Shale	12	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	9.6-12	mg/kg	Pendias & Pendias (1984)
Limestone	1.7	mg/kg	Wedepohl (1978)
Limestone	1.7	mg/kg	Bowen (1979)
Limestone, dolomite	1.7-2.9	mg/kg	Pendias & Pendias (1984)
Sandstone	1-9	mg/kg	Wedepohl (1978)
Sandstone	3.8	mg/kg	Bowen (1979)
Sandstone	1.7-3.8	mg/kg	Pendias & Pendias (1984)
Average sediment	9.6	mg/kg	Bowen (1979)
Soil	[9] 1-35	mg/kg	Bowen (1979)
Marine clay	5	mg/kg	Chester & Aston (1976)
Riverwater (dissolved)	0.1	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	14	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	0.1	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	14	mg/kg	Martin & Meybeck (1979)
Freshwater	[0.03] 0.007-0.1	µg/l	Bowen (1979)
Groundwater (crystalline)	<1	µg/l	Morland et al. (1997)
Groundwater (crystalline)	0.3-0.5	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	0.01-2.2	µg/l	Banks et al. (1995b)
Groundwater (crystalline)	0.01	µg/l	Reimann et al. (1996)
Seawater	0.00005	µg/l	Li (1991)
Seawater	0.0004	µg/l	Wedepohl (1978)
Seawater	[0.001] 0.0001-0.22	µg/l	Bowen (1979)

2.2.16 Uranium (U)

Uranium has an atomic number of 92. It is a metal and a member of the actinide elements in the periodic table. Uranium is of interest here because ^{235}U is the principal isotope in nuclear fuel and because uranium is a significant contributor to the total natural background radiation of terrestrial origin. It is an important naturally-occurring long-lived alpha emitter.

Uranium is a lithophilic element whose geochemistry is intimately linked with that of thorium. Uranium is concentrated in granite rather than in silica poor rocks. U^{4+} has an ionic radius of 0.97 Å in octahedral coordination, whereas that for U^{6+} is 0.80 Å.

Naturally-occurring uranium consists of three isotopes: ^{238}U, ^{235}U and ^{234}U. ^{238}U and ^{235}U are parent isotopes for 2 separate radioactive decay series. No natural fractionation of ^{238}U and ^{235}U has been observed and all materials have a ^{238}U/^{235}U ratio of 137.5. Half-lives are: ^{235}U = 7.1×10^{8} years; ^{238}U = 4.5×10^{9} years; ^{234}U = 2.5×10^{5} years.

Uranium occurs in a variety of minerals, but is concentrated in only a few. The most abundant uranium mineral is uraninite with a formula from UO_2 to U_3O_8. Well-crystallised UO_2 is described as uraninite and the microcrystalline form, pitchblende. Typical uranium contents of rock-forming minerals are as follows: feldspar - 0.1-10 ppm; biotite - 1-60 ppm; muscovite - 2-8 ppm; hornblende - 0.2-60 ppm; pyroxene - 0.1-50 ppm; olivine ~ 0.05 ppm; allanite - 30-1000 ppm; apatite - 10-100. In Wedepohl (1978) the following uranium minerals are listed: 15 oxides; 12 carbonates; 6 sulphates; 30 phosphate-arsenates; 10 vanadates; 15 silicates; 4 niobates and 5 molybdates.

Under oxidising conditions, pitchblende and uraninite are converted to brightly-coloured minerals such as carnotite, $K_2(UO_2)_2(VO_4)_2.3H_2O$, tyuyamunite, $Ca(UO_2)_2(VO_4)_2.nH_2O$, autunite, $Ca(UO_2)_2(PO_4)_2.nH_2O$, and rutherfordine, $UO_2.CO_3$. These minerals are soluble so that uranium may be transported by oxidising groundwater to be re-deposited under more reducing conditions.

Although valence states between 2+ and 6+ exist in nature, only the 4+ and 6+ valence states are of importance geologically. Uranous hydroxide, $U(OH)_4$ is extremely insoluble, but uranyl hydroxide, $UO_2(OH)_2$ is considerably more soluble. Sandino and Bruno (1992) have reviewed the solubility of $(UO_2)_3(PO_4)_2.4H_2O$ and the formation of U^{6+} phosphate complexes. They concluded that U will be associated with phosphate complexes in natural waters in the pH range 6-9 and if the $[PO_4^{3-}]$ / $[CO_3^{2-}]$ ratio is greater than 0.1.

Edmunds et al. (1989) noted that most analyses of uranium in groundwaters in aquifers in the U.K. were below 0.1 µg/l, although several anomalous values two orders of magnitude greater were observed. Morland et al. (1997) measured a median uranium concentration of 100 µg/l and a maximum concentration of 2 mg/l in fractured hard rocks of Norway.

Banks et al. (1995b) report uranium concentrations in the range 0.59 - 170 µg/l also in groundwaters in fractured hard rocks of Norway. Asikainen and Kahlos (1979) measured anomalously high concentrations of uranium in the range 10 - 14870 µg/l in fractured hard rocks in the Helsinki region of Finland. These high concentrations were attributed to uranium mineral veins in the bedrock.

Uranium concentrations in alkaline thermal waters in granites in southern Europe were limited by uraninite solubility (Alaux-Negrel et al., 1993). Bruno et al. (1992) measured U concentrations up to 2×10^{-8} M and concluded that waters in alkaline rocks at Poços de Caldas, Brazil were in equilibrium with pitchblende (U_3O_8). Pitchblende occurrence in the rocks was confirmed by mineralogical investigations.

McKinley et al. (1988) measured uranium concentrations in reducing hyperalkaline groundwaters in Oman as around 4×10^{-11} M. In CO_2-rich waters from Vals-les-Bains, France, uranium concentrations are in the range 1 - 3.5 nmol/l (Michard et al., 1987). Carbonate complexing of U was expected to dominate behaviour in these waters. Edmunds et al. (1987) measured uranium concentrations in deep groundwaters of the Carnmenellis granite in the range 0.00002-0.044 mg/l.

Uranium concentrations in groundwaters at Stripa are in the range 10 - 90 ppb (Andrews et al., 1989). Reimann et al. (1996) measured a median concentration of 3.514 µg/l U in 145 samples of groundwater from fractured hard rock in Norway.

Kraemer and Kharaka (1986) measured uranium concentrations in saline waters in geopressured aquifers (T = 109-166 °C) in the U.S. Gulf Coast in the range 0.003 - 0.054 µg/l which are consistent with equilibrium with uraninite and coffinite. Uranium concentrations in groundwaters associated with a uranium deposit at Crawford, Nebraska have been reported by Spalding et al. (1984). Concentrations were in the range 0.005 - 0.08 µg/g with uranium concentrations increasing with total dissolved solids content. In geothermal brines at the Salton Sea, Zukin et al. (1987) attributed high rock/brine ratios for ^{238}U (5×10^4) to uranium remaining in the U^{4+} oxidation state due to the reducing conditions of the brine.

Table 2.17: Uranium concentrations in natural materials. Data given in [ ] are the averages from a range, if given in the quoted reference.

Natural material	Elemental concentration	Concentration units	Reference
Crustal average	1.7	mg/kg	Wedepohl (1995)
Crustal average	2.4	mg/kg	Bowen (1979)
Crustal average	0.9	mg/kg	Taylor & McLennan (1995)
Upper crust	2.5	mg/kg	Wedepohl (1995)
Upper crust	2.8	mg/kg	Taylor & McLennan (1995)
Lower crust	0.93	mg/kg	Wedepohl (1995)
Granite	4.4	mg/kg	Bowen (1979)
Granite	2.2-7.6	mg/kg	Wedepohl (1978)
Basalt	0.43	mg/kg	Bowen (1979)
Basalt	0.1-1.0	mg/kg	Wedepohl (1978)
Basalt, gabbro	0.3-1.0	mg/kg	Pendias & Pendias (1984)
Granite, gneiss	2.5-6.0	mg/kg	Pendias & Pendias (1984)
Rhyolite, trachyte, dacite	5	mg/kg	Pendias & Pendias (1984)
Diorite, syenite	1.4-3.0	mg/kg	Pendias & Pendias (1984)
Peridotite, dunite	0.003-0.01	mg/kg	Pendias & Pendias (1984)
Tonalite	1.7	mg/kg	Wedepohl (1978)
Greywacke	2.0	mg/kg	Wedepohl (1978)
Shale	3.2-8	mg/kg	Wedepohl (1978)
Shale	3.7	mg/kg	Bowen (1979)
Shale	3.0-4.1	mg/kg	Pendias & Pendias (1984)
Argillaceous rocks	3-4	mg/kg	Pendias & Pendias (1984)
Limestone	2.2	mg/kg	Wedepohl (1978)
Limestone	2.2	mg/kg	Bowen (1979)
Limestone, dolomite	2.2-2.5	mg/kg	Pendias & Pendias (1984)
Sandstone	0.45-3.0	mg/kg	Wedepohl (1978)
Sandstone	0.45	mg/kg	Bowen (1979)
Sandstone	0.45-2.5	mg/kg	Pendias & Pendias (1984)
Average sediment	3.1	mg/kg	Bowen (1979)
Soil	[2] 0.7-9	mg/kg	Bowen (1979)
Marine clay	1	mg/kg	Chester & Aston (1976)
Marine clay	0.5-4.0	mg/kg	Wedepohl (1978)

Natural material	Elemental concentration	Concentration units	Reference
Riverwater (dissolved)	0.24	µg/l	Martin & Whitfield (1983)
Riverwater (suspended)	3	mg/kg	Martin & Whitfield (1983)
Riverwater (dissolved)	0.04	µg/l	Martin & Meybeck (1979)
Riverwater (suspended)	3	mg/kg	Martin & Meybeck (1979)
Freshwater	[0.4] 0.002-5	µg/l	Bowen (1979)
Groundwater	0.1	µg/l	Edmunds et al. (1989)
Groundwater (crystalline)	100	µg/l	Morland et al. (1997)
Groundwater (crystalline)	0.1-0.3	µg/l	Pearson & Scholtis (1993)
Groundwater (crystalline)	10-14870	µg/l	Asikainen & Kahlos (1979)
Groundwater (crystalline)	10-90	µg/l	Andrews et al. (1989)
Groundwater (crystalline)	0.6-170	µg/l	Banks et al. (1995b)
Seawater	3.2	µg/l	Li (1991)
Seawater	3.3	µg/l	Wedepohl (1978)
Seawater	[3.2] 0.04-6	µg/l	Bowen (1979)

2.3 Average compositions of natural materials

In this section, the data from the previous discussions of elemental abundances is reordered to give average elemental abundances occurring in some natural materials of relevance to this study, such as rocks, sediments and waters. Separate tables are given for solid materials (Table 2.18) and waters (Table 2.19). These compilations are used in the following sections of this report as input to the calculations of the natural fluxes.

It will be clear from Tables 2.2 to 2.17 that, for many of the elements of interest, there is no consensus in the literature on their average concentrations in these materials, as indicated by conflicting concentrations reported in the different references quoted. This partly reflects the fact that some of these elements are present in concentrations at or only slightly above the detection limits for the commonly used analytical techniques. It is also partly a reflection that some of these elements are not routinely analysed in studies of rocks or waters because they are not useful in 'academic' geochemical investigations. Consequently, due to a combination of very low abundances and infrequent measurements, there is a significant level of uncertainty over the actual concentrations. Nonetheless, for many of these elements, it is known that they always occur in very low concentrations.

Table 2.18: Average elemental concentrations in solid materials.

Element	Upper crust (mg/kg)	Granite (mg/kg)	Gabbro (mg/kg)	Gneiss (mg/kg)
C	3240	350	215	260
Cl	640	200	390	450
K	28650	33400	6000	10000
Ni	19	10	250	10
Cu	19	45	195	100
Zn	62	75	100	95
Se	0.07	0.05	0.05	0.05
Rb	111	150	32	75

Element	Upper crust (mg/kg)	Granite (mg/kg)	Gabbro (mg/kg)	Gneiss (mg/kg)
Cd	0.1	0.2	0.2	0.1
Sn	4	3.5	1.2	2.2
I	1.4	10	10	10
Nd	26	44	32	35
Sm	4.6	9.5	7.3	8.5
Pb	17	87	5.5	19
Th	10.5	27	2.8	16
U	2.7	4.9	0.8	3.2

Element	Shale (mg/kg)	Limestone (mg/kg)	Sandstone (mg/kg)	Soil (mg/kg)
C	30000	23000	16000	30000
Cl	400	70	500	100
K	20000	3100	15000	14000
Ni	65	12	15	50
Cu	45	10	30	30
Zn	105	25	30	90
Se	0.5	0.03	0.02	0.5
Rb	140	55	46	150
Cd	0.2	0.03	0.05	0.35
Sn	6	0.5	0.5	2
I	12	22	1	5
Nd	29	5.5	29	35
Sm	7.5	1.3	7.5	4.5
Pb	23	6	7	20
Th	12	1.7	3.2	9
U	3.5	2.2	0.6	2

When compiling these average elemental abundance tables, this uncertainty was considered and the most appropriate concentration have been chosen. In some cases, this is taken to be the average of the values given in Tables 2.2 to 2.17 but, in some cases, judgement has been used to choose an appropriate concentration when, for example, reported values are considered to be inaccurate due to early, inaccurate experimental techniques or, alternatively if they are possibly due to anthropogenic contamination of the sample.

Table 2.19: Average elemental concentrations in waters. Note: * *when no specific data for the composition of river suspended material was available for a particular element, the corresponding data for 'upper crust' composition has been adopted as proxy data.* § *Cl content in seawater is in units of g/l.*

Element	Crystalline groundwater (µg/l)	Sedimentary groundwater (µg/l)	Rive dissolved (µg/l)	River suspended (mg/kg)	Sea (µg/l)
C	60000	125000	11000	3240*	28000
Cl	110000	400000	7000	640*	19§
K	6000	40000	1500	20000	390000

Element	Crystalline groundwater (µg/l)	Sedimentary groundwater (µg/l)	Rive dissolved (µg/l)	River suspended (mg/kg)	Sea (µg/l)
Ni	0.9	10	0.5	90	0.5
Cu	5	5	1.5	100	0.2
Zn	19	50	30	250	0.3
Se	0.3	0.5	0.06	0.8	0.1
Rb	50	50	1.5	100	120
Cd	0.05	0.2	0.02	1	0.08
Sn	0.03	0.5	0.009	4*	0.006
I	8	30	5	1.4*	64
Nd	0.16	0.16	0.04	35	0.004
Sm	0.028	0.028	0.008	7	0.008
Pb	0.3	3	0.1	100	0.003
Th	0.3	0.3	0.1	14	0.00005
U	1	1	0.24	3	3.2

As was mentioned at the beginning of this chapter, natural materials do exhibit a range of compositions and this is another reason why it is difficult to define ‘average’ elemental abundances in some cases. This is further compounded when the composition of materials can display both spatial and temporal variations, which is particularly true for waters. A full account of the variability of material compositions is beyond the scope of this work. However, a few cases are described to outline the issue.

Temporal variability in the elemental abundances in river waters has been observed over a range of time periods, from diel variations up to decadal variations. In a study of trace metal concentrations in the Clark Fork River in Montana, Brick and Moore (1996) recorded diel cycles in dissolved Mn, Zn and particulate Fe, Mn, Cu and Zn. The change in concentration was typically by a factor of two to three and was associated with changes in pH and dissolved oxygen, related to the differential rates of evapotranspiration during the day and night. The elemental loads typically increased at night, with the implication that day-time measurements of elemental abundances may underestimate fluxes of metals in rivers.

Seasonal variations in river elemental loads were recorded by Shiller (1997) in the Mississippi river. Dissolved Mn and Fe concentrations increased in the autumn months and fell in the spring, in contrast to V, Mo and U which followed an opposite trend. The reasons for this seasonal changes were not completely defined but it was thought that changes in redox processes were important. Again, measurements made in any single month might over or underestimate the fluxes of metals in rivers.

Groundwater compositions also exhibit seasonal changes in composition, particularly in regions where there is a significant change in rainfall throughout the year which may cause the water table to fluctuate and residence times to change. The composition of groundwaters also exhibit spatial variations and these are the subject of much research to try to find methods for predicting the full range of variability from only a few sample locations (e.g. Ramaswami and Small, 1994).

Clearly, the definition of a meaningful ‘average’ water composition thus depends, not only on appropriate spatial sampling but also on appropriate temporal sampling. Given all this, the average compositions provided in this report have to be interpreted with some caution. It is not intended that these compositions should be taken as definitive and representative of all rock, soil and water types, across all areas. They are given here for use in the calculation of ‘typical’ fluxes that might occur in a range of geological and climatological environments. When applying the natural safety indicators methodology to a specific site, it is recommended that the necessary site-specific geochemical data are obtained rather than relying only these averages.

3 Natural processes causing elemental fluxes

Fluxes of naturally occurring materials are brought about by the action of a number of processes in the surface and subsurface environments. Those of most interest for this study, because they relate to the use of the natural safety indicators methodology in radioactive waste disposal, are:

- rock-water interactions,
- groundwater flow,
- weathering and erosion, and
- sediment transport (e.g. by water, wind and ice).

The significance of these processes relates to their relevance to the four guidelines given in Section 1.1.2 for identifying important natural fluxes for comparison with predicted repository releases.

The calculation of natural elemental and radionuclide fluxes due to these processes requires two basic pieces of information, namely the concentration of the element(s) of interest in the relevant material and the rate of the natural process causing mass movement of that material. So, for example, the elemental mass flux of uranium in groundwater is calculated from the concentration of uranium in the groundwater and the rate at which groundwater is flowing.

The elemental abundances in materials of interest (rocks, sediments, waters etc.) were compiled in the previous section. Here we are concerned with the rates of natural processes that drive the fluxes.

3.1 Rock-water interaction

It is very difficult to estimate the rates of rock-water interactions which occur in the subsurface environment. In essence, two types of reactions occur:

- dissolution reactions that provide an elemental flux from the rock to the water, and
- mineralisation and sorption reactions which provide a flux from the water to the rock.

Considering dissolution, numerous laboratory experiments have been performed to measure dissolution rates in closed ‘test-tube’ environments (for review see White and Brantley, 1996) but these investigations generally have focussed on the major rock forming minerals, such as the feldspars and quartz, rather than the accessory minerals which often contain the majority of the trace elements found in a rock.

The major rock forming minerals tend to dissolve at very different rates, even under conditions applicable to deep rock-water systems, as shown by Drever and Clow (1996) who provided comparative dissolution rates for a number of minerals (Table 3.1), relative to albite plagioclase, obtained from laboratory experiments.

Table 3.1: Mineral dissolution rates, relative to albite, obtained from laboratory experiments. From Drever and Clow (1996).

Mineral	Relative dissolution rate
Quartz	0.02
Muscovite	0.22
Biotite	0.6
Microcline	0.6
Sandine	2
Albite	1
Oligoclase	1
Andesine	7
Bytownite	15
Enstatite	57
Diopside	85
Forsterite	250
Dolomite	360000
Calcite	6000000

Unfortunately, several of the elements considered in this report are contained mostly in accessory minerals, rather than in the major rock forming minerals. Furthermore, many of these accessory minerals prove to be more resistant to dissolution than the major rock forming minerals, e.g. zircon which can contain U and Th. In a study by Miller et al. (1997), the minerals in which certain trace elements commonly occur were identified, as was their relative resistance to chemical weathering (dissolution). This information is given in Table 3.2. Given this, it is not necessarily sensible to use the laboratory determined dissolution rates for the major minerals in assessments of the fluxes of trace elements. In addition, dissolution rates are dependent on fluid chemistry and, consequently, care has to be taken to ensure laboratory data were obtained under appropriate conditions before applying them to the natural system.

Table 3.2: Host minerals for a number of trace elements and the relative resistance of these minerals to dissolution. From Miller et al. (1997).

Element	Common host minerals	Resistance to dissolution
U	zircon, apatite	high
Th	zircon, apatite	high
Ra	zircon, apatite	high
Se	sulphides	medium
Sn	mafic minerals	medium
K	feldspars	low
Rb	feldspars	low
Cs	feldspars, mafic minerals	low, medium
Cd	sulphides	medium
Cu	sulphides, mafic minerals	medium
As	sulphides	medium
Zn	sulphides	medium
Pb	sulphides	medium

In the absence of relevant, specific information for all minerals in a given rock type and their elemental concentrations, other appropriate methods for determining rock-water interaction rates at depth are required. An alternative, useful approach involves performing mass balance studies (sometimes known as input-output budgets) on small watersheds. In these studies, the difference between the masses of element leaving the watershed (e.g. via streams) and entering the watershed (e.g. as aerosols) must be due to the sum of all water-rock interactions in the system. A number of such studies have been performed (for reviews see Velbel, 1985; White and Brantley, 1996) but again, unfortunately, these generally focus on the fluxes of major elements, such as Si, Na and Ca.

One interesting feature of these mass balance studies is that they usually show a net mass loss which is assumed to relate to dissolution in the system. However, watershed estimates for dissolution rates are typically one or more orders of magnitude less than those derived from the laboratory experiments. Velbel (1986) discusses these discrepancies and suggests several possible explanations, one of which relates to the difficulty in estimating the rock (mineral) surface area involved in sub-surface rock-water interactions. These discrepancies may also relate to kinetic effects in the laboratory studies. The major problem with these watershed studies is that is impossible to know from the calculated mass balance, the relative effects of all of the different dissolution, mineralisation and sorption reactions which have occurred in the system. Nonetheless, if performed accurately, they can provide total, site-specific elemental fluxes under present-day environmental conditions, if not the dissolution rate per unit area for each mineral type.

To perform an accurate watershed calculation for any particular system on a site-specific basis would require many more precise data than are available in this study. In essence, to obtain a transfer rate in units of mass/area/time, it would be necessary to quantify the following:

- the mass of element discharged in the groundwater obtained from the volume of groundwater discharged and the elemental concentration in the groundwater,
- the water chemistry,
- the contact area which defines the reaction surface, and
- the age of the groundwater which defines the time for reaction.

However, the calculation would be complicated by two issues. The first is that not all the mineral surfaces would transfer elements to the groundwater at the same rate; in fact, many minerals do not contain the trace elements of interest and, consequently, would not provide a transfer flux at all. In addition, those minerals which do contain the trace elements would provide a flux dependent on their resistance to dissolution. The second complication is that the age of the groundwater does not give the actual duration of reaction if the groundwaters are saturated with respect to the trace elements, since no *net* dissolution will occur after saturation is reached (i.e. the duration of net dissolution reactions could be substantially less than the age of the groundwater).

In addition, as mentioned above, such an approach does not provide quantitative information on the individual retardation processes such as precipitation, sorption and biogeochemical utilisation which can remove dissolved species from the groundwater, further complicating the interpretation of the watershed data.

A better method to quantify rock-water interaction rates would be to sample groundwaters and associated solid phases from several locations along well-defined groundwater flow paths. Analysis of the variations in groundwater compositions along the flow path could then be related more directly to the rock-water processes and their rates. Such analyses have been done for small-scale systems (e.g. single fractures in a rock) but are rarely performed on the larger scales of complete natural systems and, again, do not generally focus on the trace elements of interest in this work.

To gain a simplistic indication of the rock dissolution rate at depth, it is possible to examine how much element is held in the groundwaters in a unit volume of rock. Considering a granodiorite rock and uranium as an example, with the following assumptions:

- the rock has a U concentration of 2.42 mg/kg,
- the porewater has a U concentration of 1.3×10^{-3} mg/l,
- the rock density is 2800 kg/m^3 and
- the porosity is 2 %.

Using these data, it can be calculated that the porewater holds approximately 0.0004 % of the uranium in the total rock-water system. If it is estimated that geochemical equilibrium would take 100 years to be reached in a deep system, this would imply that the bulk dissolution rate for uranium would be 2.6×10^{-7} g/m^3 of rock per year or, expressed as a percentage, dissolution removes 0.000004 % of uranium from the rock every year: that is 4×10^{-6} %/yr until chemical saturation is reached.

Such calculations clearly represent a gross simplification of the real situation; for example a number of large assumptions are made such as all the solid material is accessible to the water for dissolution, groundwater flow itself is ignored and the time taken to reach chemical saturation is actually known. Strictly, a different calculation would be required for each element because they tend to be dissolved from different minerals at different rates.

However, despite these uncertainties, this slow dissolution rate may still provide a very basic representation of old, deep crystalline groundwater systems and may act to illustrate how small the fluxes due to rock dissolution actually are. In a near-surface environment containing oxidising, acidic meteoric water, the dissolution rate is expected to be several orders of magnitude faster.

3.2 Groundwater flow

Groundwater flow characteristics of rocks and sediments are highly variable, depending on the physical and hydraulic characteristics of the materials themselves, as well as on the surface topography and climate. Groundwater flow in a rock mass can be divided into local, intermediate and regional flow systems, as shown in Figure 3.1. From this figure, it is evident that it is normal for regional flow systems to pass through deeper rock than the intermediate or local flow systems. The rate of groundwater flow at different scales and depths is dependent on the specific hydraulic characteristics of the rocks they pass through and, typically, the deep, regional flow systems will be slower than shallow flow systems.

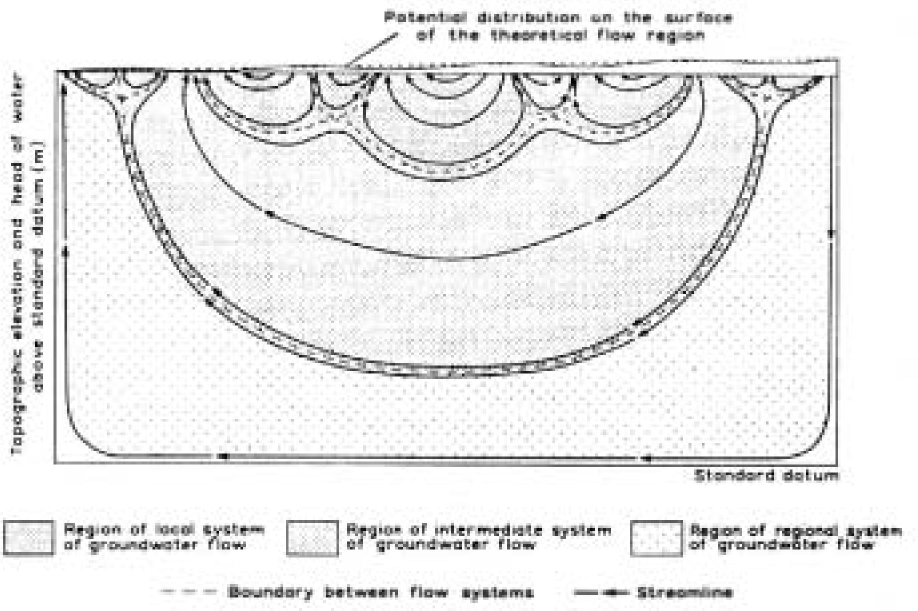

Figure 3.1; Theoretical flow patterns and boundaries between local, intermediate and regional flow systems, where the regional flow operates on the scale of tens of kilometres or larger. From Toth (1963).

Essentially, for every groundwater system, there is a maximum possible flow rate defined by the hydraulic characteristics of the rock (the hydraulic conductivity, porosity and hydraulic gradient). Actual groundwater flow rates can be less than the maximum if the hydraulic gradient (head) driving the system is lower than that physically achievable from the surface topography. This could occur in cases when the recharge rate is low due either to low rates of precipitation or high rates of evapotranspiration. In essence, this means that the climate can influence the groundwater flow rates and, thus, the elemental fluxes associated with dissolved components in the groundwater. This is indicated in Figure 3.2.

Rocks potentially suitable for the deep disposal of long-lived radioactive wastes will generally have low hydraulic conductivities (*k*) and low flow rates, and great effort is expended to characterise the hydraulic properties of such rocks. Typical values of the hydraulic properties for the rock types that might be considered for radioactive waste disposal are presented in Table 3.3. This table also includes calculated values for groundwater flux (the volume of water flowing through a unit section in a given time) and groundwater velocity, where:

- flux = hydraulic conductivity × gradient
- velocity = flux / porosity.

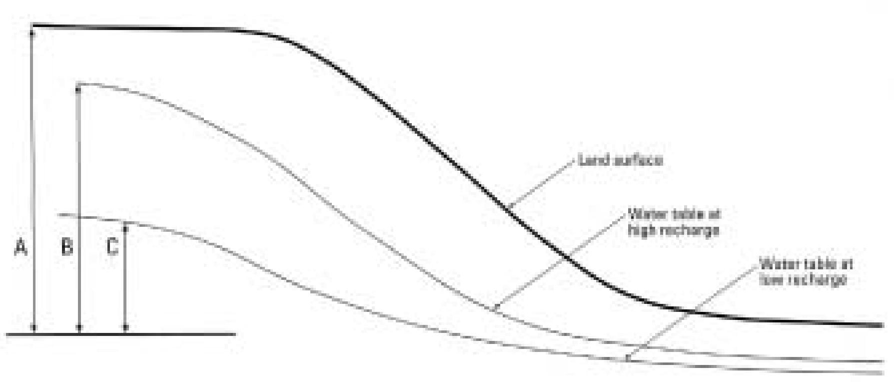

Figure 3.2: Diagrammatic representation of how climate change (by acting on recharge and the level of the water table) can alter groundwater flow rates by altering the hydraulic gradient (head) that drives groundwater flow. A = maximum potential head, B = head at high recharge rates, C = head at low recharge rates.

The values of hydraulic conductivity which are given in Table 3.3 represent the gross averages for a representative volume of rock. Values are given for rock above and below 100 m because the upper part of the rock mass is likely to have undergone some form of stress relief, thereby possessing an enhanced hydraulic conductivity and porosity compared to the deeper part.

Table 3.3: Typical ranges of hydraulic parameters for a variety of different rock types at different depths. From Savage (1995) based on previous compilations by Brace (1980), Tellam and Lloyd (1981) and Clauser (1992).

Rock type	Hydraulic conductivity (m/s)	Porosity	Gradient	Groundwater flux ($l/m^2/yr$)	Groundwater velocity (m/yr)
Plastic clay:					
Above 100 m (max)	1×10^{-7}	0.5	0.2	640	1.3
(min)	1×10^{-10}	0.3	0.05	1.6	5×10^{-4}
Below 100 m (max)	1×10^{-8}	0.5	0.2	64	0.13
(min)	1×10^{-12}	0.3	0.05	0.0016	5×10^{-6}
Shale/mudstone:					
Above 100 m (max)	1×10^{-6}	0.3	0.2	6400	21
(min)	1×10^{-9}	0.2	0.05	1.6	0.008
Below 100 m (max)	1×10^{-7}	0.25	0.2	640	2.6
(min)	1×10^{-10}	0.05	0.05	0.16	0.003
Crystalline:					
Above 100 m (max)	1×10^{-7}	0.05	0.1	320	6.4
(min)	1×10^{-9}	0.01	0.001	0.032	0.0032
Below 100 m (max)	1×10^{-8}	0.01	0.1	32	3.2
(min)	1×10^{-11}	0.001	0.001	3×10^{-4}	3×10^{-5}
Aquifer:					
(max)	1×10^{-4}	0.1	0.01	3×10^{-4}	320
(min)	1×10^{-7}	0.05	0.0005	1.6	0.03

In crystalline rocks, the rock matrix generally contains a very low porosity and, often, these pores are closed. As a consequence, in most crystalline rocks, the bulk hydraulic properties are dominated by the fracture network porosity which provides an important control on groundwater flow velocities in these rocks. As a consequence, hydraulic conductivities towards the upper values are most appropriate for use in the fluxes calculations.

In contrast to crystalline rocks, sedimentary rocks, and in particularly clays, can and often do have much slower groundwater flow velocities and greater tendencies for matrix diffusion and retardation mechanisms. Thus, in argillaceous formations (clays), hydraulic conductivities towards the lower values are most appropriate. Evaporites have generally similar low hydraulic conductivities to those of clays. In such circumstances fluxes may be so low that diffusion is the dominant transport process in some argillaceous rocks and evaporites, especially at depth.

The maximum and minimum groundwater travel times for the same rocks and environments presented in Table 3.3 have been calculated and are presented in Table 3.4. These pathlengths and travel times can be applied to rock masses at a depth of 500 m or more. They illustrate that there can be very large ranges of travel times for groundwaters in the rock types considered.

Table 3.4: Approximate maximum and minimum values of groundwater travel times on scales (depths) of 500 m or more, as derived from the data in Table 3.3. From Savage (1995) based on previous compilations by Brace (1980), Tellam and Lloyd (1981) and Clauser (1992).

Rock type	**Groundwater velocity (m/yr)**	**Path length (m)**	**Travel time (yrs)**
Plastic clay:			
Above 100 m (max)	1.3	50	40
(min)	0.0005	100	2×10^{5}
Below 100 m (max)	0.13	50	390
(min)	5×10^{-6}	100	2×10^{7}
Shale/mudstone:			
Above 100 m (max)	21	50	2
(min)	0.008	200	2×10^{4}
Below 100 m (max)	2.6	50	20
(min)	0.003	200	6×10^{4}
Crystallines:			
Above 100 m (max)	6.4	500	80
(min)	0.0032	2000	6×10^{5}
Below 100 m (max)	3.2	500	160
(min)	3×10^{-5}	2000	6×10^{6}
Aquifer:			
(max)	320	2×10^{3}	6
(min)	0.03	2×10^{4}	6×10^{5}

3.3 Weathering and erosion

Rock exposed at or near the surface will be broken up by the combined actions of physical and chemical processes to form a rock waste known as regolith. The regolith evolves into soils and sediments as it accumulates organic matter and undergoes further decomposition (a process known as ‘soil production’). The process of in situ decay and disintegration of bedrock is known as *weathering* and proceeds by two principal mechanisms:

- physical and mechanical disruption to the rock and its component minerals causing disintegration, e.g. by processes such as temperature changes, frost action and the action of organisms; and

- chemical reactions in which minerals in the bedrock are decomposed, dissolved and loosened by reaction with rainwater, porewater and the atmosphere, and by organisms and the products of their decay.

The physical, chemical and biological agents of weathering actively co-operate with each other. For example, frost action increases the opportunity for the penetration of water and consequent mineral decomposition. The mineral decomposition likewise causes a reduction in the strength of the rock making it more prone to physical and mechanical disruption, and cracks formed in the rock can be widened by the roots of growing vegetation.

In terms of natural fluxes, weathering represents an important process by which elements and radionuclides contained in the near surface rock are released. Thus weathering characterises a principal flux of elements to the surface environment, with the rock acting as a primary source of elements and radionuclides in the natural systems under investigation (within the time scales appropriate to radioactive waste disposal). Other fluxes from the rock to the surface are carried by groundwaters but the flux due to erosion can be much larger in some systems.

The materials ultimately produced by weathering are broken fragments of minerals and rocks; residual decomposition products, such as clay; and soluble decomposition products which are removed in solution. The solid weathering products may remain in their place of formation but, in dynamic surface environments, it is normal for them to be mobilised and transported by either water, wind or ice (known in this regard as ‘transporting agents’) or by simple mass movement, which is the downwards movement of solid material on a slope acting under gravity in the absence of a transporting agent.

Armed with rock fragments and aggressive chemical solvents, transporting agents can cause further physical and chemical destruction to exposed rock and regolith, as well as to surface soils and sediments. The combined action of all these destructive processes due to the effects of the transporting agents is described as *erosion*.

In real terms, erosion is the cumulative effect of a great variety of processes. In general these can be divided into two groups: two involving the transporting agent alone (chemical and physical, respectively); one combining the transporting agent with its load of transported material (detritus); and one concerning the detritus alone. These are various erosion processes are indicated in Table 3.5.

In terms of natural fluxes, erosion represents those processes by which elements and radionuclides already released from the bedrock are transported. Thus erosion characterises a range of fluxes within the surface environment and is, thus, intimately linked to surface transport processes, such as river flow which are considered in Section 3.4.

It is convenient to regard weathering as rock decay and disintegration by agents involving little or no transport of the resulting products, and erosion as land destruction by agents which simultaneously remove the debris. However, the connection between weathering and erosion is obviously a close one and, in many cases, it is not sensible to try to separate them because both sets of processes co-operate in wearing away the land surface. It is common, therefore, to refer jointly to their combined effects by the term *denudation*.

Table 3.5: Transporting agents and processes of erosion.

Type of erosion	Active agents	Chemical action on detritus and materials passed over	Physical loosening and removal of materials passed over	Wearing of surfaces by transported detritus	Mutual wear of transported detritus
Rain	Rainwater	Corrosion	Splash Rainwash Sheetwash	Localised corrasion	Attrition
River	Rivers	Corrosion	Hydraulic lifting, scouring and cavitation	Corrasion	Attrition
Glacial	Glaciers, ice-sheets	Corrosion limited to subglacial streams	Plucking and quarrying	Abrasion	Attrition
Wind (aeolian)	Wind	-	Deflation	Wind corrasion (sand blasting)	Attrition
Marine	Waves, tides and currents	Corrosion	Various hydraulic processes	Marine abrasion	Attrition

Definitions:
Abrasion: Wearing away of surfaces by mechanical processes such as rubbing, cutting and grinding.
Attrition: Reduction in size of detrital fragments by friction and impact during transport.
Cavitation: Collapse of bubbles of water vapour in streams causing shock waves that damage nearby rocks.
Corrasion: Mechanical erosion by running water or wind when charged with detritus.
Deflation: Lifting and removal of dust and sand by wind.

The thicknesses of solid weathered materials and the soils which evolve from them at any particular location represent a balance between the rate of bedrock weathering, the rate of removal of weathered material by erosional processes and the addition of organic materials from other sources to build the soil profile. Under stable conditions, a steady state can be achieved between the addition and removal of material, allowing a constant thickness of weathered material and soil to be maintained, as shown in Figure 3.3.

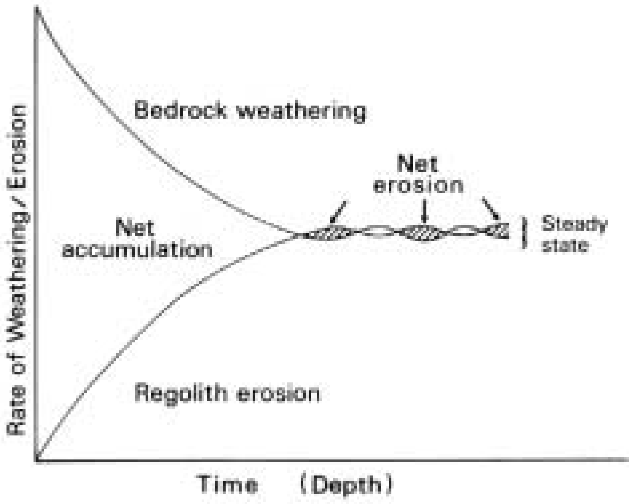

Figure 3.3. Schematic representation of the achievement of a steady state weathering profile dependent on the rates of weathering and erosion. After Crozier (1986).

The depth of the weathered material and soils which can accumulate and their compositions are dependent on the climatic controls which drive the weathering and erosional processes. In regions where transport is limited, the soils and sediments can accumulate and reach thicknesses in excess of 100 m. Such thick accumulations often occur in climates which favour chemical decomposition and minimal soil erosion. This is illustrated in Figure 3.4 which shows that the thickest sequences of weathered material arise in humid tropical climates where precipitation and temperature are high.

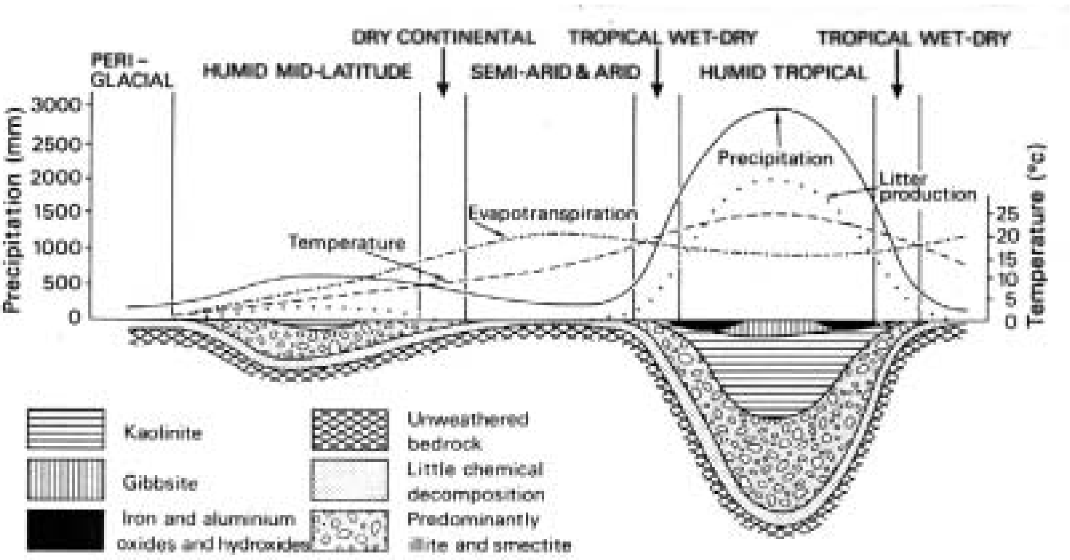

Figure 3.4: Variation in the depth of weathered material and composition in relation to climatic and biotic variables. From Strakhov (1967).

The rate of denudation of the continental land masses is highly variable around the world and, on the global scale, the dominant factors controlling denudation rates are topographic relief and climate. High relief leads to steep slopes, down which weathered detritus can move relatively quickly to expose more fresh rock to weathering processes. Consequently mountainous areas yield much greater volumes of sediment than adjacent lowlands. As the relief decreases, the amount of material being shed also decreases. Likewise, with climate, chemical weathering proceeds faster in warmer conditions (mineral dissolution rates are accelerated) and, thus, there is an increase in chemical weathering rates towards the tropical, mid-latitudes. This can be seen when the global distribution of weathering zones is mapped, as shown in Figure 3.5.

Not only does the total denudation rate vary with location, so do the various types of weathering and the different agents of erosion. In particular, as indicated above, the relative importance of physical and chemical weathering mechanisms is largely dependent on the climate and the topography. In general, mechanical disintegration is favoured by steep slopes and by the conditions characteristic of deserts and frost-affected regions, while chemical decomposition and solution are favoured by low-relief and by humid conditions, especially in tropical regions. This is shown in Figure 3.6.

The effect of climate on weathering rates is controlled through temperature and rainfall. The importance of temperature has been fairly well studied and Lasaga et al. (1994) proposed a general net rate law for chemical weathering reactions that expressed a dependence of weathering rate on, amongst other factors, temperature and mineral surface area. Thus, it is to be expected that weathering rates are higher in warm climates than in cold climates. The exact degree of temperature dependence will in turn depend on the activation energy.

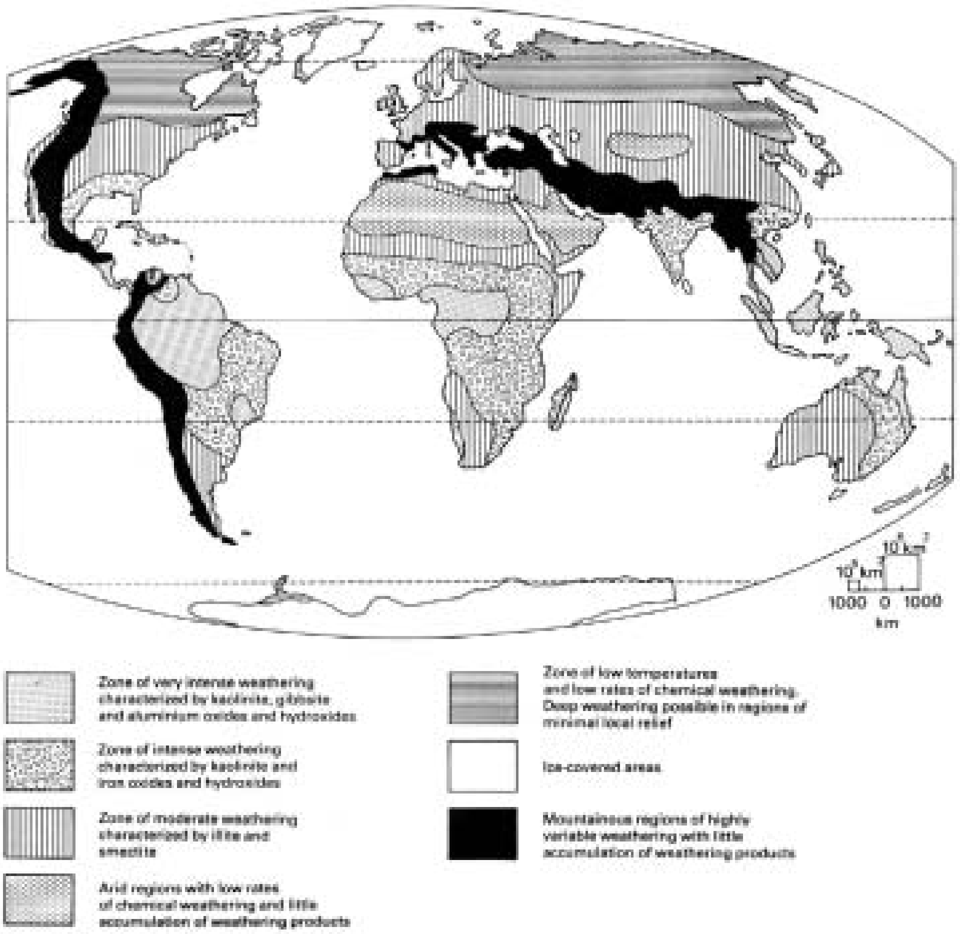

Figure 3.5 Global distribution of major weathering zones which are controlled by climatic conditions. From Strakhov (1967).

Various studies of the dependence of weathering rates on climate suggest the activation energy for chemical weathering is in the range of 40 to 80 kJ/mol (Lasaga et al., 1994; White and Blum, 1995). This is consistent with the average of activation energies of weathering reactions determined in laboratory studies. This activation energy means that in increase in temperature of 8°C would result in a doubling of the weathering rate if all other factors are constant.

Clearly, activation energies vary from mineral to mineral and this can be seen in the chemical weathering rates and mean lifetimes for minerals under specified conditions, as indicated in data from Lasaga et al. (1994) and given in Table 3.6.

Due to the fact that different minerals weather at different rates, it implies that weathering rates are dependent on rock type. By examining stream composition in relation to rock type, Meybeck (1987) derived relative chemical weathering rates for different rock types, as shown in Table 3.7. These relative weathering rates are in qualitative agreement with rates predicted from laboratory studies of reaction rates.

Table 3.6: Chemical weathering rates and mean lifetimes for mineral grains at 25°C and pH 5. From Lasaga et al. (1994).

Mineral	**Log dissolution rate (mol/m^2/s)**	**Mean lifetime (years)**
Quartz	-13.39	34 000 000
Kaolinite	-13.28	6 000 000
Muscovite	-13.07	2 600 000
Epidote	-12.61	923 000
Microcline	-12.50	579 000
Albite	-12.26	575 000
Sanidine	-12.00	291 000
Gibbsite	-11.45	276 000
Enstatite	-10.15	10 100
Diopside	-10.00	6 800
Forsterite	-9.50	2 300
Nepheline	-8.55	211
Anorthite	-8.55	112
Wollastonite	-8.00	79

Where rainfall is insufficient to continually wet all grain surfaces, the rate of chemical weathering will be lower. Thus in arid regions, chemical weathering is slow. In some cases, this also results in low overall erosion rates. In others, where high rates of erosion result from high relief, glaciation or some other factor, much of the material being removed will be fresh rock rather than weathering products.

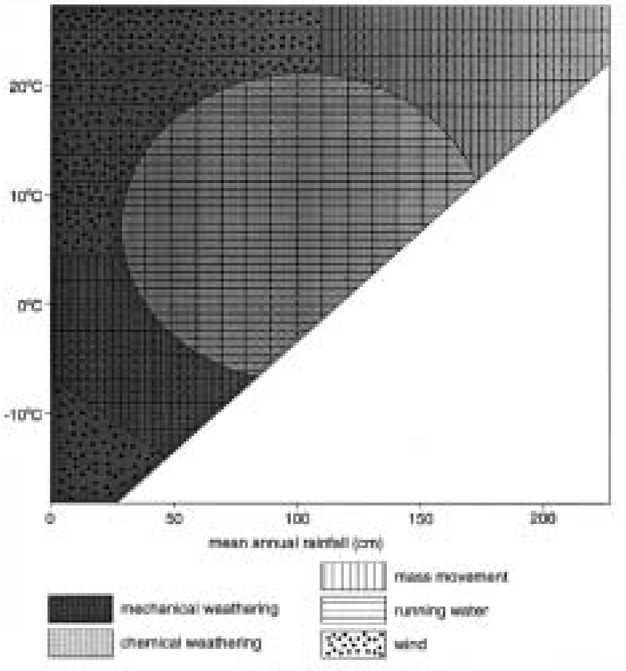

Figure 3.6: Climatic control on the relative importance of various types of weathering and various agents of erosion. After Smith (1981).

The data in Table 3.7 are for relative chemical weathering rates and cannot, necessarily, be used to define relative rates of total denudation because the rates of physical weathering are controlled by other parameters, such as topography and frost action, as discussed earlier. Lasaga et al. (1994) indicated that, in addition to temperature, the area of mineral surface in contact with water is important and this is, in turn, controlled by the rainfall and the rate of physical weathering.

Table 3.7: Relative chemical weathering rates for the major continental rock types. From Meybeck (1987).

Rock	Relative chemical weathering rate
Granite	1
Gneiss	1
Schist	1
Gabbro	1.3
Sandstone	1.3
Volcanic rocks	1.5
Shale	2.5
Serpentine, marble, amphibolite	5
Carbonate rocks	12
Gypsum	40
Evaporites	80

However, the relationship between precipitation and weathering is not simple. Bluth and Kump (1994) examined chemical weathering rates (on the basis of concentrations of bicarbonate and SiO_2 in streams) and found that the fluxes of SiO_2 and bicarbonate in streams from a given region remain constant over a large range of runoff, indicating that weathering rates increase with increasing precipitation. Nonetheless, bicarbonate and SiO_2 concentrations stay constant or even drop when runoff exceed 100 cm/yr indicating, that additional precipitation is acting to dilute weathering products rather than increase weathering rates.

Rates of chemical weathering can also be slow even in humid tropical areas if the rate of erosion is sufficiently slow to allow thick soils to develop. This results in a ‘transport limited’ regime, where thick lateritic soil (up to 100 m) insulate the underlying bedrock from chemical attack, as suggested earlier. Such transport limited regimes can occur even in areas of high elevation. The effect of climate and topographic relief were quantified by Meybeck (1976) who drew up a weathering classification based on river transport loads which were used to calculate weathering rates and the proportion due to chemical weathering for a number of climate and relief zones. This classification is summarised in Table 3.8.

This discussion serves to demonstrate that the quantification of global denudation rates is difficult because of the number of factors which influence denudation processes and because few site-specific measurements of denudation have been made to ‘calibrate’ predictive models. Most often, denudation rates are inferred from other studies, such as measurement of sediment transport in rivers, or from the thicknesses of accumulated sediment in river deltas. The best estimates of global denudation rates and their variability are shown in Figure 3.7 from Smith (1981) who showed that they vary from essential zero to over 3×10^6 kg/km^2/yr, with a global average of approximately 3×10^5 kg/km^2/yr.

Table 3.8: Weathering rate classification based on climate and relief. From Meybeck (1976).

Climate/relief zone	River solid load ($t/km^2/yr$)	River solute load ($t/km^2/yr$)	River total load ($t/km^2/yr$)	Equivalent denudation (mm/ka)	Typical solute load as % of total
Mountainous, high precipitation	200 - 1500	70 - 350	250 - 2000	95 - 740	10
Mountainous, low precipitation	100 - 1000	10 - 60	120 - 1000	45 - 370	10
Moderate relief, tropical climate	40 - 200	25 - 60	80 - 300	30 - 110	35
Low relief, dry climate	10 - 100	3 - 10	15 - 100	5 - 35	10
Low relief, temperate climate	20 - 50	12 - 50	40 - 80	15 - 30	65
Low relief, subarctic climate	1.5 - 15	5 - 35	5 - 40	5 - 15	80
Low relief, tropical climate	1 - 10	2 - 15	4 - 30	1.5 - 10	50

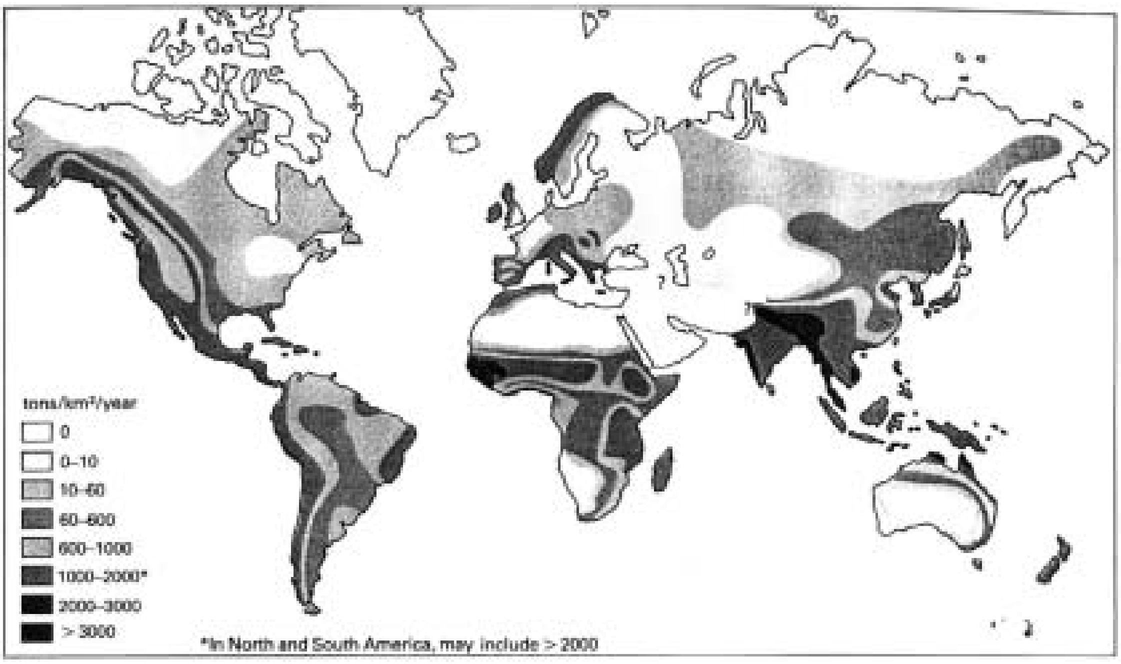

Figure 3.7: Global variation in the rates of denudation of the continental land masses. After Smith (1981).

Most of the information presented in Figure 3.7 and in Table 3.8 relate to denudation at the global scale and, at this scale and as mentioned earlier, the dominant factors controlling denudation are relief and climate. The ranges in denudation rate given in Table 3.8 for the different climate/relief zones reflect the impact of other factors that are significant at the local and regional scale. The most important of these is lithology and, put simply, the rocks most resistant to erosion (hard crystalline rocks) are represented by the lower end of the denudation ranges while the more least resistant rocks (soft sedimentary rocks such as shales and mudstones) are represented by the higher end of the denudation ranges.

Only quite recently have methods other than river sediment balances been used to determine weathering and total denudation rates for the continents. Novel isotopic methods which investigate the abundance of cosmogenic isotopes (^{3}He, ^{10}Be, ^{26}Al) generated by the interaction of cosmic rays with rock and soil minerals can now be used to obtain precise measures of recent weathering rates. Bierman (1994) compared weathering rates obtained by a number of different methods and found that, overall, there is quite a good agreement. Typically, rates range over two orders of magnitude, from 1 to 100 m/Ma, as indicated in Figure 3.8.

Glacial erosion

The rates of glacial erosion are normally much higher than those due to subaerial weathering. Glaciers may erode rock by a number of processes including crushing and fracturing, abrasion (by both ice and embedded rock fragments), cavitation and chemical decomposition (Drewry, 1986). The relative importance of these processes is controlled by several factors, the most important of which are the thickness of the ice, the nature of the rock, the temperature of the base of the glacier and the speed of the glacier over the rock. The total mass of material eroded per unit area from the glacier bed includes the mass of material eroded by abrasion, the mass of crushed and fractured material, the mass of material removed by meltwater erosion and the mass of material removed by chemical decomposition by the meltwater.

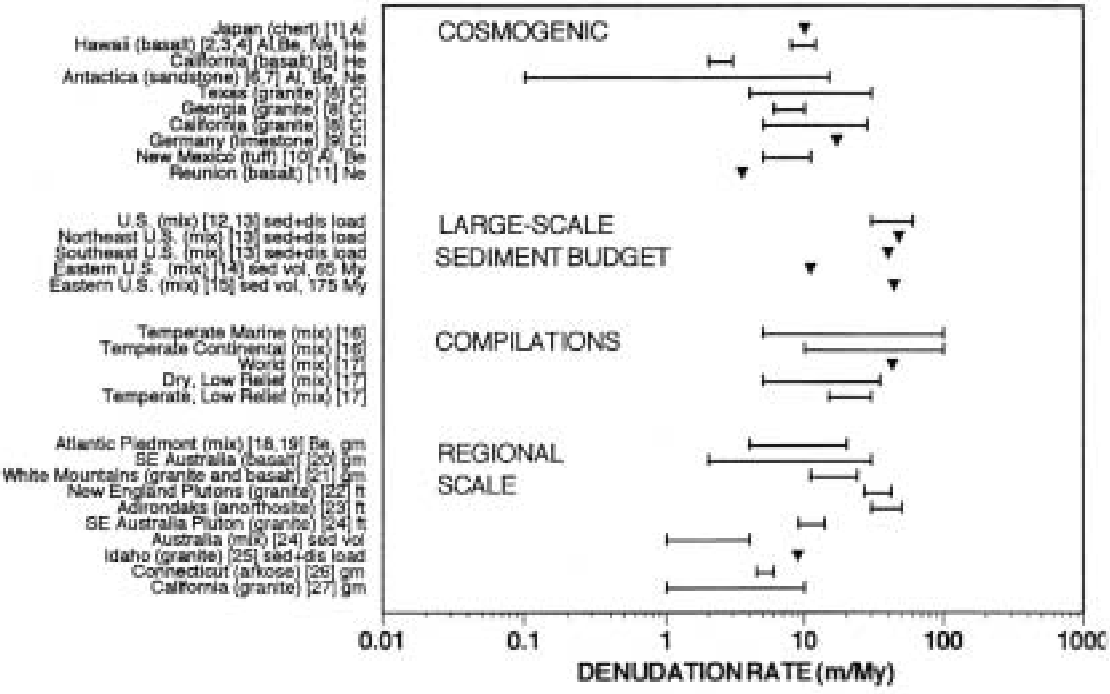

Figure 3.8: Denudation rates determined by a range of different methods. Rock types are given in parentheses: ft = fission track, gm = geomorphic arguments adopted. From Bierman (1994). The numbers in [ ] refer to original references. See Bierman (1994) for details.

Normally it is impossible to ascribe quantities to each parameter and often only an indirect assessment of total erosion can be made by measuring sediment and solute transport in rivers. Few direct measurements of abrasion have been made but one notable study was that of Boulton (1974) who measured directly the abrasion beneath the Breidamerkurjökull glacier in Iceland. Smooth plattens of marble and basalt were fixed to the bedrock beneath the ice and, sometime later, the depth of abrasion at the raised edges of the plattens was measured. The results for the rock plattens indicated average abrasion rates of 0.95 mm/yr for basalt and 3.4 mm/yr for marble.

Typically, glacial erosion rates are inferred from measurements of the sediment transport in glacial rivers. Numerous studies have employed this method to determine erosion rates for various glaciers around the world. The range of inferred glacial erosion rates varies from around 1 to 30 mm/yr, as reported in Drewry (1986). This variation relates to the different strengths of rock types and, in general, the resistance to glacial erosion for different rocks will be similar to the resistance to weathering as indicated in Table 3.7. Hard crystalline rocks are most resistant to glacial erosion. One interesting study of glacial erosion rates on granite in Norway was reported by Kjeldsen (1981) who showed a variation in erosion rates of 73 to 610 mm/ka, with a median rate of 340 mm/ka.

In addition to measuring present-day glacial erosion rates, some workers have estimated erosion rates for the last few glaciations on the basis of the volume of glacial sediments (tills, moraines etc.) and the depth of glacial valleys. Evidence such as this indicates that in mountainous areas, the floor of a glacial valley can lowered by as much as 600 m in one glacial cycle (Hamblin, 1982). Given that a single glaciation event may last, say, 10 000 years, this suggests an erosion rate of a few centimetres per year. This is very much a maximum erosion rate and is likely to be several orders of magnitude greater than the erosion which is likely to occur in relatively low-lying areas. Evidence from glacial landforms in northern Europe suggests that erosion during the last few glaciations was not generally significant (although locally variable) partly because those landforms and deposits susceptible to erosion had been removed in previous glacial episodes (Eronen and Olander, 1990).

3.4 Sediment transport

As mentioned earlier, eroded and weathered material released from the bedrock can be transported across the land surface by a number of different transporting agents. Winds blowing over the land can pick up small, sand-sized or smaller fragments of minerals and carry them long distances. Glaciers can carry rock fragments of all sizes, including boulders weighing many tonnes. Rainwash, sliding scree slopes and landslides transport material from hillsides to the valley floors and plains where they may be picked up by rivers and carried towards the seas.

With regard to the fluxes of natural materials (and their constituent elements) on a global scale, the most important transporting agent is water in the form of steams and rivers. However, transport by ice may become significant for some sites in high latitudes during glacial periods. Likewise, wind transport may be significant in certain environments, where active erosion by water and ice does not occur. However, in terms of total global mass sediment movement, rivers are, by far, the most important mechanism for transporting weathered material over the continental land masses.

The transport by water, wind and ice is discussed in the following sections.

Water

Over long periods of time (say 10^4 to 10^5 years) on the scale of a single river catchment, the mass of material denuded from the land surface will approximately equal the mass of material transported by the river to the sea. Over shorter periods of time, it is likely that variations in the denudation rate and the river flow rate may mean that eroded material may accumulate in the river basin or, alternatively, previously accumulated sediment may be striped away.

Material can be transported in rivers either as large solid particles bounced along the river bottom (the bed load), or as fine particulates that are carried in the stream water itself (suspended load), or as dissolved species (the dissolved load). Normally, studies of river transport are concerned only with the dissolved load because it is much simpler to sample, analyse and quantify the river waters rather than the suspended materials in it. However, the dissolved load analyses are likely to include colloidal material in addition to true dissolved species.

Several determinations have been made on the masses of solid material (suspended load) carried by the major rivers of the world (e.g. Milliman and Meade, 1983; Milliman and Syvitski, 1992). In addition, a number of chemical analyses have been made on the dissolved components in these river waters but fewer have analysed the suspended load. A comprehensive compilation of these data was carried-out by Martin and Meybeck (1979) who determined that the total masses of material carried by all the worlds rivers to the oceans are:

- solid load = 15.5×10^{12} kg/yr,
- dissolved load = 4.0×10^{12} kg/yr, and thus
- total load = 19.5×10^{12} kg/yr.

In addition, these authors also compiled chemical analyses on the dissolved and particulate components of river water, and these data are reported in Chapter 2 on an element-by-element basis.

These transport rates do not account either for normal bedload or for the transport of material during catastrophic floods, since these components of river transport are very difficult to quantify using standard river measurement techniques. Milliman and Meade (1983), when evaluating river transport, estimated that the solid load mass transported due to bedload and floods would be approximately 1.5×10^{12} kg/yr in additional to the loads given above by Martin and Meybeck (1979).

Although there are many hundreds of rivers around the world, a relatively small number together carry a high proportion of the total global sediment load. In Tables 3.9a and 3.9b, data from 30 of the world's largest rivers are listed, including information on their solid and dissolved loads, and the denudation rates of their catchment areas.

Table 3.9a: Transport load and denudation data for some of the world's largest river basins. From Summerfield and Hulton (1994).

River basin	Annual solid load (Mt/yr)	Annual specific solid load (t/km^2/yr)	Physical denudation rate (mm/kyr)	Annual solute load (Mt/yr)	Annual denudation load (Mt/yr)
Amazon	1320	221	82	275	171
Amur	57	28	10	22	12
Brahmaputra	1157	1808	670	51	31
Chiang Jiang	468	281	104	226	124
Colorado	167	239	89	16	13
Columbia	32	48	18	33	21
Danube	74	94	35	63	35
Dnepr	1	2	1	11	7
Ganges	680	694	257	75	41
Huang He	100	127	47	22	14
Indus	300	323	120	62	38
Kolyma	6	9	3	4	2
La Plata	87	30	11	38	25
Lena	17	7	3	88	55
Mackenzie	110	62	23	65	40
Mekong	176	232	86	47	27
Mississippi	605	189	70	105	64
Murray	33	30	11	8	6
Nelson	-	-	-	31	20
Niger	40	19	7	13	8
Nile	100	28	10	20	11
Ob	18	6	2	50	31
Orange	58	65	24	17	10
Orinoco	165	179	66	29	21
Rio Grande	30	48	18	3	2
Sao Francisco	7	11	4	-	-
Shatt-el-Arab	50	56	21	19	13
St Lawrence	2	2	1	60	35
Yenisei	14	5	2	73	45
Yukon	79	94	35	34	19
Zaire	51	14	5	37	23
Zambezi	48	34	13	13	9

The global pattern of suspended sediment yields is dependent on a number of factors, most importantly the climate (precipitation and runoff), and the surface geological and geomorphological conditions. The range of yields is from under 50 to over 1000 t/km^2/yr as indicated in Figure 3.9.

The suspended sediment and solute yields for individual rivers can be related to the total denudation rate of the surface rocks within each river catchment. This relationship is shown in Figure 3.10 for 35 of the largest rivers, on the assumption that the average continental rock has a density of 2700 kg/m^3. This figure has been compiled by making allowances for the non-denudational component of the solute loads. The balance between the suspended sediment and solute yields for some of these large rivers is shown in Figure 3.11.

Table 3.9b: Transport load and denudation data for some of the world's largest river basins. From Summerfield and Hulton (1994).

River basin	Annual specific denudational load (t/km^2/yr)	Chemical denudation rate (mm/kyr)	Total denudation rate (mm/kyr)	Chemical denudation as percent of total (%)
Amazon	29	11	93	11.6
Amur	6	2	12	17.6
Brahmaputra	49	18	688	2.6
Chiang Jiang	72	27	131	20.4
Colorado	19	7	96	7.4
Columbia	32	12	30	40.0
Danube	45	17	52	32.4
Dnepr	12	4	5	85.7
Ganges	42	16	273	5.7
Huang He	18	7	54	12.4
Indus	42	16	136	11.5
Kolyma	4	1	4	30.8
La Plata	9	3	14	23.1
Lena	22	8	11	75.9
Mackenzie	23	9	32	27.1
Mekong	36	13	99	13.4
Mississippi	20	7	77	9.6
Murray	6	2	13	9.7
Nelson	16	6	-	-
Niger	4	1	8	17.4
Nile	3	1	11	9.7
Ob	11	4	6	64.7
Orange	11	4	28	14.5
Orinoco	23	9	75	11.4
Rio Grande	4	1	19	7.7
Sao Francisco	-	-	-	-
Shatt-el-Arab	14	5	26	20.0
St Lawrence	34	13	14	94.4
Yenisei	18	7	9	78.3
Yukon	23	9	44	19.7
Zaire	6	2	7	30.0
Zambezi	6	2	15	15.0

Wind

Wind is a relatively weak transporting agent compared to water. Due to the low density and viscosity of air, wind can transport only very fine particles, except at very high wind velocities but, even then, sand-sized grains are generally the largest which can be blown significant distances.

Moisture and vegetation tend to bind sediment particles together, so that wind (aeolian) transport is only really efficient in arid regions devoid of vegetation. Thus, aeolian transport dominates in deserts but, even then, occasional high rainfall events can move greater masses of material in a few days than wind can over the course of a year. Wind can also be an important transport mechanism on bare fields, sandy coasts, river plains and deltas, and on the margins of glaciers and permafrost regions. In such environments, natural fluxes of material at the Earth's surface may be locally wind controlled.

Figure 3.9. Global patterns of yields of suspended sediment as determined from intermediate sized basins of 10^4 to 10^5 km^2. From Summerfield (1991).

The most obvious aeolian landforms are desert dunes, which are concentrated in sand seas known as *ergs*. However, another important aeolian feature are loess deposits, which are extensive blankets of silt-sized materials, which often accumulated at the marginal areas of Pleistocene ice sheets and, less frequently, in lower latitudes. Most wind blown sands are derived from the aeolian reworking of sediments rather than from the bedrock itself. These sands are comprised of quartz because the other minerals have usually degraded away by this stage in the sedimentary cycle. Thus, although desert winds can move significant masses of sandy material, the elemental fluxes associated with them are low because most elements of interest have already been removed.

Due to the lower viscosity and energy of wind, compared to water, wind is less able to transport large particles, except at very high wind speeds. For example, a typical grain of sand with a diameter of 1 mm requires a 10 m/s vertical updraft to lift the grain. Such uplifts are typically associated with winds with an average horizontal speed of between 20 and 30 m/s. Since these winds are at the top end of the wind speed range, grains over 2 mm diameter are rarely picked-up by wind and tend to move by bouncing over the ground - 'saltation'.

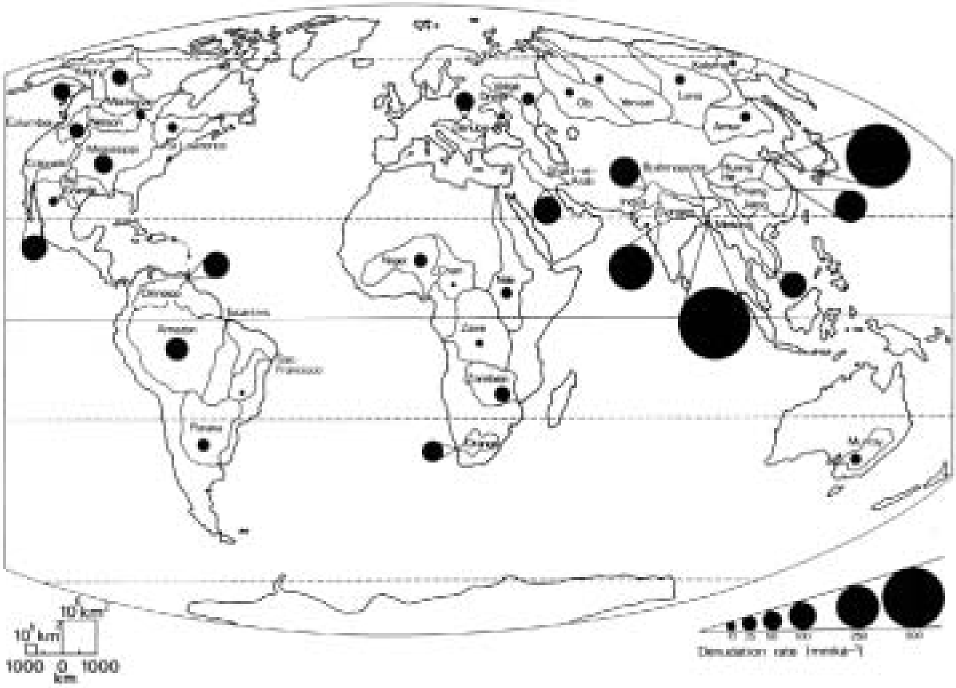

Figure 3.10: Denudation rates for some of the largest rivers in the world based on measured solid and solute loads, after making allowances for the non-denudational solute load and assuming a rock density of 2700 kg/m^3*. From Summerfield (1991).*

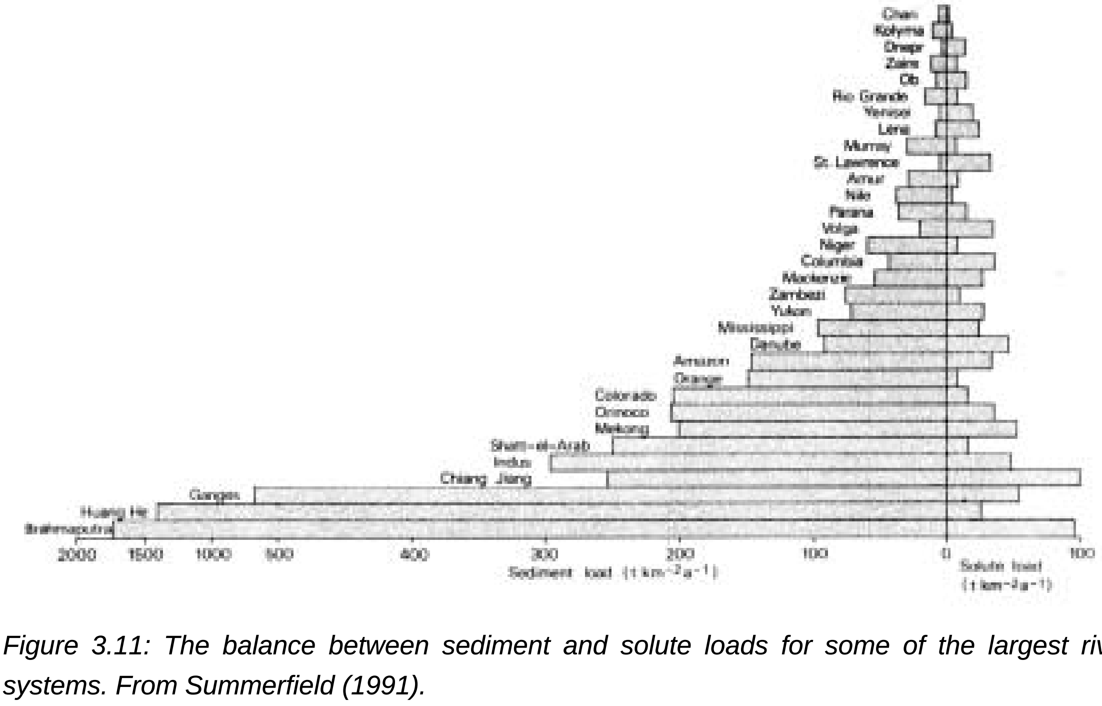

Figure 3.11: The balance between sediment and solute loads for some of the largest river systems. From Summerfield (1991).

At the other end of the scale, fine clay dust particles are usually bonded together by electrostatic cohesion. As such, these fine clays are hard for wind to pick-up if the sediment is moist. Consequently, it is middle sized particles which are most efficiently moved by wind: the grainsize that travels most easily is 0.3 mm (Summerfield, 1991).

However, in dry, desert environments, this dust material can be picked-up by wind, and can represent a very efficient transport process in short-term, high wind speed events. For example, in large dust storms, one cubic kilometre of air can hold up to 1000 tonnes of dust (Press and Siever, 1982) and, once picked-up, this dust can be transported several hundred kilometres. The rate of aeolian transport is controlled by wind speed, particle size and, to lesser extents, by surface topography and air density (which varies according to temperature and altitude). Greater rates of sand movement can occur at high wind speeds but such winds are infrequent. Thus, most sand transport occurs at moderate wind speeds which are most common (around 12 to 18 m/s), as shown in Figure 3.12.

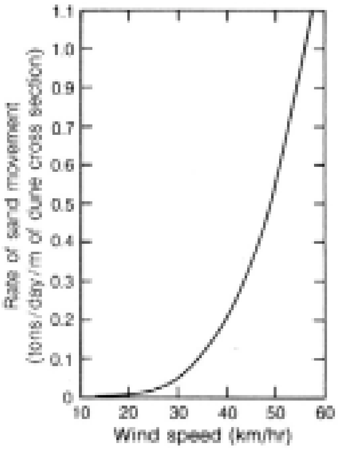

Figure 3.12: Relationship between wind speed and sand movement across a dune. From Press and Siever (1982).

Ice

Ice is a very powerful sediment transporting agent. Due to the power of an advancing ice sheet or glacier, the physical erosion rate can be very high (as indicated earlier) and all sizes of eroded material can be transported, from sand-sized grains to very large boulders of bedrock.

However, ice (as glaciers or ice sheets) can only dominate surface transport in regions where snow persists from year to year, allowing it to accumulate, and where the ice is flowing. This typically is restricted to either high latitudes or high elevations. Thus, in regions where ice persists year round, natural fluxes of material at the Earth’s surface will be ice controlled.

Transported materials can occur on top of the flowing ice (supraglacial debris), within the mass of the ice (englacial debris) or at the base of the ice (subglacial debris). The latter is responsible for increasing the erosion rate of the bedrock below the ice. The rates of ice flow can vary considerably but typically lie in the range 3 to 300 m/yr but this can also vary spatially and temporally within an individual ice sheet. The upper end of this rate is the speed of valley glaciers while the lower end relates more closely with the speed of a continental scale icesheet - the icesheet at the South Pole is moving at around 8 m/yr (Press and Siever, 1982).

Although the total mass of debris carried on and in an ice sheet can be very large, these slow rates of movement (relative to a river), mean that the actual flux of ice transported material could be quite low. Much greater fluxes of sediment transport occur at the front (snout) of a glacier, especially a retreating glacier, due to fast flowing glacial meltwaters which rework the glacial deposits.

Thus, in total global terms, ice is not a dominant transporting agent for natural fluxes associated with sediments, but ice is a significant mechanism for eroding material from bedrock to form surface sediments. Subsequent reworking by water (or possibly wind) is more important for moving this eroded material about.

4 Global scale fluxes

The surface and near-surface rocks, sediments and waters of the continents are subject to active geological, geomorphological and climatological processes that can cause mass movement of material, as discussed in Chapter 3. The amount of material which is moved by these processes appears large in comparison to every-day, human measures of scale but actually represents only a very small proportion of the total mass of the continents. In general, over long time periods, these processes act to remove material from the continents and transport them to the oceans, although certain atmospheric processes can transport material in the other direction (as aerosols and as precipitation). In addition, a small amount of ‘new’ material is added to the surface from extraterrestrial sources, at a rate of around 3.6×10^9 kg/yr.

Figure 4.1 provides a graphical indication of the principal mechanisms of mass movement and the masses of material transported annually. As can be seen from this illustration, rivers are the dominant mechanism driving mass movement. The majority of the solid material transported by the processes shown in Figure 4.1 will comprise silicate-mineral based rocks and their degradation products (e.g. clays, soils and sediments). In terms of elemental fluxes, therefore, the dominant mobile species will be the principal components of these minerals, notably Si, O, Ca, Na, K, Al, Fe and Mg. Added to these will be organic C from biological activity at the surface. Of these dominant elements, only K and C are considered in this report. The remainder of the elements considered in this work are trace elements, occurring typically at around the ppm or ppb level [1 ppm = 1 mg/kg and 1 ppb = 1 µg/kg].

The quantification of global elemental fluxes (i.e. elemental fluxes averaged for the entire Earth) due to the different mass movement processes requires many assumptions to be made and averages to be defined. For example, the calculation of global elemental fluxes due to erosion requires that a global average erosion rate is known together with a global average composition for the eroding material.

Although it is evident that global fluxes must represent some spatial average, it is less clear that they also represents some element of temporal averaging. The reason for this relates to the techniques used in the field to obtain process rates or material compositions, and to the interpretation of these data. For example, erosion rates are frequently based on the masses of sediment carried by rivers. However, the sediment that is currently carried in rivers may have been eroded from the surface rocks over, say, the last few hundred or thousand years and which is still in the sedimentary cycle. In other words, measuring sediment transfer rates in rivers today does not tell us about present-day erosion rates but, rather, the average erosion rate over the past few hundred or thousand years. Likewise, elemental concentrations in deep groundwaters do not tell us how rapidly these elements are leached from the rock today but relate to leaching processes occurring over time along the groundwater flowpath. Consequently, many of the fluxes calculated here have inherited some degree of temporal as well as spatial averaging. Frequently, however, it is not easy clearly to define what the extent of this temporal averaging actually is.

As a result of the varied assumptions and uncertainties behind these calculations, the fluxes which are calculated here must be treated with some caution and interpreted with care. It would be wrong, say, to take the calculated global elemental fluxes due to erosion presented here and assume that they are equivalent to the erosion fluxes which are occurring at a given location, at any particular time. This is because the global average flux values mask the considerable variability which exists in natural systems. Nonetheless, these global elemental fluxes are considered to be a useful starting point to the natural safety indicators method because they provide a datum against which site specific (or environment specific) fluxes can be compared. If a site specific elemental flux were to be used as some comparator with repository releases, it would be valuable to know if that site specific natural flux was particularly high or low compared to natural fluxes at other locations, and the calculation of global elemental fluxes allows such an evaluation to be made.

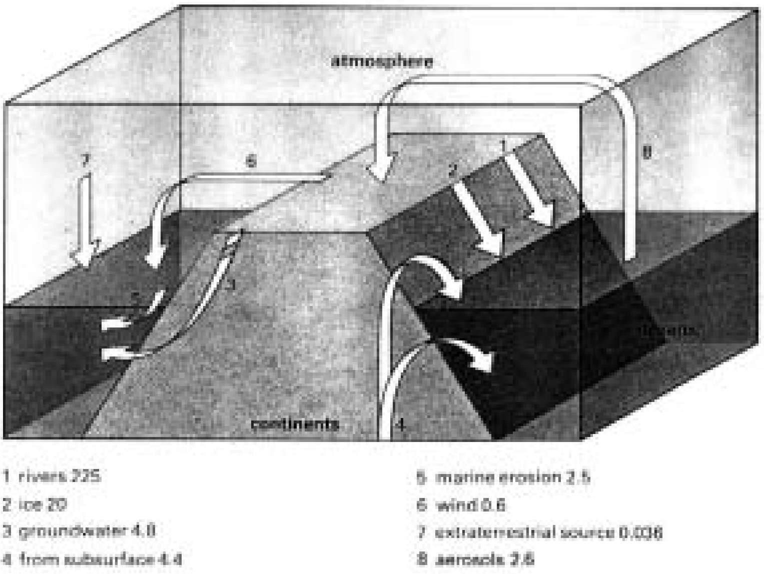

Figure 4.1: The principal mechanisms causing mass movement in the surface and near-surface continental rocks, and the masses of material transported annually (in units of $\times 10^{11}$ *kg/yr). After Smith (1981).*

As discussed in Section 1.1.2, many of the processes which cause global scale fluxes are endogenic, particularly those related to deep crustal and mantle processes, and, therefore, have little or no relevance to the types of processes or fluxes which may be compared to repository releases. However, certain exogenic processes are directly relevant because these give rise to elemental fluxes that are accessible at the surface and are comparable to repository release mechanisms. These fluxes can be represented in a compartment diagram such as the one given in Figure 4.2.

This figure is clearly a gross simplification of the real Earth system but, for the broad nature of these global average calculations, is adequate. For ease of presentation, the calculations for the global elemental fluxes along each of the pathways shown on Figure 4.2 are presented separately below.

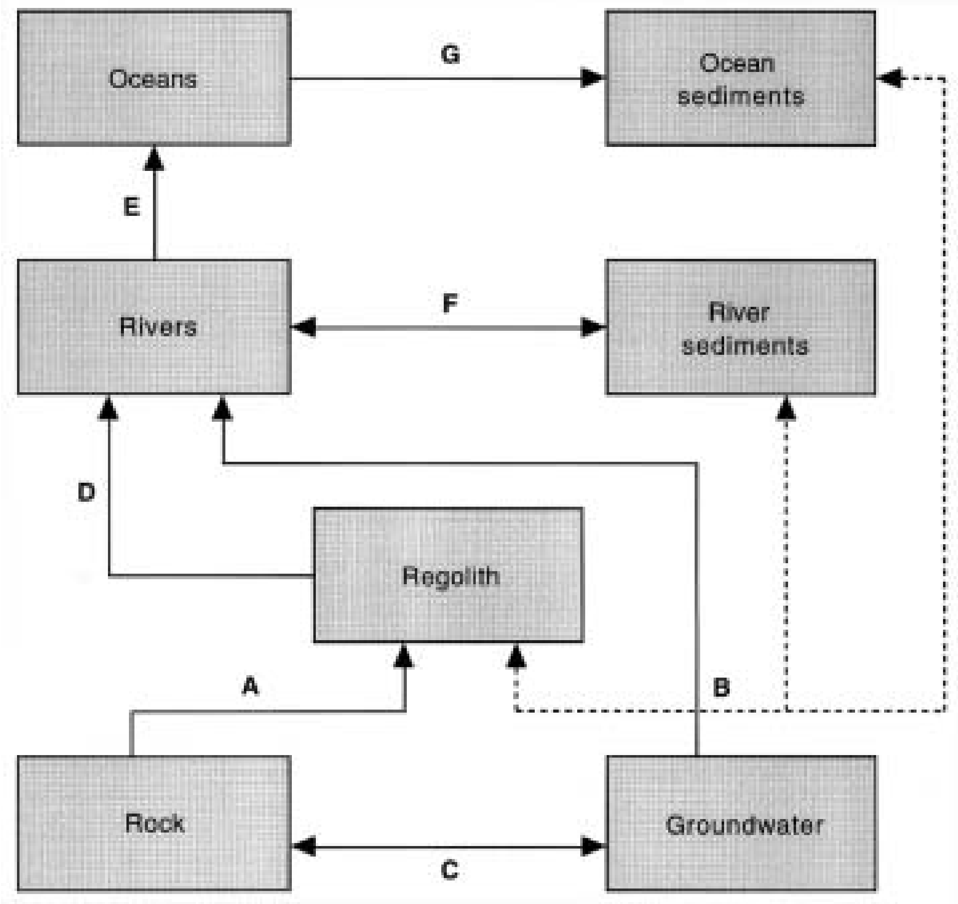

Figure 4.2: A compartment model for the Earth showing the processes/pathways that result in mass movement at or near the Earth's surface that cause significant element fluxes. The letters refer to pathways for which fluxes have been calculated.

4.1 Erosion (Pathway A)

Pathway A is the erosion of the upper rock mass to form the surface sediments, such as gravels, sands and soils (collectively termed 'regolith'). There are a number of ways that the global average elemental fluxes due to erosion can be calculated using different estimates of erosion rates published in the literature.

1st approximation

Garrels and Lerman (1977) calculated, by extrapolation from the volumes of sedimentary rocks of different ages found in the geological record, that the global erosion rate for the continents, averaged over the entire Phanerozoic Era (the last 570 Ma) was 8×10^{12} kg/yr. Given that the surface area of the continents is 153×10^{6} km^2, this equates to a global average erosion rate of 5.23×10^{4} kg/km^2/yr. According to Garrels and Lerman, the sedimentary rock record revealed that this erosion rate showed random fluctuations of between 25 to 400 % of the average but with no clear cyclical behaviour.

Garrels and Lerman also calculated that the mean residence time of material in sedimentary rocks is 200 Ma. Therefore, given that their average erosion rate relates to a period three times longer than the average residence time, it implies that Garrels and Lerman's erosion rate defines the erosion of material from the basement rocks (upper crustal rocks) and is not significantly affected by the reworking of sedimentary rocks at the Earth's surface. Hence, using the erosion rate from Garrels and Lerman gives a relevant estimate of the long-term fluxes from basement crustal rocks due to erosion.

On this basis, the total erosion flux for each element can be calculated using the upper crust composition given in Table 2.18 and the global average erosion rate given by Garrels and Lerman (i.e. 8×10^{12} kg/yr). These fluxes are calculated and presented in Table 4.1. In addition, this table also shows the specific erosion flux which is simply the total erosion flux dividing by the surface area of the continents (i.e. 153×10^{6} km^2).

Table 4.1: Long-term (10^8 years) average elemental fluxes due to erosion of the basement upper crustal rocks.

Element	**Total erosion flux (kg/yr)**	**Specific erosion flux ($kg/km^2/yr$)**
C	2.59×10^{10}	169.4
Cl	5.12×10^{9}	33.5
K	2.29×10^{11}	1498.0
Ni	1.52×10^{8}	1.0
Cu	1.52×10^{8}	1.0
Zn	4.96×10^{8}	3.2
Se	5.60×10^{5}	4.0×10^{-3}
Rb	8.88×10^{8}	5.8
Cd	8.00×10^{5}	5.0×10^{-3}
Sn	3.20×10^{7}	0.2
I	1.12×10^{7}	7.0×10^{-2}
Nd	2.08×10^{8}	1.4
Sm	3.68×10^{8}	0.2
Pb	1.36×10^{8}	0.9
Th	8.40×10^{8}	0.5
U	2.16×10^{8}	0.1

Garrels and Lerman noted from their data that the mass of sediments and sedimentary rocks has not shown any significant growth or loss trends over the Phanerozoic. As a direct consequence, the mass of material deposited on the ocean floor, averaged over this time-period, must approximate to the mass eroded from the upper crustal rocks. Given that the dominant mechanism removing sediment from the continents is river transport, then the fluxes due to erosion given in Table 4.1 must also approximate closely to the elemental fluxes due to river transport for the same time period (the last 570 Ma). In this case, the majority of the eroded material would be in solid form, carried in suspension or as bedload.

2^{nd} approximation

The erosion rate used in the 1st approximation relates to a time period (10^8 years) which is orders of magnitude longer than is relevant to PA. Erosion occurring over times more applicable to PA (i.e. 10^4 to 10^6 years) needs to take account of the fact that, during these times, formation and reworking of sedimentary rocks now becomes significant because we are considering times shorter than the 200 Ma average residence time of material in the sedimentary rock record, according to Garrels and Lerman (1977).

Since erosion and reworking of the sedimentary rocks is now of interest, it is necessary to know the proportions of the different rock types on the continents which are being eroded, their compositions and rates of erosion in order to calculate global elemental fluxes due to erosion. Meybeck (1977) determined the outcrop abundances of the major rock types on the continents in terms of percent by area, and these are presented in Table 4.2.

Table 4.2: Relative surface outcrop abundances of the major continental rock types. From Meybeck (1977).

Rock	Proportion (%)
Plutonic rocks (mostly granite/granodiorite)	11
Metamorphic rocks (mostly gneiss)	15
Volcanic rocks (mostly basalt)	7.9
Sandstone	15.8
Shale	33.1
Carbonate (mostly limestone)	15.9
Evaporites (mostly gypsum/halite)	1.3

Differentiating crystalline from sedimentary rocks in Table 4.2, reveals that the surface outcrop abundance of crystalline rocks on the continental crust is 33.9 % (plutonic, metamorphic and volcanic rocks), while the abundance of sedimentary rocks is 66.1 % (sandstone, shale, carbonates and evaporites).

Average elemental abundances for these rocks can be read from Table 2.18, assuming granite composition for plutonic rocks, gneiss composition for metamorphic rocks, basalt for volcanic rocks, clay composition for shale, limestone composition for carbonates and ignoring the minor evaporites.

As discussed in Section 3.3, global erosion rates reflecting erosive process operating over the last few thousand years (10^3 to 10^4 year) were presented by Smith (1981). Various factors control the erosion rate at different locations around the world, including topographic elevation and climate, as well as rock type. Smith showed that the erosion rates vary from essential zero to over 3×10^6 kg/km^2/yr, with a global average of approximately 3×10^5 kg/km^2/yr. The spatial distribution of erosion rates over the continents was shown in Figure 3.7.

The medium term (10^3 to 10^4 year), global average erosion rate of 3×10^5 kg/km^2/yr from Smith corresponds to a total rock erosion flux of 4.6×10^{13} kg/yr for all the continental land area. This is approximately 5 times greater than the long term (10^8 year) value of 8×10^{12} kg/yr given by Garrels and Lerman (1977) for the erosion of the basement rocks over the Phanerozoic Era.

The medium term average rate is higher because it reflects recycling of material in the sedimentary cycle at the Earth's surface.

As discussed in Section 3.4, Martin and Meybeck (1979) determined the total mass of material transported in the world's largest rivers (including dissolved load) and concluded the average transport rate was 19.5×10^{12} kg/yr, excluding bedload and catastrophic flooding. This is order of magnitude equivalent to the erosion flux from Smith (1981) of 4.6×10^{13} kg/yr, being approximately only a factor of two smaller. Given the uncertainties in measuring transport rates and in determining a global average value, it is not clear whether the difference between these two values is real. If it is real, it suggests that, in the medium term, there is a net accumulation of sediment on the continents because the erosion rate is twice as large as the rate of sediment transport in rivers. However, it is most likely that some of the difference is due to the fact that Martin and Meybeck (1979) data did not account for the catastrophic events. Even though catastrophic flooding events may occur infrequently and last for short periods of time, they are capable of transporting large amounts of material. If these events were accounted for, it might be expected that the total mass of material transported in the world's largest rivers would equate more closely with the erosion flux from Smith (1981). However, in the absence of reliable data on the catastrophic flooding events, this conclusion must be treated with caution. This is an example of the insensitivity of the method inherited from the input data.

The average elemental fluxes due to erosion can be determined for each major rock type using the elemental abundances for each rock type (Table 2.18), its outcrop abundances (Table 4.2) and the medium term average erosion rate from Smith (1981), i.e. 3×10^{5} kg/km^{2}/yr. These fluxes are calculated and presented in Table 4.3, together with a total global erosion flux for each element determined by adding together the individual elemental fluxes for each rock type. Of course, the different rock types will not all erode at the same average rate: it can be expected that carbonates will erode faster than plutonic rocks for example. However, since a large control on the erosion rates is climate and we have no information on a general relationship between climate and rock type distribution, it seems most appropriate to apply the average erosion rate from Smith (1981) to all rock types, rather than to introduce another source of uncertainty into the calculations.

Table 4.3: Medium-term (10^{4} to 10^{6} years) average elemental fluxes due to erosion of the major continental rock types.

Element	**Plutonic flux (kg/yr)**	**Metamorphic flux (kg/yr)**	**Volcanic flux (kg/yr)**	**Sandstone flux (kg/yr)**
C	1.77x10^{9}	1.79 x10^{9}	7.81 x10^{8}	1.16 x10^{11}
Cl	1.01 x10^{9}	3.11 x10^{9}	1.42 x10^{9}	3.63 x10^{9}
K	1.69 x10^{11}	6.90 x10^{10}	2.18 x10^{10}	1.09 x10^{11}
Ni	5.06 x10^{7}	6.90 x10^{7}	9.09 x10^{8}	1.09 x10^{8}
Cu	2.28 x10^{8}	6.90 x10^{8}	7.09 x10^{8}	2.18 x10^{8}
Zn	3.80 x10^{8}	6.56 x10^{8}	3.63 x10^{8}	2.18 x10^{8}
Se	2.53 x10^{5}	3.45 x10^{5}	1.82 x10^{5}	1.45 x10^{5}
Rb	7.59 x10^{8}	5.18 x10^{8}	1.16 x10^{8}	3.34 x10^{8}
Cd	1.01 x10^{6}	6.90 x10^{5}	7.27 x10^{5}	3.63 x10^{5}
Sn	1.77 x10^{7}	1.52 x10^{7}	4.36 x10^{6}	3.63 x10^{6}
I	5.06 x10^{7}	6.90 x10^{7}	3.63 x10^{7}	7.27 x10^{6}

Nd	2.23 x10^{8}	2.42 x10^{8}	1.16 x10^{8}	2.11 x10^{8}
Sm	4.81 x10^{7}	5.87 x10^{7}	2.65 x10^{7}	5.45 x10^{7}
Pb	4.40 x10^{8}	1.31 x10^{8}	2.00 x10^{7}	5.09 x10^{7}
Th	1.37 x10^{8}	1.10 x10^{8}	1.02 x10^{7}	2.33 x10^{7}
U	2.48 x10^{7}	2.21 x10^{7}	2.91 x10^{6}	4.36 x10^{6}

Element	Shale flux (kg/yr)	Carbonate flux (kg/yr)	Total flux (kg/yr)	Specific erosion flux (kg/km^{2}/yr)
C	4.57 x10^{11}	1.68 x10^{11}	7.46 x10^{11}	4.87 x10^{3}
Cl	6.09 x10^{9}	5.12 x10^{8}	1.58 x10^{10}	1.03 x10^{2}
K	3.05 x10^{11}	2.27 x10^{10}	6.96 x10^{11}	4.55 x10^{3}
Ni	9.90 x10^{8}	8.78 x10^{7}	2.21 x10^{9}	14.5
Cu	6.85 x10^{8}	7.31 x10^{7}	2.60 x10^{9}	17.0
Zn	1.60 x10^{9}	1.83 x10^{8}	3.40 x10^{9}	22.2
Se	7.61 x10^{6}	2.19 x10^{5}	8.76 x10^{6}	5.72 x10^{-2}
Rb	2.13 x10^{9}	4.02 x10^{8}	4.26 x10^{9}	27.8
Cd	3.05 x10^{6}	2.19 x10^{5}	6.06 x10^{6}	3.96 x10^{-2}
Sn	9.14 x10^{7}	3.66 x10^{6}	1.36 x10^{8}	0.88
I	1.83 x10^{8}	1.61 x10^{8}	5.07 x10^{8}	3.31
Nd	4.42 x10^{8}	4.02 x10^{7}	1.27 x10^{9}	8.32
Sm	1.14 x10^{8}	9.51 x10^{6}	3.11 x10^{8}	2.04
Pb	3.50 x10^{8}	4.39 x10^{7}	1.04 x10^{9}	6.77
Th	1.83 x10^{8}	1.24 x10^{7}	4.76 x10^{8}	3.11
U	5.33 x10^{7}	1.61 x10^{7}	1.24 x10^{8}	0.81

The total global elemental fluxes given in Table 4.3 are generally larger than those from the 1st approximation by a factor of around 3 to 5 for two reasons. First, the erosion rate used here is larger than in the first approximation by a factor of about 5, as discussed earlier. Second, some elements are preferentially concentrated in sedimentary rocks compared to the upper crust and hence reveal larger fluxes here due to the reworking of the sedimentary material. This is particularly the case for C and I which are 28 and 45 % larger, respectively, in this calculation than in the 1st approximation to the global elemental fluxes due to erosion.

These second approximations to the global elemental fluxes due to erosion are considered to be more significant that the 1st approximations as comparators to repository fluxes because they represent the fluxes of elements actually moving about in natural systems over time periods comparable to those considered in PA.

4.2 Groundwater discharge (Pathway B)

Pathway B is the transport of dissolved material from the geosphere to the biosphere via groundwater discharge. This is a crucial pathway to consider, since this is also the pathway by which the majority of radionuclides released from a repository would return to the surface environment. Therefore, of all the natural fluxes, this one is most interesting to compare to repository releases. Surprisingly, very few studies have examined fluxes between the geosphere and the biosphere via groundwater and those that have are generally concerned only with major elements and with small spatial areas.

Two factors must be known in order to calculate the masses of elements transported with groundwater. These are the flux of groundwater from the geosphere and the elemental concentrations within the groundwater. Gaseous and colloidal transport in the groundwater are not considered here.

The basic assumption behind the calculation made here is that the global groundwater discharge rate is equivalent to the global recharge rate resulting from precipitation: i.e. the volume of groundwater is constant, which seems to be a reasonable assumption. The volume of groundwater held in continental rocks is poorly constrained but is typically quoted to be approximately $60x10^6$ km^3 with an average residence time of 5000 years (e.g. Freeze and Cherry, 1979; Shaw, 1988). Dividing the reservoir volume by the residence time gives an annual groundwater recharge/discharge flux of $1.2x10^{16}$ l/yr [1 km^3 = $1x10^{12}$ l].

This total groundwater volume is distributed throughout the entire volume of continental crust, most of which comprises crystalline basement. Assuming deep crystalline basement has an average thickness of is 33 km and an average porosity of 0.5 % which is water saturated, the volume of groundwater in the crystalline basement is 2.52 $x10^7$ km^3, which is about 42 % of the total groundwater volume. The remaining groundwater will be contained in the top 2 km of crustal rock (above the basement) which comprises both crystalline and sedimentary rocks. The fact that the remaining 58 % of groundwater can be held in a much smaller volume of rock than the crystalline basement is explained by the fact that the near-surface sedimentary rocks have a much larger porosity (as much as 30 % according to Table 3.3) than the crystalline basement rocks. On this basis, the volume of groundwater held in the near-surface rocks (at or above typical repository depths) will be 58 % of the total groundwater volume (i.e. 3.5×10^7 km^3).

A similar calculation can be done using the data in Table 4.2 which gives the relative surface outcrop abundances of the major continental rock types, from Meybeck (1977). The data in this table indicates that, combined, the surface outcrop abundance of crystalline rocks on the continental crust is 33.9 % (plutonic, metamorphic and volcanic rocks), while the abundance of sedimentary rocks is 66.1 % (sandstone, shale, carbonates and evaporites). Assuming that surface outcrop abundances are roughly proportional to volumetric abundances in the near-surface rocks (for the upper 2 km), and that the crystalline and sedimentary rocks have average, saturated porosities of 1 % and 10 %, respectively, then the volumes of groundwater held in the near-surface rocks are:

- volume of groundwater in near-surface crystalline rocks = 1.04×10^6 km^3, and
- volume of groundwater in near-surface sedimentary rocks = 2.02×10^7 km^3.

This gives a combined groundwater volume in the upper 2 km of rock of 2.12×10^7 km^3 which is order of magnitude equivalent to the 58 % of total groundwater (3.5×10^7 km^3) calculated from the Freeze and Cherry (1979) groundwater volume, giving confidence in the groundwater volumetric distributions. Adopting these distributions and the 5000 year average residence time of groundwater from Freeze and Cherry (1979), this means that the typical groundwater discharge fluxes from the near-surface rocks will be:

- discharge flux of groundwater in near-surface crystalline rocks = 2.08×10^{14} l/yr, and
- discharge flux of groundwater in near-surface sedimentary rocks = 4.04×10^{15} l/yr.

These groundwater discharge fluxes can be used to calculate the elemental fluxes of dissolved components in the groundwater if the average groundwater compositions are known. Unfortunately, it is not really practicable to calculate an accurate average global groundwater composition which is directly applicable to this calculation. This is because too few deep groundwater analyses have been made that include all the elements of interest to this study to enable accurate mean compositions to be determined for different rock types. In fact, very few groundwater analyses which include the trace elements of concern in this study are ever undertaken outside of radioactive waste oriented research programmes. Nonetheless, individual elemental abundances from a range of groundwater types were obtained in the compilation of elemental abundances (Chapter 2) and, from this, estimated average trace element abundances in groundwaters from both crystalline and sedimentary rocks were defined in Table 2.19. However, it should be recognised that considerable uncertainty is associated with these data.

Using these average groundwater elemental abundances and the global groundwater fluxes for sedimentary and crystalline rocks, the total global elemental fluxes due to groundwater discharge are calculated and presented in Table 4.4, together with their combined values. In addition, the specific groundwater discharge fluxes are given. These are simply the total elemental discharge fluxes divided by the surface area of the continents (153×10^{6} km^{2}). This is not intended to indicate that each km^{2} would actually provide such elemental fluxes because there will be significant spatial variability in the groundwater discharge rates. Nonetheless, these values do act to give order of magnitude elemental fluxes due to global groundwater discharges. From these values, it can be seen that typically for the trace elements, the global average amount of element released in groundwater is on the order of a few grams per year for each km^{2} area of land.

Table 4.4: Global elemental fluxes due to groundwater discharge for both sedimentary and crystalline rocks.

Element	**Sedimentary groundwater flux (kg/yr)**	**Crystalline groundwater flux (kg/yr)**	**Total groundwater discharge flux (kg/yr)**	**Specific groundwater discharge flux (kg/km^{2}/yr)**
C	5.00x10^{11}	1.20 x10^{10}	5.12 x10^{11}	3.35 x10^{3}
Cl	1.60 x10^{12}	2.20 x10^{10}	1.62 x10^{12}	1.06 x10^{4}
K	1.60 x10^{11}	1.20 x10^{9}	1.61 x10^{11}	1.05 x10^{3}
Ni	4.00 x10^{7}	1.80 x10^{5}	4.02 x10^{7}	0.26
Cu	2.00 x10^{7}	1.00 x10^{6}	2.10 x10^{7}	0.14
Zn	2.00 x10^{8}	3.80 x10^{6}	2.04 x10^{8}	1.33
Se	2.00 x10^{6}	6.00 x10^{4}	2.06 x10^{6}	1.35 x10^{-2}
Rb	2.00 x10^{8}	1.00 x10^{7}	2.10 x10^{8}	1.37
Cd	8.00 x10^{5}	1.00 x10^{4}	8.10 x10^{5}	5.29 x10^{-3}
Sn	2.00 x10^{6}	6.00 x10^{3}	2.01 x10^{6}	1.31 x10^{-2}
I	1.20 x10^{8}	1.60 x10^{6}	1.22 x10^{8}	0.80
Nd	6.40 x10^{5}	3.20 x10^{4}	6.72 x10^{5}	4.39 x10^{-3}
Sm	1.12 x10^{5}	5.60 x10^{3}	1.18 x10^{5}	7.69 x10^{-4}

Element	Sedimentary groundwater flux (kg/yr)	Crystalline groundwater flux (kg/yr)	Total groundwater discharge flux (kg/yr)	Specific groundwater discharge flux (kg/km^2/yr)
Pb	1.20 x10^7	6.00 x10^4	1.21 x10^7	7.88 x10^{-2}
Th	1.20 x10^6	6.00 x10^4	1.26 x10^6	8.24 x10^{-3}
U	4.00 x10^6	2.00 x10^5	4.20 x10^6	2.75 x10^{-2}

There are clearly many assumptions inherent in the determination of both the global groundwater discharge rate and global average groundwater compositions and, consequently, the results should be viewed only as first approximations. However, if it is a requirement that repository releases should be compared to a proportion of the total global natural fluxes (as suggested in some proposals), rather than the natural fluxes within, say, one country or region, then it is necessary to perform these broad based calculations.

The predominant discharge path for groundwaters will be to the rivers. However, some groundwaters may also discharge to the regolith, and to river and ocean sediments, although the exact proportions are not known. This is represented on Figure 4.2 by the dashed lines from the groundwater compartment. It follows that a proportion of the dissolved trace element load in the Earth's rivers is due to leaching of rock by groundwaters. The remainder of the dissolved trace-element load in rivers will be due to chemical weathering of the rocks by surface processes.

4.3 Rock dissolution (Pathway C)

Pathway C represents leaching of the elements of interest from the rocks by the groundwater and is somewhat analogous to the leaching of the radioactive wastes within a repository. Clearly the basement rock leaching rate will depend on the physico-chemical conditions of the rock-water system at any one location and, of course, actual leaching rates will be highly variable both spatially and temporally and, so, the global averages calculated here must be seen only as a first approximation.

However, it is clear that the mass of trace-element leached from the rocks must equal the mass of elements discharged with the groundwater if it is assumed that the composition of groundwaters is not changing; in other words, if the 'global' rock-groundwater system is in equilibrium. This is not an unreasonable assumption on the global although, on a local scale, it is likely that mass balance may not always be preserved due to a range of processes, such as precipitation, which act locally to reconcentrate some of the dissolved trace elements before they can be discharged with the groundwater.

The volume of rock that is leached by these groundwaters can be calculated if it is assumed that only, say, the upper 2 km of rock are hosting active groundwater flow systems (the same depth assumed for the groundwater discharge calculations). The rock below this depth will contain groundwaters but the flow rates of this water are probably so slow that no significant linkage occurs between this water and the groundwater circulating in the upper crustal rocks. Of course, the depth of active groundwater flow systems will vary from place to place but 2 km is believed to be a reasonable average.

Thus, given that the area of the continents is about 153×10^6 km^2 and assuming rock to a depth of 2 km is leached by the groundwater, this gives a potential leached volume of rock of 3.06×10^8 km^3. Using the calculated fluxes of trace elements discharged with groundwaters globally ('Total groundwater discharge flux' from Table 4.4), it is possible to calculate the average rate of rock leaching. This calculation has been performed and the results are shown in Table 4.5. The calculated fluxes (per element) are expressed as the 'specific leaching flux' which is the mass of element leached per unit volume of rock per year.

Table 4.5: Global elemental fluxes due to rock leaching by groundwater.

Element	**Specific rock leaching rate (g/km^3/yr)**
C	1.67×10^6
Cl	5.30×10^6
K	5.27×10^5
Ni	1.31×10^2
Cu	68.6
Zn	666.0
Se	6.73
Rb	686.0
Cd	2.65
Sn	6.56
I	397.0
Nd	2.20
Sm	0.38
Pb	39.4
Th	4.12
U	13.7

The implicit assumptions behind these calculations of elemental fluxes due to rock dissolution are that:

- the entire volume of rock is in contact with groundwater and accessible for leaching (porous medium assumption),
- all minerals in the rock leach and releases dissolved elements at the same rate, and
- once dissolved, elements stays in solution and are not removed by sorption or precipitation processes.

Clearly, these assumptions are not truly representative of 'real' rock-water interaction processes. In particular, only a small proportion of the rock is actually in intimate contact with groundwater (the 'wetted surface area'), governed by the porosity and permeability of the rock mass. However, porous medium assumptions are frequently made in groundwater calculations in PA and, without detailed data for wetted surface areas and specific mineral leaching rates, the calculation presented here is believed to represent a useful first approximation to the average bulk rock leaching rates due to rock-water interaction.

4.4 River transport (Pathways D, E and F)

Pathway D is the flux to the rivers of surface sediments formed by erosion (e.g. soils, gravels etc.). In a stable system, the mass of material eroded from the rocks to form sediments would equal the mass of sediment being removed by rivers and, over long time-periods, it is probably true that the mass of the surface sediments has been constant. Therefore, over a 10^8 year time-period, the elemental fluxes along pathway D would be roughly equal to those calculated for the 1st approximation to the erosion fluxes (Pathway A) and given in Table 4.1. Furthermore, in the long-term, the fluxes along pathways A and D will also approximate the fluxes along pathway E, the transport of material by rivers to the oceans.

On a shorter time-period of more relevance to PA (10^4 to 10^6 years), the rates of erosion and transport of sediments may be different to the long-term averages; for example, due to fluctuations in the rates of these processes caused by climate change. In this case, there may be a change in the total mass of sediment stored on land or in the river basins (it may either be accumulating or being eroded away). Thus, over the short-term, the elemental fluxes along Pathway A may not equal those along D or E.

Pathway F represents the transfer of solid material between the river water and the river sediments. This two-way situation occurs because deposition of material in river sediments is a temporary process which is dependent on the energy of the river. During periods of low energy (low river flow rates) material is deposited, however when the energy increases (flow rates increase) material is picked-up from the river bed by the river. River flow rates change, principally, in response to changes in precipitation and, thus, the net direction of transport along this pathway is controlled by changes in the seasons on a short time-period. However, over long time-periods, these fluctuations are evened-out and, on average, the mass of sediment stored in the river sediments will be constant when the system is in equilibrium. Therefore, over long periods, there would be no net flux along Pathway F.

A demonstration of temporary storage is given in Figure 4.3, which shows that, for a tributary of the Mississippi (the Coon Creek), the entire sediment budget for the period 1938 to 1975 does not travel along with the river water but is stored in local valleys.

Estimates of the mass of sediment stored in rivers are not precise and are based on the bedload transport within rivers. The bedload is the movement of material along the bottom of a river, material which is too large to be picked-up by the river but may be rolled or bounced along the bottom. This material will be transported so far down a river until the river widens or the topographic gradient decreases and the energy of the river drops. The bedload, therefore, is a first approximation to the mass of material stored in the Earth's river sediments.

It is worth noting that materials in surface sediments, especially soils, often have compositions that are substantially different from the rocks from which it is formed. This is because some elements are easily leached from the soils and so become depleted with respect to the parent rock while other elements may become enriched in the soils with respect to the parent rock because they are poorly soluble in the surface environment or they may be sorbed onto the organic and clay fractions of the soil. In addition, biologically-mediated processes will affect elemental distributions in organic-rich sediments. As a consequence of their variable behaviour, different elements will have different residence times in the sediments. These residence times have been determined for a few elements (e.g. plutonium and iodine in soils) but not for the majority of the elements considered here. Numerous analyses have been made of soils and average soil compositions are given in Section 2.3 (Table 2.18).

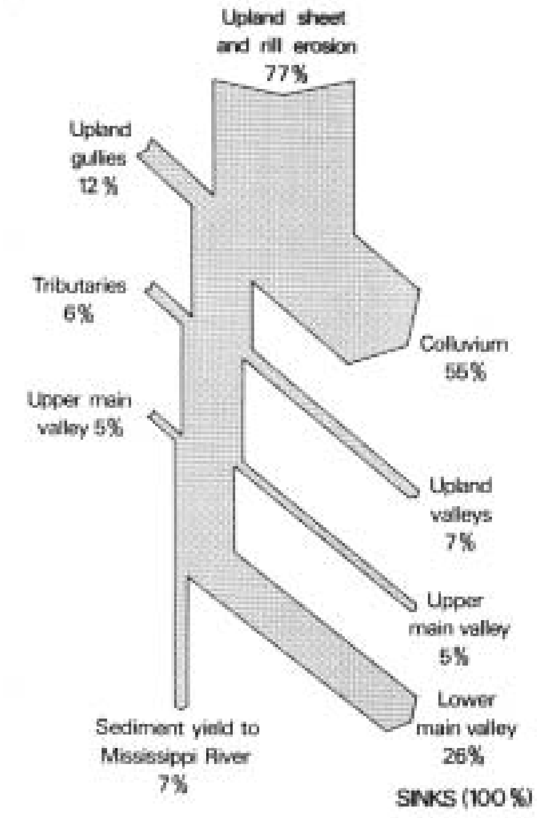

Figure 4.3: Sediment budget for the Coon Creek, Mississippi for the period 1938 to 1975. From Summerfield (1991).

Pathway E is the transport of sediment and dissolved species from the continents to the seas and oceans. As discussed in Section 3.4, several determinations have been made on the masses of solid material (suspended particulates) carried by the major rivers of the world (e.g. Holeman, 1968; Meybeck, 1977; Martin and Meybeck, 1979; Milliman and Meade, 1983; Meade, 1985; Milliman and Syvitski, 1992).

In addition, a number of analyses have been made on the dissolved components in these river waters but fewer have analysed the suspended load. As mentioned earlier, a comprehensive compilation of river transport data was carried-out by Martin and Meybeck (1979) who determined that the total masses of material carried by all the worlds rivers to the oceans are:

- solid load = 15.5×10^{12} kg/yr,
- dissolved load = 4.0×10^{12} kg/yr, and thus
- total load = 19.5×10^{12} kg/yr.

In addition, Martin and Meybeck also compiled the chemical analyses and determined the averages of the dissolved and particulate components of river water available up to that (see Chapter 2).

For the calculation of the elemental fluxes carried by the world's rivers, it is considered most accurate to use actual river water and sediment analyses (e.g. from Martin and Meybeck, 1979) rather than simply to assume equivalence with the erosion fluxes. Rivers transport material in three principal phases: dissolved, suspended and bedload. Since the variable chemical behaviour of elements means that they may be variously partitioned between these phases, the elemental fluxes associated with each phase is calculated separately below.

Dissolved river load

The fluxes of elements carried as dissolved load in the world's rivers can be calculated from the global average composition of river water and the global riverwater discharge rate. In Table 2.19, the best estimates of average elemental abundances in riverwater is provided from the compilation of elemental distributions in natural materials given in Section 2. Here, the elemental data are largely from Martin and Whitfield (1983) with a few exceptions (e.g. Se) when Martin and Whitfield (1983) did not provide relevant data.

The total annual water discharge from the world's major rivers has been estimated by Baumgartner and Reichel (1975) to be 3.7×10^4 km^3/yr and this value is used in these calculations. The calculated fluxes (per element) are shown in Table 4.6. These are expressed as a total mass flux, rather than as a flux per unit area because there is no sensible means of 'distributing' equally the river flow to all areas of the continental landmass.

Suspended river load

The fluxes of elements carried as suspended load in the world's rivers can be calculated from the global average composition of the suspended material and the global suspended material mass transport rate. The composition of the suspended material can be approximated in two ways. The first is based on measurements of suspended particle compositions as presented in Table 2.19, which is largely based on the data from Martin and Whitfield (1983). However, this composition is biased to the larger rivers these researchers investigated and may not be representative of the world average composition of suspended particles. The second approach is based on the assumption that suspended particles have the same composition as the upper crust (as given in Table 2.18), given that this is the source rock for the eroded material suspended in the rivers. As discussed in Section 3.4, the suspended material mass transport rate used in the calculations is the total river particulate load from Martin and Meybeck (1979) which has a value of 15.5×10^{12} kg/yr.

Two sets of flux calculations have been performed using both approaches to the suspended material composition from Table 2.19 and the river particulate load. The calculated fluxes (per element) are shown in Table 4.6. As with the dissolved load, these are expressed as a total mass flux, rather than as a flux per unit area.

Bedload

Global estimates of bedload are around 1.5×10^{12} kg/yr (Martin and Meybeck, 1979), although there is considerable uncertainty over this value. Since bedload material is generally comprised of fragments of rock (i.e. gravel, boulders etc.), it will have a composition which approximates to that of the upper crust, as given in Table 2.18, given that this is the source rock for the eroded material carried in rivers. The calculated fluxes (per element) are shown in Table 4.6. As with the dissolved and suspended loads, these are expressed as a total mass flux, rather than as a flux per unit area.

Table 4.6: Global elemental fluxes due to river transport as dissolved, suspended and bedload. Suspended* *is using the average suspended load composition from Table 2.19 and Suspended*§ *is using the upper crust composition from Table 2.18 for the suspended load composition. Total river flux is the addition of dissolved, suspended* and bedload.*

Element	**Riverwater dissolved flux (kg/yr)**	**Riverwater suspended* flux (kg/yr)**	**Riverwater suspended§ flux (kg/yr)**	**Bedload solid flux (kg/yr)**	**Total river elemental flux (kg/yr)**
C	4.07×10^{11}	5.02×10^{10}	5.02×10^{10}	4.86×10^{9}	4.62×10^{11}
Cl	2.59×10^{11}	9.92×10^{9}	9.92×10^{9}	9.60×10^{8}	2.70×10^{11}
K	5.55×10^{10}	3.10×10^{11}	4.44×10^{11}	4.30×10^{10}	4.08×10^{11}
Ni	1.85×10^{7}	1.40×10^{9}	2.95×10^{8}	2.85×10^{7}	1.44×10^{9}
Cu	5.55×10^{7}	1.55×10^{9}	2.95×10^{8}	2.85×10^{7}	1.63×10^{9}
Zn	1.11×10^{9}	3.88×10^{9}	9.61×10^{8}	9.30×10^{7}	5.08×10^{9}
Se	2.22×10^{6}	1.24×10^{7}	1.09×10^{6}	1.05×10^{5}	1.47×10^{7}
Rb	5.55×10^{7}	1.55×10^{9}	1.72×10^{9}	1.67×10^{8}	1.77×10^{9}
Cd	7.40×10^{5}	1.55×10^{7}	1.55×10^{6}	1.50×10^{5}	1.64×10^{7}
Sn	3.33×10^{5}	6.20×10^{7}	6.20×10^{7}	6.00×10^{6}	6.83×10^{7}
I	1.85×10^{8}	2.17×10^{7}	2.17×10^{7}	2.10×10^{6}	2.09×10^{8}
Nd	1.48×10^{6}	5.43×10^{8}	4.03×10^{8}	3.90×10^{7}	5.83×10^{8}
Sm	2.96×10^{5}	1.09×10^{8}	7.13×10^{7}	6.90×10^{6}	1.16×10^{8}
Pb	3.70×10^{6}	1.55×10^{9}	2.64×10^{8}	2.55×10^{7}	1.58×10^{9}
Th	3.70×10^{6}	2.17×10^{8}	1.63×10^{8}	1.58×10^{7}	2.36×10^{8}
U	8.88×10^{6}	4.65×10^{7}	4.19×10^{7}	4.05×10^{6}	5.94×10^{7}

Although the sediment and dissolved river transport values given by Martin and Meybeck (1979) are widely quoted in the literature, Milliman and Syvitski (1992) have suggested that they may not be representative of the long term average. Milliman and Syvitski (1992) suggest that, before the proliferation of dam construction in the latter half of the twentieth century, rivers probably discharged about 20×10^{12} kg/yr of suspended sediment to the oceans. Furthermore, prior to widespread farming and deforestation (beginning 2000 to 2500 years ago), suspended sediment discharge probably was less than half the present level; i.e. about 7×10^{12} kg/yr. In other words, modern river sediment loads seldom represent natural loads due to deforestation, poor soil management and urbanisation. The only probable exception to this are the rivers of the high Arctic where human civilisation has had little impact.

Since the aim of this study is to determine natural fluxes of elements to compare with repository releases, it may be argued that the sediment fluxes determined by Martin and Meybeck (1979) should not, therefore, be used because they do not represent truly natural conditions. However, it is possible (may be probable) that for a significant proportion of the next 10^4 to 10^4 years the sediment load in rivers will continue to be affected by the activities of Man and, because this is a period of significant assessment interest, it seems sensible to take this into account but recognising that these fluxes have been modified.

4.5 Ocean sedimentation (Pathway G)

Pathway G represents the transfer of material from the ocean water to the ocean sediments. Over long time-periods, the flux of material to the ocean sediments will equal the flux of materials carried to the oceans by the Earth's rivers (i.e. as given in Table 4.6) because the composition of the ocean waters has remained relatively constant over the last 1000 Ma (Martin and Whitfield, 1983). The material carried by rivers to the oceans arrives in both dissolved and solid form. In this case, atmospheric precipitation to the oceans is ignored. The solid material, will be dropped in the near-shore sediments as riverwater energy is rapidly dissipated at the estuary regions. Accumulations of sediment in the near-shore are sporadically transported and deposited to the ocean floor over the continental shelf in large material flows called turbidity currents.

In contrast to the solid material, the dissolved material will not, necessarily, be precipitated immediately in the estuary regions but is likely to be carried far into the oceans by the ocean currents. Eventually, however, all the dissolved species will be precipitated to the sea-floor. The residence time of the different dissolved elements in the ocean waters are given in Table 4.7.

Table 4.7: Residence times of elements in the oceans. The residence time for C is uncertain and is controlled by organic processes. From Bowen (1979).

Element	Residence time (yrs)
C	*
Cl	1000000
K	6800000
Ni	440000
Cu	3000
Zn	12000
Se	38000
Rb	4500000
Cd	40000
Sn	17000
I	1100000
Nd	700
Sm	280
Pb	380
Th	1200
U	300000

4.6 Discussion

Following these calculation of global scale elemental fluxes, a number of interesting points are worth highlighting. Perhaps the most notable feature of these calculated fluxes is their magnitude. Even for elements which are considered to be relatively uncommon in crustal rocks and natural waters, such as uranium which has an average concentration in granite of approximately 5 ppm [1 ppm = 1 mg/kg], the total amount of element moving around the world each year by natural processes is very large. As an example, the amount of uranium released from the upper crustal rocks by erosion is 124000 tonnes, which is rather more than the mass of uranium which may be emplaced in a typical spent fuel or HLW repository. The elemental flux due to the major processes are summarised in Table 4.8.

Table 4.8: Summary of the total global elemental fluxes due to erosion (Table 4.3), groundwater discharge (Table 4.4) and river transport (Table 4.6), together with a few comparisons between certain fluxes.

Element	**Total erosion flux (kg/yr)**	**Total groundwater flux (kg/yr)**	**Total river flux (kg/yr)**	**Groundwater flux as % of erosion flux**	**River flux as % of erosion + groundwater fluxes**
C	7.46×10^{11}	5.12×10^{11}	4.62×10^{11}	68.7	36.7
Cl	1.58×10^{10}	1.62×10^{12}	2.70×10^{11}	10284.9	16.5
K	6.96×10^{11}	1.61×10^{11}	4.08×10^{11}	23.2	47.7
Ni	2.21×10^{9}	4.02×10^{7}	1.44×10^{9}	1.8	64.0
Cu	2.60×10^{9}	2.10×10^{7}	1.63×10^{9}	0.8	62.3
Zn	3.40×10^{9}	2.04×10^{8}	5.08×10^{9}	6.0	141.0
Se	8.76×10^{6}	2.06×10^{6}	1.47×10^{7}	23.5	136.1
Rb	4.26×10^{9}	2.10×10^{8}	1.77×10^{9}	4.9	39.6
Cd	6.06×10^{6}	8.10×10^{5}	1.64×10^{7}	13.4	238.7
Sn	1.36×10^{8}	2.01×10^{6}	6.83×10^{7}	1.5	49.6
I	5.07×10^{8}	1.22×10^{8}	2.09×10^{8}	24.0	33.2
Nd	1.27×10^{9}	6.72×10^{5}	5.83×10^{8}	0.1	45.8
Sm	3.11×10^{8}	1.18×10^{5}	1.16×10^{8}	0.0	37.1
Pb	1.04×10^{9}	1.21×10^{7}	1.58×10^{9}	1.2	150.6
Th	4.76×10^{8}	1.26×10^{6}	2.36×10^{8}	0.3	49.6
U	1.24×10^{8}	4.20×10^{6}	5.94×10^{7}	3.4	46.5

An important observation is that the fluxes due to groundwater are generally only a small proportion (a few percent) of the fluxes due to erosion of the crustal rocks. The major exception to this is Cl but this is likely to be an artefact of the high Cl contents of the groundwater analyses reported in Section 2.2.2 which were biased by abnormal high-Cl hydrothermal waters. Examination of Cl contents in groundwaters from ‘normal’ groundwaters shows them to be several orders of magnitude lower. A similar explanation may explain the high I groundwater flux. The C groundwater flux is also high at almost 69 % and this is possibly due to recycling of surface-derived organic carbon in recharging groundwaters (and thus not derived from the crustal rocks). Cd, Se and K also exhibit relatively high groundwater fluxes. In the case of K, this may be due to the relatively fast degradation of K-bearing feldspars by groundwaters in shallow rocks. In contrast, for Cd and Se this could be the result of anthropogenic contamination of the groundwaters.

As discussed earlier and indicated in Figure 4.2, rivers are, by far, the predominant pathway for material to be transported to the oceans. Therefore, over long time periods, there should be a balance between the mass of material eroded from the land surface and discharged in groundwater compared to the mass of material transported in rivers. The data in Table 4.7 shows that for most elements there is an apparent shortfall in the river fluxes, which generally are only about 50 to 60% of the combined fluxes from erosion and groundwater. This would imply surface storage of these elements in the sediments on land or in the river basins. This is possibly a correct explanation, given that sediments have generally been accumulating on the landmass during the current interglacial period. However, it should be noted that this discrepancy between erosion and river transport fluxes may be an artefact of the data, which are unlikely to be very accurate. This is an example of the insensitivity of the method at the global scale, where it is not possible uniquely to interpret the difference in the input and output fluxes in the global system due to inherent inaccuracies and uncertainties in the input data.

In some cases, heavy metals show a larger river flux than erosion flux and this is very likely to be due to anthropogenic contamination being reflected in the river water chemical analyses reproduced in Section 2.

So far, the global scale fluxes have only been considered in terms of mass. However, as discussed in Section 1.2, it is possible to convert the mass fluxes for U, Th, K and Rb to activity fluxes. For U and Th, activity fluxes can be calculated for the radioelements alone (in normal isotopic proportions) as well as for their respective decay chains, assuming secular equilibrium in the chains and considering only the longer-lived nuclides with half-lives longer than one day. On the basis of the elemental mass fluxes given in Table 4.8, the activity fluxes have been calculated and are given in Table 4.9.

Table 4.9: Activity fluxes for the various processes for which global scale elemental fluxes have been calculated in this work. Total alpha is the total of the U and Th chain activities, and total non-alpha is total of K and Rb.

Nuclide or decay chain	Total erosion activity flux (Bq/yr)	Total groundwater activity flux (Bq/yr)	Total river activity flux (Bq/yr)
U (^{234}U, ^{235}U, ^{238}U)	3.2×10^{15}	1.1×10^{14}	1.5×10^{15}
Th (^{232}Th)	2.0×10^{15}	5.2×10^{12}	9.7×10^{14}
U chains	1.5×10^{16}	5.0×10^{14}	7.0×10^{15}
Th chain	7.8×10^{15}	2.1×10^{13}	3.9×10^{15}
K (^{40}K)	1.7×10^{16}	4.0×10^{15}	1.0×10^{16}
Rb (^{87}Rb)	3.8×10^{15}	1.9×10^{14}	1.6×10^{15}
Total alpha	2.3×10^{16}	5.2×10^{14}	1.1×10^{16}
Total non-alpha	2.1×10^{16}	4.2×10^{15}	1.2×10^{16}

These activity fluxes seem at first sight to be very large but it must be remembered that they are total activities over the entire continental land mass for each of the processes indicated. For the erosion fluxes, more useful values are the specific fluxes per unit area (km^2) for the land mass area (153×10^6 km^2), which are:

- total alpha flux = 1.5×10^8 Bq/km^2/yr, and
- total non-alpha = 1.4×10^8 Bq/km^2/yr.

For the groundwater fluxes, the specific activity fluxes are (assuming groundwater were to discharge equally over the land surface):

- total alpha flux = 3.4×10^6 Bq/km^2/yr, and
- total non-alpha = 2.8×10^7 Bq/km^2/yr.

For the river fluxes, useful values are the specific fluxes per unit volume (km^3) of river water discharge per year (3.7×10^4 km^3) which are:

- total alpha flux = 2.9×10^{11} Bq/km^3/yr, and
- total non-alpha = 3.2×10^{11} Bq/km^3/yr.

Of course these activity fluxes inherit the same uncertainty which is present in the input data. However, given that the input and output fluxes for the global system agree to within an order of magnitude, it is believed that it is reasonable to conclude that these activity flux values represent order of magnitude approximations to the actual global average values. As such they provide an extremely useful comparator to the activity releases from a repository calculated in PAs. These global average values will later be compared to the specific activity fluxes for the reference environment locations in which deep geological repositories may be located.

5 Reference environments

In the previous section, global elemental fluxes were calculated because they provide the best datum against which site or geological environment specific natural fluxes can be compared to evaluate if they are higher or lower than average and, thus, are useful for providing a more complete natural context for predicted repository releases. As discussed in Section 1.3, another scale which is relevant for investigation is the 'local' or 'catchment' scale around a repository because this may represent the same system, with the same rock, groundwater and surface conditions as those controlling the release and transport of contaminants from the repository.

At present, because very few actual repository locations have been identified and characterised in detail, it is not possible to calculate natural fluxes for specific disposal environments for comparison with predicted repository releases. As an alternative, therefore, this section has the objective of calculating fluxes at the catchment scale for a range of reference (or generic) environments which are designed to be representative of the types of locations which might potentially host a radioactive waste repository. The aim of these reference environment flux calculations is to quantify fluxes for processes which move material from the geosphere to the biosphere (essentially groundwater discharge and rock weathering) and for processes which move material across the surface (e.g. by water, wind and ice, as appropriate).

5.1 Defining reference environments

Reference environments are defined here largely on the basis of two parameters: geology and climate. Geology (rock type) controls the primary 'source term' for released elements in natural fluxes, while climate controls the 'driving force' for the fluxes by changing the nature of the processes which can occur and their rates (e.g. of erosion, groundwater flow etc). The types of geology and climate states that are considered in the reference environments are described in the following sections.

5.1.1 Geology

A starting point for the definition of the types of geology of interest to this study is the work of Chapman et al. (1986) who defined a number of geological environments which would be suitable for hosting a HLW repository. Although this work was done from a United Kingdom perspective, the geological environments identified are relatively general and at least one could be found in most countries.

The approach adopted by Chapman et al. (1986) to identify suitable geological environments was to concentrate on the definition of hydrogeology and geology, and on their potential containment characteristics. This is particularly relevant for this work because these are the same characteristics which largely influence geochemical fluxes, at least in the subsurface. The geological environments identified by Chapman et al. (1986) were:

- inland sedimentary basin,

- modified sedimentary basin limb,
- seaward-dipping and offshore sediments,
- low permeability basement under sedimentary cover,
- hard rocks in low relief coastal terrains, and
- small islands.

These geological environments are illustrated in Figure 5.1. For the purposes of this work, the three sedimentary environments (inland basin, modified basin limb and seaward-dipping sediments) can be considered together since the geological ('source term') control on natural fluxes in these environments is likely to be similar. Likewise, aspects of the low relief coastal terrains and small island can be considered together.

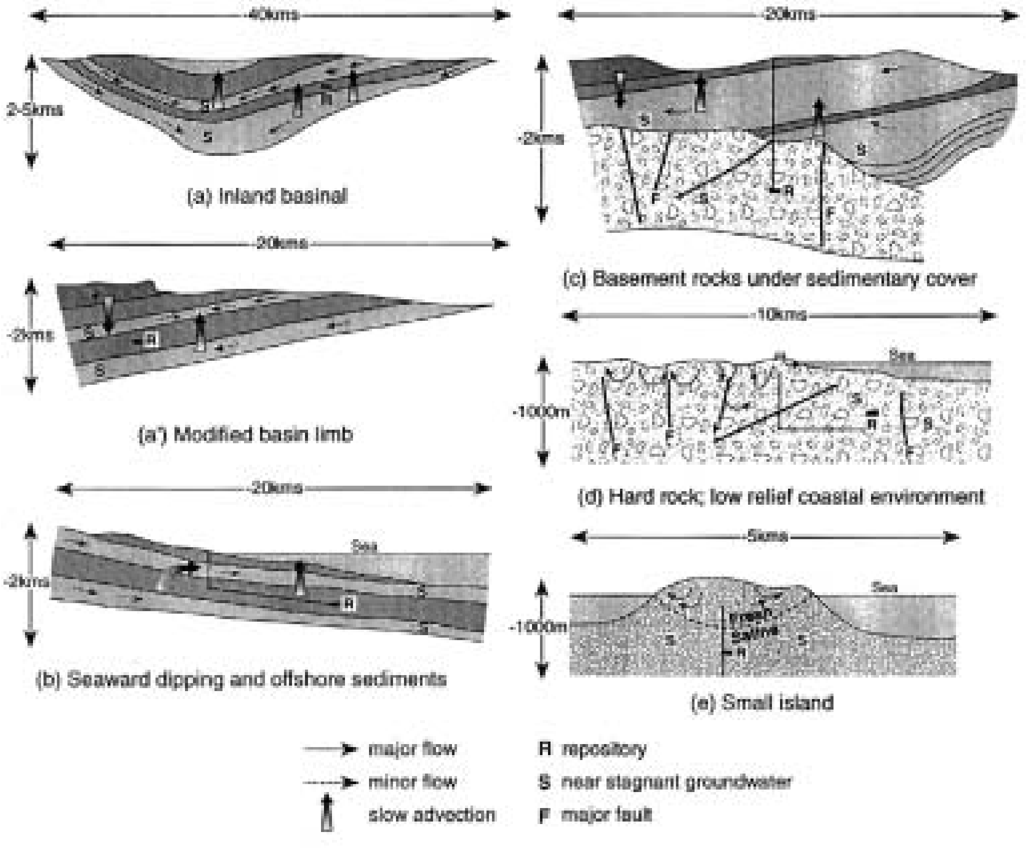

Figure 5.1: Potentially suitable environments for the deep disposal of long-lived radioactive waste. From Chapman et al. (1986).

By combining characteristics of these geological environments, three geological systems were identified which are considered to reflect the likely variability in natural fluxes at potential repository sites. These three geological systems are thus:

- an inland pluton with little or no sedimentary cover,
- a crystalline basement rock with sedimentary cover close to the coast, and

- a sedimentary basin.

In some cases, variants to each of these reference geological systems may be considered to reflect different rock compositions. For example, the inland pluton can be considered to be either granitic or gabbroic.

These three reference geological systems are variously combined with the different climate states described below to define a number of environments for which natural elemental concentrations and fluxes are quantified.

In addition, orebodies and geo/hydrothermal systems are also considered briefly even though they are unlikely ever to be considered as sites for a radioactive waste repository. These systems are considered here because they represent, respectively, locations with high flux and high concentration. They might, sensibly, then be considered to represent the upper bounds to elemental concentrations and fluxes in natural systems.

5.1.2 Climate

The three reference geological systems identified in the previous section can be found at many locations around the world, at different latitudes, and thus exposed to different climate states. Climate is a complex parameter to define and can be controlled on both a regional and local scale by features such as latitude, elevation, rainfall, temperature, distance from the coast, local topography etc. The major morphoclimatic zones around the world and their characteristics are presented in Table 5.1, based on information from Summerfield (1991), and their distribution is shown graphically in Figure 5.2.

The number of morphoclimatic zones and their parameters provide too many variables which could not sensibly be accounted for here in the definition of reference environments. Consequently, a simpler approach to the definition of climate was adopted based only on mean annual temperature and mean annual precipitation since, as was discussed in Chapter 3, these are dominant controls on the rates of many processes which drive natural fluxes, such as groundwater flow and weathering.

Table 5.1: The major morphoclimatic zones of the Earth. From Summerfield (1991).

Morphoclimatic zone	**Mean annual temperature (°C)**	**Mean annual precipitation (mm/yr)**	**Notes**
Humid tropical	20 - 30	> 1500	High potential rates of chemical weathering; mechanical weathering limited; highly active, episodic mass movement; moderate to low rates of stream corrasion but locally high rates of dissolved and suspended load transport.
Tropical wet-dry	20 - 30	600 - 1500	Chemical weathering active during wet season; rates of mechanical weathering low to moderate; mass movement fairly active; fluvial action high during wet season with overland and channel flow; wind action generally minimal but locally moderate in wet season.
Tropical semi-arid	10 - 30	300 - 600	Chemical weathering rates moderate to low; mechanical weathering locally active especially on drier and cooler margins; mass movement locally active but sporadic; fluvial action rates high but episodic; wind action moderate to high.

Morphoclimatic zone	Mean annual temperature (°C)	Mean annual precipitation (mm/yr)	Notes
Tropical arid	10 - 30	0 - 300	Mechanical weathering rates high; chemical weathering rates minimal; mass movement minimal; rates of fluvial activity generally very low but sporadic high; wind action at a maximum.
Humid mid-latitude	0 - 20	400 - 1800	Chemical weathering rates moderate, increasing to high at lower latitudes; mechanical weathering activity moderate with frost action important at higher latitudes; mass movement activity moderate to high; moderate rates of fluvial processes; wind action confined to coasts.
Dry continental	0 - 10	100 - 400	Chemical weathering rates low to moderate; mechanical weathering, especially frost action, seasonally active; mass movement moderate and episodic; fluvial processes active in wet season; wind action locally moderate.
Periglacial	< 0	100 - 1000	Mechanical weathering very active with frost action at a maximum; chemical weathering rates low to moderate; mass movement very active; fluvial processes seasonally active; wind action rates locally high.
Glacial	< 0	0 - 1000	Mechanical weathering rates (especially frost action) high; chemical weathering rates low; mass movement rates low except locally; fluvial action confined to seasonal melt; glacial action at a maximum; wind action significant.
Azonal mountain zone	Variable	Variable	Rates of all processes vary significantly with altitude; mechanical and glacial action become significant at high elevations.

On the basis of temperature and precipitation, five simple climate states were defined and, for each, a present-day representative city was identified which has approximately similar climatic conditions. These climate states are defined in Table 5.2.

*Table 5.2: The five climate states used to define reference environments for the local-scale flux calculations. *Godthab is not strictly glacial itself but is the largest settlement close to the edge of the Greenland icesheet.*

Climate state	Representative city or location	Mean annual temperature (°C)	Mean annual precipitation (cm/yr)	Principal erosion mechanism
Temperate	London	11	60	Water
Subarctic	Anchorage	2	40	Water/ice
Tropical	Hong Kong	25	220	Water
Desert	Las Vegas	20	10	Wind/water
Polar	Godthab*	-1.4	60	Ice

In this table, the principal erosion mechanism is simply defined as the medium (water, wind or ice) which dominates the weathering and erosion processes occurring at the surface, and the movement of material across the land surface. These five climate states are variously combined with the three reference geological systems identified earlier to define a number of environments for which natural elemental concentrations and fluxes are quantified.

Natural elemental fluxes are first calculated for the dominant processes which potentially can cause movement of material from the geosphere to the surface. These generally are:

- groundwater flow and discharge, and
- denudation of the surface rock.

These processes are highlighted because they are the most interesting for comparison with predicted repository releases when considering the four guidelines for the identification of relevant pathways discussed in Section 1.1.2. The calculations are presented in turn for the three reference geological systems presented earlier and considering various of the different climate states.

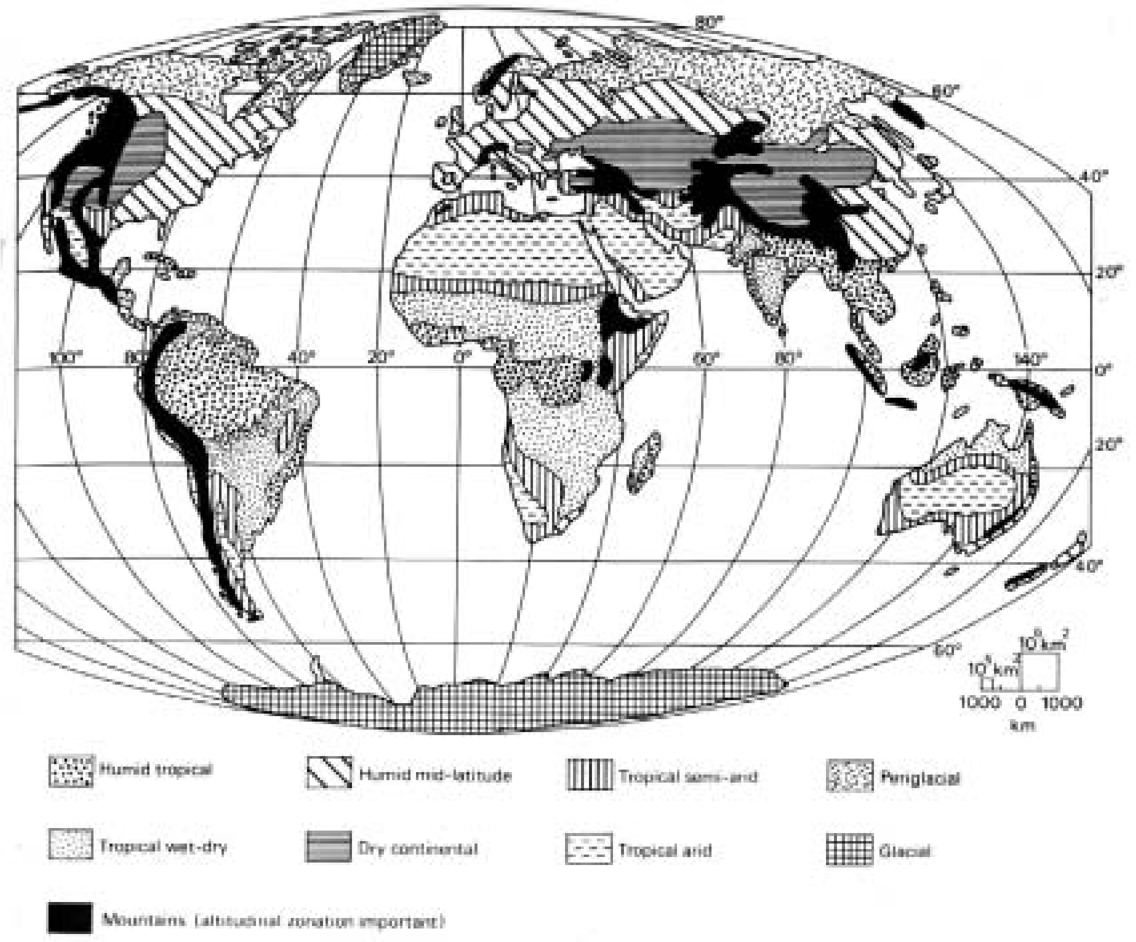

Figure 5.2: The global distribution of morphoclimatic zones on the Earth. From Summerfield (1991).

5.2 Inland pluton fluxes

Inland plutons are attractive as potential host rocks for a repository due to the very low permeabilities of crystalline rock and their potentially low hydraulic gradients (in the absence of significant surface topography). Thus plutonic rocks have been widely considered as repository host rocks in a number of site selection programmes in different countries (e.g. Sweden, Finland, Canada, UK and Spain).

Plutonic (intrusive igneous) rocks occur widely throughout the world and normally range in composition from granitic to gabbroic (acidic to basic) varieties. The essential differences between the pluton types concerns their mineral geochemistry, with basic rocks having potentially more advantageous geochemical attributes (greater redox buffering potential) in comparison with acidic rocks. In geologically inactive regions with low relief, plutonic rocks can be exposed at the surface, particularly in countries with areas of peneplained, old basement, such as is commonly found in Sweden, Finland and Canada. However, in regions which are geologically more active (such as Japan), exposed plutonic rocks are less common and plutons may be covered with thicknesses of recent sediments and sedimentary rocks.

For this reference environment, the pluton is assumed to lie inland (away from any coastal effects), in an area with low topographic relief environment and with only a relatively thin sediment cover. The pluton is roughly circular with a diameter of 25 km (an area of approximately 490 km^2). The structural geological setting is of a large syn-tectonic pluton which has been emplaced into metamorphic country rocks. The pluton is cut by semi-regular sets of joints, visible in outcrop, and also by larger-scale fracture zones. A simple cross section of the inland pluton reference environment is shown in Figure 5.3.

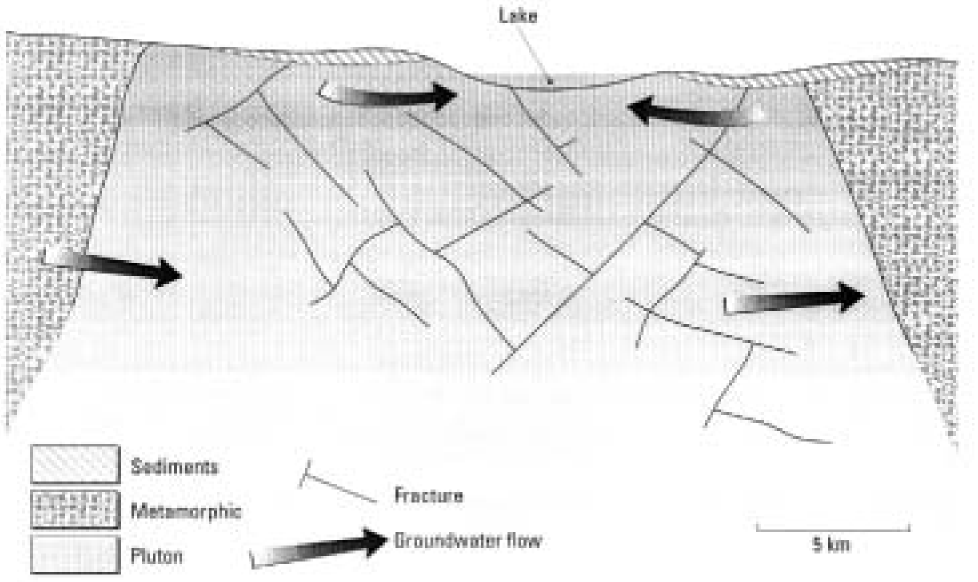

Figure 5.3: Cross section of the inland pluton reference environment.

The low relief means that there are only small head gradients to drive the groundwaters. This in combination with the low hydraulic conductivity of the rock means that the groundwaters move very slowly through the rock. These groundwaters are restricted to the hydraulically-active fractures which cut through the pluton and no groundwater movement occurs in the rock matrix itself, as discussed in Section 3.2. A feature of this environment is that, due to the topography, the pluton does not represent a closed groundwater flow system and is, instead, connected to the larger regional flow pattern. This means that not all of the groundwater recharging the pluton may be discharged locally.

The fractures and fracture zones exhibit multi-phase alteration and infilling. Hydrothermal alteration has resulted in sericitisation adjacent to the fractures. Fracture filling minerals consist of quartz, calcite, chlorite and mixed-layer clays. Reducing conditions are present at depth in the pluton while, in the shallow rock, there is a zone of altered rock, where oxidising, acidic waters are recharging.

The slow rate of deep groundwater movement means that these groundwaters have time to interact and reach chemical equilibrium with the rock. The concentrations of trace elements in these groundwater will thus be as high as thermodynamically possible. Shallow groundwaters will have shorter residence times and, consequently, will be dilute compared to the deeper, more saline waters.

Two geological variants are considered here: the first is a granitic pluton and the second is a gabbroic pluton. The variants are distinguished by the geochemistry of the rock mass in terms of the natural abundances of the elements in the rock. All five climate states are also considered for the flux calculations. The strength of the plutonic rock and the low topography combine to ensure that the rate of denudation of the pluton is relatively slow. Depending on the climate state, weathered material is added to the shallow sediment horizon and/or transported from the system by water, wind or ice.

The elemental abundances for the various materials in the inland pluton environment that are used in the flux calculations are shown in Table 5.3. These data have been derived from the compilation of elemental abundances in Chapter 2.

Table 5.3: Elemental abundances in the various materials present in the inland pluton reference environment.

Element	Granite (mg/kg)	Gabbro (mg/kg)	Soil (mg/kg)	Shallow groundwater (µg/l)	Deep groundwater (µg/l)
C	350	215	30000	15000	60000
Cl	200	390	100	27500	110000
K	33400	6000	14000	1500	6000
Ni	10	250	50	0.2	0.9
Cu	45	195	30	1.2	5
Zn	75	100	90	5	19
Se	0.05	0.05	0.5	0.1	0.3
Rb	150	32	150	12	50
Cd	0.2	0.2	0.35	0.02	0.05
Sn	3.5	1.2	2	0.01	0.03
I	10	10	5	2	8
Nd	44	32	35	0.04	0.16
Sm	9.5	7.3	4.5	0.01	0.028
Pb	87	5.5	20	0.1	0.3
Th	27	2.8	9	0.1	0.3
U	4.9	0.8	2	0.2	1

Groundwater flow and discharge

As discussed in Section 3.2, groundwater flow rates can be influenced by climate through the surface topography which controls the maximum potential hydraulic gradient (head) in the flow system. However, in the inland pluton environment, the low topographic relief means that the extent to which groundwater flow rates at depth can be modified by climate change is lessened, assuming there are no higher relief areas outside of the pluton driving the deep groundwater flow system.

Nonetheless, changing climate can significantly alter the local groundwater discharge rate within the pluton due to changes in the groundwater recharge. If recharge is low, then local groundwater discharge within the pluton could be zero if the water table falls below the land surface, meaning that groundwater discharge would occur some distance away as part of the regional groundwater flow system. In contrast, if recharge is high, then the water table will be raised, groundwater flow will be at a maximum and local groundwater discharge within the pluton is likely to occur to lakes and rivers. Excess precipitation will result only in additional surface runoff. In this case, local groundwater discharge within the area of the pluton would be a proportion of the recharge, with the remaining recharging groundwater joining the deep regional flow system and discharging outside of the pluton area.

In Section 3.2, typical hydraulic parameters for crystalline rocks at depths above and below 100 m were given, these were (from Savage, 1995):

- above 100 m, groundwater flux of 0.032 to 320 l/m^2/yr and a groundwater velocity of 0.0032 to 6.4 m/yr, and
- below 100 m, groundwater flux of 3×10^{-4} to 32 l/m^2/yr and a groundwater velocity of 3×10^{-5} to 3.2 m/yr.

For the deep, regional groundwater flow system, it can be assumed this flows in a roughly horizontal direction at a rate of between 3×10^{-4} and 32 l/m^2/yr (from the data above). This range is a consequence of the likely variation in the hydraulic characteristics of deep crystalline rocks. These flow rates suggest that the volume of water flowing through the deeper part of the pluton would be 3.8×10^{3} to 4.0×10^{8} l/yr, given a cross-sectional area for the deep pluton of approximately 12.5 km^2 [25 km pluton diameter × assumed depth of 0.5 km for the deep groundwater flow system]. These deep groundwaters would be likely to contain dissolved elemental abundances similar to those given in Table 5.3. On the basis of this groundwater composition and the range of groundwater flow rates, the elemental fluxes associated with the deep groundwater are calculated and presented in Table 5.4. The fluxes are given in units of g/m^2/yr for the horizontal groundwater flowing through the pluton.

Table 5.4: Elemental fluxes due to both deep and shallow groundwater flow through the inland pluton reference environment.

	Deep groundwater		**Shallow groundwater**	
Element	**Maximum (g/m^2/yr)**	**Minimum (g/m^2/yr)**	**Maximum (g/m^2/yr)**	**Minimum (g/m^2/yr)**
C	1.9	1.8×10^{-5}	4.8	4.8×10^{-4}
Cl	3.5	3.3×10^{-5}	8.8	8.8×10^{-4}
K	0.19	1.8×10^{-6}	0.48	4.8×10^{-5}
Ni	2.9×10^{-5}	2.7×10^{-10}	7.2×10^{-5}	7.2×10^{-9}
Cu	1.6×10^{-4}	1.5×10^{-9}	4.0×10^{-4}	4.0×10^{-8}
Zn	6.1×10^{-4}	5.7×10^{-9}	1.5×10^{-3}	1.5×10^{-7}
Se	9.6×10^{-6}	9.0×10^{-11}	2.4×10^{-5}	2.4×10^{-9}
Rb	1.6×10^{-3}	1.5×10^{-11}	4.0×10^{-3}	4.0×10^{-7}
Cd	1.6×10^{-6}	1.5×10^{-11}	4.0×10^{-6}	4.0×10^{-10}
Sn	9.6×10^{-7}	9.0×10^{-12}	2.4×10^{-6}	2.4×10^{-10}
I	2.6×10^{-4}	2.4×10^{-9}	6.4×10^{-4}	6.4×10^{-8}

	Deep groundwater		Shallow groundwater	
Element	**Maximum ($g/m^2/yr$)**	**Minimum ($g/m^2/yr$)**	**Maximum ($g/m^2/yr$)**	**Minimum ($g/m^2/yr$)**
Nd	5.1×10^{-6}	4.8×10^{-11}	1.3×10^{-5}	1.3×10^{-9}
Sm	9.0×10^{-7}	8.4×10^{-12}	2.2×10^{-6}	2.2×10^{-10}
Pb	9.6×10^{-6}	9.0×10^{-11}	2.4×10^{-5}	2.4×10^{-9}
Th	9.6×10^{-6}	9.0×10^{-11}	2.4×10^{-5}	2.4×10^{-9}
U	3.2×10^{-5}	3.0×10^{-10}	8.0×10^{-5}	8.0×10^{-9}

For the shallow groundwater flow system, it can be assumed this flows at a rate of between 0.032 and 320 $l/m^2/yr$ (from the data above). Some of this shallow groundwater may discharge to the surface within the pluton area, provided the water table is sufficiently high to allow local discharge to occur, in which case there would be a vertical component to the shallow groundwater flow. The shallow flowing groundwaters will have relatively short residence times and, thus, they would be likely to have low contents of dissolved elements. For these calculations, it is assumed they carry dissolved loads equal to one quarter of those in the deep groundwater, as indicated in Table 5.3. On the basis of this dilute groundwater composition and the range of groundwater flow rates, the elemental fluxes associated with the shallow groundwater are calculated and presented in Table 5.4. The fluxes are given in units of $g/m^2/yr$.

As discussed earlier, the fluxes given in Table 5.4 are essential unaffected by the changes in climate because there is little scope for increased or decreased precipitation to alter the hydraulic gradient in the absence of surface topography. However, the fluxes of elements carried in the groundwaters that actually discharge to the surface within the pluton may be affected. Unfortunately, it is very hard to quantify the amount of discharge that would occur in any particular environment, without detailed information on the hydrogeology and hydrology of the site.

One approach would be to consider the pluton as a closed hydrological system. While this is a gross assumption, which would not be correct for all plutons, it allows the discharge to be set equal to the recharge, assuming no change in groundwater storage volume. Recharge is typically a small proportion of precipitation, which is known for the different climate states (defined in Table 5.1). Actual recharge rates are hard to define for typical generic environments and no simple rule-of-thumb exists to quantify them. However, generally the proportion of precipitation which recharges the groundwater is small. In a recharge area, the simple water-balance equation is (Freeze and Cherry, 1979):

$$P = Q_s + R + E_R$$

Where P is precipitation, Q_s is surface water runoff, R is recharge and E_R is evapotranspiration. In most cases, Q_s and E_R dominate, and R will be only a few percent. As an indication, the total annual precipitation to the land surface is estimated to be between 99×10^3 and 119×10^3 km^3 while the corresponding annual recharge to the groundwaters has been estimated to be approximately 12×10^3 km^3 (Ward and Robinson, 1990). This means that the average rate of groundwater recharge for the continents is of the order of 10 to 12 % of the total precipitation but it could be expected that this is considerably variable.

Hydrological experience shows that practical controls on the recharge and local discharge rates include the nature of vegetation, thickness of soils, hydraulic conductivity of the near-surface rocks, and whether the precipitation occurs evenly throughout the year or in short, high rainfall events. This global average recharge proportion is heavily weighted by the large area of permeable sedimentary rocks exposed on the continental land surface. It would be expected that for crystalline rocks (such as the inland pluton) with much lower hydraulic conductivities than most sedimentary rocks, the proportion of precipitation which recharges would be considerably less than the global average.

In the absence of detailed water balance information, the best that can be achieved here is to estimate the recharge and local discharge proportions to the pluton for the different climate states. The values chosen for the calculations are:

- for the temperate climate, 5 % of precipitation recharges (high evapotranspiration due to abundant vegetation) and 50 % of this discharges locally to the pluton, with the remainder joining the deep regional flow system, giving a local discharge volume of 7.4×10^9 l/yr;
- for the subarctic climate, 3 % of precipitation recharges (high runoff) and 50 % of this discharges locally to the pluton, with the remainder joining the deep regional flow system, giving a local discharge volume of 2.9×10^9 l/yr;
- for the tropical climate, 15 % of precipitation recharges (equal to global average) and 50 % of this discharges locally to the pluton, with the remainder joining the deep regional flow system, giving a local discharge volume of 8.1×10^{10} l/yr;
- for the desert climate, 2 % of precipitation recharges (high evaporation) and none of this discharges locally to the pluton (depressed water table), so it all joins the deep regional flow system, giving a local discharge volume of 0 l/yr; and
- for the polar climate, 0 % of precipitation recharges (arrives as snow and accumulates on the ice sheet) giving a local discharge volume of 0 l/yr.

The local discharging groundwater is not likely to have penetrated to any depth in the inland pluton environment and so will have relatively short residence times and low contents of dissolved elements. As with the groundwater flow calculations above, it is assumed the locally discharging groundwaters carry dissolved loads equal to one quarter of those in the deep groundwater, as indicated in Table 5.3. On the basis of this dilute groundwater composition and the groundwater discharge volumes for the different climate states derived above, the elemental fluxes associated with the discharging shallow groundwater are calculated and presented in Table 5.5. The fluxes are given in units of kg/yr (as opposed to a flux per unit area as given for the fluxes associated with groundwater flow).

Table 5.5: Elemental fluxes due to groundwater discharge to the surface within the inland pluton reference environment for the different climate states.

Element	Temperate climate (kg/yr)	Subarctic climate (kg/yr)	Tropical climate (kg/yr)
C	$1.1\text{x}10^5$	$4.4\text{x}10^4$	$1.2\text{x}10^6$
Cl	$2.0\text{x}10^5$	$8.0\text{x}10^4$	$2.2\text{x}10^6$
K	$1.1\text{x}10^4$	$4.4\text{x}10^3$	$1.2\text{x}10^5$
Ni	1.67	0.65	18.23
Cu	9.25	3.63	101.25
Zn	35.15	13.78	384.75

Element	Temperate climate (kg/yr)	Subarctic climate (kg/yr)	Tropical climate (kg/yr)
Se	0.56	0.22	6.08
Rb	92.50	36.25	$1.0x10^3$
Cd	0.09	0.04	1.01
Sn	0.06	0.02	0.61
I	14.80	5.80	162.00
Nd	0.30	0.12	3.24
Sm	0.05	0.02	0.57
Pb	0.56	0.22	6.08
Th	0.56	0.22	6.08
U	1.85	0.73	20.25

In Table 5.5, no elemental fluxes are given for the desert and polar climate states because no groundwater discharges locally to the pluton surface in these conditions. In this case, all elemental fluxes associated with groundwater flow are associated with regional groundwater and will discharge elsewhere some distance from the pluton.

The groundwater discharge fluxes in Table 5.5 are given in terms of mass. However, it is possible to convert the mass fluxes for U, Th, K and Rb to alpha and non-alpha activity fluxes for individual radioelements and for their respective decay chains, assuming secular equilibrium in the chains. The details of the assumptions underlying these activity calculations were discussed in Section 1.2. On the basis of these assumptions, the activity fluxes for groundwater discharge in the inland pluton reference environment have been calculated and are given in Table 5.6.

Table 5.6: Activity fluxes for groundwater discharge in the inland pluton reference environment. Total alpha is the total of the U and Th chain activities, and total non-alpha is total of ^{40}*K and* ^{87}*Rb.*

Nuclide or decay chain	Temperate climate (Bq/yr)	Subarctic climate (Bq/yr)	Tropical climate (Bq/yr)
U (^{234}U, ^{235}U, ^{238}U)	4.8×10^7	1.9×10^7	5.2×10^6
Th (^{232}Th)	2.3×10^6	9.0×10^5	2.5×10^7
U chains	2.2×10^8	8.6×10^7	2.4×10^9
Th chain	9.2×10^6	3.6×10^6	1.0×10^6
K (^{40}K)	2.7×10^8	1.1×10^9	3.0×10^9
Rb (^{87}Rb)	8.2×10^7	3.2×10^7	8.9×10^6
Total alpha	2.3×10^8	9.0×10^7	2.5×10^9
Total non-alpha	3.5×10^8	1.1×10^9	3.9×10^9

These activity fluxes seem at first sight to be large but it must be remembered that they are total groundwater discharge activities over the entire inland pluton environment. Alternative values are the specific fluxes per unit area (km^2) for the pluton surface (490 km^2), assuming groundwaters were to discharge equally over the pluton. These specific activity fluxes are given in Table 5.7.

Table 5.7: Specific activity fluxes for groundwater discharge in the inland pluton reference environment, assuming discharge over the entire pluton surface area.

Activity	Temperate climate ($Bq/km^2/yr$)	Subarctic climate ($Bq/km^2/yr$)	Tropical climate ($Bq/km^2/yr$)
Total alpha	4.7×10^5	1.8×10^5	5.1×10^6
Total non-alpha	7.1×10^5	2.2×10^6	7.9×10^6

Denudation of the surface rock

The crystalline rock of the inland pluton (granite and gabbro variants) is relatively resistant to both physical and chemical weathering processes, in comparison to sedimentary rock types. However, the actual rate of weathering is strongly dependent on the climate state, as is the relative importance of chemical compared to physical weathering processes. As discussed in Section 3.3, mechanical disintegration is favoured by steep slopes and by the conditions characteristic of deserts and frost-affected regions, while chemical decomposition and solution are favoured by low-relief and by humid conditions, especially in tropical regions. This was shown graphically in Figure 3.4.

Table 5.8: The parameters used for the denudation flux calculation for the inland pluton reference environment.

Climate state	Total denudation rate (mm/ka)	Proportion chemical weathering (%)
Temperate	15	65
Subarctic	5	80
Tropical	1.5	50
Desert	5	10
Polar	340	0

For the inland pluton environment, potential average weathering (denudation) rates can be derived for the different climate states from the information given in Table 3.8 for low relief zones. As indicated in Table 3.7, granite is the most resistant of the rock types to weathering and, thus, it is sensible to take the lower estimates of denudation from Table 3.8 as the most appropriate for the inland pluton. The rate for glacial erosion is taken to be 340 mm/ka from the work of Kjeldsen (1981) which was discussed in Section 3.3. On this basis, the denudation rates that are adopted for the flux calculations are given in Table 5.8.

Table 5.9: Elemental fluxes due to total denudation of the rock surface for the different climate states at the inland pluton reference environment.

Element	Temperate climate ($g/m^2/yr$)	Subarctic climate ($g/m^2/yr$)	Tropical climate ($g/m^2/yr$)	Desert climate ($g/m^2/yr$)	Polar climate ($g/m^2/yr$)
Granite variant:					
C	1.4×10^{-2}	4.8×10^{-3}	1.4×10^{-3}	4.8×10^{-3}	0.33
Cl	8.3×10^{-3}	2.8×10^{-3}	8.3×10^{-4}	2.8×10^{-3}	0.19
K	1.4	0.46	0.14	0.46	31
Ni	4.1×10^{-4}	1.4×10^{-4}	4.1×10^{-5}	1.4×10^{-4}	9.4×10^{-3}
Cu	1.9×10^{-3}	6.2×10^{-4}	1.9×10^{-4}	6.2×10^{-4}	0.04

Element	Temperate climate (g/m^2/yr)	Subarctic climate (g/m^2/yr)	Tropical climate (g/m^2/yr)	Desert climate (g/m^2/yr)	Polar climate (g/m^2/yr)
Zn	3.1x10^{-3}	1.0x10^{-3}	3.1x10^{-4}	1.0x10^{-3}	0.07
Se	2.1x10^{-6}	6.9x10^{-7}	2.1x10^{-7}	6.9x10^{-7}	4.7x10^{-5}
Rb	6.2x10^{-3}	2.1x10^{-3}	6.2x10^{-4}	2.1x10^{-3}	0.14
Cd	8.3x10^{-6}	2.8x10^{-6}	8.3x10^{-7}	2.8x10^{-6}	1.9x10^{-4}
Sn	1.4x10^{-4}	4.8x10^{-5}	1.4x10^{-5}	4.8x10^{-5}	3.3x10^{-3}
I	4.1x10^{-4}	1.4x10^{-4}	4.1x10^{-5}	1.4x10^{-4}	9.4x10^{-3}
Nd	1.8x10^{-3}	6.1x10^{-4}	1.8x10^{-4}	6.1x10^{-4}	0.04
Sm	3.9x10^{-4}	1.3x10^{-4}	3.9x10^{-5}	1.3x10^{-4}	8.9 x10^{-3}
Pb	3.6x10^{-3}	1.2x10^{-3}	3.6x10^{-4}	1.2x10^{-3}	0.08
Th	1.1x10^{-3}	3.7x10^{-4}	1.1x10^{-4}	3.7x10^{-4}	0.03
U	2.0x10^{-4}	6.7x10^{-5}	2.0x10^{-5}	6.7x10^{-5}	4.6x10^{-3}
Gabbro variant:					
C	8.9x10^{-3}	3.0x10^{-3}	8.9x10^{-4}	3.0x10^{-3}	0.20
Cl	0.02	5.4x10^{-3}	1.6x10^{-3}	5.4x10^{-3}	0.36
K	0.25	0.08	0.03	0.08	5.6
Ni	0.01	3.4x10^{-3}	1.0x10^{-3}	3.4x10^{-3}	0.23
Cu	8.0x10^{-3}	2.7x10^{-3}	8.0x10^{-4}	2.7x10^{-3}	0.18
Zn	4.1x10^{-3}	1.4x10^{-3}	4.1x10^{-4}	1.4x10^{-3}	0.09
Se	2.1x10^{-6}	6.9x10^{-7}	2.1x10^{-7}	6.9x10^{-7}	4.7x10^{-5}
Rb	1.3x10^{-3}	4.4x10^{-4}	1.3x10^{-4}	4.4x10^{-4}	0.03
Cd	8.3x10^{-6}	2.8x10^{-6}	8.3x10^{-7}	2.8x10^{-6}	1.9x10^{-4}
Sn	5.0x10^{-5}	1.7x10^{-5}	5.0x10^{-6}	1.7x10^{-5}	1.1x10^{-3}
I	4.1x10^{-4}	1.4x10^{-4}	4.1x10^{-5}	1.4x10^{-4}	9.4x10^{-3}
Nd	1.3x10^{-3}	4.4x10^{-4}	1.3x10^{-4}	4.4x10^{-4}	0.03
Sm	3.0x10^{-4}	1.0x10^{-4}	3.0x10^{-5}	1.0x10^{-4}	6.8x10^{-3}
Pb	2.3x10^{-4}	7.6x10^{-5}	2.3x10^{-5}	7.6x10^{-5}	5.1x10^{-3}
Th	1.2x10^{-4}	3.9x10^{-5}	1.2x10^{-5}	3.9x10^{-5}	2.6x10^{-3}
U	3.3x10^{-5}	1.1x10^{-5}	3.3x10^{-6}	1.1x10^{-5}	7.5x10^{-4}

Given these denudation rates and assuming that the pluton has variant compositions of granite and gabbro, as given in Table 5.3, and a density of 2750 kg/m^3, the elemental fluxes are calculated and presented in Table 5.9 for total erosion. The elemental fluxes due to just chemical weathering can be calculated from the total weathering fluxes using the proportions given in Table 5.8.

The denudation fluxes in Table 5.9 are given in terms of mass. However, it is possible to convert the mass fluxes for U, Th, K and Rb to alpha and non-alpha activity fluxes for individual radioelements and for their respective decay chains, assuming secular equilibrium in the chains. The details of the assumptions underlying these activity calculations were discussed in Section 1.2. On the basis of these assumptions, the activity fluxes for denudation of the inland pluton reference environment have been calculated and are given in Table 5.10. The activity fluxes in Table 5.10 are given in units of Bq/m^2/yr. To compare with the activity fluxes due to groundwater discharge calculated earlier, the total alpha and total non-alpha fluxes are recast as specific fluxes per unit area (km^2) for both total and chemical weathering, assuming the chemical weathering proportions given in Table 5.8, and the results are given in Table 5.11.

Table 5.10: Activity fluxes for denudation of the inland pluton reference environment. Total alpha is the total of the U and Th chain activities, and total non-alpha is ^{40}K plus ^{87}Rb.

Nuclide or decay chain	**Temperate climate ($Bq/m^2/yr$)**	**Subarctic climate ($Bq/m^2/yr$)**	**Tropical climate ($Bq/m^2/yr$)**	**Desert climate ($Bq/m^2/yr$)**	**Polar climate ($Bq/m^2/yr$)**
Granite variant:					
U (^{234}U, ^{235}U, ^{238}U)	5.1	1.7	0.51	1.7	120
Th (^{232}Th)	4.5	1.5	0.45	1.5	120
U chains	24.0	7.9	2.4	7.9	540
Th chain	18.0	6.1	1.8	6.1	490
K (^{40}K)	35.0	11.0	3.5	11.0	760
Rb (^{87}Rb)	5.5	1.9	0.55	1.9	120
Total alpha	42.0	14.0	4.2	14.0	1000
Total non-alpha	40.0	13.0	4.0	13.0	890
Gabbro variant:					
U (^{234}U, ^{235}U, ^{238}U)	0.85	0.28	0.08	0.28	19.0
Th (^{232}Th)	0.49	0.16	0.05	0.16	11.0
U chains	3.9	1.3	0.39	1.3	88.0
Th chain	2.0	0.64	0.20	0.64	43.0
K (^{40}K)	6.2	2.0	0.74	2.0	140.0
Rb (^{87}Rb)	1.2	0.39	0.12	0.39	27.0
Total alpha	5.9	1.9	0.59	1.9	130.0
Total non-alpha	7.3	2.4	0.86	2.4	160.0

Comparison of the specific activity fluxes due to denudation (Table 5.11) and due to groundwater discharge (Table 5.7) for the inland pluton environment, shows that those due to denudation are typically one to two orders of magnitude larger than those due to groundwater discharge. The exceptions are the desert and polar climates in which no groundwater discharge was assumed to occur.

Table 5.11: Specific activity fluxes for denudation in the inland pluton reference environment for both total denudation and chemical weathering.

Nuclide or decay chain	**Temperate climate ($Bq/km^2/yr$)**	**Subarctic climate ($Bq/km^2/yr$)**	**Tropical climate ($Bq/km^2/yr$)**	**Desert climate ($Bq/km^2/yr$)**	**Polar climate ($Bq/km^2/yr$)**
Granite variant - total denudation:					
Total alpha	4.2×10^7	1.4×10^7	4.2×10^6	1.4×10^7	1.0×10^9
Total non-alpha	4.0×10^7	1.3×10^7	4.0×10^6	1.3×10^7	8.9×10^8
Granite variant - chemical weathering:					
Total alpha	2.7×10^7	1.1×10^7	2.1×10^6	1.4×10^6	0
Total non-alpha	2.6×10^7	1.0×10^7	2.0×10^6	1.3×10^6	0
Gabbro variant - total denudation:					
Total alpha	5.9×10^6	1.9×10^6	5.9×10^5	1.9×10^6	1.3×10^8
Total non-alpha	7.3×10^6	2.4×10^6	8.6×10^5	2.4×10^6	1.6×10^8
Gabbro variant - chemical weathering:					
Total alpha	3.8×10^6	1.5×10^6	3.0×10^5	1.5×10^6	0
Total non-alpha	4.8×10^6	1.9×10^6	4.3×10^5	1.9×10^6	0

The activity flues due to denudation of the granite are approximately 7 times larger than those for the gabbro. The reason for this is that the radioelements U, Th, K and Rb are all more concentrated in acidic igneous rocks such as granites than they are in basic igneous rocks such as gabbro. This can be seen in the data in Table 5.3 where, for example, U is present in granite at 4.9 mg/kg but only at 0.8 mg/kg in the gabbro. A further interesting observation from Table 5.11, is that the total alpha and total non-alpha activity fluxes due to denudation of the inland pluton (particularly the granite variant) are very similar. This is coincidental and due to the relative proportions in the rock of the radioelements U, Th, K and Rb.

5.3 Crystalline basement rock with sedimentary cover fluxes

The crystalline basement under sedimentary cover environment (sometimes referred to as ‘BUSC’) was first proposed by Chapman et al. (1986) and has been investigated in detail as a potential repository host environment in a number of countries, such as the UK, France and Switzerland. The potential advantages of this type of environment, over and above those expected from a crystalline rock exposed at the surface, are dependent on the thickness and lithologies of the overlying sediments and the expected hydraulic connection between the basement rocks and the sediments. Scoping calculations generally suggest that very long groundwater travel times could be expected in situations where the overlying sediments were relatively flat lying and where there was an alternation of sediment lithologies to produce large hydraulic anisotropies, i.e. a ‘layer cake’ type stratigraphy of alternating formations with high and low hydraulic conductivities. Overlying sediments with high hydraulic conductivities may have a beneficial safety role because they tend to insulate the underlying basement from topographically-driven flow (by acting as a partial hydraulic cage) and can provide a large potential for dilution of radionuclides migrating from the crystalline basement rock.

Crystalline basement under sedimentary cover environments occur in many countries and can exhibit considerable variation. The basement crystalline rocks can comprise regional scale metamorphic rocks or smaller scale intrusive (igneous) plutons, or a mixture of both. As a consequence, the basement rocks can vary in composition from acidic to basic. The overlying sediments can be equally variable and may include shales, sandstones, limestones etc. In certain volcanically active locations, such as parts of Japan, it is possible for the sedimentary sequences to be interlayered with volcanic lithologies. The thickness of the sedimentary cover can be variable but, to have a significant role in safety, would need to be more than around 100 m thick.

For this reference environment, the basement crystalline rock under sedimentary cover geological system is assumed to be in a coastal setting in an area with moderate topographic relief. The crystalline rocks are taken to be basic metasediments with a composition equal to that of ‘gneiss’ from Table 2.18. In the inland, upland areas, the basement rocks are exposed at the surface where the sediments have been eroded away. The crystalline rocks will be cut by semi-regular sets of joints and by larger-scale fracture zones. The overlying sediments are taken to be 200 m thick, with beds with varying hydraulic conductivity, although for simplicity are all assumed to have a composition equal to that of ‘shale’ from Table 2.18. In reality, the sedimentary sequences may be considerably more complicated and may comprise many different lithologies, from two or more phases of deposition separated by a angular unconformities. A simple cross-section of the basement under sedimentary rock reference environment is shown in Figure 5.4.

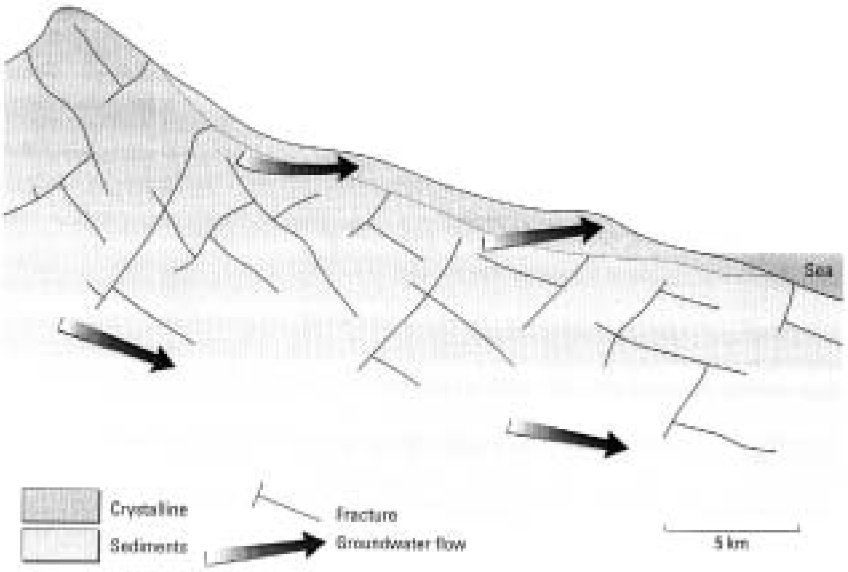

Figure 5.4: Cross-section of the basement under sedimentary rock reference environment.

The surface topography in this reference environment is of moderate relief, with the upland areas reaching a maximum altitude of 300 m above sea level. The uplands create a valley or ‘basin’ opening to the sea, creating a small, closed catchment area with dimensions of approximately 20 km × 15 km. Surface drainage takes place by a single river system discharging to the sea. Groundwater flow in the crystalline basement rock is restricted to the hydraulically-active fractures, with groundwater flow driven by the hydraulic head gradient created by the inland, upland areas. Due to the generally low hydraulic conductivity of the crystalline rock, the groundwater flow rates will be relatively slow. Groundwater flow in the sedimentary sequences will occur throughout the rock matrix, which acts as a porous medium. Flow will be concentrated in the layers with higher hydraulic conductivity where it will take place significantly faster than in the basement rocks. No geological variants are considered here, although all five climate states defined in Table 5.2 are considered. The elemental abundances that are used in the flux calculations are shown in Table 5.12. These data have been derived from the compilation of elemental abundances in Chapter 2.

Table 5.12: Elemental abundances in the various materials present in the basement under sedimentary cover reference environment.

Element	**Gneiss (mg/kg)**	**Shale (mg/kg)**	**Soil (mg/kg)**	**Crystalline groundwater (μg/l)**	**Sedimentary groundwater (μg/l)**
C	260	30000	30000	60000	125000
Cl	450	400	100	110000	400000
K	10000	20000	14000	6000	40000

Element	Gneiss (mg/kg)	Shale (mg/kg)	Soil (mg/kg)	Crystalline groundwater (µg/l)	Sedimentary groundwater (µg/l)
Ni	10	65	50	0.9	10
Cu	100	45	30	5	5
Zn	95	105	90	19	50
Se	0.05	0.5	0.5	0.3	0.5
Rb	75	140	150	50	50
Cd	0.1	0.2	0.35	0.05	0.2
Sn	2.2	6	2	0.03	0.5
I	10	12	5	8	30
Nd	35	29	35	0.16	0.16
Sm	8.5	7.5	4.5	0.028	0.028
Pb	19	23	20	0.3	3
Th	16	12	9	0.3	0.3
U	3.2	3.5	2	1	1

Groundwater flow and discharge

In contrast to the inland pluton, the basement under sedimentary cover environment has greater topographic relief (maximum 300 m above sea level). The inland, upland area will generally act as a recharge zone, and the effect of changing climate (precipitation) will be to raise or lower the water table in the upland area and, thus, the hydraulic gradient (head) acting on the groundwater flow system. For simplicity, it is assumed that the head during the temperate climate is close to the maximum possible from the topography (i.e. 300 m) and during climates with less precipitation, the head is proportional to rainfall, as indicated in Table 5.13. For the tropical climate, with high precipitation (220 cm/yr), the excess water above that need to maintain maximum head simply adds to surface runoff. Although, in reality, other factors (such as vegetation) will complicate this picture by changing the proportion of precipitation that recharges the groundwater, this is both a simple and a useful approach to evaluating the impact of climate (precipitation) on groundwater flow.

As discussed in Section 3.2, the groundwater flux ($l/m^2/yr$) through the rock is proportional to the hydraulic gradient, according to the formula:

- groundwater flux = hydraulic conductivity $\times$ gradient

Consequently, to calculate the elemental fluxes occurring in the groundwater for different climates, the simplest approach is to calculate fluxes for the temperate climate (maximum groundwater flux) and then scale these proportionally to the different in heads for the various climate states (i.e. fluxes in the subarctic climate will be two thirds of the fluxes in the temperate climate). This assumes no change in groundwater composition with climate which, again, may not strictly be true but assuming adequate time in all cases for rock-water interactions to occur, the groundwater compositions towards the ends of the flow paths should be similar for all climates.

However, this approach does not work for the polar climate because, on a land area covered by a warm-bottomed ice-sheet, the thickness of the ice effectively becomes the hydraulic head (if the ice-sheet thickness is greater than the height of the topography of the land). If the ice-sheet is relatively flat over the region, then there is no significant hydraulic gradient despite the topography of the land surface. Thus, for the polar climate, the actual head will be very small and is assumed to be 10 m.

These hydraulic conditions for the different climates mean that, in all but the driest climate, some proportion of the groundwater can be expected to discharge to the surface and comprise part of the input to the river system.

Table 5.13: The five climate states and the impact on hydraulic head in the basement under sedimentary cover reference environment.

Climate state	**Mean annual precipitation (cm/yr)**	**Head (m)**
Temperate	60	300
Subarctic	40	200
Tropical	220	300
Desert	10	50
Polar	60	10

The contrasting hydraulic characteristics of the basement crystalline rocks and the overlying sedimentary rocks means essentially that two different groundwater flow systems occur, although some mixing between the two will be inevitable. In Section 3.2, typical hydraulic parameters were given for crystalline rocks at depths below 100 m and for sedimentary rocks (assuming data for shales and mudstones) above and below 100 m, these are (from Savage, 1995):

- crystalline rock below 100 m, groundwater flux of 3×10^{-4} to 32 l/m^2/yr and a groundwater velocity of 3×10^{-5} to 3.2 m/yr,
- sedimentary rock above 100 m, groundwater flux of 1.6 to 6400 l/m^2/yr and a groundwater velocity of 0.008 to 21 m/yr, and
- sedimentary rock below 100 m, groundwater flux of 0.16 to 640 l/m^2/yr and a groundwater velocity of 0.003 to 2.6 m/yr.

For the groundwater flow system in the upper portion of the basement rock, a median value from the ‘crystalline rock’ hydraulic parameters would be an adequate representation of the likely flow system. This is because these basement rocks, although now buried by the sediments, would previously have been exposed to the surface and the upper portion of the rock would have experienced some degree of destressing and fracturing. Thus for the crystalline basement rocks, a groundwater flux of 1×10^{-2} l/m^2/yr and a groundwater velocity of 1×10^{-3} m/yr are assumed for the temperate climate, and, for the other climates, the groundwater fluxes are scaled as discussed earlier.

The groundwaters in the basement crystalline rock would be likely to contain dissolved elemental abundances similar to those given for ‘crystalline groundwater’ in Table 5.12. On the basis of this groundwater composition and the groundwater flow rate assumed above, the elemental fluxes associated with the basement groundwater are calculated and presented in Table 5.14. The fluxes are given in units of g/m^2/yr for the groundwater flowing through the basement rock.

For the sedimentary rock, it is clear from the hydraulic parameters from Savage (1995) above, that there is considerable variation and that the range in the parameters for shallow rock overlaps that for the deep rock. This is not at all surprising given that sedimentary rocks can be extremely heterogeneous in both the vertical and horizontal directions, resulting from changes in environmental conditions during and subsequent to sedimentation. Given this, it is more sensible to assign the range in hydraulic parameters to the alternating formations with high and low hydraulic conductivities, rather than simply to depth. Therefore, median values from the deep and shallow sedimentary rock ranges are assigned to the high and low hydraulic conductivity layers. Thus for the high hydraulic conductivity sedimentary layers, a groundwater flux of 3000 l/m^2/yr and a groundwater velocity of 10 m/yr are assumed, and for the low hydraulic conductivity layers, a groundwater flux of 100 l/m^2/yr and a groundwater velocity of 1 m/yr are assumed. These values are for the temperate climate and, for the other climates, the groundwater fluxes are scaled as discussed earlier.

The groundwaters in the overlying sedimentary rock would be likely to contain dissolved elemental abundances similar to those given for ‘sedimentary groundwater’ in Table 5.12. No distinction is made between the composition of groundwaters in the high and low hydraulic conductivity layers. On the basis of this groundwater composition and the groundwater flow rates assumed above, the elemental fluxes associated with the groundwater in the sedimentary rocks are calculated and presented in Table 5.14. The fluxes are given in units of g/m^2/yr for the groundwater flowing through the high and low hydraulic conductivity layers.

Table 5.14: Elemental fluxes due to groundwater flow in both the crystalline and sedimentary rocks in the basement under sedimentary cover reference environment for the temperate and tropical climates.

Element	**Crystalline rock groundwater (g/m^2/yr)**	**High *k* sedimentary rock groundwater (g/m^2/yr)**	**Low *k* sedimentary rock groundwater (g/m^2/yr)**
C	6.0×10^{-4}	375	12.50
Cl	1.1×10^{-3}	1.2×10^{3}	40
K	6.0×10^{-5}	120	4
Ni	9.0×10^{-9}	0.03	1.0×10^{-3}
Cu	5.0×10^{-8}	0.02	5.0×10^{-4}
Zn	1.9×10^{-7}	0.15	5.0×10^{-3}
Se	3.0×10^{-9}	1.50×10^{-3}	5.0×10^{-5}
Rb	5.0×10^{-7}	0.15	5.0×10^{-3}
Cd	5.0×10^{-10}	6.0×10^{-4}	2.0×10^{-5}
Sn	3.0×10^{-10}	1.5×10^{-3}	5.0×10^{-5}
I	8.0×10^{-8}	0.09	3.0×10^{-3}
Nd	1.6×10^{-9}	4.8×10^{-4}	1.6×10^{-5}
Sm	2.8×10^{-10}	8.4×10^{-5}	2.8×10^{-6}
Pb	3.0×10^{-9}	9.0×10^{-3}	3.0×10^{-4}
Th	3.0×10^{-9}	9.0×10^{-4}	3.0×10^{-5}
U	1.0×10^{-8}	3.0×10^{-3}	1.0×10^{-4}

As mentioned earlier, the elemental fluxes due to groundwater flow in the other climate states can be approximated by proportionately scaling the elemental fluxes for the temperate climate according to the differences in assumed head according to Table 5.13. On this basis the scaling factors for the climate states are:

- temperate, 1
- subarctic, 0.67 (two thirds)
- tropical, 1
- desert, 0.16 (one sixth), and
- polar, 0.03 (one thirtieth).

However, it should be recognised that these are approximations based on the assumptions described earlier and that they relate to assumed steady state conditions. As conditions change, it could be expected that the groundwater flow rates may alter quite rapidly. This is particularly true for the polar climate. Here it is assumed a polar climate involves a permanent ice-sheet.

However, during advance or retreat of the ice-sheet, considerable perturbances to the groundwater flow system would be inevitable and may involve fresh, oxygenating waters penetrating to considerable depth. Therefore, in a change to or from a polar climate, the groundwater flow systems may be considerably faster than assumed here, although, if the groundwater was dilute, the associated elemental fluxes could still be low.

Turning now to the fluxes of elements associated with the groundwater which discharges to the surface, these also will be affect by the changing climate. However, realistically, it is hard to quantify the amount of discharge which would occur in any particular system without detailed information on the hydrogeology and hydrology of the site. In this case, the topographic relief of the basement under sedimentary cover environment means that it is effectively a closed hydrological system.

As was discussed earlier for the inland pluton environment, discharge can be estimated from likely proportions of precipitation which recharge the groundwaters (recharge = discharge in a steady state system). In this system, the recharge will occur predominantly in the upland areas which comprise the exposed crystalline rocks (gneiss). Gneiss has similar hydrogeological properties to the granite and, thus, the recharge estimates for the inland pluton could also be applied to the crystalline rock in this environment. The area of the upland recharge zone is assumed to be one third of the area of the total reference environment, i.e. 100 km^2.

Unlike the inland pluton, most of the recharge water will be discharged to the surface in this environment. In the pluton situation, because it was not a closed hydrogeological system, approximately half of the recharge water was assumed to join the deep, regional flow system and be discharged outside of the pluton area. In contrast, here it is assumed that typically 90 % of recharge waters will be discharged to the surface, with the remaining 10 % discharging to the sea floor. Using these assumptions, the estimates for recharge and discharge groundwater volumes for the different climate states are:

- for the temperate climate, 5 % of precipitation recharges (high evapotranspiration due to abundant vegetation) and 90 % of this discharges locally to the surface, with the remainder discharging to the sea, giving a local discharge volume of 2.7×10^9 l/yr;

- for the subarctic climate, 3 % of precipitation recharges (high runoff) and 90 % of this discharges locally to the surface, with the remainder discharging to the sea, giving a local discharge volume of 1.1×10^{9} l/yr;
- for the tropical climate, 15 % of precipitation recharges (equal to global average) and 90 % of this discharges locally to the surface, with the remainder discharging to the sea, giving a local discharge volume of 3.0×10^{10} l/yr;
- for the desert climate, 2 % of precipitation recharges (high evaporation) and 50 % of this discharges locally to the surface (depressed water table), with the remainder discharging to the sea, giving a local discharge volume of 1.1×10^{8} l/yr; and
- for the polar climate, 0 % of precipitation recharges (arrives as snow and accumulates on the ice sheet) giving a local discharge volume of 0 l/yr.

The local discharging groundwater is assumed to carry dissolved loads equal to those in the ‘crystalline’ groundwater, as indicated in Table 5.12. On the basis of this groundwater composition and the groundwater discharge volumes for the different climate states derived above, the elemental fluxes associated with the discharging groundwater are calculated and presented in Table 5.15. The fluxes are given in units of kg/yr (as opposed to a flux per unit area as given for the fluxes associated with groundwater flow).

Table 5.15: Elemental fluxes due to groundwater discharge to the surface within the basement under sedimentary cover reference environment for the different climate states.

Element	Temperate climate (kg/yr)	Subarctic climate (kg/yr)	Tropical climate (kg/yr)	Desert climate (kg/yr)
C	1.6×10^{5}	6.6×10^{4}	1.8×10^{6}	6.6×10^{3}
Cl	3.0×10^{5}	1.2×10^{5}	3.3×10^{6}	1.2×10^{4}
K	1.6×10^{4}	6.6×10^{3}	1.8×10^{5}	660.00
Ni	2.43	0.99	27.00	0.10
Cu	13.50	5.50	150.00	0.55
Zn	51.30	20.90	570.00	2.09
Se	0.81	0.33	9.00	0.03
Rb	135.00	55.00	1.5×10^{3}	5.50
Cd	0.14	0.06	1.50	5.5×10^{-3}
Sn	0.08	0.03	0.90	3.3×10^{-3}
I	21.60	8.80	240.00	0.88
Nd	0.43	0.18	4.80	0.02
Sm	0.08	0.03	0.84	3.1×10^{-3}
Pb	0.81	0.33	9.00	0.03
Th	0.81	0.33	9.00	0.03
U	2.70	1.10	30.00	0.11

In Table 5.15, no elemental fluxes are given for the polar climate state because no groundwater discharges locally to the surface in these conditions.

The groundwater discharge fluxes in Table 5.15 are given in terms of mass. However, it is possible to convert the mass fluxes for U, Th, K and Rb to alpha and non-alpha activity fluxes for individual radioelements and for their respective decay chains, assuming secular equilibrium in the chains. The details of the assumptions underlying these activity calculations were discussed in Section 1.2. On the basis of these assumptions, the activity fluxes for groundwater discharge in the inland pluton reference environment have been calculated and are given in Table 5.16.

Table 5.16: Activity fluxes for groundwater discharge in the basement under sedimentary cover reference environment. Total alpha is the total of the U and Th chain activities, and total non-alpha is total of ^{40}K and ^{87}Rb.

Nuclide or decay chain	**Temperate climate (Bq/yr)**	**Subarctic climate (Bq/yr)**	**Tropical climate (Bq/yr)**	**Desert climate (Bq/yr)**
U (^{234}U, ^{235}U, ^{238}U)	6.9×10^7	2.8×10^7	7.7×10^8	2.8×10^6
Th (^{232}Th)	3.3×10^6	1.4×10^6	3.7×10^7	1.2×10^5
U chains	3.2×10^8	1.3×10^8	3.5×10^9	1.3×10^7
Th chain	1.3×10^7	5.4×10^6	1.5×10^8	4.9×10^5
K (^{40}K)	3.9×10^8	1.6×10^8	4.4×10^9	1.6×10^7
Rb (^{87}Rb)	1.2×10^8	4.9×10^7	1.3×10^9	4.9×10^6
Total alpha	3.3×10^8	1.4×10^8	3.7×10^9	1.3×10^7
Total non-alpha	5.1×10^8	2.1×10^8	5.8×10^9	2.1×10^7

These activity fluxes seem at first sight to be large but it must be remembered that they are total groundwater discharge activities for the basement under sedimentary cover environment. Alternative values are the specific fluxes per unit area (km^2) for the total surface of the discharge region (200 km^2), assuming groundwaters were to discharge equally over the low lying plains area (assumed to be two thirds of the total area given that one third was previously assumed to be the recharge zone). These specific activity fluxes are given in Table 5.17.

Table 5.17: Specific activity fluxes for groundwater discharge in the basement under sedimentary cover reference environment, assuming discharge over the entire surface area.

Activity	**Temperate climate (Bq/km^2/yr)**	**Subarctic climate (Bq/km^2/yr)**	**Tropical climate (Bq/km^2/yr)**	**Desert climate (Bq/km^2/yr)**
Total alpha	1.7×10^6	6.8×10^5	1.8×10^7	6.7×10^4
Total non-alpha	2.6×10^6	1.1×10^6	2.9×10^7	1.1×10^5

These specific activity fluxes for groundwater discharge in the basement under sedimentary cover environment are typically around a factor of 3 to 5 larger than the equivalent fluxes for the inland pluton reference environment given in Table 5.7. This is due to a combination of faster groundwater flow through the rocks in the basement under sedimentary cover environment than in the pluton, and due to differences in the groundwater compositions in the two environments.

Denudation of the surface rock

Denudation of the rocks in the basement under sedimentary cover environment is dependent not only on rock type and climate but also on location of exposure. The crystalline basement rocks are exposed only in the upland area which can be classed as having moderate relief. In contrast, the younger sedimentary (shale) sequences are exposed on the flanks of the upland area and in the coastal plains, which collectively can be classed as low relief areas.

The lithological control on denudation rates was expressed in Table 3.7 which shows that gneiss and shale have relative weathering rates of 1 and 2.5, respectively. The climate control on denudation was expressed in Table 3.8 which gives ranges for each climate state. Combining all this information, it is sensible to take the lower estimates for denudation in moderate relief areas from Table 3.8 as the most appropriate for the crystalline basement and the median of the denudation ranges for the sedimentary (shale) rocks. Note, however, that the data from Meybeck (1976) in Table 3.8 only provides one range of denudation rates for all climates for moderate relief areas, indicating that at these elevations, the relief is a greater control than climate. The rate for glacial erosion on the crystalline rock is taken to be approximately 340 mm/ka from the work of Kjeldsen (1981) and 3400 mm/ka for the shale, based on the marble glacial abrasion measurements from Boulton (1974) which were discussed in Section 3.3. On this basis, the denudation rates that are adopted for the flux calculations are given in Table 5.18.

Table 5.18: The parameters used for the denudation flux calculations for the basement under sedimentary cover reference environment.

	Crystalline basement		**Sedimentary cover**	
Climate state	**Total denudation rate (mm/ka)**	**Proportion chemical weathering (%)**	**Total denudation rate (mm/ka)**	**Proportion chemical weathering (%)**
Temperate	30	35	22	65
Subarctic	30	35	10	80
Tropical	30	35	6	50
Desert	30	35	20	10
Polar	340	0	3400	0

Given these denudation rates and assuming the compositions for gneiss and shale given in Table 5.12, and densities of 2750 and 2200 kg/m^3 respectively, the elemental fluxes are calculated and presented in Table 5.19 for total erosion. The elemental fluxes due to just chemical weathering can be calculated from the total weathering fluxes using the proportions given in Table 5.18.

*Table 5.19: Elemental fluxes due to total denudation of the rock surface for the different climate states at the basement under sedimentary cover reference environment. *The fluxes for the temperate climate also apply to the subarctic, tropical and desert climates because the total denudation rates for these climates are the same.*

	Crystalline basement		**Sedimentary cover**				
Element	**Temperate* (g/m^2/yr)**	**Polar (g/m^2/yr)**	**Temperate (g/m^2/yr)**	**Subarctic (g/m^2/yr)**	**Tropical (g/m^2/yr)**	**Desert (g/m^2/yr)**	**Polar (g/m^2/yr)**
C	0.02	0.24	1.45	0.66	0.40	1.32	224.40
Cl	0.04	0.42	0.02	8.8×10^{-3}	5.3×10^{-3}	0.02	2.99
K	0.83	9.35	0.97	0.44	0.26	0.88	149.60
Ni	8.3×10^{-4}	9.4×10^{-3}	3.1×10^{-3}	1.4×10^{-3}	8.6×10^{-4}	2.9×10^{-3}	0.49
Cu	8.3×10^{-3}	0.09	2.2×10^{-3}	9.9×10^{-4}	5.9×10^{-4}	2.0×10^{-3}	0.34
Zn	7.8×10^{-3}	0.09	5.1×10^{-3}	2.3×10^{-3}	1.4×10^{-3}	4.6×10^{-3}	0.79
Se	4.1×10^{-6}	4.7×10^{-5}	2.4×10^{-5}	1.1×10^{-5}	6.6×10^{-6}	2.2×10^{-5}	3.7×10^{-3}
Rb	6.2×10^{-3}	0.07	6.8×10^{-3}	3.1×10^{-3}	1.8×10^{-3}	6.2×10^{-3}	1.05

	Crystalline basement		Sedimentary cover				
Element	**Temperate* ($g/m^2/yr$)**	**Polar ($g/m^2/yr$)**	**Temperate ($g/m^2/yr$)**	**Subarctic ($g/m^2/yr$)**	**Tropical ($g/m^2/yr$)**	**Desert ($g/m^2/yr$)**	**Polar ($g/m^2/yr$)**
Cd	8.3×10^{-6}	9.4×10^{-5}	9.7×10^{-6}	4.4×10^{-6}	2.6×10^{-6}	8.8×10^{-6}	1.5×10^{-3}
Sn	1.8×10^{-4}	2.1×10^{-3}	2.9×10^{-4}	1.3×10^{-4}	7.9×10^{-5}	2.6×10^{-4}	0.04
I	8.3×10^{-4}	9.4×10^{-3}	5.8×10^{-4}	2.6×10^{-4}	1.6×10^{-4}	5.3×10^{-4}	0.09
Nd	2.9×10^{-3}	0.03	1.4×10^{-3}	6.4×10^{-4}	3.8×10^{-4}	1.3×10^{-3}	0.22
Sm	7.0×10^{-4}	7.9×10^{-3}	3.6×10^{-4}	1.7×10^{-4}	9.9×10^{-5}	3.3×10^{-4}	0.06
Pb	1.6×10^{-3}	0.02	1.1×10^{-3}	5.1×10^{-4}	3.0×10^{-4}	1.0×10^{-3}	0.17
Th	1.3×10^{-3}	0.01	5.8×10^{-4}	2.6×10^{-4}	1.6×10^{-4}	5.3×10^{-4}	0.09
U	2.6×10^{-4}	3.0×10^{-3}	1.7×10^{-4}	7.7×10^{-5}	4.6×10^{-5}	1.5×10^{-4}	0.03

The denudation fluxes in Table 5.19 are given in terms of mass. However, it is possible to convert the mass fluxes for U, Th, K and Rb to alpha and non-alpha activity fluxes for individual radioelements and for their respective decay chains, assuming secular equilibrium in the chains. The details of the assumptions underlying these activity calculations were discussed in Section 1.2. On the basis of these assumptions, activity fluxes for denudation in the basement under sedimentary cover reference environment have been calculated and are given in Table 5.20.

Table 5.20: Activity fluxes for denudation of the basement under sedimentary cover reference environment. Total alpha is the total of the U and Th chain activities, and total non-alpha is ^{40}K *plus* ^{87}Rb.

Nuclide or decay chain	**Temperate climate ($Bq/m^2/yr$)**	**Subarctic climate ($Bq/m^2/yr$)**	**Tropical climate ($Bq/m^2/yr$)**	**Desert Climate ($Bq/m^2/yr$)**	**Polar Climate ($Bq/m^2/yr$)**
Crystalline basement:					
U (^{234}U, ^{235}U, ^{238}U)	6.7	6.7	6.7	6.7	77.1
Th (^{232}Th)	5.3	5.3	5.3	5.3	41.0
U chains	30.6	30.6	30.6	30.6	353.6
Th chain	21.3	21.3	21.3	21.3	164.0
K (^{40}K)	20.5	20.5	20.5	20.5	230.6
Rb (^{87}Rb)	5.5	5.5	5.5	5.5	62.4
Total alpha	52.0	52.0	52.0	52.0	517.6
Total non-alpha	26.0	26.0	26.0	26.0	293.0
Sedimentary cover:					
U (^{234}U, ^{235}U, ^{238}U)	4.4	2.0	1.2	3.9	7.7×10^{2}
Th (^{232}Th)	2.4	1.1	0.7	2.2	3.7×10^{2}
U chains	20.0	9.1	5.4	17.7	3.5×10^{3}
Th chain	9.5	4.3	2.6	8.7	1.5×10^{3}
K (^{40}K)	23.9	10.9	6.4	21.7	3.7×10^{3}
Rb (^{87}Rb)	6.1	2.8	1.6	5.5	9.4×10^{2}
Total alpha	29.5	13.3	8.0	26.4	5.0×10^{3}
Total non-alpha	30.0	13.6	8.0	27.2	4.6×10^{3}

The activity fluxes in Table 5.20 are given in units of $Bq/m^2/yr$. To compare with the activity fluxes due to groundwater discharge calculated earlier, the total alpha and total non-alpha fluxes are recast as specific fluxes per unit area (km^2) for both total and chemical weathering, assuming the chemical weathering proportions given in Table 5.18, and the results are given in Table 5.21.

Comparison of these specific activity fluxes with those due to groundwater discharge (Table 5.17) for the basement under sedimentary cover environment, shows that those due to denudation are typically one to two orders of magnitude larger than those due to groundwater discharge. The exceptions is the polar climate in which no groundwater discharge was assumed to occur.

Table 5.21: Specific activity fluxes for denudation in the basement under sedimentary cover reference environment for both total denudation and chemical weathering.

Nuclide or decay chain	**Temperate climate ($Bq/km^2/yr$)**	**Subarctic climate ($Bq/km^2/yr$)**	**Tropical climate ($Bq/km^2/yr$)**	**Desert climate ($Bq/km^2/yr$)**	**Polar climate ($Bq/km^2/yr$)**
Crystalline basement - total denudation:					
Total alpha	5.2×10^7	5.2×10^7	5.2×10^7	5.2×10^7	5.2×10^8
Total non-alpha	2.6×10^7	2.6×10^7	2.6×10^7	2.6×10^7	2.9×10^8
Crystalline basement - chemical weathering:					
Total alpha	1.8×10^7	1.8×10^7	1.8×10^7	1.8×10^7	0
Total non-alpha	9.1×10^6	9.1×10^6	9.1×10^6	9.1×10^6	0
Sedimentary cover - total denudation:					
Total alpha	2.9×10^7	1.3×10^7	8.0×10^6	2.6×10^7	5.0×10^9
Total non-alpha	3.0×10^7	1.4×10^7	8.0×10^6	2.7×10^7	4.6×10^9
Sedimentary cover - chemical weathering:					
Total alpha	1.9×10^7	1.0×10^7	4.0×10^6	2.6×10^6	0
Total non-alpha	2.0×10^7	1.1×10^7	4.0×10^6	2.7×10^6	0

Comparison of the activity fluxes due to denudation between the pluton and the basement under sedimentary cover environments shows that those in the basement under sedimentary cover environment are slightly greater, especially compared to the gabbro pluton variant. This is due to a combination of fast erosion of the sedimentary rocks compared to the crystalline rocks and because the gabbro contains low abundances of the radioelements U, Th, K and Rb.

A further interesting observation from Table 5.21, is that the total alpha and total non-alpha activity fluxes due to denudation of the sedimentary cover are very similar. This is coincidental and due to the relative proportions in the rock of the radioelements U, Th, K and Rb.

5.4 Sedimentary basin

Sedimentary basins occur widely throughout the world and the range of sediment lithologies and chemistries they contain can be highly variable, including mudstones, shales, clays and evaporites. In volcanically active regions (e.g. Japan), interbedded volcanic horizons can also be found in these basins. The sedimentary lithologies of most interest for radioactive waste disposal are the clay-rich (argillaceous) rocks. These have attractive characteristics due largely to the low permeabilities of clays, the potentially very long return times for contaminants to reach the surface and the high sorption capacity provided by clay minerals.

Sedimentary basins containing substantial thicknesses of argillaceous rocks (suitable for hosting a repository) occur in a number of countries around the world and, thus, argillaceous rocks have been widely considered in a number of site selection programmes in different countries (e.g. Switzerland, Spain, France and Belgium). The dimensions of these basins can vary considerably, both in lateral extent and in thickness. Furthermore, their physical and structural heterogeneity can be large, particularly if the original depositional environment was not stable.

Groundwater flow in sedimentary basins generally will be focussed in the coarser grained (sandier) lithologies with higher hydraulic conductivities than the clay-rich lithologies. In this way, there can be advantages if the argillaceous horizons in a basin (which may host a repository) are overlain with sandy layers because these tend to insulate the argillaceous horizons from topographically-driven flow (by acting as a partial hydraulic cage) and can provide a large potential for the dilution of radionuclides migrating from the argillaceous horizons. Departures from this simple model can occur if the argillaceous horizons have been indurated and subsequently fractured, in which case they can behave in a broadly similar manner to fractured crystalline rocks with respect to groundwater flow.

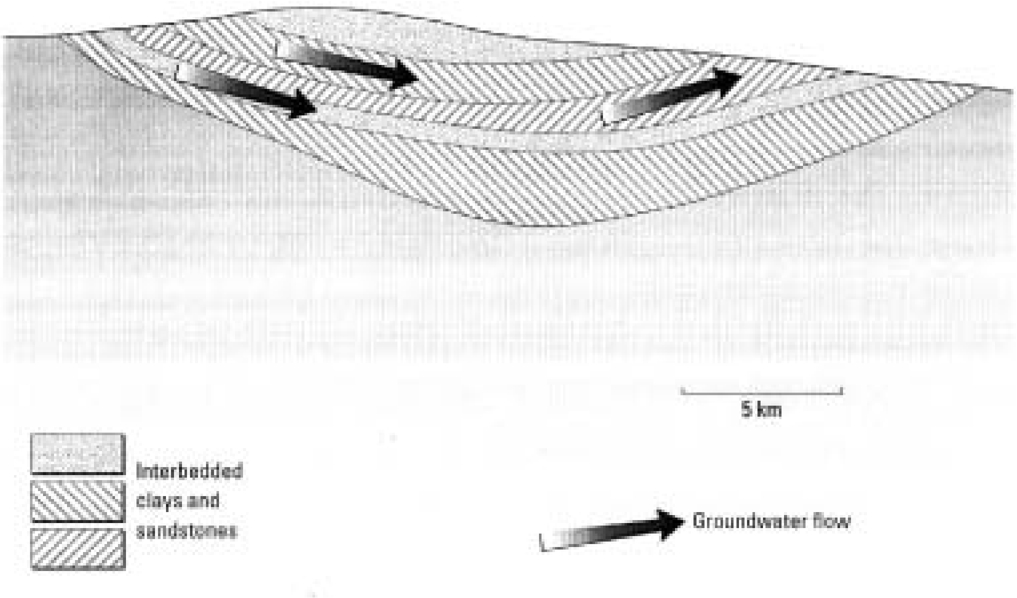

Figure 5.5: Cross section of the sedimentary basin reference environment.

On the scale of the basin, groundwater movement would tend to be down dip towards the centre of the basin, with recharge occurring on the basin limbs. Towards the centre of the basin, groundwater fluxes would tend to be lower and very low groundwater velocities could be expected, with mixing of groundwaters due to diffusional processes or due to sub-vertical advection, caused by pressure differences between different formations or by thermal buoyancy of groundwaters related to regional heat flows.

Sedimentary rocks are relatively soft and easily weathered by both physical and chemical processes. The carbonate cement which typically bonds together the grains in a sedimentary rock is readily soluble in oxidising, mildly acidic near-surface waters. As a consequence, the weathering and erosion rates of sedimentary rocks are considerably faster than those of harder, crystalline rocks which means that the surface topography around sedimentary basins is often quite low. This further helps to minimise hydraulic gradients and groundwater flow velocities in the basin.

For this reference environment, the sedimentary basin is assumed to be inland, away from any coastal effects. The basin is elongate with dimensions of approximately 25 km × 20 km. For simplicity, the lithologies are assumed to be plastic clays with some interbedded sandier horizons without significant post depositional structures to complicate the system. A simple cross section of the sedimentary basin reference environment is shown in Figure 5.5.

The surface topography in this reference environment is of low relief, with only rolling hills reaching a maximum height of 30 m. The descending limbs of the sedimentary basin effectively create a slow moving, closed groundwater flow system, although surface waters are drained by a single river system that crosses the basin and flows to the coast.

No geological variants are considered here, although all five climate states defined in Table 5.2 are considered. The elemental abundances that are used in the flux calculations are shown in Table 5.22. These data have been derived from the compilation of elemental abundances in Chapter 2.

Table 5.22: Elemental abundances in the various materials present in the sedimentary basin reference environment.

Element	Clay (mg/kg)	Sandstone (mg/kg)	Soil (mg/kg)	Sedimentary groundwater (µg/l)
C	30000	16000	30000	125000
Cl	400	500	100	400000
K	20000	15000	14000	40000
Ni	65	15	50	10
Cu	45	30	30	5
Zn	105	30	90	50
Se	0.5	0.02	0.5	0.5
Rb	140	46	150	50
Cd	0.2	0.05	0.35	0.2
Sn	6	0.5	2	0.5
I	12	1	5	30
Nd	29	29	35	0.16
Sm	7.5	7.5	4.5	0.028
Pb	23	7	20	3
Th	12	3.2	9	0.3
U	3.5	0.6	2	1

Groundwater flow and discharge

The low surface relief in most sedimentary basins (due partly to their easily erodable lithologies) means that their groundwater flow systems are driven by small topographic heads. This also means that the extent to which groundwater flow rates at depth can be modified by climate change is lessened, assuming there are no higher relief areas outside of the sedimentary basin driving the deep groundwater flow system.

As with the inland pluton reference environment, changing climate can, however, alter the local groundwater discharge rate within the sedimentary basin due to changes in groundwater recharge. If recharge is low, then local groundwater discharge within the sedimentary basin could be zero if the water table falls below the ground surface, meaning that groundwater discharge would occur some distance away as part of the regional groundwater flow system. In contrast, if recharge is high, then the water table will be raised, groundwater flow will be at a maximum and local groundwater discharge within the sedimentary basin is likely to occur to surface lakes and rivers.

In Section 3.2, typical hydraulic parameters for plastic clays at depths above and below 100 m were given, these were (from Savage, 1995):

- above 100 m, groundwater flux of 1.6 to 640 $l/m^2/yr$ and a groundwater velocity of 5×10^{-4} to 1.3 m/yr, and
- below 100 m, groundwater flux of 0.0016 to 64 $l/m^2/yr$ and a groundwater velocity of 5×10^{-6} to 0.13 m/yr.

It is clear from these data that there is considerable variation in the hydraulic parameters and that the range for shallow rock overlaps that for the deep rock. This is because clay rocks can be considerably heterogeneous in both the vertical and horizontal directions, resulting from changes in environmental conditions during and subsequent to sedimentation. In the absence of detailed hydrogeological information, the simplest approach is to calculate fluxes for both the maximum and minimum values for rocks above and below 100 m.

The groundwaters in the clays would be likely to contain dissolved elemental abundances similar to those given for 'sedimentary groundwater' in Table 5.22. No distinction is made between the composition of groundwaters in the upper and lower layers. On the basis of this groundwater composition and the ranges for groundwater flow rates assumed above, the elemental fluxes associated with the groundwater in the sedimentary basin are calculated and presented in Table 5.23. The fluxes are given in units of $g/m^2/yr$ for the groundwater flowing through the upper and lower horizons.

Table 5.23: Elemental fluxes due to both deep and shallow groundwater flow through the sedimentary basin reference environment.

	Deep groundwater		**Shallow groundwater**	
Element	**Maximum $(g/m^2/yr)$**	**Minimum $(g/m^2/yr)$**	**Maximum $(g/m^2/yr)$**	**Minimum $(g/m^2/yr)$**
C	8.0	2.0×10^{-4}	80.0	4.0×10^{-3}
Cl	25.6	6.4×10^{-4}	256.0	1.3×10^{-2}
K	2.6	6.4×10^{-5}	25.6	1.3×10^{-3}
Ni	6.4×10^{-4}	1.6×10^{-8}	6.4×10^{-3}	3.2×10^{-7}
Cu	3.2×10^{-4}	8.0×10^{-9}	3.2×10^{-3}	1.6×10^{-7}
Zn	3.2×10^{-3}	8.0×10^{-8}	3.2×10^{-2}	1.6×10^{-6}
Se	3.2×10^{-5}	8.0×10^{-10}	3.2×10^{-4}	1.6×10^{-8}
Rb	3.2×10^{-3}	8.0×10^{-8}	3.2×10^{-2}	1.6×10^{-6}
Cd	1.3×10^{-5}	3.2×10^{-10}	1.3×10^{-4}	6.4×10^{-9}
Sn	3.2×10^{-5}	8.0×10^{-10}	3.2×10^{-4}	1.6×10^{-8}
I	1.9×10^{-3}	4.8×10^{-8}	1.9×10^{-2}	9.6×10^{-7}

	Deep groundwater		Shallow groundwater	
Element	Maximum ($g/m^2/yr$)	Minimum ($g/m^2/yr$)	Maximum ($g/m^2/yr$)	Minimum ($g/m^2/yr$)
Nd	1.0×10^{-5}	2.6×10^{-10}	1.0×10^{-4}	5.1×10^{-9}
Sm	1.8×10^{-6}	4.5×10^{-11}	1.8×10^{-5}	9.0×10^{-10}
Pb	1.9×10^{-4}	4.8×10^{-9}	1.9×10^{-3}	9.6×10^{-8}
Th	1.9×10^{-5}	4.8×10^{-10}	1.9×10^{-4}	9.6×10^{-9}
U	6.4×10^{-5}	1.6×10^{-9}	6.4×10^{-4}	3.2×10^{-8}

The fluxes given in Table 5.23 are essential unaffected by the changes in climate because there is little scope for increased or decreased precipitation to alter the hydraulic gradient in the absence of any significant surface topography. However, the fluxes of elements carried in the groundwaters which actually discharge to the surface within the sedimentary basin may be affected but it is difficult to quantify the amount of discharge which would occur, without detailed information on the hydrogeology and hydrology of the site.

In the absence of further information, similar assumptions for changing discharge volumes with climate are made for the sedimentary basin environment as were made for the inland pluton. These assumptions are:

- for the temperate climate, 5 % of precipitation recharges (high evapotranspiration due to abundant vegetation) and 50 % of this discharges locally to the ground surface, with the remainder joining the deep regional flow system, giving a local discharge volume of 7.5×10^9 l/yr;
- for the subarctic climate, 3 % of precipitation recharges (high runoff) and 50 % of this discharges locally to the ground surface, with the remainder joining the deep regional flow system, giving a local discharge volume of 3.0×10^9 l/yr;
- for the tropical climate, 15 % of precipitation recharges (equal to global average) and 50 % of this discharges locally to the ground surface, with the remainder joining the deep regional flow system, giving a local discharge volume of 8.3×10^{10} l/yr;
- for the desert climate, 2 % of precipitation recharges (high evaporation) and none of this discharges locally to the ground surface (depressed water table), so it all joins the deep regional flow system, giving a local discharge volume of 0 l/yr; and
- for the polar climate, 0 % of precipitation recharges (arrives as snow and accumulates on the ice sheet) giving a local discharge volume of 0 l/yr.

On the basis of the ‘sedimentary groundwater’ composition given in Table 5.22 and the groundwater discharge volumes for the different climate states given above, the elemental fluxes associated with the discharging groundwater are calculated and presented in Table 5.24. The fluxes are given in units of kg/yr (as opposed to a flux per unit area as given for the fluxes associated with groundwater flow).

In Table 5.24, no elemental fluxes are given for the desert and polar climate states because no groundwater discharges locally to the ground surface in these conditions. In this case, all elemental fluxes associated with groundwater flow are associated with regional groundwater and will discharge elsewhere some distance from the sedimentary basin.

Table 5.24: Elemental fluxes due to groundwater discharge to the surface within the sedimentary basin reference environment for the different climate states.

Element	Temperate climate (kg/yr)	Subarctic climate (kg/yr)	Tropical climate (kg/yr)
C	9.4×10^{5}	3.8×10^{5}	1.0×10^{7}
Cl	3.0×10^{6}	1.2×10^{6}	3.3×10^{7}
K	3.0×10^{5}	1.2×10^{5}	3.3×10^{6}
Ni	75.0	30.0	830.0
Cu	37.5	15.0	415.0
Zn	375.00	150.00	4.2×10^{3}
Se	3.75	1.50	41.5
Rb	375.00	150.00	4.2×10^{3}
Cd	1.5	0.6	16.6
Sn	3.8	1.5	41.5
I	225.0	90.0	2.5×10^{3}
Nd	1.2	0.5	13.3
Sm	0.2	8.4×10^{-2}	2.3
Pb	22.5	9.0	249.0
Th	2.3	0.9	24.9
U	7.5	3.0	83.0

The groundwater discharge fluxes in Table 5.24 are given in terms of mass. However, it is possible to convert the mass fluxes for U, Th, K and Rb to alpha and non-alpha activity fluxes for individual radioelements and for their respective decay chains, assuming secular equilibrium in the chains. The details of the assumptions underlying these activity calculations were discussed in Section 1.2. On the basis of these assumptions, the activity fluxes for groundwater discharge in the inland pluton reference environment have been calculated and are given in Table 5.25.

Table 5.25: Activity fluxes for groundwater discharge in the sedimentary basin reference environment. Total alpha is the total of the U and Th chain activities, and total non-alpha is total of ^{40}K and ^{87}Rb.

Nuclide or decay chain	Temperate climate (Bq/yr)	Subarctic climate (Bq/yr)	Tropical Climate (Bq/yr)
U (^{234}U, ^{235}U, ^{238}U)	1.9×10^{8}	7.7×10^{7}	2.1×10^{9}
Th (^{232}Th)	9.4×10^{6}	3.7×10^{6}	1.0×10^{8}
U chains	8.8×10^{8}	3.5×10^{8}	9.8×10^{9}
Th chain	3.8×10^{7}	1.5×10^{7}	4.1×10^{8}
K (^{40}K)	7.4×10^{9}	3.0×10^{9}	8.1×10^{10}
Rb (^{87}Rb)	3.3×10^{8}	1.3×10^{8}	3.7×10^{9}
Total alpha	9.2×10^{8}	3.7×10^{8}	1.0×10^{10}
Total non-alpha	7.7×10^{9}	3.1×10^{9}	8.5×10^{10}

These activity fluxes seem at first sight to be large but it must be remembered that they are total groundwater discharge activities over the entire sedimentary basin environment. Alternative values are the specific fluxes per unit area (km^{2}) for the basin surface (500 km^{2}), assuming groundwaters were to discharge equally over the area. These specific activity fluxes are given in Table 5.26.

Table 5.26: Specific activity fluxes for groundwater discharge in the sedimentary basin reference environment, assuming discharge over the entire basin area.

Activity	**Temperate climate ($Bq/km^2/yr$)**	**Subarctic climate ($Bq/km^2/yr$)**	**Tropical climate ($Bq/km^2/yr$)**
Total alpha	1.8×10^{6}	7.4×10^{5}	2.0×10^{7}
Total non-alpha	1.5×10^{7}	6.2×10^{6}	1.7×10^{8}

Denudation of the surface rock

For the sedimentary basin environment, potential average weathering (denudation) rates can be derived for the different climate states from the information given in Table 3.8 for low relief zones. As indicated in Table 3.7, the argillaceous rocks in the sedimentary basin will be more prone to both physical and chemical weathering processes, in comparison to hard, crystalline rock types and, thus, it is sensible to take the higher estimates of denudation from Table 3.8 as the most appropriate for the inland pluton. There are no reliable rates for glacial erosion of argillaceous rocks. However, a semi-approximate value may be the 3.4 mm/yr glacial erosion rate recorded by Boulton (1974) on a marble platten, which was discussed in Section 3.3. Although marble is a somewhat different material to argillaceous rocks, it is a relatively soft rock and one which weathers easily, as do clays. This glacial erosion rate is one order of magnitude faster than the rate adopted for the glacial erosion of granite for the inland pluton environment (340 mm/ka: Kjeldsen, 1981). On this basis, the denudation rates that are adopted for the flux calculations are given in Table 5.27.

Table 5.27: The parameters used for the denudation flux calculation for the sedimentary basin reference environment.

Climate state	**Total denudation rate (mm/ka)**	**Proportion chemical weathering (%)**
Temperate	30	65
Subarctic	15	80
Tropical	10	50
Desert	35	10
Polar	3400	0

Given these denudation rates and assuming that the clay has a the compositions given in Table 5.22, and a density of 2200 kg/m^3, the elemental fluxes are calculated and presented in Table 5.28 for total erosion. The elemental fluxes due to just chemical weathering can be calculated from the total weathering fluxes using the proportions given in Table 5.27.

Table 5.28: Elemental fluxes due to total denudation of the rock surface for the different climate states in the sedimentary basin reference environment.

Element	**Temperate Climate ($g/m^2/yr$)**	**Subarctic Climate ($g/m^2/yr$)**	**Tropical Climate ($g/m^2/yr$)**	**Desert climate ($g/m^2/yr$)**	**Polar climate ($g/m^2/yr$)**
C	2.0	1.0	0.7	2.3	224.4
Cl	2.6×10^{-2}	1.3×10^{-2}	8.8×10^{-3}	3.1×10^{-2}	3.0
K	1.3	0.7	0.4	1.5	149.6
Ni	4.3×10^{-3}	2.1×10^{-3}	1.4×10^{-3}	5.0×10^{-3}	0.5

Element	Temperate Climate (g/m^2/yr)	Subarctic Climate (g/m^2/yr)	Tropical Climate (g/m^2/yr)	Desert climate (g/m^2/yr)	Polar climate (g/m^2/yr)
Cu	3.0×10^{-3}	1.5×10^{-3}	9.9×10^{-4}	3.5×10^{-3}	0.3
Zn	6.9×10^{-3}	3.5×10^{-3}	2.3×10^{-3}	8.1×10^{-3}	0.8
Se	3.3×10^{-5}	1.7×10^{-5}	1.1×10^{-5}	3.9×10^{-5}	3.7×10^{-3}
Rb	9.2×10^{-3}	4.6×10^{-3}	3.1×10^{-3}	1.1×10^{-2}	1.0
Cd	1.3×10^{-5}	6.6×10^{-6}	4.4×10^{-6}	1.5×10^{-5}	1.5×10^{-3}
Sn	4.0×10^{-4}	2.0×10^{-4}	1.3×10^{-4}	4.6×10^{-4}	4.5×10^{-2}
I	7.9×10^{-4}	4.0×10^{-4}	2.6×10^{-4}	9.2×10^{-4}	9.0×10^{-2}
Nd	1.9×10^{-3}	9.6×10^{-4}	6.4×10^{-4}	2.2×10^{-3}	0.2
Sm	5.0×10^{-4}	2.5×10^{-4}	1.7×10^{-4}	5.8×10^{-4}	5.6×10^{-2}
Pb	1.5×10^{-3}	7.6×10^{-4}	5.1×10^{-4}	1.8×10^{-3}	0.2
Th	7.9×10^{-4}	4.0×10^{-4}	2.6×10^{-4}	9.2×10^{-4}	9.0×10^{-2}
U	2.3×10^{-4}	1.2×10^{-4}	7.7×10^{-5}	2.7×10^{-4}	2.6×10^{-2}

The denudation fluxes in Table 5.28 are given in terms of mass. However, it is possible to convert the mass fluxes for U, Th, K and Rb to alpha and non-alpha activity fluxes for individual radioelements and for their respective decay chains, assuming secular equilibrium in the chains. The details of the assumptions underlying these activity calculations were discussed in Section 1.2. On the basis of these assumptions, the activity fluxes for denudation of the sedimentary basin reference environment have been calculated and are given in Table 5.29.

Table 5.29: Activity fluxes for denudation of the sedimentary basin reference environment. Total alpha is the total of the U and Th chain activities, and total non-alpha is ^{40}K plus ^{87}Rb.

Nuclide or decay chain	Temperate climate (Bq/m^2/yr)	Subarctic climate (Bq/m^2/yr)	Tropical climate (Bq/m^2/yr)	Desert climate (Bq/m^2/yr)	Polar climate (Bq/m^2/yr)
U (^{234}U, ^{235}U, ^{238}U)	5.9	3.1	2.0	6.9	668.2
Th (^{232}Th)	3.2	1.6	1.1	3.8	369.0
U chains	27.1	14.1	9.1	31.8	3064.1
Th chain	13.0	6.6	4.3	15.1	1476.0
K (^{40}K)	32.1	17.3	9.9	37.0	3699.3
Rb (^{87}Rb)	8.2	4.1	2.8	9.8	891.2
Total alpha	40.1	20.7	13.3	46.9	4540.1
Total non-alpha	40.3	21.4	12.6	46.2	4590.5

The activity fluxes in Table 5.29 are given in units of Bq/m^2/yr. To compare with the activity fluxes due to groundwater discharge calculated earlier, the total alpha and total non-alpha fluxes are recast as specific fluxes per unit area (km^2) for both total and chemical weathering, assuming the chemical weathering proportions given in Table 5.27, and the results are given in Table 5.30.

Comparison of these specific activity fluxes due to denudation (Table 5.30) and due to groundwater discharge (Table 5.26) for the sedimentary basin environment, shows that those due to denudation are typically one to two orders of magnitude larger than those due to groundwater discharge. The exceptions are the desert and polar climates in which no groundwater discharge was assumed to occur.

Table 5.30: Specific activity fluxes for denudation in the sedimentary basin reference environment for both total denudation and chemical weathering.

Nuclide or decay chain	Temperate climate ($Bq/km^2/yr$)	Subarctic climate ($Bq/km^2/yr$)	Tropical climate ($Bq/km^2/yr$)	Desert climate ($Bq/km^2/yr$)	Polar climate ($Bq/km^2/yr$)
Total denudation:					
Total alpha	4.0×10^{7}	2.1×10^{7}	1.3×10^{7}	4.7×10^{7}	4.5×10^{9}
Total non-alpha	4.0×10^{7}	2.1×10^{7}	1.3×10^{7}	4.6×10^{7}	4.6×10^{9}
Chemical weathering:					
Total alpha	2.6×10^{7}	1.7×10^{7}	6.7×10^{6}	4.7×10^{6}	0
Total non-alpha	2.6×10^{7}	1.7×10^{7}	6.3×10^{6}	4.6×10^{6}	0

Although the actual rates of denudation of the clay are several times faster than those of hard crystalline rocks (3 to 10 depending on climate), the activity fluxes are only 1 to 4.5 times greater than those associated with denudation of the granite variant of the inland pluton. The reason for this is that the clay contains smaller concentrations of the radioelements U, Th, K and Rb than the granite. This illustrates the point that a high process rate does not, necessarily, produce a particularly high elemental or activity flux. For this to occur, a high concentration in the mobile material is also required. A further interesting observation from Table 5.21, is that the total alpha and total non-alpha activity fluxes due to denudation of the sedimentary cover are almost identical to each other. This is coincidental and due to the relative proportions in the rock of the radioelements U, Th, K and Rb.

5.5 Sediment movement

Once material has been released from the geosphere to the surface by groundwater discharge or by denudational processes, this material can then move about the surface driven by the action of water, wind or ice. These processes thus drive additional elemental fluxes in natural geological systems. In Section 4.4, the elemental mass fluxes associated with global average river transport (dissolved, suspended and bedload) were calculated and presented in Table 4.6. In this section, the likely transport fluxes in the three reference geological environments are considered.

5.5.1 Water (river) transport

The three references geological environments represent small catchment systems with areal extents of a few hundred km^2. The rivers which potentially might flow through land areas of this size are most likely to be part of small, local drainage systems rather than major continental-scale river systems, such as the Amazon or Mississippi.

The capability of a river to transport suspended and dissolved materials is dependent on the water discharge such that (Meybeck, 1977):

$Cs = a'.Q^{b'}$ with $b' > 1$, and

$Cd = a.Q^{b}$ with $-1<b<0$.

Where Cs = suspended water content, a' = turbidity, Cd = dissolved water content, a = salinity, Q = river discharge rate. Thus there is a broadly linear relationship between increasing size of river and the mass of material transported, although there is considerable scatter due to the characteristics of individual river systems.

Milliman and Syvitski (1992) catalogued transport data for over 280 of the world's smaller rivers, with drainage basins less than 10 000 km^2. These data are divided by topography of the river basin, from high mountain to lowland (100 to 500 m). Data from several of the smaller rivers in the latter lowland group are listed in Table 5.31 because these most approximate to the size and topography of the reference geological environments considered in this report.

Table 5.31: River transport data from some small rivers. From Milliman and Syvitski (1992).

River	Catchment area (km^2)	Suspended load ($\times 10^6$ t/yr)	Sediment yield (t/km^2/yr)	Runoff (mm/yr)
Esk, UK	310	0.018	58	-
Welland, UK	530	0.01	14	200
Clyde, UK	1900	0.11	60	430
Chehalis, USA	3400	0.11	34	-
St Jean, Canada	5600	0.25	48	-
Munio Ålv	24000	0.36	15	500
Kalkkinen, Finland	25000	0.06	0.26	250
Apalachicola, USA	44000	0.17	4	470

The average suspended load from these rivers is 0.14×10^9 kg/yr and this could be taken to be representative of the loads which might be carried in rivers in the reference environments. Assuming the solid load particulates are derived from the rock (have the same composition as the rock), and using the average suspended load, the equivalent elemental fluxes are calculated and presented in Table 5.32 for the different geological reference environments. In the case of the basement under sedimentary cover, since a variety of rocks crop out at the surface, the proportions are taken to be 50% gneiss and 50% shale.

The river discharge rates can be calculated from the runoff and the catchment area values. For the five rivers for which both sets of values are available, an average river discharge rate of approximately 8 km^3/yr is obtained. Again, this could be taken to be representative of a river in any of the reference environments. No specific analyses of these riverwater compositions are available. However, assuming these rivers have water compositions equivalent to the global average river water which was described in Section 2 (Table 2.19) and using the average river discharge rate, the elemental fluxes for the dissolved loads are calculated, and these are presented in Table 5.32.

Since the rivers listed in Table 5.31 come from broadly temperate climates, the calculated fluxes given in Table 5.32 must be representative of the temperate climate. No data are available for rivers in different climate zones but an approximation to the fluxes which would occur for different climates may be obtained by scaling these fluxes according to the different rainfalls which occur in the different climates, and which were given in Table 5.2. The exception is the polar climate because, in this state, glacial transport replaces river transport. On this basis the scaling factors for the climate states are:

- temperate, 1
- subarctic, 0.6
- tropical, 3.6, and
- desert, 0.17.

Table 5.32: Elemental fluxes due to river water transport for a typical 'small' river in the different geological environments. The dissolved load applies to all geological environments.

Element	**Dissolved load (kg/yr)**	**Suspended load: granite pluton (kg/yr)**	**Suspended load: gabbro pluton (kg/yr)**	**Suspended load: basement under sediment cover (kg/yr)**	**Suspended load: sedimentary basin (kg/yr)**
C	8.8×10^{7}	4.9×10^{4}	3.0×10^{4}	2.1×10^{6}	4.2×10^{6}
Cl	5.6×10^{7}	2.8×10^{4}	5.5×10^{4}	6.0×10^{4}	5.6×10^{4}
K	1.2×10^{7}	4.7×10^{6}	8.4×10^{5}	2.1×10^{6}	2.8×10^{6}
Ni	4.0×10^{3}	1.4×10^{3}	3.5×10^{4}	5.3×10^{3}	9.1×10^{3}
Cu	1.2×10^{4}	6.3×10^{3}	2.7×10^{4}	1.0×10^{4}	6.3×10^{3}
Zn	2.4×10^{5}	1.1×10^{4}	1.4×10^{4}	1.4×10^{4}	1.5×10^{4}
Se	4.8×10^{2}	7.0	7.0	39.0	70.0
Rb	1.2×10^{4}	2.1×10^{4}	4.5×10^{3}	1.5×10^{4}	2.0×10^{4}
Cd	1.6×10^{2}	28.0	28.0	21.0	28.0
Sn	72.0	4.9×10^{2}	1.7×10^{2}	5.7×10^{2}	8.4×10^{2}
I	4.0×10^{4}	1.4×10^{3}	1.4×10^{3}	1.5×10^{3}	1.7×10^{3}
Nd	3.2×10^{2}	6.2×10^{3}	4.5×10^{3}	4.5×10^{3}	4.1×10^{3}
Sm	64.0	1.3×10^{3}	1.0×10^{3}	1.1×10^{3}	1.1×10^{3}
Pb	8.0×10^{2}	1.2×10^{4}	7.7×10^{2}	2.9×10^{3}	3.2×10^{3}
Th	8.0×10^{2}	3.8×10^{3}	3.9×10^{2}	2.0×10^{3}	1.7×10^{3}
U	1.9×10^{3}	6.9×10^{2}	1.1×10^{2}	4.7×10^{2}	4.9×10^{2}

These elemental fluxes are surprisingly large and act to demonstrate how large fluxes may be generated from materials with low elemental concentrations if large volumes of material are actually being transported across the surface.

Of course, these fluxes are only for an 'example' small river of the type which may cross the area in the vicinity of a repository in the temperate climate. As such these fluxes can be considered only as indicators of the magnitude of river fluxes. It is not possible to be more precise at this point and more detailed flux calculations would need to wait until a repository site has been chosen and the characteristics of any river at the site investigated.

The activity fluxes associated with this example small river in the temperate climate can be calculated from the mass fluxes of U, Th, K and Rb, as discussed in Section 1.2, and these are given in Table 5.33.

These fluxes seem very large at first sight but it must be remembered that they relate to the total activity associated with the total annual river flow. To put these fluxes into perspective, the river water discharge in the average river is 8 km^3/yr and the suspended load is 1.4×10^{8} kg/yr (or 17.5 mg/l if the suspended load is equally distributed throughout the river water). On this basis, the activity associated with each litre of river water (from both dissolved and suspended loads) are calculated and given in Table 5.34.

Table 5.33: Activity fluxes associated with the dissolved and suspended loads of an example small river in the different geological environments. The dissolved load activity flux applies to all environments. Total alpha is the total of the U and Th chain activities, and total non-alpha is ^{40}K plus ^{87}Rb.

Nuclide or decay chain	Dissolved load (Bq/yr)	Suspended load: granite pluton (Bq/yr)	Suspended load: gabbro pluton (Bq/yr)	Suspended load: basement under sediment cover (Bq/yr)	Suspended load: sedimentary basin (Bq/yr)
U (^{234}U, ^{235}U, ^{238}U)	4.9×10^{10}	1.8×10^{10}	2.8×10^{9}	1.2×10^{10}	1.3×10^{10}
Th (^{232}Th)	3.3×10^{9}	1.6×10^{10}	1.6×10^{9}	8.2×10^{10}	7.0×10^{9}
U chains	2.2×10^{11}	8.1×10^{10}	1.3×10^{10}	5.5×10^{10}	5.8×10^{10}
Th chain	1.3×10^{10}	6.2×10^{10}	6.4×10^{9}	3.3×10^{10}	2.8×10^{10}
K (^{40}K)	3.0×10^{11}	1.2×10^{11}	2.1×10^{10}	5.2×10^{10}	6.9×10^{7}
Rb (^{87}Rb)	1.1×10^{10}	1.9×10^{10}	4.0×10^{9}	1.3×10^{10}	1.8×10^{10}
Total alpha	2.4×10^{11}	1.4×10^{11}	1.9×10^{10}	8.8×10^{10}	8.6×10^{10}
Total non-alpha	3.1×10^{11}	1.3×10^{11}	2.5×10^{10}	6.5×10^{10}	1.8×10^{10}

These values can be compared with typical activities in surface waters which are in the range of 0.001 to 0.1 Bq/l, with a mean of 0.01 Bq/l (Nordic Radiation Protection and Nuclear Safety Authorities, 1993). This shows that the calculated fluxes are in accordance with measured values and provides some confidence in these activity flux calculations.

Table 5.34: Specific activity fluxes associated with flow in an example small river in the different geological environments.

Nuclide or decay chain	Granite pluton (Bq/l)	Gabbro pluton (Bq/l)	Basement under sedimentary cover (Bq/l)	Sedimentary basin (Bq/l)
Total alpha	4.8×10^{-2}	3.2×10^{-2}	4.1×10^{-2}	4.1×10^{-2}
Total non-alpha	5.5×10^{-2}	4.2×10^{-2}	4.7×10^{-2}	4.1×10^{-2}

5.5.2 Wind transport

As discussed in Section, 3.4, wind transport may be significant in certain types of environments. Moisture and vegetation tend to bind sediment particles together, so that wind transport is only really efficient in arid regions devoid of vegetation. Thus, aeolian transport dominates in only the desert reference environment but, even in this climate, occasional high rainfall events can move greater masses of material in a few days than wind can over the course of a year. Wind can also be an measurable transport mechanism in some of the other climates in restricted locations, such as on bare fields, sandy coasts, river plains and deltas, and on the margins of glaciers and permafrost regions.

Due to the lower viscosity and energy of wind, compared to water, wind is less able to transport large particles, except at very high wind speeds. For example, a typical grain of sand with a diameter of 1 mm requires a 10 m/s vertical updraft to lift the grain. Such uplifts are typically associated with winds with an average horizontal speed of between 20 and 30 m/s. Since these winds are at the top end of the wind speed range, grains over 2 mm diameter are rarely picked-up by wind and tend to move by bouncing over the ground, by a process known as ‘saltation’. At the other end of the scale, fine clay dust particles are usually bonded together by electrostatic cohesion. As such, these fine clays are hard for wind to pick-up if the sediment is moist. Consequently, it is middle sized particles which are most efficiently moved by wind: the grainsize that travels most easily is 0.3 mm (Summerfield, 1991).

However, in dry, desert environments, this dust material can be picked-up by wind, and can represent a very efficient transport process in short-term, high wind speed events. For example, in large dust storms, one cubic kilometre of air can hold up to 1000 tonnes of dust (Press and Siever, 1982) and, once picked-up, this dust can be transported several hundred kilometres.

It is assumed here that such a dust storm represent a maximum rate of wind transport. A typical dust storm may extent over an area of 100 km^2 and reach a height of 500 m, meaning that around 50 000 tonnes of dust (50×10^6 kg) may be in transport in each dust storm. Assuming this dust is derived from the rock (has the same composition as the rock), the equivalent elemental fluxes are calculated and presented in Table 5.35 for the different geological reference environments. In the case of the basement under sedimentary cover, since a variety of rocks crop out at the surface, the proportions are taken to be 50% gneiss and 50% shale.

Table 5.35: Elemental fluxes due to wind transport in a typical dust storm for the different geological environments.

Element	Granite pluton (kg/storm)	Gabbro pluton (kg/storm)	Basement under sediment cover (kg/storm)	Sedimentary basin (kg/storm)
C	1.8×10^{4}	1.1×10^{4}	7.6×10^{5}	1.5×10^{6}
Cl	1.0×10^{4}	2.0×10^{4}	2.1×10^{4}	2.0×10^{4}
K	1.7×10^{6}	3.0×10^{5}	7.5×10^{5}	1.0×10^{6}
Ni	5.0×10^{2}	1.3×10^{4}	1.9×10^{3}	3.3×10^{3}
Cu	2.3×10^{3}	9.8×10^{3}	3.6×10^{3}	2.3×10^{3}
Zn	3.8×10^{3}	5.0×10^{3}	5.0×10^{3}	5.3×10^{3}
Se	2.5	2.5	14.0	25.0
Rb	7.5×10^{3}	1.6×10^{3}	5.4×10^{3}	7.0×10^{3}
Cd	10.0	10.0	7.5	10.0
Sn	1.8×10^{2}	66.0	2.1×10^{2}	3.0×10^{2}
I	5.0×10^{2}	5.0×10^{2}	5.5×10^{2}	6.0×10^{2}
Nd	2.2×10^{3}	1.6×10^{3}	1.6×10^{3}	1.5×10^{3}
Sm	4.8×10^{2}	3.7×10^{2}	4.0×10^{2}	3.8×10^{2}
Pb	4.4×10^{3}	2.8×10^{2}	1.1×10^{3}	1.2×10^{3}
Th	1.4×10^{3}	1.4×10^{2}	7.0×10^{2}	6.0×10^{2}
U	2.5×10^{2}	40.0	1.7×10^{2}	1.8×10^{2}

These elemental fluxes would reflect the transport of juvenile dust material: i.e. dust derived by recent comminution of the rock. This might reflect dust at the fringes of icesheets where glacial action has created a rock flour. However, as discussed in Section 3.4, most wind blown sands are derived from the aeolian reworking of sediments rather than from the bedrock itself. These reworked sands are comprised of mostly of quartz because the other minerals from the rock have usually degraded away by this stage in the sedimentary cycle.

Since quartz does not usually contain a high concentration of trace elements, the elemental fluxes associated with wind transported quartz-rich dust must be very low. Hence, the fluxes given in Table 5.35, are likely to reflect the very maximum fluxes which could occur due to wind transport. Given the very large uncertainties associated with the calculation of the wind driven fluxes, it is not considered sensible to attempt to calculate activity fluxes for this transport process.

5.5.3 Ice transport

As discussed in Section 3.4, ice is a very powerful sediment transporting agent. This is because the physical erosion rate of an icesheet or glacier can be very high and all sizes of eroded material can be transported, from sand-sized grains to very large boulders of bedrock. However, the rates of ice flow are generally quite slow (in the range 3 to 300 m/yr) compared to either water or wind and, thus, the actual flux of ice transported material could be quite low. The upper end of this rate is the speed of valley glaciers while the lower end relates more closely with the speed of a continental scale icesheet. For example, the icesheet at the South Pole is moving at around 8 m/yr (Press and Siever, 1982).

Transported materials can occur on top of the flowing ice (supraglacial debris), within the mass of the ice (englacial debris) or at the base of the ice (subglacial debris). A typical maximum debris loading is about 10% (i.e. 90% is ice). Considering a valley glacier travelling at 300 m/yr which is 250 m wide, 200 m thick and with a debris loading of 10%, this provides a debris flux of 1.5×10^{-3} km^3/yr. If the debris is derived from the rock (has the same composition as the rock), the equivalent elemental fluxes are calculated and presented in Table 5.36 for the different geological reference environments. In the case of the basement under sedimentary cover, since a variety of rocks crop out at the surface, the proportions are taken to be 50% gneiss and 50% shale.

Table 5.36: Elemental fluxes due to ice transport in a typical valley glacier for the different geological environments.

Element	Granite pluton (kg/yr)	Gabbro pluton (kg/yr)	Basement under sediment cover (kg/yr)	Sedimentary basin (kg/yr)
C	1.4×10^{6}	8.9×10^{5}	5.1×10^{7}	9.9×10^{7}
Cl	8.3×10^{5}	1.6×10^{6}	2.5×10^{6}	1.3×10^{6}
K	1.4×10^{8}	2.5×10^{7}	7.4×10^{7}	6.6×10^{7}
Ni	4.1×10^{4}	1.0×10^{6}	1.5×10^{5}	2.1×10^{5}
Cu	1.9×10^{5}	8.0×10^{5}	4.9×10^{5}	1.5×10^{5}
Zn	3.1×10^{5}	4.1×10^{5}	5.7×10^{5}	3.5×10^{5}
Se	2.1×10^{2}	2.1×10^{2}	1.0×10^{3}	1.7×10^{3}
Rb	6.2×10^{5}	1.3×10^{5}	5.4×10^{5}	4.6×10^{5}
Cd	8.3×10^{2}	8.3×10^{2}	7.4×10^{2}	6.6×10^{2}
Sn	1.4×10^{4}	5.0×10^{3}	1.9×10^{4}	2.0×10^{4}
I	4.1×10^{4}	4.1×10^{4}	6.1×10^{4}	4.0×10^{4}
Nd	1.8×10^{5}	1.3×10^{5}	1.9×10^{5}	9.6×10^{4}
Sm	3.9×10^{4}	3.0×10^{4}	4.7×10^{4}	2.5×10^{4}

Element	Granite pluton (kg/yr)	Gabbro pluton (kg/yr)	Basement under sediment cover (kg/yr)	Sedimentary basin (kg/yr)
Pb	3.6×10^5	2.3×10^4	1.2×10^5	7.6×10^4
Th	1.1×10^5	1.2×10^4	8.6×10^4	4.0×10^4
U	2.0×10^4	3.3×10^3	1.9×10^4	1.2×10^4

These elemental fluxes are relatively large, although it needs to be remembered that the physical size of this debris is generally quite large which, combined with the inhospitable glacial climate, means that the exposure to humans from these fluxes is very small indeed.

Of course, these fluxes are only for an ‘example’ valley glacier of the type which may cross the area in the vicinity of a repository. As such these fluxes can be considered only as indicators of the magnitude of glacial fluxes. It is not possible to be more precise at this point and more detailed flux calculations would need to wait until a repository site has been chosen and detailed climate predictions for the site undertaken. Given the very large uncertainties associated with the calculation of the ice driven fluxes, it is not considered sensible to attempt to calculate activity fluxes for this transport process.

5.6 Orebodies and geo/hydrothermal systems

As discussed in Section 5.1, orebodies and geo/hydrothermal systems are considered here because they provide additional information on the distributions of naturally-occurring chemical species and, as such, they may provide further context to the hazard presented by radionuclide releases from a repository, even though these systems are unlikely ever to be considered as potential repository sites. Specifically, orebodies are considered because they represent high concentrations of elements and radionuclides, while geo/hydrothermal systems can represent high fluxes. The term *orebody* is used to here very loosely to represent any geochemical anomaly with elemental concentrations above the average elemental abundances found in normal rocks (e.g. as listed in Table 2.18): it is not intended to imply economic significance. Likewise, the use of the term *hydrothermal* is meant to imply any hot aqueous fluid, regardless of geological origin or behaviour.

Orebodies and hydrothermal systems have a genetic link because many (but not all) orebodies are formed by the precipitation of elements from hydrothermal fluids due to a change in the ambient chemical conditions, such as temperature, salinity, Eh, pH etc. The hydrothermal fluids derive their load of dissolved elements from leaching of large volumes of rock. Other types of orebodies (e.g. placer deposits) form by the accumulation of dense ore minerals in sedimentary, depositional environments, such as a river estuary or beach. Thus, although the details of the formation mechanisms may vary between different orebodies, they all share the same basic origin involving the transport and reconcentration of elements in either solid or liquid form. As such, the existence of an orebody is direct evidence of earlier elemental fluxes involved in orebody formation.

The many different types of orebody which occur exhibit a considerable range of elemental distributions and concentrations. In certain types, the ore minerals are distributed at low concentrations throughout the rock over large areas (a *dispersed* orebody) while, in other types, the ore minerals are concentrated within a small volume of rock (a *confined* orebody). As such, the elemental concentrations found in orebodies are highly variable from subeconomic chemical anomalies with concentrations just above normal background levels, through to high grade ores which are economic to mine. This is indicated in Table 5.37 by the variation in uranium concentrations found in different rocks, and in some ores.

Table 5.37: Uranium concentrations in various rocks (from Chapter 2) and in uranium source rocks and ore (from Carmichael, 1990).

Rock	U (mg/kg)
Upper crust	2.7
Granite	4.9
Gabbro	0.8
Gneiss	3.2
Shale	3.5
Limestone	2.2
Sandstone	0.6
Barren Salt Wash Sandstone, Colorado	11.0
Mudstone, Yellow Cat uranium district, Colorado	12.8
Mineralised Salt Wash Sandstone, Colorado	183
Composite uranium ore, Salt Wash Sandstone, Colorado	3800
Composite ore, Jurassic sandstone, Colorado	1500

It is clear from Table 5.37, that the concentration of uranium in orebodies can be two or three times higher than the concentrations found in normal ‘barren’ rocks. The same observation is generally true for most other elements which are normally present in rocks in trace amounts, although the degree of concentration in orebodies varies from element to element.

It is very common for several elements to be concentrated together in an orebody, and various elemental associations are frequently used to categorise orebody types. The more common associations found in different uranium orebodies are listed in Table 5.38, together their maximum size. It is clear from this table that orebodies can reflect both very high elemental concentrations and large elemental masses.

Table 5.38: Characteristics of the main uranium orebody types.

Type	Typical uranium grade (%)	Commonly associated elements	Largest known deposit (tonnes)
Pegmatites and magmatic deposits	0.03 - 0.13	Th, P, Zr, S, REE	100 000
Vein type deposits	0.1 - 2.0	Th, Mo, REE	20 000
Unconformity hosted deposits	0.4 - 4.0	Ni, Co, As, Au	250 000
Sandstone hosted deposits	0.05 - 0.5	V, Pb, Cu, Se, Mo, C, S	40 000
Conglomerate hosted deposits	0.01 - 0.1	V, Pb, Cu, Se, Mo, C, Au	15 000
Placer deposits	0.001 - 0.05	Ti, Au, Zr, C, S	100 000
Limestones	0.2 - 0.3	Ba, C	10 000
Phosphates	0.001 - 0.06	P, Co, C, As	10 000
Black shales	0.001 - 0.03	Pb, Ag, Zn, Ni	500 000

Although orebodies do represent high elemental abundances, they do not necessarily imply the presence of associated large-scale elemental fluxes. This is because many orebodies have remained physically and chemically stable since formation, sometimes for hundreds of millions of years. This is exemplified by the Cigar Lake uranium orebody in Canada, which is the second largest and richest uranium orebody yet discovered (with an average grade of 14% but reaching up to 55% in some parts). However, despite this very high concentration, there is essentially no flux of uranium or any other trace element from the orebody to the surface (no surface geochemical signature). The reason for this is that the chemical conditions in the vicinity of the ore ensure that uranium and other associated elements remain insoluble.

However, this is not always the case and orebodies which are exposed to chemical conditions in which trace elements are soluble can generate large elemental fluxes. For example, orebodies which originally formed and remained stable at depth, are subject to extensive leaching when erosion brings the orebody into the oxidising, near-surface zone. An example of this is the El Berrocal uranium orebody in Spain which was examined as a natural analogue of uranium transport in fractured granites (Rivas et al., 1997). This uranium orebody is hosted by a mineralised quartz vein within the large El Berrocal granitic pluton. Erosion has brought the orebody close to the surface, and the open fractures and veins provide high conductivity pathways through the rock and the ore. Uranium dissolved from the orebody and the granite by oxidising meteoric groundwater travels downwards with the groundwater. Some of this uranium then reprecipitates at depth in more chemically reducing conditions. As part of the investigations at the site, various geochemical, kinetic and mass balance calculations were undertaken in an attempt to quantify the fluxes of uranium and other elements between the fresh (reference) granite, weathered granite and the quartz vein.

The modelling considered a 100 m^2 'slice' of rock from the surface to a depth of 600 m. Using measured groundwater elemental abundances, flow rates and rock porosities, the fluxes for a number of chemical species were quantified: these are shown in Figure 5.6. The calculated fluxes were found to correlate well with the observed rock-water interactions, such as the association of trace elements (U, Mn and Ba) with carbonate and iron oxyhydroxide co-precipitates during dissolution and precipitation reactions. The calculated elemental fluxes of U from the dissolving vein (the UQV) to the altered granite are given as 1.9×10^{-5} mol/dm^3/yr. This corresponds to a U concentration which is high compared to the uranium concentrations in normal (non-hydrothermal) groundwaters, which are typically around 1 µg/l as shown in Table 2.19. These data are obviously site specific and could not be applied to other systems. However, this example demonstrates the more detailed modelling which is possible if comprehensive site specific data are available and which should be possible for proposed repository sites using the site characterisation data.

The fluxes of elements away from near-surface orebodies experiencing dissolution are very useful for the natural safety indicators methodology because, potentially, they can provide the largest natural fluxes at the geosphere-biosphere interface carried in solution. They, therefore, provide a maximum natural flux against which repository releases can be compared to provide context. Nonetheless, as well as the orebody dissolution fluxes, it is also interesting to consider the elemental fluxes which were responsible for the formation of the larger orebodies. Investigations at the Cigar Lake orebody and other similar deposits have shed some light on these fluxes. The very large kilometre scale uranium orebodies, such as Cigar Lake, contain up to 250 000 tonnes of uranium and are believed to have formed, from isotopic measurements, in under 500 000 years. This suggests a uranium mass flux in the region of 500 kg/yr and, assuming typical groundwater flow rates for these geological systems, this requires aqueous fluids with uranium concentrations of around 30 mg/l (Barnes, 1997).

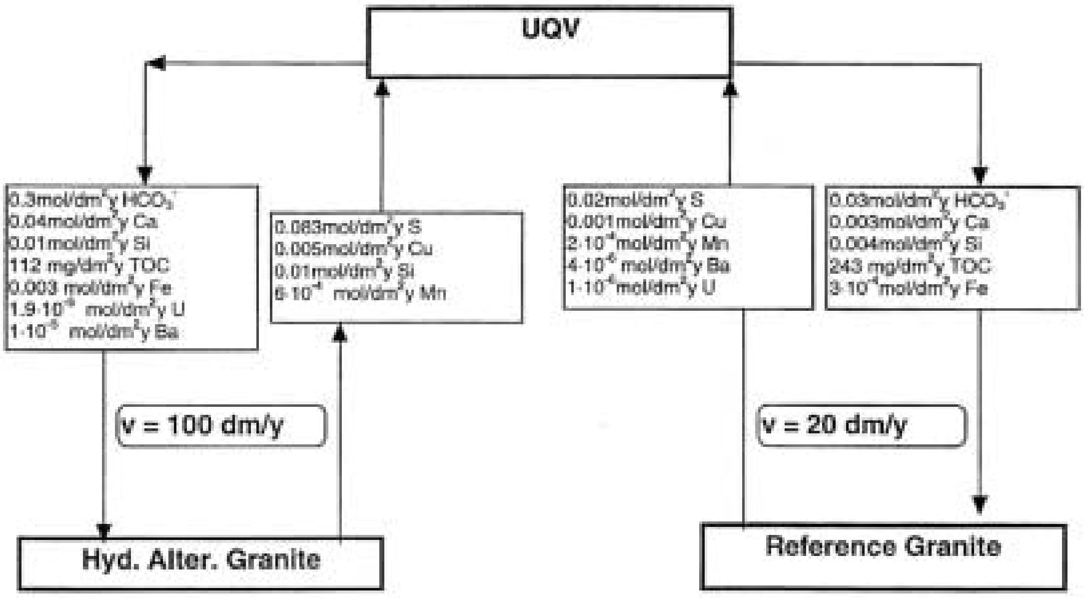

Figure 5.6: Calculated elemental fluxes at the El Berrocal uranium orebody, Spain. UQV = the mineralised quartz vein; reference granite is fresh granite; V = groundwater flow rate between compartments. From Rivas et al. (1997).

Such elemental concentrations for the ore forming fluids are around four orders of magnitude higher than those found in normal (non-hydrothermal) groundwaters, as indicated in Table 2.19, and three orders of magnitude higher than the concentrations in the groundwater close to the El Berrocal uranium orebody. They are, however, typical of the concentrations of ore metals in hydrothermal fluids, such as copper, lead, zinc, tin, molybdenum and silver which are present normally in the range of a few tens to hundreds of parts per million (Barnes, 1997). This is illustrated graphically in Figure 5.7, which shows the concentrations in ore forming hydrothermal fluids of the dominant metals in a number of different orebody types, as determined from fluid inclusion analysis or from geochemical calculation. Similar elemental concentrations and fluxes are possibly occurring today at depth in active hydrothermal systems where new orebodies may presently be forming.

This discussion indicates that the elemental concentrations and fluxes which occur in the vicinity of some orebodies currently undergoing leaching (e.g. El Berrocal) can be very high and probably reflect the largest natural concentrations and fluxes occurring at the geosphere-biosphere interface. In contrast, measurements at other orebodies which are stable (e.g. Cigar Lake) indicate that no trace element fluxes are occurring in these environments despite the very high concentrations in the ore. Such a contrast is significant for the natural safety indicators methodology because it implies that natural elemental concentrations and natural elemental fluxes are not directly interchangeable indicators: a high concentration need not imply a high flux and visa versa. This is clearly the same with a repository, where the high concentrations of radionuclides in the repository do not present a potential hazard unless they become mobile.

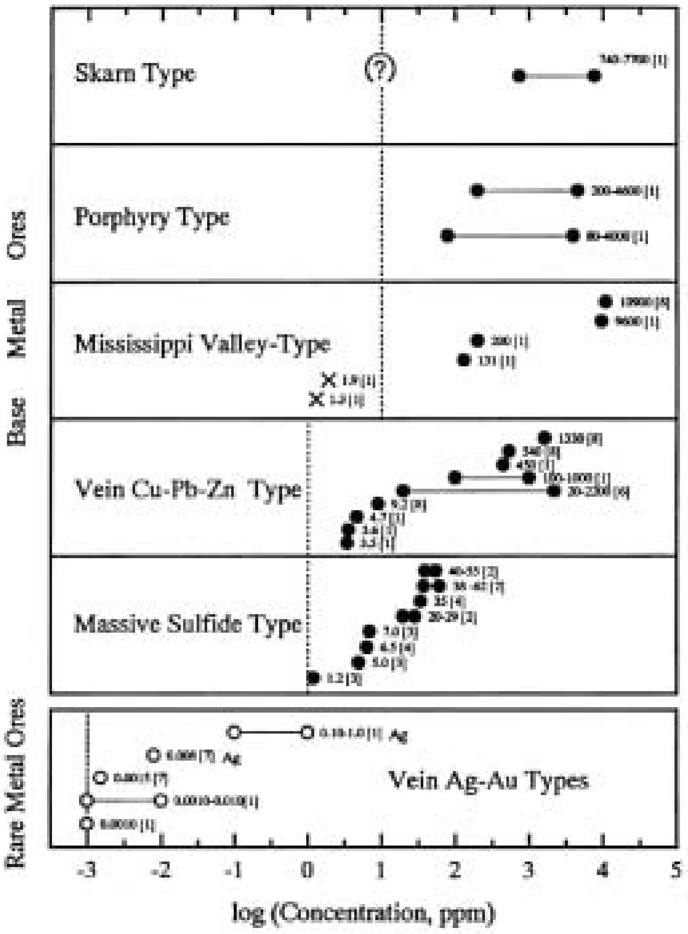

Figure 5.7: Elemental concentrations in ore forming hydrothermal fluids of the dominant metals in a number of different orebody types. Filled dots are for Cu, Pb and Zn, open dots are for Ag, Au and Hg, and × represents non ore-forming concentrations. The dotted vertical line represents the minimum concentration necessary for orebodies to form. From Barnes (1997). The numbers in [ ] refer to original references. See Barnes (1997) for details.

It follows that the choice of elemental concentrations or fluxes as natural safety indicators in a safety assessment will need to be made carefully to ensure the most appropriate indicator is chosen to meet the objectives of the safety assessment in hand.

6 Coupled flux modelling

In the previous sections, elemental fluxes have been calculated for discrete processes, such as groundwater discharge and denudation, based on simple, unvarying process rates and on the elemental abundances in the material being mobilised. This approach is adequate for understanding the elemental fluxes which occur due to a single mechanism at a particular point in time (e.g. today), or when averaged over a very long time period, provided an appropriate long-term average process rate can be defined. However, natural systems are dynamic, not static, which means that a single rate may not be applicable to an individual process over the time scales of interest to PA, when climate change and other dynamic events are is likely to have a significant impact on the system. Furthermore, in a real geological system, all processes are coupled, so that a change in the rate of one process may have an affect on a second process. A simple example of this might be where an increase in the denudation rate causes the soil thickness to be reduced which, in turn, could cause a change to the proportion of rainfall which recharges the groundwater.

In an attempt to scope the effect of coupled processes and changing climate on natural elemental fluxes, a crystalline rock system has been modelled using the QuantiSci code AMBER which was appropriately modified to deal with non-linearity in geological systems, such as solubility limit controls on groundwater compositions.

Using AMBER, it is possible to represent natural systems using a series of compartments between which transfers of chemical species can be represented and quantified. A compartment can be any suitable part of the system being modelled, for instance a lung in a model of the human body or a river in a model of the biosphere. Careful discretisation of the system allows processes to be represented in three dimensions. For example, modelling advection in an aquifer may be represented by a series of compartments each representing a volume of rock along the groundwater flow path. Compartmentalisation of problems simplifies the modelling required and enables interfaces between different parts of the system to be represented in a convenient manner.

In AMBER, the chemical species being modelled, referred to as contaminants, are assumed to be uniformly mixed in each of the compartments. Every transfer between compartments is ‘donor controlled’, depending directly on the amount of the material present in the compartment from which the material is moving, and can change with time. AMBER allows contaminants to decay with time into other contaminants, if required. For example, a parent radionuclide may decay into a daughter nuclide, or a particular organic compound may degrade into a different one. However, for the modelling work undertaken in this study, radionuclide decay was not represented because only stable or very long-lived radionuclides are considered.

A crystalline rock system was chosen for this modelling exercise because crystalline rocks are common to both the inland pluton and the basement under sedimentary cover reference environments, and because the flux calculations described in Chapter 5 suggested that the range of elemental mass fluxes which can occur in these environments as a result of different climate states may be very large. A conceptual model for the crystalline rock system was constructed to describe:

- the geometry of the system,
- partitioning of elements in the system,
- movement of groundwaters through the system, and
- the mechanisms for elemental transfer from the geosphere to the surface environment.

The objective was to calculate elemental fluxes between compartments, and to investigate which processes are responsible for these fluxes, during a time dependent climate scenario. The details of the mathematical modelling approach underpinning this modelling work are described in Appendix A. In the following sections, the conceptual model of the crystalline system and the AMBER results are presented.

6.1 The conceptual model

The crystalline rock system is based around features of both the inland pluton and the basement under sedimentary cover reference environments, which were discussed in Sections 5.2 and 5.3 respectively, modified in certain ways (as discussed below) to emphasise certain aspects of the behaviour of natural fluxes.

The system comprises a large granitic pluton which is assumed to lie inland (away from any coastal effects) partially covered with variable thicknesses of soil. A cross-section of the crystalline rock system is shown in Figure 6.1. The pluton is roughly circular with a diameter of 25 km. The structural geological setting is of a large syn-tectonic pluton which has been emplaced into metamorphic country rocks. The pluton is cut by semi-regular sets of joints, visible in outcrop, and also by larger-scale fracture zones. The granite is subdivided into an upper, oxidising zone which is assumed to be approximately 200 m thick and a lower, chemically reducing zone.

The surface topography in the crystalline rock system is of moderate relief, with the upland areas rising to approximately 300 m above the lowest local ground level. The uplands create a valley which forms a small, closed catchment area. Surface drainage takes place by a single river system. Groundwater flow in the granite is restricted to the hydraulically-active fractures, with groundwater flow driven by the hydraulic head gradient created by the upland areas. Due to the generally low hydraulic conductivity of the crystalline rock, the groundwater flow rates will be relatively slow. Groundwaters in the shallow and deep rocks mix as waters flow downwards and upwards. In the area of recharge, water infiltrates through the soil into the shallow rock and then into the deep rock. In the area of discharge, water from deep basement rock flows upwards and mixes with water from the shallow rock.

Groundwater flowing in the fractures reacts with the granite causing mineral dissolution and release of elements into the flowing porosity. The concentration of dissolved species is balanced by the mineral dissolution rate, the solubility limits and the groundwater flow. Higher solubility limits generally apply in the upper, oxidising zone than in the deeper reducing zone.

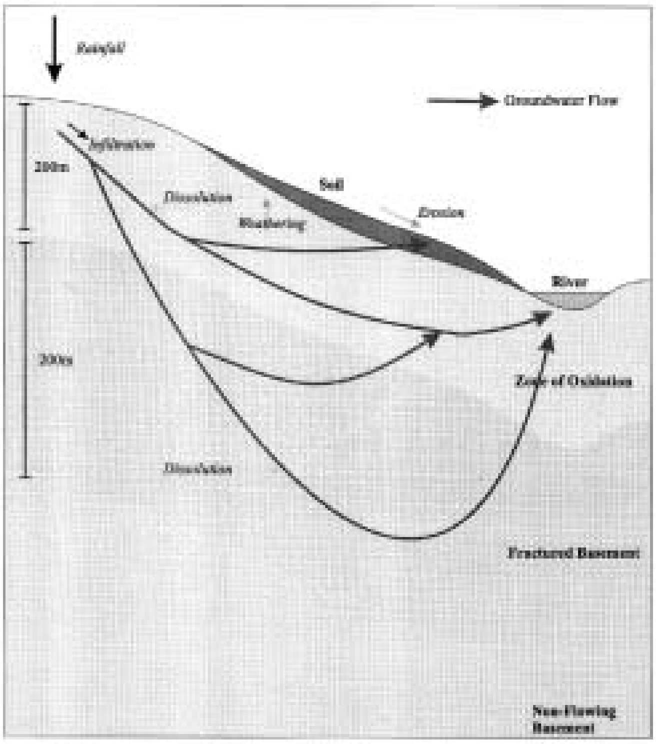

Figure 6.1: Cross-section of the crystalline rock system, showing a number of the features and processes which are explicitly considered in the AMBER modelling.

The pluton is partially covered by a soil horizon which is most extensive on the valley floor. The soil thickness changes over time in response to climate which controls the balance between soil formation (due to weathering of the near-surface granite and the addition of organic material, a process known as 'soil production') and erosion of the upper surface of the soil.

The movement of material after it has been eroded from the soil is not modelled in detail. A simple assumption is made that a river removes weathered material and soils from the area, and deposits them to a sink, which could be a river estuary or the sea floor sediments. River flows are fed by surface run-off and groundwater discharge in the form of a baseflow.

The full extent of the pluton was not modelled in AMBER. To focus the work on fluxes which occur within the crystalline rock and across the geosphere-biosphere interface, a model area of 4 km × 8 km was adopted which lies entirely within the pluton. The rock was modelled to a depth of only 1 km because, below this depth, groundwater flow is assumed to be negligible.

6.2 Model parameters and climate scenario

The AMBER model of the crystalline rock system with all the compartments and transfers is described in Appendix A, together with all of the AMBER model parameters required for the flux calculations are defined. Many of these parameters were fixed (e.g. the dimensions of the model system) but others were calculated by AMBER during the model runs (e.g. elemental concentrations). However, a number of parameters were user defined to 'set' the model system and these largely related to the climate state and the impact of climate on the conceptual model. A simple climate change scenario was constructed which involved four distinct climate states which ‘flipped’ instantaneously from one to the other. Each climate state was considered to last 50 000 years. The climate states considered were based on four of the five climates discussed in Section 5.1.2 and identified in Table 5.2. The climate scenario which was constructed for the AMBER modelling is defined in Table 6.1. In the AMBER model, climate directly influenced a number of parameters:

- the proportion of rainfall infiltrating the ground,
- weathering,
- erosion and
- soil production.

Table 6.1: The climate scenario adopted in the AMBER model of the crystalline rock system.

Time period (ka)	Climate state	Mean annual temperature (°C)	Mean annual precipitation (cm/yr)
0 - 50	Temperate	11	60
50 - 100	Subarctic	2	40
100 - 150	Temperate	11	60
150 - 200	Desert	20	10
200 - 250	Temperate	11	60
250 - 300	Tropical	25	220

The climate controlled parameter values for the modelling are defined in Table 6.2. The proportion of rainfall as infiltration values were taken from the discussion of groundwater discharge for the inland pluton reference environment given in Section 5.2 and the weathering rate of granite was taken from data given in Table 5.8. The soil production and soil erosion rates were chosen to produce soil thicknesses in accordance with the general relationship between soil depth and climate as shown graphically in Figure 3.4.

The geochemical parameters in the model system are defined in Table 6.3, these relate to:

- initial elemental abundances in each compartment,
- the solubility limits in shallow and deep groundwaters, and
- the distribution coefficients (K_ds) in the rock/water and soil/water zones.

In the system, the only source term for elemental fluxes was taken to be the granite. Therefore, at time zero in the modelling, the elemental concentrations in all groundwater, soil and sink compartments was set at zero. The initial elemental abundances in the granite were taken from the elemental abundance compilation in Chapter 2 and relate to the ‘average granite’ composition in Table 2.18. The solubility limits have been chosen such that they correspond to the average ‘crystalline groundwater’ composition given in Table 2.19, on the basis that most deep, old groundwaters in a stable environment will be close to equilibrium with the crystalline rock and, thus, the concentration of these elements will approximate to an ‘average’ solubility limit (except for source term controlled elements).

Table 6.2: Climate controlled parameter values in the AMBER model of the crystalline rock system.

Climate state	Proportion of rainfall as infiltration	Weathering rate of granite (m/yr)	Soil production rate (m/yr)	Erosion rate of soil (m/yr)
Temperate	0.05	1.5×10^{-5}	9.0×10^{-6}	2.1×10^{-6}
Subarctic	0.03	5.0×10^{-6}	5.0×10^{-7}	3.0×10^{-6}
Desert	0.02	5.0×10^{-6}	0	5.0×10^{-6}
Tropical	0.07	1.5×10^{-6}	1.5×10^{-5}	1.1×10^{-7}

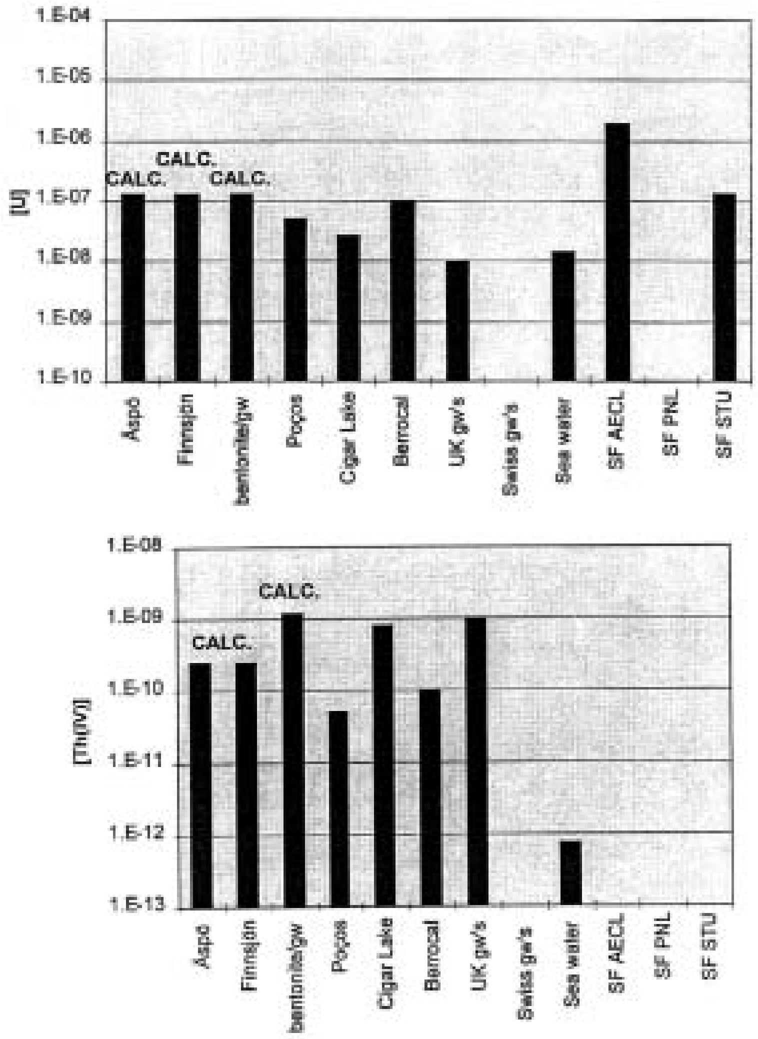

Figure 6.2: Comparison between predicted (calculated) solubility limits for the SKB SR97 PA and measured elemental abundances in natural waters. From Bruno et al. (1997).

This approach to defining real solubility limits, as opposed to limits measured in a laboratory, has been discussed by Bruno et al. (1997) who showed that it was a valuable method for 'validating' the solubility limits adopted in the Swedish SR97 PA. Comparisons derived by Bruno et al. (1997) between predicted (calculated) solubility limits and measured natural elemental abundances for U and Th are shown graphically in Figure 6.2. Solubility limits for the shallow groundwaters were set to be one order of magnitude higher than those for the deep rock on the basis that most elements are more soluble in near-surface oxidising waters than in deep, reducing waters.

The distribution coefficients adopted in this work for the granite/groundwater system were taken from the Nagra 1995 sorption database using the ‘realistic’ values for crystalline rock (Stenhouse, 1995). The values chosen for the soil/porewater system were taken from various sources in the literature and set at an ‘average’ value for organic rich soils.

Table 6.3: Geochemically controlled parameter values in the AMBER model of the crystalline rock system.

Element	**Initial abundance in granite (mg/kg)**	**Solubility limit in deep groundwater (M)**	**Solubility limit in shallow groundwater (M)**	**Distribution coefficient in rock/water (m^3/kg)**	**Distribution coefficient in soil/water (m^3/kg)**
Ni	10.0	1.5×10^{-8}	1.5×10^{-7}	0.5	0.9
Se	0.05	3.8×10^{-9}	3.8×10^{-8}	0.01	0.09
Sm	9.5	1.9×10^{-10}	1.9×10^{-9}	0.05	0.05
Th	27.0	1.2×10^{-9}	1.2×10^{-8}	1	5
U	4.9	4.5×10^{-9}	4.5×10^{-8}	1	10

6.3 Model results

A number of specific issues related to the distribution of elements in the crystalline rock system were examined using the AMBER model. These were:

1) the modelled elemental concentrations in the groundwaters and whether solubility limits had been reached,
2) the elemental fluxes from deep to shallow groundwaters,
3) the elemental fluxes associated with discharging groundwaters,
4) the modelled elemental concentrations in the soil horizon,
5) the thickness of the soil horizon,
6) the elemental fluxes associated with the erosion of the soil horizon, and
7) the impact of climate changes on the above parameters.

Only five elements were considered in this modelling exercise to reduce the run-times for the AMBER code and to simplify the presentation of the results: these were Ni, Se, Sm, Th and U. These elements were chosen because they have a range of abundances in the granite (source term) and a range of K_ds in the rock-water system. They were expected, thus, to display divergent behaviour in the model system. The U and Th abundances can be used to calculate the alpha activity associated with the elemental distributions and fluxes.

The modelled (calculated) elemental concentrations in the deep and shallow groundwaters are shown in Figures 6.3 and 6.4 respectively. In the case of the deep groundwater, most of the elements (with the exception of U) reach stable concentrations within a period of approximately 1000 years. These stable concentrations do not necessarily reflect solubility limits because a balance can be established between the flux of element to the groundwater by dissolution and the flux out of the system due to groundwater flow. However, in most cases, these stable concentrations do approximate to the solubility limits, but this is not the case for Se which only approaches solubility limits during the desert climate (150 - 200 ka) when slow groundwater movement will allow longer rock-water reaction times.

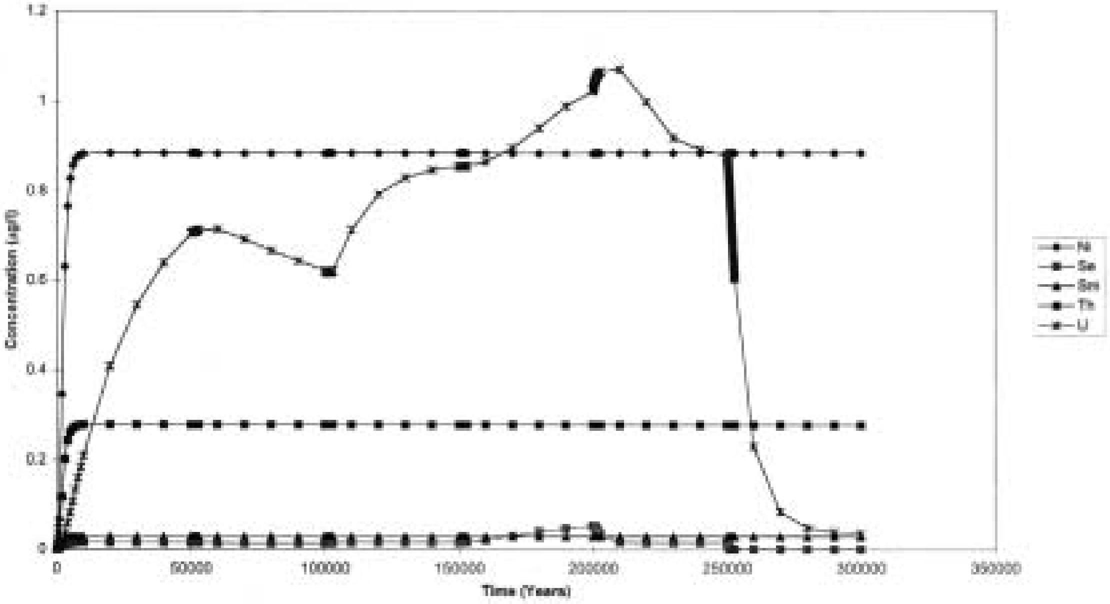

Figure 6.3: Modelled elemental concentrations in the deep groundwater in the crystalline rock system.

The unusual behaviour of U is due to a low initial elemental abundance in the rock (4.9 mg/kg) which means that the slow dissolution rate of the rock does not allow it to reach equilibrium in the time available during any climate state period. As with Se, U only approaches solubility limits during the desert climate. The U concentration falls significantly at 250 ka at the onset of the tropical climate, when a larger groundwater flux ‘dilutes’ the groundwater composition. Se is similarly affected by the tropical groundwaters but to a lesser extent.

In the case of the shallow groundwaters, the elements display similar behaviour to the deep waters. However, solubility limits are now higher (due to the oxidising conditions) and, thus, most elemental concentrations are higher than those at depth. Some elements achieve their solubility limits but Ni, in addition to U and Se, is now unable to reach an equilibrium concentration within the period of the individual climate states and shows considerable variability in concentration, decreasing during the subarctic climate (50 - 100 ka) and tropical climates (250 - 300 ka), and rising in the desert climate when residence times are greatest.

The maintenance of solubility limit concentrations for elements such as Th is partly due to their abundance in the rock relative to their solubility limits (meaning that less time is required to dissolve the rock and buffer the groundwater concentration) and partly due to the fact that their high abundance allows some buffering of concentration between shallow and groundwaters as the two systems mix. The behaviour of U in both the deep and shallow groundwaters is explicitly shown on Figures 6.5 and 6.6, respectively.

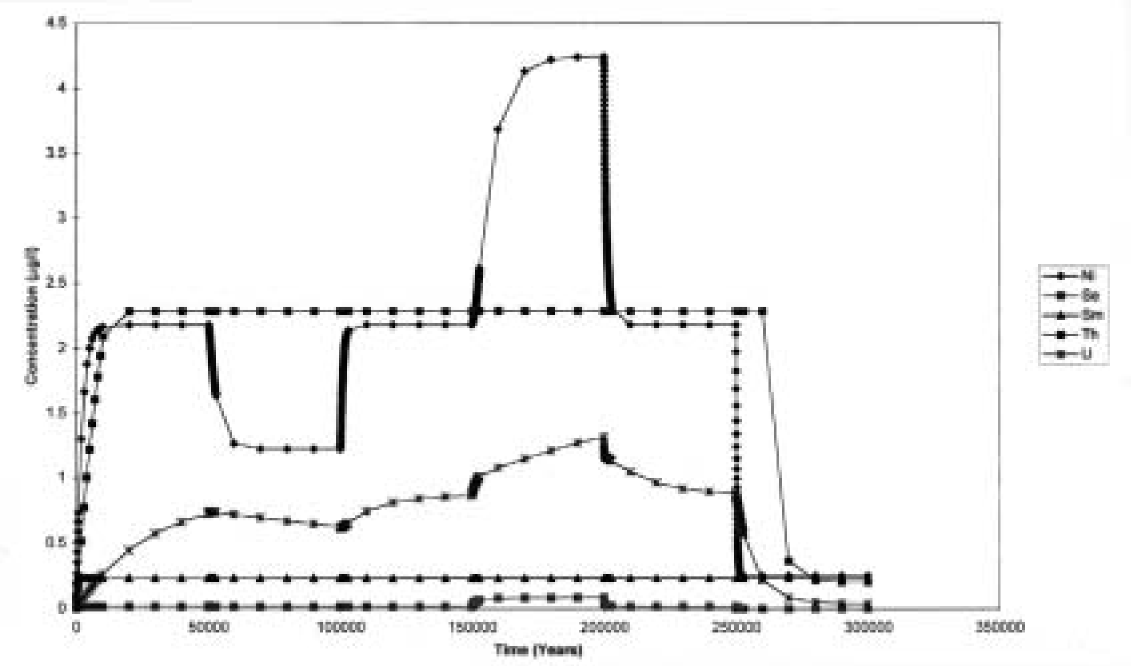

Figure 6.4: Modelled elemental concentrations in the shallow groundwater in the crystalline rock system.

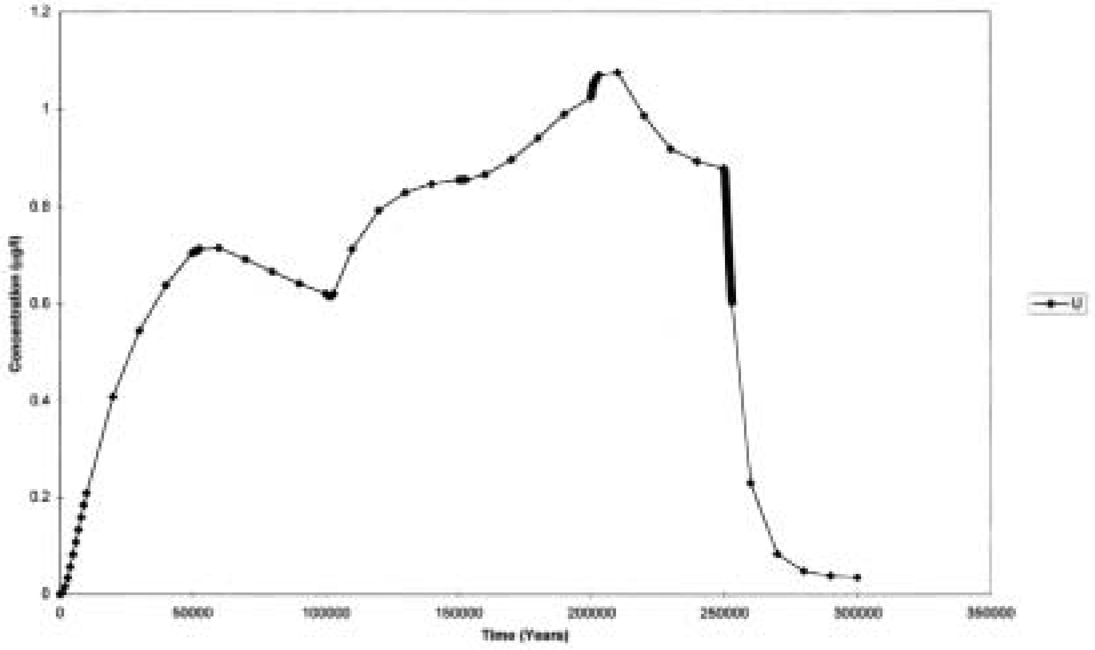

Figure 6.5: Modelled U concentrations in the deep groundwater in the crystalline rock system.

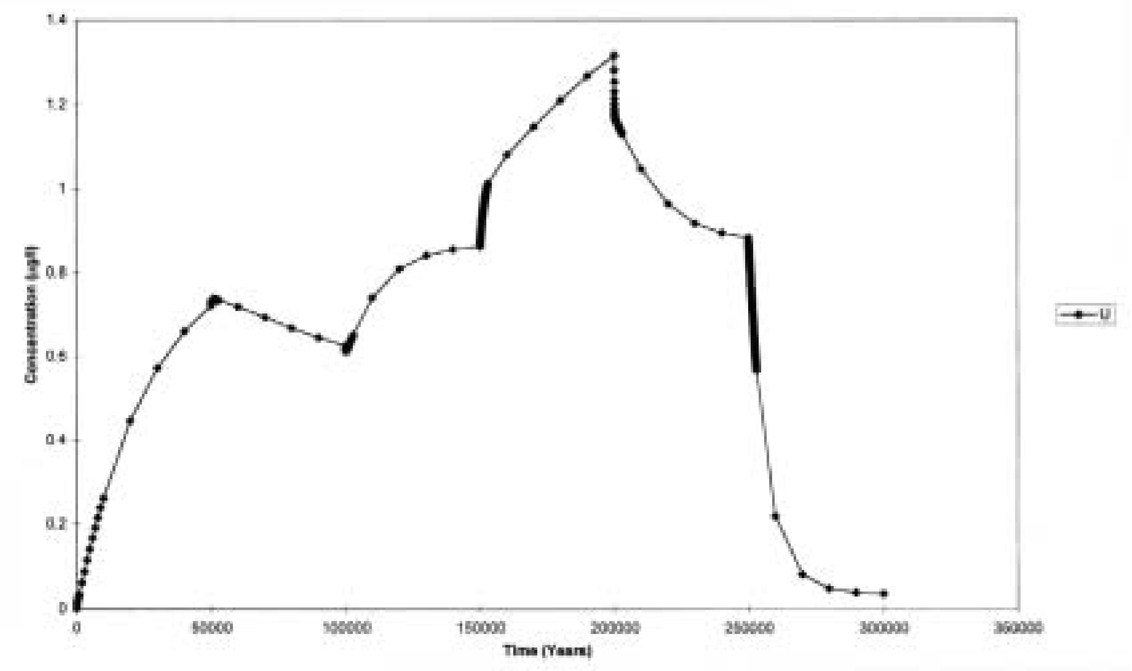

Figure 6.6: Modelled U concentrations in the shallow groundwater in the crystalline rock system.

In general, the AMBER model simulates elemental concentrations in the groundwaters which are consistent with measured values from natural groundwaters (Table 2.19). The overall conclusion from the groundwater elemental concentrations is that the flux from the rock to the groundwater is complex and that, in a rapidly changing system, stable elemental abundances and fluxes may not be attained. This could be particularly relevant for northern latitude countries where rock-water system may still be responding to earlier glacial events, and where future glacial events are required to be addressed in PAs for deep repositories.

The elemental fluxes associated with discharging groundwaters are shown on Figure 6.7. It is assumed that these waters are all passing through the soil horizon on the way to the river system. There is a very clear dependence of the flux on the changing climate and, essentially, elemental fluxes are related to the groundwater flow (set here as a proportion of rainfall). Nonetheless, the individual behaviour is more complex than a simple step function response to climate, due to the difference in the rates of groundwater flow and rock dissolution. This is indicated by the behaviour of Th at 100 ka, at the change from subarctic to temperate climate, where it can be seen that a few thousand years are required to reach a new equilibrium Th flux for the new climate state.

Likewise, at the change from desert to temperate climates (at 200 ka), a sudden peak in Th flux is achieved due to the high concentration, slow flowing (long residence time) desert groundwaters suddenly being flushed out of the system by the larger groundwater flows in the temperate climate. Similar behaviour is indicated by U. After the initial flushing, the elemental fluxes return to an equilibrium state. However, this is followed by an even larger flushing event at the change from temperate to tropical climates (at 250 ka) in which most elements show a ‘pulse’ release in the groundwater.

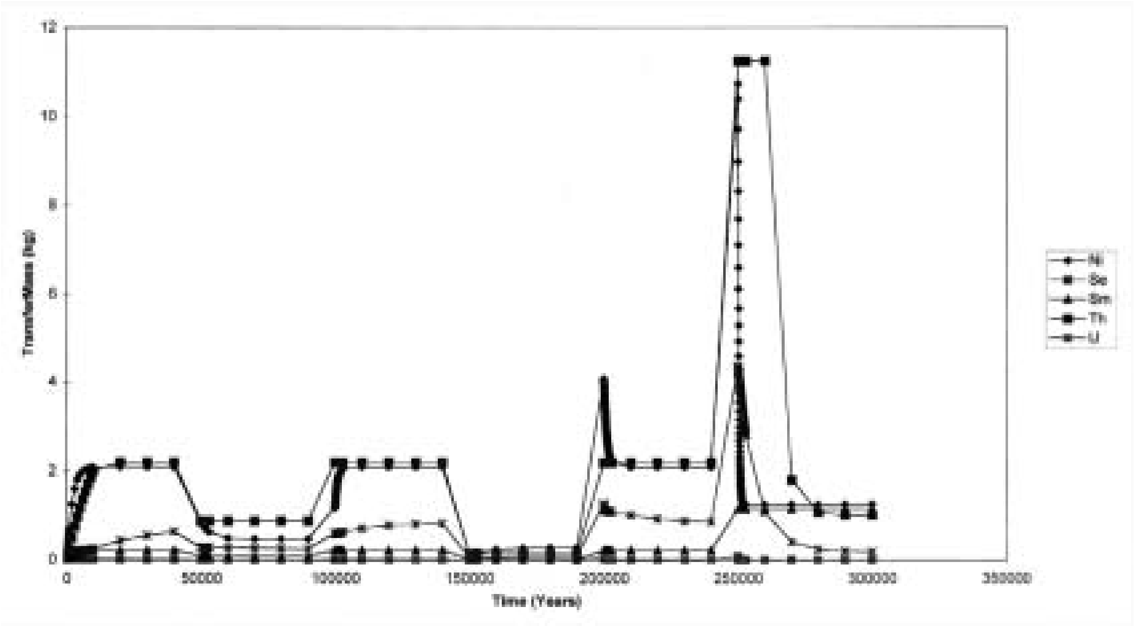

Figure 6.7: Modelled elemental fluxes associated with discharging groundwater in the crystalline rock system.

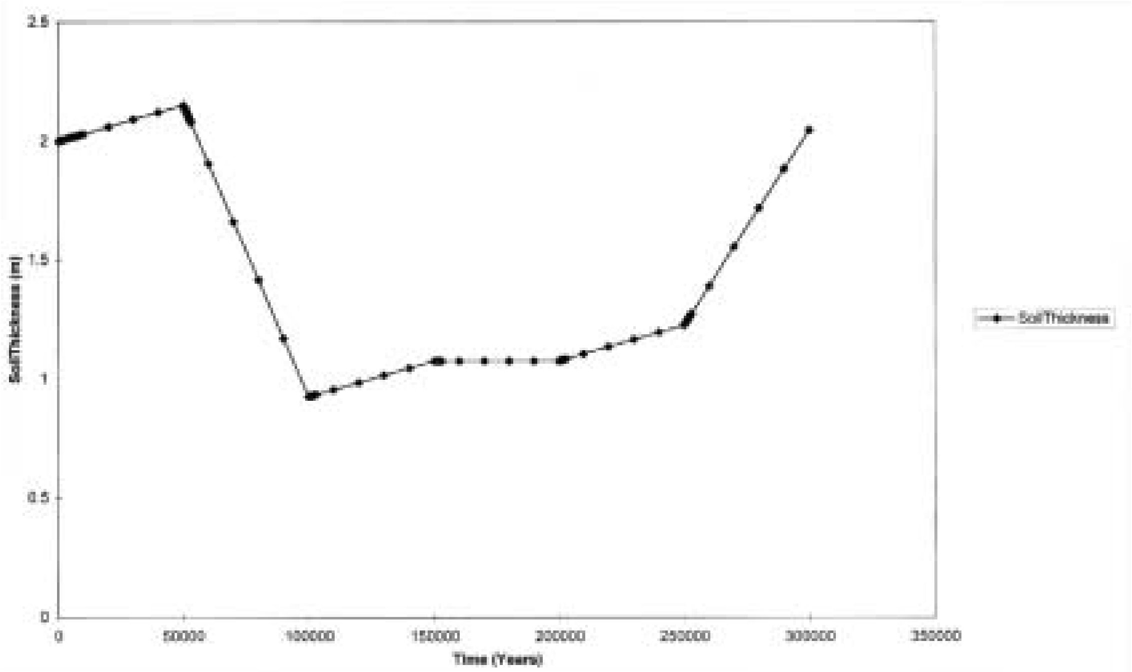

Figure 6.8: Modelled soil thickness associated with climate change in the crystalline rock system.

The fluxes shown on Figure 6.7 are in units of mass (kg) for the entire modelled system (4 km × 8 km). It is evident from the magnitude of the fluxes that the groundwater discharges are roughly a few kilograms per year per element in a stable system. These magnitudes are comparable to those calculated in Section 5.2 for fluxes associated with groundwater discharge in the inland pluton reference environment. However, Figure 6.7 also shows that these fluxes can be considerably higher during short-term pulses associated with rapid environmental changes.

At the land surface, the thickness of the soil horizon changes with climate in response to the balance between the processes of granite weathering, soil production (the addition of organic material to the weathered granite material) and soil erosion. Figure 6.8 shows the changing thickness of the soil horizon during the different climate states. The most obvious features are the rapid thinning of the soil during the subarctic climate (50 - 100 ka) when soil is removed by water, ice and mass movement, and the deepening of the soil during the tropical climate (250 - 300 ka), when chemical weathering of rock is at a maximum, as discussed in Section 3.4. During the desert climate (150 - 200 ka), the soil thickness is at a minimum and constant, due in part to the lack of surface water and vegetation (zero soil production). The elements carried in the discharging groundwaters (as indicated in Figure 6.7) are assumed to pass through the surface soil and a proportion of these elements will be retarded in accordance with their soil/water K_d values, which were given in Table 6.3.

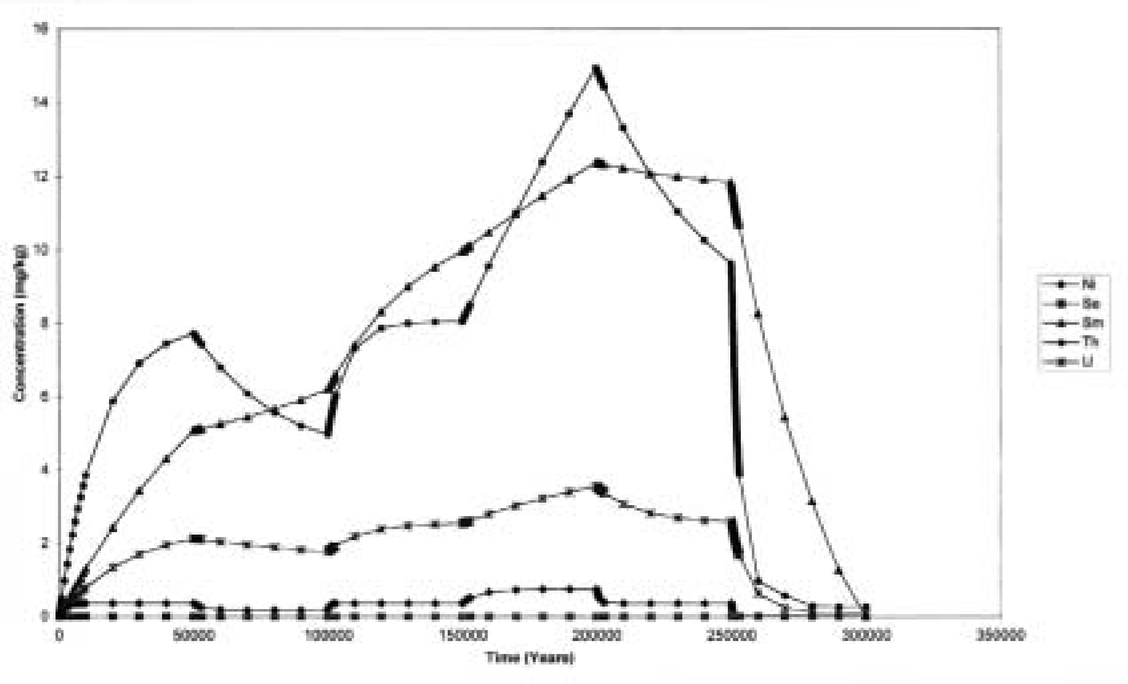

Figure 6.9: Modelled elemental concentrations in the soil horizon in the crystalline rock system.

Figure 6.9 shows the effect of elemental retardation on the elemental abundances in the soil (given in mg/kg, equal to ppm). In fact, the modelled concentrations are not attributable only to the input and retardation of element but also to the changing volume (thickness) of the soil in response to the variable erosion rates as discussed above and shown in Figure 6.8. Nonetheless, it is clear that elements with a high K_d, such as Th, generally become enriched in the soil over time. The sudden drop off in concentration at 250 ka is due to the onset of the tropical climate and the rapid increase in soil thickness (effectively 'diluting' the elements in the soil). This is a consequence of modelling the soil as a single, well-mixed compartment.

A better appreciation of elemental retardation within the soil horizon could be obtained in a more detailed model which accounts for elemental distributions in separate soil layers.

Nonetheless, in general, the AMBER model simulates elemental concentrations in the soil which are consistent with measured values from natural materials. It is also clear that elemental behaviour in the soil is strongly controlled by the balance between the elemental fluxes in the discharging groundwater and the soil/water K_d values. The concentration of U in the soil is explicitly shown in Figure 6.10.

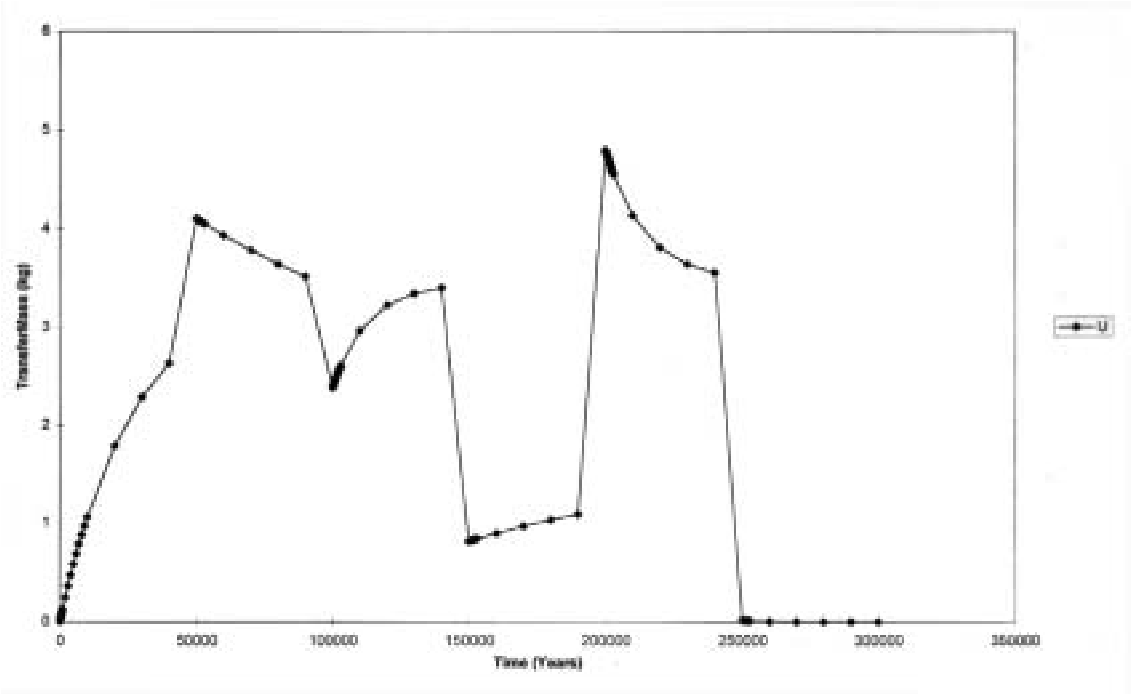

Figure 6.10: Modelled U concentrations in the soil horizon in the crystalline rock system.

The elemental fluxes from the soil to the sink are due to the passage of unretarded elements in the discharging groundwater and to the erosion of soil. The changing climate has a significant impact on the erosion rate, as quantified in Table 6.2, and thus on the fluxes from the soil to the sink. In this AMBER model, this flux pathway is not explicitly defined and is assumed simply to be a river. However, in reality, the mechanism for the erosion of soil could involve water, wind or ice. The physical nature of the sink would also be climate specific and could be, for example, estuarine or ocean sediments, desert sands or loess deposits.

Nonetheless, although the nature of the mechanisms which transfer material to the sink are not defined, the mass fluxes along the pathway are calculated (and are appropriate for the climate state) and these are shown in Figure 6.11. On this figure, the impact of climate is obvious. The lowest fluxes occur in the desert climate (150 - 200 ka), when only wind blown transport of smaller dust and small sand particles would be possible. The largest fluxes occur at the end of the desert climate (200 ka) and, again, a high flux event associated with a changing system is evident. Overall, the fluxes of individual elements roughly corresponds to their relative abundances in the soil horizon, as was shown in Figure 6.9.

The alpha activity associated with the U and Th mass fluxes from the soil to the sink can be calculated. The peak mass fluxes are approximately 20 kg/yr for Th and 5 kg/yr for U, which arise from the entire surface of the model area (4 km × 8 km). Based on the assumptions for activity calculations given in Section 1.2, the activity fluxes associated with U and Th (assuming the U is in normal isotopic proportions) will be:

- U = 4.0×10^6 Bq/km^2/yr, and
- Th = 2.6×10^6 Bq/km^2/yr.

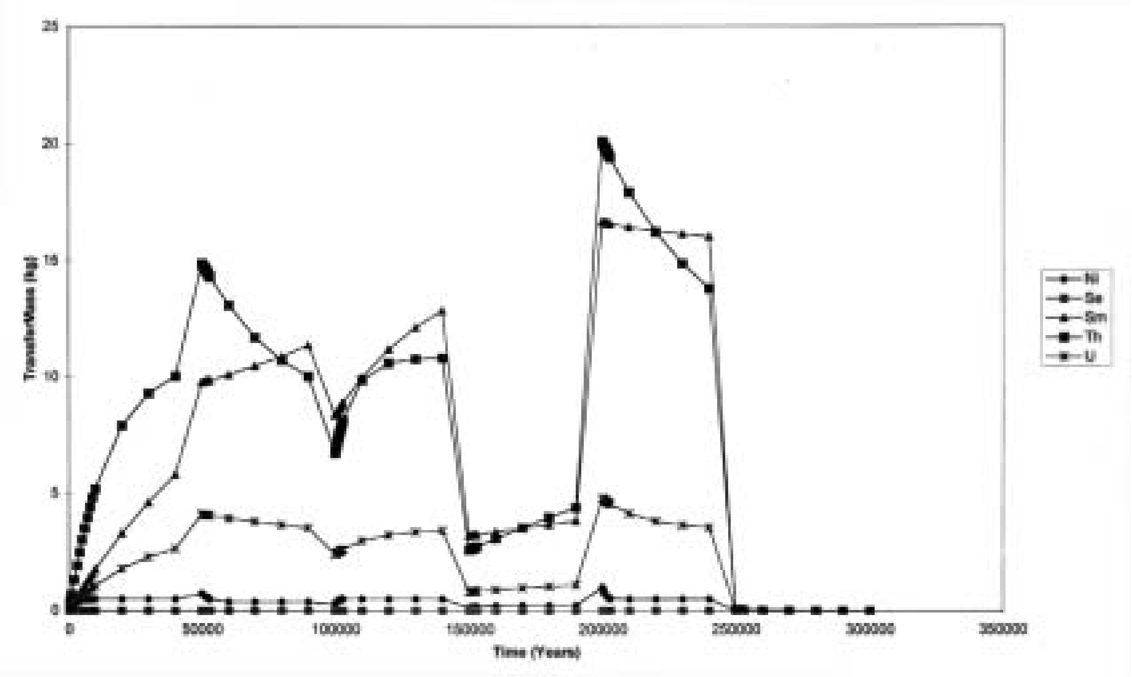

Figure 6.11: Modelled elemental fluxes associated with passage of material from the soil to the sink in the crystalline rock system.

If it is further assumed that U and Th are in secular equilibrium with the longer-lived daughters, as discussed in Section 1.2, then the activity fluxes for the U and Th chains are:

- U chains = 1.8×10^7 Bq/km^2/yr, and
- Th chain = 1.0×10^7 Bq/km^2/yr.

In which case the peak total alpha activity flux due to passage of material from the soil to the sink is 2.8×10^7 Bq/km^2/yr. These values are order of magnitude equivalent to the activity fluxes due to denudation of the granitic inland pluton, which are given in Table 5.11.

An important observation from this modelling work is that the maximum elemental fluxes are not associated with particular steady-state systems in any climate state, even those with high process rates. Instead, the largest magnitude fluxes appear to occur as transient events associated with climate change events. In this model, climates are assumed to change instantaneously and, therefore, there is an inevitable period during which a new equilibrium state has to be established. Nonetheless, the real world climate system is capable of rapid changes and it seems probable that climate changes will often be more rapid than the geological and geomorphological processes which have to adapt in response to them. Therefore, although the peak fluxes associated with transient events may not be as large as indicated in this modelling work, they are very likely to occur.

This raises particular issues for using fluxes as natural safety indicators because the impact of these high magnitude, short duration flux events will be lost in the longer term averages and, thus, predicted ranges of fluxes (and concentrations) may not be as representative as is often assumed. However, this is also true for the repository releases because these are affected by the same natural processes which drive the natural elemental fluxes. It is probable, therefore, that some processes may cause pulse releases of waste radionuclides to the surface environment, leading to short but high activities which are not accounted for in standard PA calculations.

In an attempt, therefore, to examine these transient features in a little more detail, a revised AMBER model was constructed which mimics large environmental changes. The most likely environments in which high magnitude, short duration flux events could occur are those where there is a mechanism by which elements are retarded (and reconcentrated) in a medium which is relatively unstable (i.e. easily transportable, such as a soft sediment). Such environments are relatively common around the world and occur in many climate states. Two examples are presented here:

1) High latitude, wet climates with unconsolidated, organic-rich sediments through which groundwaters discharge. This could be a peat bog in Sweden or Ireland. The organic sediment will retard many dissolved elements from the groundwater and, over periods of time, they may develop high elemental concentrations. Similar mechanisms are responsible for the elevated concentrations of U in some coals. If the climate changes, these unconsolidated sediments can be easily eroded by ice, if the climate gets colder, or by wind if the climate gets warmer and the sediment dries and desiccates. Either way, rapid erosion of the sediment will cause a pulse release of the reconcentrated elements.
2) Mid latitude, dry climates where groundwater discharges in an arid environment. This is analogous to the situation at the proposed US repository at Yucca Mountain where the discharge points for the groundwaters which pass through the repository zone are located in dry lake beds. Discharging groundwaters evaporate from the surface, leaving behind an ‘evaporite-type’ deposit of previously dissolved elements. Potentially, in a situation like this, a changing climate could remobilise the evaporite concentrate in water, if the climate gets wetter, or by wind.

To examine mechanisms of this kind, a simple transient system model was developed in AMBER which incorporated a basic mechanism whereby the soil horizon eroded only very slowly in early climate states but eroded rapidly (10^3 times faster) in a subsequent climate state at 200 ka. The granite weathering, soil production and soil erosion rates adopted in the transient system are defined in Table 6.4. Only two elements were considered in this simple model: Sr and U. These elements were chosen because they have significantly different K_d values in soil/porewater systems, with Sr acting in a semi-conservative manner (K_d = 0.5 m^3/kg) with respect to U (K_d = 10 m^3/kg).

For this simple transient system model, the elemental fluxes associated with the discharging groundwater passing through the soils are shown in Figure 6.12. The impact on climate is evident in the fluxes of both elements, with the magnitude being partly dependent on the groundwater flow (rainfall proportion as recharge) and, as seen in the earlier example, peak fluxes are associated with climate change events.

Table 6.4: Climate controlled parameter values in the AMBER model of the transient system.

Climate state	Time period (ka)	Weathering rate of granite (m/yr)	Soil production rate (m/yr)	Erosion rate of soil (m/yr)
1	0 - 50	1.5×10^{-5}	0	1.0×10^{-7}
2	50 - 100	5.0×10^{-6}	0	1.0×10^{-7}
3	100 - 150	1.5×10^{-5}	0	1.0×10^{-7}
4	150 -200	5.0×10^{-6}	0	1.0×10^{-7}
5	200 - 250	1.5×10^{-5}	9.0×10^{-6}	3.0×10^{-4}
6	250 - 300	1.5×10^{-6}	1.5×10^{-5}	1.1×10^{-7}

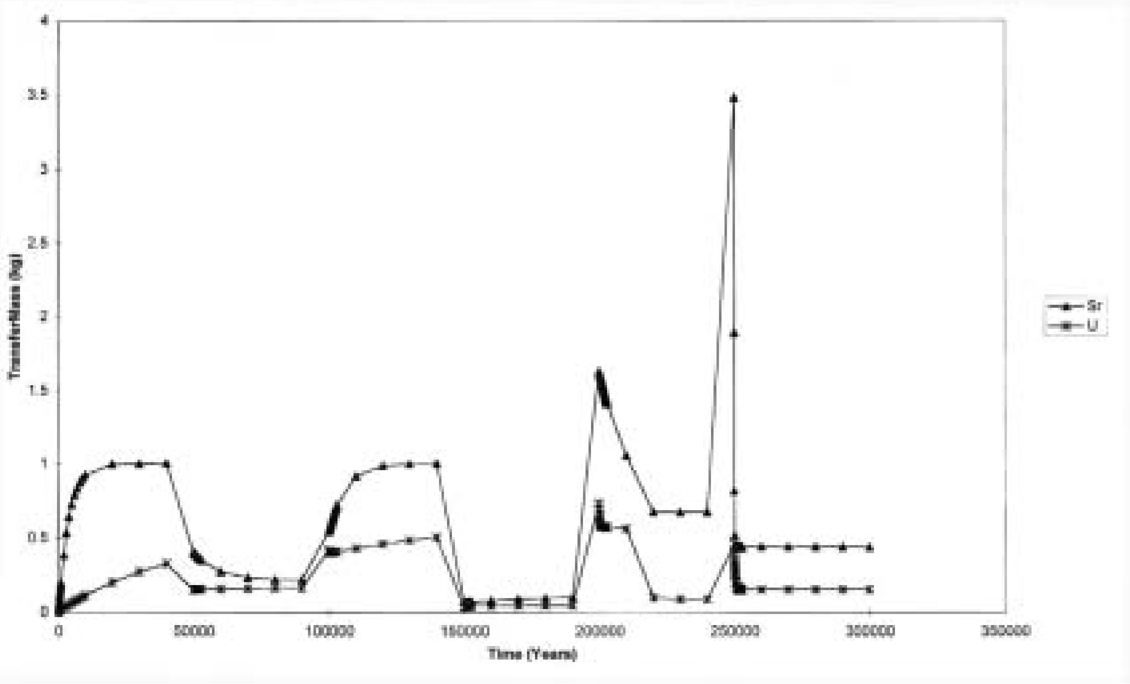

Figure 6.12: Modelled elemental fluxes associated with discharging groundwater in the transient system.

In this model, the soil thickness increases over the first 200 ka, during the period of slow soil erosion (weathering rate > soil erosion rate), until the high erosion event occurred in response to a changing climate, as indicated in Figure 6.13. The nature of this erosion event does not need to be explicitly defined here but could be imagined as the onset of glaciation in an easily erodable sedimentary basin. In any event, the model assumes a new erosion rate (10^3 times faster than previously). As can be seen in Figure 6.13, the soil thickness changes rapidly (in geological terms) from approximately 4 m to almost zero. At the end of this climate state (at 250 ka), soil thickness again begin to increase.

The changing concentrations of Sr and U in the soil horizon over this time period are shown in Figure 6.14. Despite the high fluxes of Sr in the discharging groundwaters and the changing soil thickness, the concentration of Sr in the soil remains relatively constant (at around 0.5 mg/kg) over the entire 300 ka model period. This is due to the low K_d value for Sr in the soil/porewater system. In other words, the Sr acts conservatively and passes through the soil to the sink more or less regardless of the climate state and soil thickness. In contrast U, which is preferentially retarded by the organic-rich soil, increases in concentration over the first 200 ka, reaching a maximum of approximately 4.5 mg/kg, until the onset of the high erosion event, at which point its concentration drops to close to zero (as the soil is removed).

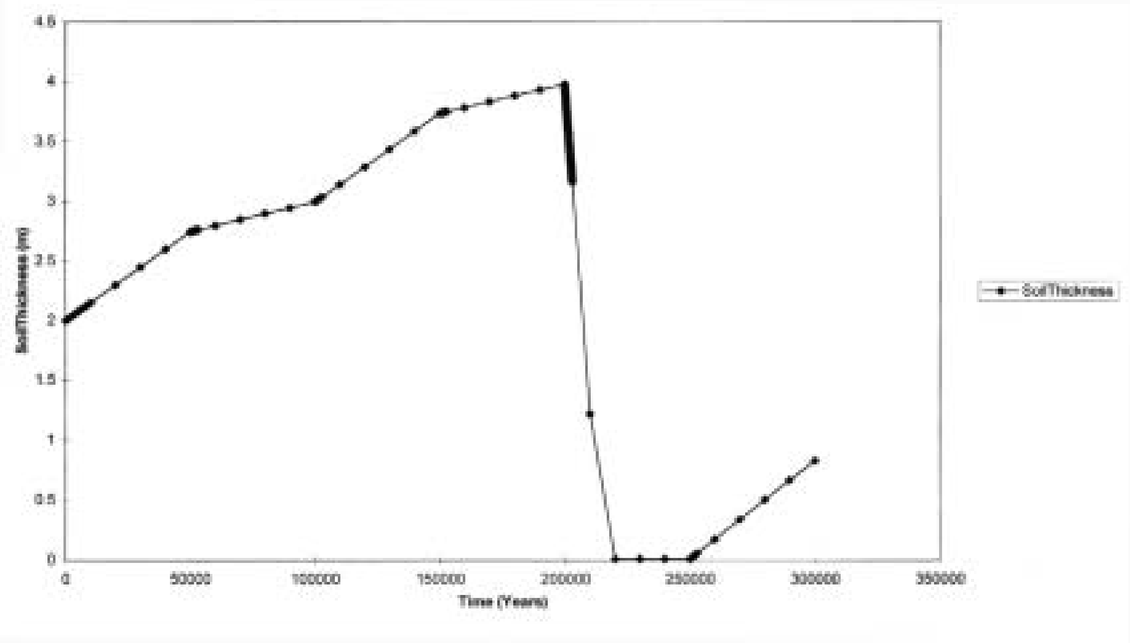

Figure 6.13: Modelled soil horizon thickness in the transient system.

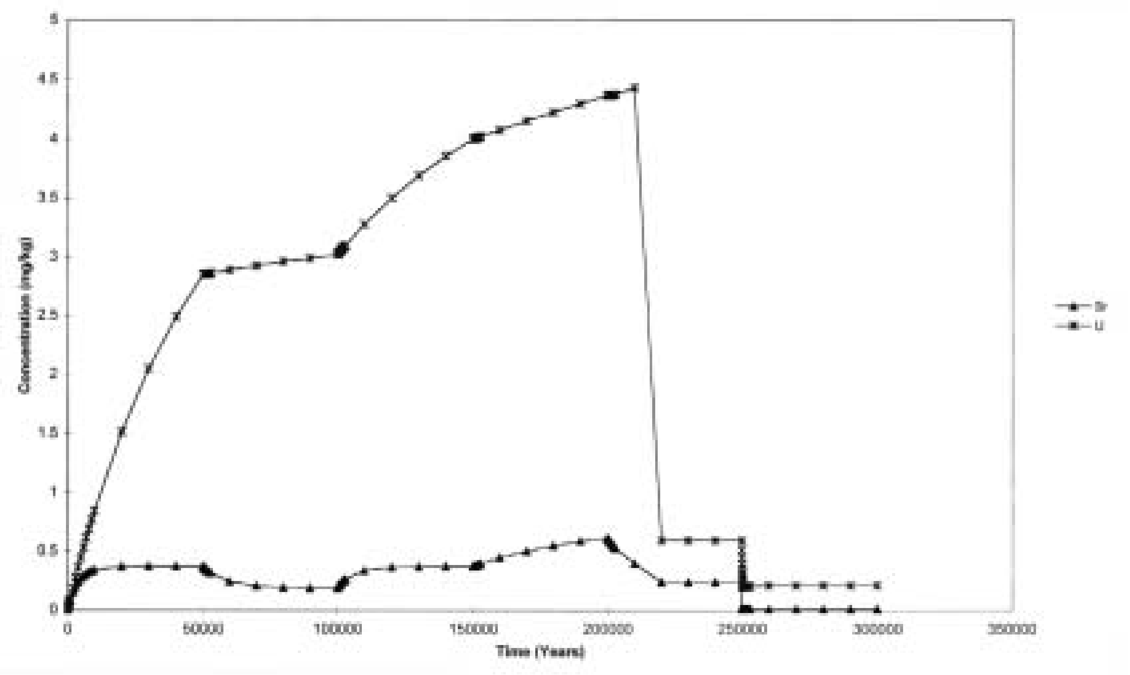

Figure 6.14: Modelled elemental concentrations in the soil horizon in the transient system.

The impact of these processes on the elemental fluxes leaving the soil and passing through to the accessible biosphere is indicated in Figure 6.15. The constant slow flux of Sr is broken only by a relatively small peak associated with the high erosion flux event. In contrast, the U flux is dominated by the high erosion, at which point the magnitude of the flux increases from just a few kg/yr to over 80 kg/yr.

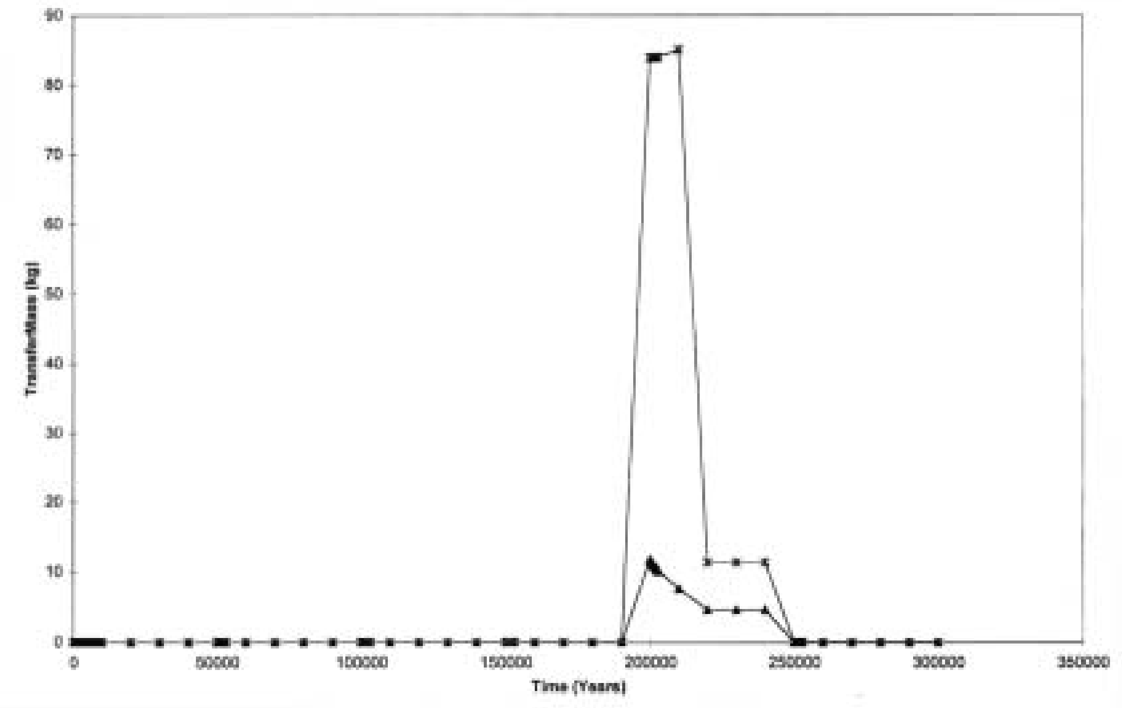

Figure 6.15: Modelled elemental fluxes associated with passage of material from the soil to the sink in the transient system.

Although the transient system modelled here is only very simple and not directly related to any specific geological environment or event, it demonstrates clearly the implications of climate change on systems in which elemental reconcentration can occur in the near-surface. There are wider implications beyond only natural fluxes because, as mentioned earlier, the same reconcentration processes can act on releases from a repository.

7 Discussion and conclusions

The calculated post-closure performance of a radioactive waste repository is generally quantified in terms of radiological dose or risk to humans, with safety being determined by whether the calculated exposure values are consistent with predetermined target criteria which are deemed to represent acceptable radiological hazards. Radiological exposure based target criteria are used widely by licensing authorities, and dose and risk have been universally calculated in all recent PAs. However, despite their general acceptance, dose and risk are not ideal measures of repository safety because, in order to calculate them, gross assumptions must be made for future human behaviour patterns. Such predictions clearly become increasingly uncertain as forecasts are made further into the future. As a consequence, it could be argued that it is not scientifically valid to base licensing criteria on predicted exposures to humans for times in excess of a few hundred or thousand years into the future.

As a consequence, there has been a growing interest in developing other ways of assessing repository safety which do not require assumptions to be made for future human behaviour. One proposed assessment method is to use the distributions of naturally-occurring chemical species in the environment, expressed either as concentrations or fluxes of elements, radionuclides or radioactivity, as *natural safety indicators* which may be compared with the PA predictions of repository releases. Numerous comparisons are possible between the repository and natural systems (e.g. a comparison between natural and repository derived radioactivity fluxes in groundwater discharges). The primary objective would be to use the natural system to provide context to the hazard presented by the repository releases. Put simply, if it can be demonstrated that the flux to the biosphere from the repository is not significant compared with the natural flux from the geosphere, then its radiological significance should not be of great or priority concern.

Natural safety indicators may be quantified on a site specific basis, using information derived from a repository site characterisation programme, and can be compared to the outputs from the associated site specific PAs. Such calculations and comparisons may be very detailed and might examine, for example, the spatial and temporal variations in the distributions and fluxes of naturally-occurring chemical species arising from individual processes, such as groundwater discharge, river flow and erosion at specific locations.

However, the natural safety indicators methodology can also be of value at the generic level of repository development, before site characterisation programmes have been undertaken. They could be used, for example, as a component in comparative evaluations of alternative generic disposal concepts. The objective at the generic level would be to define typical or average natural elemental concentrations and fluxes in geological systems representative of the environments which might host a repository, and to compare these with the outputs from the associated generic PAs.

To define average elemental concentrations and fluxes requires that sufficient information is available on natural elemental distributions in the different rocks, sediments and waters which comprise typical disposal environments, as well as the rates of processes which drive the elemental fluxes in these systems. Much of this information is available but is widely scattered across a broad spectrum of the earth science literature (including geology, geochemistry and physical geography). Thus, to facilitate the use of the natural safety indicators methodology at the generic level, this study has undertaken to bring together and to compile much of the required information.

This information has been used to quantify average elemental mass fluxes at the global scale for a range of processes, including groundwater discharge, erosion and sediment transport. The point of these calculations is that they provide a baseline against which site or geological environment specific natural fluxes, from anywhere in the world, can be compared on an equal basis to evaluate if they are higher or lower than the global average and, thus, are useful for providing a broad natural context for predicted repository releases.

In separate calculations, elemental mass fluxes were quantified for a number of *reference environments* which are chosen to be representative of the types of sites and geological systems which may host a deep repository. The reference environments were an inland pluton, basement under sedimentary cover and a sedimentary basin. The fluxes for these environments were calculated for systems with spatial scales of a few hundred square kilometres and, as such, approximate closely to the repository systems modelled in PAs because a reference environment represents the same system, with the same rock, groundwater and surface conditions as those controlling the release and transport of contaminants from the repository.

In further calculations, the elemental mass fluxes of U, Th, K and Rb were used to calculate total alpha and non-alpha radioactive fluxes. For U and Th, activity fluxes were calculated for the radioelements alone (in normal isotopic proportions) as well as for their respective decay chains, assuming secular equilibrium in the chains and considering only the longer-lived nuclides with half-lives longer than one day. For K and Rb, activity fluxes were calculated for the non-series nuclides ^{40}K and ^{87}Rb. These natural activity fluxes are considered to be particularly useful safety indicators because they can be readily compared with the results from PAs, because the calculated repository releases normally expressed as dose can be recast in terms of equivalent activity fluxes.

Lastly, orebodies and hydrothermal systems were considered briefly because they provide the potential for maximum concentrations and maximum fluxes, respectively, in geological systems. Although it would be unlikely that a repository would ever be located in these geological systems, they are useful to consider here because they provide further context to the broadest variability in natural systems for comparison with the repository releases.

The detailed elemental distributions and calculated elemental mass and activity fluxes for the global and reference environment systems are presented in Chapters 4 and 5. However, the more immediately interesting and useful natural safety indicator parameters are summarised in Tables 7.1 to 7.4. A number of comments can be made and conclusions reached from the results of this study. These are discussed below in relation to the practical application of the natural safety indicators methodology to repository safety assessment and demonstration.

Table 7.1: Selected natural safety indicator parameters for the global scale system. See Chapter 4 for full details.

Parameter	**Value**
Average U content in upper crustal rocks	2.7 mg/kg
Average Th content in upper crustal rocks	10.5 mg/kg
Average K content in upper crustal rocks	28.7 g/kg
Average Rb content in upper crustal rocks	111 mg/kg
Average Sn content in upper crustal rocks	4 mg/kg
Average erosion rate of continents	$3\text{x}10^{5}$ kg/km^{2}/yr
Mass of U eroded from continents	$1.2\text{x}10^{8}$ kg/yr
Mass of Th eroded from continents	4.8×10^{8} kg/yr
Mass of K eroded from continents	7.0×10^{11} kg/yr
Mass of Rb eroded from continents	4.3×10^{9} kg/yr
Mass of Sn eroded from continents	1.4×10^{8} kg/yr
Activity of U due to erosion of the continents	3.2×10^{15} Bq/yr
Activity of Th due to erosion of the continents	2.0×10^{15} Bq/yr
Activity of ^{40}K due to erosion of the continents	1.7×10^{16} Bq/yr
Specific alpha activity (U, Th chains) due to erosion of the continents	1.5×10^{8} Bq/km^{2}/yr
Specific beta activity (^{40}K, ^{87}Rb) due to erosion of the continents	$1.4\text{x}10^{8}$ Bq/km^{2}/yr
Mass of U discharged in continental groundwater	4.2×10^{6} kg/yr
Mass of Th discharged in continental groundwater	1.3×10^{6} kg/yr
Mass of K discharged in continental groundwater	1.6×10^{11} kg/yr
Mass of Rb discharged in continental groundwater	2.1×10^{8} kg/yr
Mass of Sn discharged in continental groundwater	$2.0\text{x}10^{6}$ kg/yr
Activity of U due to continental groundwater discharge	1.1×10^{14} Bq/yr
Activity of Th due to continental groundwater discharge	5.2×10^{12} Bq/yr
Activity of ^{40}K due to continental groundwater discharge	4.0×10^{15} Bq/yr
Total alpha activity (U, Th chains) due to continental groundwater discharge	5.2×10^{14} Bq/yr
Total beta activity (^{40}K, ^{87}Rb) due to continental groundwater discharge	4.2×10^{15} Bq/yr
Total mass of suspended material carried in global rivers	15.5×10^{12} kg/yr
Total mass of dissolved material carried in global rivers	4.0×10^{12} kg/yr
Total riverwater discharge volume	3.7×10^{4} km^{3}/yr
Average dissolved U content in riverwater	0.24 µg/l
Average dissolved Th content in riverwater	0.1 µg/l
Average suspended U content in riverwater	3.0 mg/kg
Average suspended Th content in riverwater	14 mg/kg
Mass of U discharged in global rivers	6.0×10^{7} kg/yr
Mass of Th discharged in global rivers	2.4×10^{8} kg/yr
Mass of K discharged in global rivers	4.1×10^{11} kg/yr
Mass of Rb discharged in global rivers	1.8×10^{9} kg/yr
Mass of Sn discharged in global rivers	6.8×10^{7} kg/yr
Activity of U due to global riverwater discharge	1.5×10^{15} Bq/yr
Activity of Th due to global riverwater discharge	9.7×10^{14} Bq/yr
Activity of ^{40}K due to global riverwater discharge	1.0×10^{16} Bq/yr
Specific alpha activity (U, Th chains) due to global riverwater discharge	2.9×10^{11} Bq/km^{3}/yr
Specific beta activity (^{40}K, ^{87}Rb) due to global riverwater discharge	3.2×10^{11} Bq/km^{3}/yr

Table 7.2: Selected natural safety indicator parameters for the inland pluton reference environment. See Section 5.2 for full details.

Parameter	**Value**
Average U content in granite	4.9 mg/kg
Average Th content in granite	27.0 mg/kg
Average K content in granite	33.4 g/kg
Average Rb content in granite	150 mg/kg
Average Sn content in granite	3.5 mg/kg
Average U content in gabbro	0.8 mg/kg
Average Th content in gabbro	2.8 mg/kg
Average K content in gabbro	6.0 g/kg
Average Rb content in gabbro	32 mg/kg
Average Sn content in gabbro	1.2 mg/kg
Deep groundwater flow rate	3×10^{-4} to 32 $l/m^2/yr$
Shallow groundwater flow rate	0.032 to 320 $l/m^2/yr$
Average U content of deep groundwater	1.0 µg/l
Average Th content of deep groundwater	0.3 µg/l
Average K content of deep groundwater	6.0 mg/l
Average Rb content of deep groundwater	50 µg/l
Average Sn content of deep groundwater	0.03 µg/l
Mass of U flowing in deep groundwater	3.0×10^{-10} - 3.2×10^{-5} $g/m^2/yr$
Mass of Th flowing in deep groundwater	$9.0x10^{-11}$ - 9.6×10^{-6} $g/m^2/yr$
Mass of K flowing in deep groundwater	1.8×10^{-6} - 0.19 $g/m^2/yr$
Mass of U discharging in groundwater in temperate climate	1.9 kg/yr
Mass of Th discharging in groundwater in temperate climate	0.6 kg/yr
Mass of U discharging in groundwater in tropical climate	20.3 kg/yr
Mass of U discharging in groundwater in tropical climate	6.1 kg/yr
Activity of U due to groundwater discharge in temperate climate	4.8×10^{7} Bq/yr
Activity of Th due to groundwater discharge in temperate climate	2.3×10^{6} Bq/yr
Activity of ^{40}K due to groundwater discharge in temperate climate	2.7×10^{8} Bq/yr
Specific alpha activity due to groundwater discharge in temperate climate	4.7×10^{5} $Bq/km^2/yr$
Specific beta activity due to groundwater discharge in temperate climate	7.1×10^{5} $Bq/km^2/yr$
Total denudation rate in temperate climate	15 mm/ka
Total denudation rate in tropical climate	1.5 mm/ka
Mass of U eroded from granite pluton in temperate climate	2.0×10^{-4} $g/m^2/yr$
Mass of Th eroded from granite pluton in temperate climate	1.1×10^{-3} $g/m^2/yr$
Mass of K eroded from granite pluton in temperate climate	1.4 $g/m^2/yr$
Mass of Rb eroded from granite pluton in temperate climate	6.2×10^{-3} $g/m^2/yr$
Mass of U eroded from gabbro pluton in temperate climate	3.3×10^{-5} $g/m^2/yr$
Mass of Th eroded from gabbro pluton in temperate climate	1.2×10^{-4} $g/m^2/yr$
Mass of Rb eroded from gabbro pluton in tropical climate	1.3×10^{-4} $g/m^2/yr$
Activity of U due to erosion of granite pluton in temperate climate	5.1 $Bq/m^2/yr$
Activity of Th due to erosion of granite pluton in temperate climate	4.5 $Bq/m^2/yr$
Activity of ^{40}K due to erosion of granite pluton in temperate climate	35.0 $Bq/m^2/yr$
Specific alpha activity due to erosion of granite pluton in temperate climate	4.2×10^{7} $Bq/m^2/yr$
Specific beta activity due to erosion of granite pluton in temperate climate	4.0×10^{7} $Bq/m^2/yr$

Table 7.3: Selected natural safety indicator parameters for the basement under sedimentary cover reference environment. See Section 5.3 for full details.

Parameter	**Value**
Average U content in gneiss basement	3.2 mg/kg
Average Th content in gneiss basement	16 mg/kg
Average K content in gneiss basement	10.0 g/kg
Average Rb content in gneiss basement	75 mg/kg
Average Sn content in gneiss basement	2.2 mg/kg
Average U content in shale	3.5 mg/kg
Average Th content in shale	12 mg/kg
Average K content in shale	14.0 g/kg
Average Rb content in shale	140.0 mg/kg
Average Sn content in shale	6.0 mg/kg
Groundwater flow rate in gneiss basement	3×10^{-4} to 32 $l/m^2/yr$
Groundwater flow rate in shale	0.16 to 6400 $l/m^2/yr$
Average U content of crystalline groundwater	1.0 µg/l
Average Th content of crystalline groundwater	0.3 µg/l
Average K content of crystalline groundwater	6.0 mg/l
Average Rb content of crystalline groundwater	50.0 µg/l
Average U content of sedimentary groundwater	1.0 µg/l
Average Th content of sedimentary groundwater	0.3 µg/l
Average K content of sedimentary groundwater	40.0 mg/l
Average Sn content of sedimentary groundwater	0.5 µg/l
Mass of U discharging in groundwater in temperate climate	2.7 kg/yr
Mass of Th discharging in groundwater in temperate climate	0.8 kg/yr
Mass of U discharging in groundwater in tropical climate	30.0 kg/yr
Mass of Th discharging in groundwater in tropical climate	9.0 kg/yr
Activity of U due to groundwater discharge in temperate climate	6.9×10^{7} Bq/yr
Activity of Th due to groundwater discharge in temperate climate	3.3×10^{6} Bq/yr
Activity of ^{40}K due to groundwater discharge in temperate climate	3.9×10^{8} Bq/yr
Specific alpha activity due to groundwater discharge in temperate climate	1.7×10^{6} $Bq/km^2/yr$
Specific beta activity due to groundwater discharge in temperate climate	2.6×10^{6} $Bq/km^2/yr$
Total denudation rate of gneiss basement in temperate climate	30.0 mm/ka
Total denudation rate of shale in tropical climate	10.0 mm/ka
Mass of U eroded from shale in subarctic climate	1.7×10^{-4} $g/m^2/yr$
Mass of Th eroded from shale in temperate climate	5.8×10^{-4} $g/m^2/yr$
Mass of K eroded from shale in temperate climate	1.0 $g/m^2/yr$
Mass of Rb eroded from shale in temperate climate	6.8×10^{-3} $g/m^2/yr$
Mass of U eroded from gneiss basement in polar climate	3.0×10^{-5} $g/m^2/yr$
Mass of Th eroded from gneiss basement in polar climate	0.01 $g/m^2/yr$
Mass of Rb eroded from gneiss basement in polar climate	0.07 $g/m^2/yr$
Activity of U due to erosion of shale in temperate climate	4.4 $Bq/m^2/yr$
Activity of Th due to erosion of shale in temperate climate	2.4 $Bq/m^2/yr$
Activity of ^{40}K due to erosion of shale in temperate climate	23.9 $Bq/m^2/yr$
Specific alpha activity due to erosion of shale in temperate climate	2.9×10^{7} $Bq/m^2/yr$
Specific beta activity due to erosion of shale in temperate climate	3.0×10^{7} $Bq/m^2/yr$

Table 7.4: Selected natural safety indicator parameters for the sedimentary basin reference environment. See Section 5.4 for full details.

Parameter	Value
Average U content in clays	3.5 mg/kg
Average Th content in clays	12.0 mg/kg
Average K content in clays	20.0 g/kg
Average Rb content in clays	140 mg/kg
Average Sn content in clays	6.0 mg/kg
Average U content in sandstones	0.6 mg/kg
Average Th content in sandstones	3.2 mg/kg
Average K content in sandstones	15.0 g/kg
Average Rb content in sandstones	46.0 mg/kg
Average Sn content in sandstones	0.5 mg/kg
Groundwater flow rate in clays	1.6×10^{-3} to 640 $l/m^2/yr$
Average U content of sedimentary groundwater	1.0 µg/l
Average Th content of sedimentary groundwater	0.3 µg/l
Average K content of sedimentary groundwater	40.0 mg/l
Average Rb content of sedimentary groundwater	50 µg/l
Average Sn content of sedimentary groundwater	0.5 µg/l
Mass of U flowing in deep groundwater	1.6×10^{-9} - 6.4×10^{-5} $g/m^2/yr$
Mass of Th flowing in deep groundwater	4.8×10^{-10} - 1.9×10^{-5} $g/m^2/yr$
Mass of U discharging in groundwater in temperate climate	7.5 kg/yr
Mass of Th discharging in groundwater in temperate climate	2.3 kg/yr
Mass of U discharging in groundwater in tropical climate	83.0 kg/yr
Mass of Th discharging in groundwater in tropical climate	24.9 kg/yr
Activity of U due to groundwater discharge in temperate climate	1.9×10^{8} Bq/yr
Activity of Th due to groundwater discharge in temperate climate	9.4×10^{6} Bq/yr
Activity of ^{40}K due to groundwater discharge in temperate climate	7.4×10^{9} Bq/yr
Specific alpha activity due to groundwater discharge in temperate climate	1.8×10^{6} $Bq/km^2/yr$
Specific beta activity due to groundwater discharge in temperate climate	1.5×10^{7} $Bq/km^2/yr$
Total denudation rate of clay in temperate climate	30.0 mm/ka
Total denudation rate of clay in polar climate	3400 mm/ka
Mass of U eroded from clay in temperate climate	2.3×10^{-4} $g/m^2/yr$
Mass of Th eroded from clay in temperate climate	7.9×10^{-4} $g/m^2/yr$
Mass of K eroded from clay in temperate climate	1.3 $g/m^2/yr$
Mass of Rb eroded from clay in temperate climate	9.2×10^{-3} $g/m^2/yr$
Mass of U eroded from clay in polar climate	2.6×10^{-2} $g/m^2/yr$
Mass of Th eroded from clay in polar climate	9.0×10^{-2} $g/m^2/yr$
Mass of K eroded from clay in polar climate	149.6 $g/m^2/yr$
Mass of Rb eroded from clay in polar climate	1.0 $g/m^2/yr$
Activity of U due to erosion of clay in temperate climate	5.9 $Bq/m^2/yr$
Activity of Th due to erosion of clay in temperate climate	3.2 $Bq/m^2/yr$
Activity of ^{40}K due to erosion of clay in temperate climate	32.1 $Bq/m^2/yr$
Specific alpha activity due to erosion of clay in temperate climate	4.0×10^{7} $Bq/m^2/yr$
Specific beta activity due to erosion of clay in temperate climate	4.0×10^{7} $Bq/m^2/yr$

The use of elemental concentration as a natural safety indicator

Concentration has sometimes been suggested as a useful safety indicator. At its most basic, concentration could be used to demonstrate that the amount of repository derived contaminant reaching the geosphere and biosphere is very small compared to the amounts of natural chemical species in the same materials, either in solid or solute form. Problems arise, however, for the non-natural chemical species in the waste (transuranic elements) which do not occur in nature because no straight concentration comparison can then be made.

Looking at the amounts of natural elements which are distributed throughout common rocks (as compiled in Chapter 2), it is evident that there is no particularly large variation in the abundance of the trace elements in the different rock types. For example, U has an average concentration of 2.7 mg/kg in the upper crustal rocks, with a variation from 0.6 mg/kg (sandstone) to 4.9 mg/kg (granite). This represents a total variation of less than one order of magnitude. A broadly similar concentration range and variation is exhibited by the other trace elements. However, potassium, being a major element (an essential component of many common rock forming minerals) is much more abundant with an average concentration of 28.7 g/kg in the upper crustal rocks, but this element still shows a variation of less than one order of magnitude between common rock types: from 6.0 g/kg (gabbro) to 33.4 g/kg (granite).

The variation in the concentrations of the trace elements in groundwaters is also small (as shown in Table 2.19), although the relatively few trace element analyses of deep groundwaters makes it difficult fully to appreciate the actual variability. As a consequence of these generally invariant (but low) abundances of the trace elements in most rocks and waters, any large variations in the calculated elemental mass and activity fluxes must owe more to differences in the process rates than the concentration variations themselves.

The exception to this generalisation are the above average elemental concentrations which occur in orebodies and some hydrothermal fluids. As discussed in Section 5.6, elemental abundances in these systems can be three or four orders of magnitude higher in ‘typical’ orebodies than in normal rocks, and can be even more enriched in the highest grade ores. The extreme illustration is the uranium concentration in the Cigar Lake uranium orebody which has an average grade of 14% (i.e. 140 g/kg).

In general, it would appear that elemental concentration has some value as a natural safety indicator but its use may be limited to simple comparisons to demonstrate that the amount of material in repository releases is very minor compared to the abundances of natural species which would be present in the rocks and groundwaters comprising a typical disposal environment. Concentration can be used to demonstrate that natural species are widely distributed throughout most materials in trace amounts without any obvious health impacts.

The high elemental concentration values from orebodies and hydrothermal fluids may also be used as natural safety indicators, but their value as a direct comparator is lessened because they relate to geological environments which would not normally be considered to host a deep geological repository. They do, however, provide upper (bounding) limits to the distributions of naturally-occurring elements and radionuclides which help to define the broadest contextual range for PA predictions of repository releases.

The use of elemental flux as a natural safety indicator

Elemental fluxes, along with concentration, have often been suggested as natural safety indicators, although relatively few PAs have ever explicitly compared fluxes of naturally-occurring chemical species with repository releases.

In essence, a flux is a mobile concentration and, hence, fluxes and concentrations are intimately linked. As discussed in Chapter 3, the rates of the natural processes which drive elemental fluxes can be significantly variable. As an example, the measured hydraulic conductivities of different geological materials (a primary control on maximum possible groundwater flow rates) varies by about 13 orders of magnitude, as indicated in Figure 7.1. This means that the variation in the fluxes of trace elements carried in groundwaters through these materials can be considerably larger than the variation due simply to differences in the groundwater elemental abundances. The range in hydraulic conductivity for potential repository host rocks is about four orders of magnitude, compared to about a one order of magnitude variation in the range of elemental abundances for the same rocks.

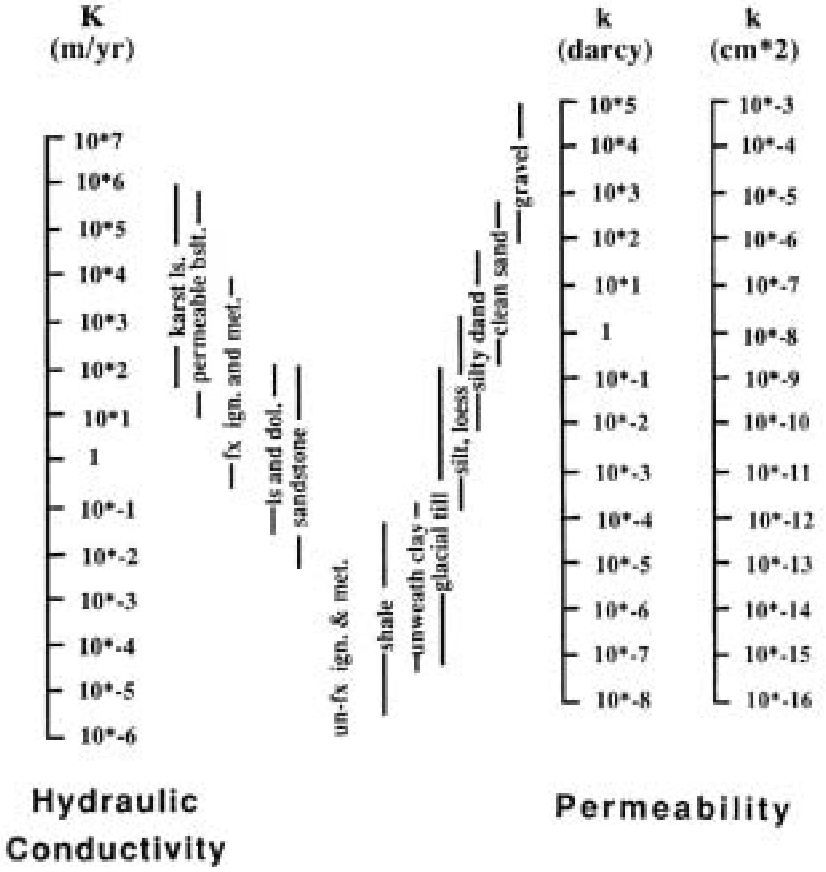

Figure 7.1: Hydraulic conductivities and permeabilities of common geological materials. From Freeze and Cherry (1979).

Other processes driving natural fluxes also demonstrate considerable variation in their rates. However, these variations are not always due to differences in the inherent properties of the geological materials (such as hydraulic conductivities). They can also be a consequence of external factors such as climate change which alter the impact of certain processes (e.g. erosion) and, indeed, climate change is indicated in this report to be one of the largest causes of variability in the natural elemental fluxes. This can be demonstrated with reference to the rate of erosion of a granitic pluton (Section 5.2) which varies from 1.5 mm/ka in a tropical climate to 340 mm/ka in a polar (glacial) environment. Similarly, the groundwater discharge volumes for the same pluton vary from zero in the desert and polar climates to 8×10^{10} l/yr in the tropical climate. This is because climate change affects groundwater recharge and, thus, the position of the water table and the overall geometry of the groundwater flow system. This has most significance for the application of the natural safety indicators methodology to repositories planned to be located at locations where future climate change will be most extreme (e.g. the Scandinavian countries).

The end point of a calculation of elemental fluxes is a mass flux (e.g. in units of kg/yr) or, if integrated over a known area or volume, a specific mass flux (e.g. in units of $kg/km^2/yr$). Separate mass fluxes can be calculated for all the naturally-occurring elements of interest and these can be compared with the masses of repository-derived contaminants calculated in PA. However, as with concentration, direct comparisons are not possible for the non-natural radioelements in the waste, which can limit the applicability of the methodology. Elemental fluxes may be calculated for specific processes and so a range of mass fluxes corresponding to different processes can be generated for the same element (e.g. groundwater discharge, erosion, river flow etc). In this manner, the most significant flux by *mass* can be readily identified. However, in terms of providing direct comparisons with repository releases, it is the fluxes associated with processes which drive the transfer of materials from the geosphere to the biosphere which are potentially most interesting. This generally means groundwater discharge (solute transfer) and erosion (solid transfer). For most systems, the mass flux due to erosion is significantly larger than that due to groundwater discharge, as seen in Tables 7.1 to 7.4.

This report has shown that, provided suitable process rates are known, elemental fluxes can be readily calculated for a range of elements and for most geological processes. These elemental fluxes are considered to be very useful natural safety indicators. They may be more appropriate than concentration in many cases because they can be used to identify natural processes which potentially introduce a natural radiotoxic or chemotoxic hazard to the surface environment. A high concentration in rocks at depth presents no hazard unless some process can mobilise the material. Likewise, a repository presents no hazard unless the waste is mobilised. Given that PAs focus on the mobile waste fraction, rather than the immobile, it seems consistent for the natural safety indicators similarly to pay most attention to mobile natural materials (fluxes) rather than to static materials (concentrations).

The range of elemental fluxes calculated in this study is very large. The most appropriate fluxes for comparison with calculated repository releases would be those from the reference environments and these fluxes can be described as having ‘average’ magnitudes. This is because the reference environments reflect stable geological systems with normal ‘barren’ rocks. However, the largest fluxes are those associated with either very fast process rates (e.g.

very fast groundwater flow) or with above normal elemental concentrations (e.g. hydrothermal fluids). These large magnitude fluxes are obviously less directly comparable to repository releases but have contextual value for demonstrating maximum limits to geological systems.

The use of radioactive flux as a natural safety indicator

In this work, the elemental mass fluxes of U, Th, K and Rb arising due to a number of processes in different geological environments were used to calculate alpha and non-alpha radioactivity fluxes. A number of assumptions (e.g. of secular equilibrium) were necessarily made to simplify the activity calculations. Although these assumptions will not hold true for all situations, as discussed in Section 1.2, they are similar to the assumptions which are often made in some PAs.

The end point of these calculations is an activity flux (e.g. in units of Bq/yr) or, if integrated over a known area or volume, a specific activity flux (e.g. in units of Bq/km^2/yr). Separate activity fluxes can be calculated for individual processes. These activity fluxes provide a useful means of making direct comparisons between natural fluxes and repository releases, since both may be expressed in the same radiological units.

Comparing total activities in this way does not explicitly take account of the nature of the chemical species contributing to those activities. As such, this comparison would mask the fact that some of the contributors to the repository activity fluxes would be non-natural or have non-natural isotopic abundances. Nonetheless, while it is true that different nuclides can give rise to different levels of radiation dose per unit activity, it also seems likely to be true that if it can be demonstrated, using total activity fluxes alone, that the repository releases are minor in comparison to the natural activity fluxes, then the radiological hazard posed by individual nuclides in the repository release inventory should be of great or priority concern.

An interesting observation from the alpha and beta activity fluxes is that, in many cases, they are essentially equivalent to each other in terms of magnitude, for fluxes arising due to individual geological processes. For example, on the global scale, the specific activity fluxes due to erosion of the continental landmasses, given in Table 7.1, are 1.5×10^8 Bq/km^2/yr for the alpha activity (U and Th chains) and 1.4×10^8 Bq/km^2/yr for the beta activity (^{40}K and ^{87}Rb). This equivalence is simply coincidental and arises from fortuitous concentrations of U, Th, K and Rb in the common continental rocks. This would not necessarily be the case for the activity fluxes associated with repository releases.

Most PAs present their outputs in terms of dose or risk. Although these are calculated from the activities of individual nuclides, total activity fluxes associated with the repository releases are not always explicitly given in the PA documentation. Given this, to facilitate direct comparisons between activity fluxes due to natural processes and repository releases, it would require intermediate PA calculation of total activity to be made.

The significance of spatial scale

In this work, fluxes were calculated on a number of different spatial scales, from the global to the catchment scale. In terms of using the natural safety indicators methodology to provide the fullest context to the repository releases, both scales have value. As mentioned earlier, the global scale flux calculations provide a baseline against which site or geological environment specific natural fluxes, from anywhere in the world, can be compared on an equal basis to evaluate if they are higher or lower than the global average and, thus, are useful for providing a broad natural context for predicted repository releases. However, the global average flux values mask the considerable variability which exists in natural systems and, as a result, these flux values are not sufficient as natural safety indicators on their own, and must be used and interpreted with some caution.

The catchment scale has the potential advantage that it allows the total natural mass fluxes to be calculated for the same closed hydrological system in which repository releases will occur because it represents the same system, with the same rock, groundwater and surface conditions as those controlling the release and transport of contaminants from the repository. This simplifies comparison between the natural fluxes and repository releases. However, this is only true if the repository is to be located in a small, well-defined catchment system and there are systems for which catchment scale flux calculations would be inappropriate. This is the case in central Canada, for example, where the groundwater flow systems and river catchments are very large and essentially take place on a continental scale. In such a large system, it might not be sensible to look at the natural fluxes over the entire catchment area.

As an alternative, it may be more practical to define an area or volume of rock local to any proposed repository and calculate the natural fluxes for just this system. As an example of this approach, Miller et al. (1996) proposed the Repository Equivalent Rock Volume (RERV) as a method for defining an appropriate scale for the direct comparison of natural and repository fluxes. The RERV approach has not been further investigated in this report but it offers an alternative scale on which to calculate fluxes.

Overall, when considering the spatial scale issue, the catchment scale is the preferred choice for natural flux calculations which will be compared directly to the output from a PA, due to the greater similarity between the natural and repository systems. However, to provide the fullest context, it is useful to also provide for comparison the global average flux values and, possibly, the fluxes associated with orebodies or hydrothermal systems, given that these potentially represent the maximum natural fluxes.

The importance of climate change

As discussed earlier, climate can have a significant impact on the rates of processes driving natural fluxes. The effect of climate change on fluxes was specifically investigated in Chapter 6 which examined the behaviour of coupled processes in a granitic pluton subjected to climate change.

A significant conclusion from this work is that the magnitudes of the fluxes do not change in a simple, step-wise manner in response to climate change but, rather, exhibit short-term pulse events. In some cases, these pulse events relate to the ‘flushing’ of slowly moving saline groundwaters by faster oxidising waters during wetter climates or the sudden removal of surface sediments (e.g. soils and lake sediments) which previously had been reconcentrating sorbing species discharged with groundwaters. The instantaneous ‘flipping’ of the climate in the modelling exercise is likely to have exaggerated the magnitude of these pulse events but it is probable that such events do occur in natural geological systems. More comprehensive analysis is required to evaluate the actual significance of this process, not just for the fluxes of naturally-occurring species but also for the releases of repository-derived radionuclides at the geosphere-biosphere interface.

The fact that climate change will alter the magnitude of the fluxes which operate in a particular system over time needs to be considered. Given that the PA output is time dependent, it may be sensible to attempt to predict the future changes in the natural fluxes and compare these to the calculated repository releases on a time-for-time basis. Alternatively, the calculated repository releases for all future times could be compared to the present-day fluxes on the basis that the significance of the present-day fluxes for human existence (as a hazard) is well understood.

Final thoughts

This study has demonstrated that it is possible to compile from the published literature a substantial database of elemental abundances in natural materials and, using this data, to calculate a range of elemental and activity fluxes arising due to different processes at different spatial scales. Although it was not attempted in this work, these fluxes should be comparable to standard PA results, with some modification to the PA calculations explicitly to output the concentrations and activities associated with the repository releases (at present only dose or risk are usually explicitly given as output).

The most appropriate spatial scale over which to perform the calculation of natural fluxes is the catchment scale because a catchment can represent the same geometry, materials and processes which control the release of radionuclides from the repository. This provides the closest like-for-like comparison. However, the global average fluxes are also useful in order to place the catchment scale fluxes in a wider geological perspective. Elemental mass fluxes could be calculated for a range of elements (including chemotoxic species) to provide a wide contextual view of the chemical character of the natural system. However, for comparison with the PA results, activity fluxes calculated from the mass fluxes of U, Th, K and Rb are probably the most useful.

It is recommended that, whatever form natural safety indicators are calculated and presented, their use should be restricted to the evaluation of repository safety rather than for the quantitative definition of safety limits (release criteria). An important factor here is that natural safety indicators would be used as *complementary* indicators of safety to dose and risk, rather than as an *alternative* or replacement for them. This is in accordance with the general view that repository safety has to be demonstrated using multiple and independent lines of evidence.

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Appendix A: The AMBER model

Using AMBER, it is possible to represent natural systems using a series of compartments between which transfers of chemical species can take place and be quantified. A compartment can be any suitable part of the system being modelled, for instance a lung in a model of the body, or a river in a model of the biosphere. Careful discretisation of the system allows processes to be represented in three dimensions. For example, modelling advection in an aquifer may be represented by a series of compartments each representing a volume of rock along the groundwater flow path. Compartmentalisation of problems simplifies the modelling required and enables interfaces between different parts of the system to be represented in a convenient manner.

In AMBER, the chemical species of interest, referred to as contaminants, are assumed to be uniformly mixed in the compartments. Each transfer is 'donor controlled', depending directly on the amount of the material present in the compartment from which the material is moving, and can change with time. AMBER allows contaminants to decay with time into other contaminants, if required. For example, one radionuclide may decay into another, or a particular chemical may be degraded into a different one. However, for the modelling work undertaken in this study, radionuclide decay was not represented because only stable or very long-lived species are considered. In the absence of radioactive decay, the amount I_i^m (moles) of contaminant *m* in a compartment *i* is determined by the equation (1).

$$\frac{dI_i^m}{dt} = \sum_j \lambda_{ji} I_j^m - \sum_j \lambda_{ij} I_i^m \tag{1}$$

where λ_{ij} is the exchange rate between compartment *i* and compartment *j* (y^{-1}).

A requirement for the natural fluxes project has been to include the representation of solubility limitations. These capabilities are achieved using a new concept in Amber, Availability schemes. In a transfer which is limited by solubility, for example, the transfer equation becomes:

$$\frac{dI_i^m}{dt} = \sum_j \lambda_{ji} I_j^m a_{im} \tag{2}$$

where a_{im} is the availability of radionuclide i in compartment m. The availability is a fractional parameter (0 to 1) which defines the amount of a contaminant in a donor compartment which is available for transfer. All the material in a donor compartment is available for transport until a "Limit" is reached (in this example the solubility limit) whereupon no further material can be taken into the aqueous phase. Once the limit is exceeded only a proportion of the material in a compartment is available for transport, hence the availability becomes less than unity.

Modelling flux, transfer rates and concentrations

Mass balance (water fluxes)

The total flux of water entering the system (Q_{in} [$m^3 y^{-1}$]) is simply:

$$Q_{in} = r_{(t)}A$$

$r_{(t)}$ is the rainfall rate [m/yr] and A is the area of the land surface. For each climate state the proportions of this flux which is assumed to infiltrate into the lithosphere and which enters the river system via surface run-off are specified. The Infiltration velocity [m/yr] into the lithosphere ($\chi_{s..sr}$ is the area of intersection between the soil and the lithosphere) is:

$$v_{s..sr} = \frac{Q_{(in)}\phi}{\theta\chi_{s..sr}}$$

ϕ is the proportion of rainfall which infiltrates into the lithosphere. The velocity of surface run-off ($_{s..r}$) is:

$$v_{s..sr} = \frac{Q_{(in)}(1-\phi)}{\theta\chi_{s..r}}$$

Figure A1 is a schematic diagram of the water fluxes flowing between the different parts of the system. It is necessary to specify the proportion of the flux entering the shallow rock which flows horizontally versus that which flows vertically downwards (Ψ)

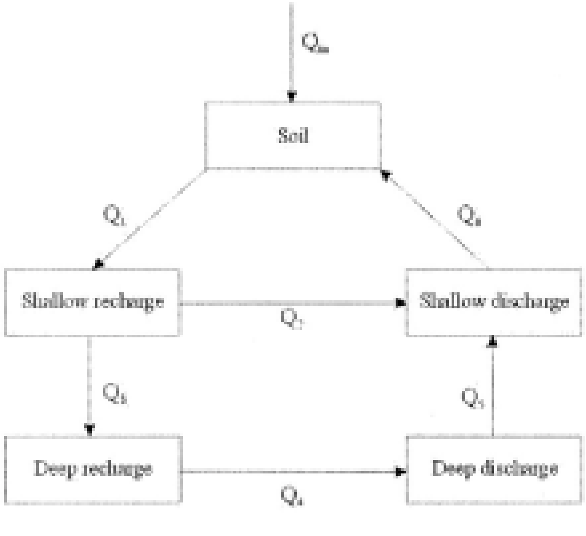

Figure A1: The water fluxes modelled for the crystalline rock system.

$$Q_1 = Q_{(in)}\phi$$
$$Q_2 = Q_{(in)}\phi\psi$$
$$Q_3 = Q_{(in)}\phi(1-\psi)$$
$$Q_4 = Q_3$$
$$Q_5 = Q_3$$
$$Q_6 = Q_1$$

Once the fluxes have been calculated it is relatively simple to calculate the flow velocities between compartments in a similar manner to the method used to calculate the infiltration velocity (see above).

Transport mechanisms

Advection

If the advective flux f_{ij} (mol y^{-1}) of a radionuclide between two compartments *i* and *j* is determined by an advective velocity v_i (m y^{-1}) then:

$$f_{ij} = \theta_i v_i \chi_{ij} C_i$$

where χ_{ij} is the common area between compartments *i* and *j* (m^2), C_i is the concentration of the radionuclide in the donor compartment *i* (mol m^{-3}) and θ_i is the kinematic porosity of the donor compartment *i* (-).

v_i is generally calculated using:

$$v_i = \frac{k_i}{\theta_i}\frac{\partial H}{\partial x}$$

where k_i is the hydraulic conductivity donor compartment *i* (m y^{-1}), and $\frac{\partial H}{\partial x}$ is the avarage head gradient (-). However, for this purposes of the models presented here, the flow velocities in the fractured zone, near the surface, were evaluated by mass balancing infiltration rate of rainwater with the flow in each compartment. Assuming a constant infiltration rate and that the flux in a compartment is driven only by the infiltration of rainwater, the total flux of water (Q_i). The flow velocity (v_i) of water between two compartments is calculated by dividing Q_i by the area of intersection between adjacent compartments.

The flux of radionuclides can be written in terms of the exchange rate λ_{ij} between the two compartments:

$$f_{ij} = \lambda_{ij}(\theta_i R_i C_i)V$$

where R_i is the retardation factor of the radionuclide in donor compartment *i* (-), and V_i is the volume of donor compartment *i* (m^3). The combination of terms in parentheses is the total amount of material per unit volume in the compartment.

The exchange rate between compartment *i* and compartment *j* is directly represented by:

$$\lambda_{ij} = \frac{Q_{ij}}{R_i V \theta}$$

which can also be expressed as:

$$\lambda_{ij} = \frac{v_i}{R_i L_i}$$

where L_i is the length of donor compartment *i* in the direction of the advective flow (m).

Erosion and Weathering

For a compartment which is subject to erosion the transfer rate of mass from these compartments is simply:

$$\lambda = \frac{e}{H(t)} \qquad t \le t_0 + \frac{H_0 - H_{\min}}{e}$$

where e is the erosion rate (m/yr), H_0 is the initial Length (or thickness) of the compartment and H_{min} is the minimum length (or thickness) of the compartment.

The thickness of the compartment will obviously diminish as a result of erosion, as follows:

$$H_t = H_0 - {}_0^t e \qquad H_t > H_{\min}$$

$$H_t = H_{\min} \qquad H_t < H_{\min}$$

The conceptual model of the inland pluton defines shallow rocks to occur in an oxidising zone, which penetrates to a depth of 200 m below the surface. If rock is removed from the surface via erosion, it would imply that rocks must pass from the deep rocks (in the zone of reduction) to shallow rocks, at the same rate as the erosion of the surface rocks.

Weathering of the shallow basement rocks to form soil is modelled in the same manner as physical erosion. It is important to note that the weathering of the shallow rocks has no influence upon the shallow rock/deep rock interface, which remains fixed.

The thickness of the soil layer is dependent on both sub-aerial erosion and weathering of the basement, as follows

$$H_{(t)} = H_{(0)} - {}_0^t e_{(s)} + {}_0^t w_{(sr)} + {}_0^t \pi_{(s)}$$

where $H_{(t)}$ is the length of the compartment, $H_{(0)}$ is the initial height of the compartment, $e_{(s)}$ $w_{(sr)}$ and $\pi_{(s)}$ are the soil erosion rate, the weathering rate of the shallow rocks and the soil production rate respectively.

The influence of time dependent climate changes, erosion rates and weathering rates are represented in the AMBER model. Erosion and weathering rates are taken to be piecewise constant functions of time, so the change in thickness of a compartment due to erosion is given by:

$$H_{(t)} = H_{(t = i)} - \left[e(t - t_{(i)})\right]$$

Where i represents the time previous to t where there was a discontinuous change in the erosion rate. A similar expression may be formulated relating the change in soil thickness to the weathering of the basement rocks.

Dissolution

Dissolution of minerals from the solid rock phase is responsible for transporting elements to the groundwater. The method for modelling dissolution makes use of concepts that have been developed for modelling solubility within AMBER, and is discussed in section 8.4.2.

Solubility

The transport of elements around the system is affected by elemental solubility limits within aqueous phases. Solubility limits have implications for the definition of the concentration of elements within compartments and more importantly will control the precipitation or dissolution within the system modelled.

Solubility limits are modelled by the use of the concept of "Availability". The availability refers to the fraction (0 to 1) of the material in a compartment, which is available for transport. All the material is available for transport until a "Limit" is reached whereupon no further material can be taken into the aqueous phase. Once the limit is exceeded only a proportion of the material in a compartment is available for transport, hence the availability becomes less than unity.

The Limit in compartment *i* is calculated using:

$$Limit = V_i \theta_i R_i SL_i$$

V_i is the volume of a compartment, R_i the retardation coefficient θ_i the porosity and SL_i the solubility limit, Given this limit, the Availability is the minimum of Limit/Amount and unity.

It is necessary to account for the Availability of an element when calculating the transfer flux between two compartments. The flux becomes:

$$TransferFlux = TransferRate * \alpha * A_i$$

Concentration of aqueous phase

Concentrations of elements within a compartment are partitioned between an aqueous, sorbed and precipitated phases.

The concentration of an element in the aqueous phase of a compartment ($C_{(i,a)}$) is dependant on the availability in the following manner:

$$C_{(i,a)} = \frac{(A_i * \alpha)}{V_i R_i \theta_i}$$

For compartments which represent only a water phase the retardation factor should not be included in the denominator, however since these compartments have a porosity of 1, the retardation becomes unity and hence the factor is included in the equation defining concentration in all compartments in the Amber model.

Precipitation and sorption

Precipitation out of an aqueous phase solution occurs when the solubility limit has been exceeded. In order to calculate the amount of material precipitated it is necessary to first calculate the amount of material within the aqueous solution and the amount of material sorbed within a compartment (*i*).

$$AmountInSolution = V_i * \theta_i * (C_{(i,a)})$$

$$AmountSorbed = (R_i - 1) * V_i * \theta_i * (C_{(i,a)})$$

The amount of an element precipitated within a compartment then becomes:

$$AmountPpt = A_i - AmountInSolution - AmountSorbed$$

Dissolution

Material enters the aqueous phase within a compartment via dissolution, until the solubility limit is reached, at which point dissolution ceases. Modelling the flux of mineral entering an aqueous solution is a complex kinetic problem, which requires detailed geochemical modelling using codes such as PHREEQC. For the purposes of the models presented here the dissolution rate will be calculated simply as:

$$DissolutionFlux = \frac{A_{sol} * V_i R_i e_i}{\tau}$$

Asol is the solubility limited amount and τ is the equilibration timescale, the estimated time taken for a mineral to reach the solubility limit of an aqueous solution, at which point the aqueous solution is in equilibrium with the host rock. As soon as the solubility limit of an element within the aqueous solution is reached, dissolution of that element from the host is modelled to cease.

This transfer is represented in Amber by using two transfers between the solid rock and the fractured porosity:

1) A flux from the intact rock to the fracture water determined by the equilibration timescale and the capacity of the receiving compartment at solubility limitation. This effectively reproduces the constant dissolution flux from the rock.
2) A flux from the fracture water to the intact rock determined by the equilibration timescale. In the absence of any other transfers, the amount of radionuclide in the fractured porosity compartment (A) would approach equilibrium according to

$$A = A_{sol}(1 - \exp(-t/\tau))$$

In fact, for some parts of the system matters are more complicated because of advective fluxes into and out of the region. Where the amount in a fracture porosity compartment exceeds the solubility limited amount, this is interpreted as material having been precipitated out. Everything is consistent provided the additional following change is made:

- The definition of aqueous concentration is limited by the solubility limit- excess amounts are precipitated.

For both the transfers the transfer rate as implemented in AMBER is:

$$\lambda = \frac{1}{\tau}$$

Compartments in the crystalline rock system

The system modelled consists of a catchment area 8000 m by 8000 m which feeds a river system. The geosphere is modelled to a depth of 1000 m. It is considered that rocks below this depth will have low chemical fluxes due to the absence of flowing features. The main features of the system and the AMBER model compartments that represent them are listed in Table A1.

Properties of Intact Rock

Intact rock, i.e. the non-flowing basement rock matrix is modelled as one compartment for both the zones of recharge and discharge. Dissolution is modelled as a constant flux for each element into the fracture network. The flux itself is defined using the simple geochemical model defined in earlier. The purpose for modelling the intact rock as a compartment is to enable the model to calculate the transfer of material upwards towards the surface as erosion occurs.

Properties of Fractured Rock

A series of compartments represent the flowing porosity (faults and fractures) within the basement rock. Groundwater flow in the model is restricted to these compartments. The fractured rock compartments are a single fluid phase, retention processes on to the wall rock of fractures are ignored.

Soil Compartment

The soil compartment is a homogeneous layer overlying basement rocks. Weathering of the basement rocks is responsible for soil production; conversely, erosion by sub-aerial processes removes soil. The layer is modelled as a rectangular compartment with a variable thickness dependent on the relative rates of chemical weathering of the basement erosion rates and biological soil production.

Table A1: The features of the conceptual crystalline rock system and the AMBER compartments that represent them.

Feature of system	**Description**	**Amber compartment**
Near-surface rock	Solid phase of shallow rock	ShallowRock
Deep rock	Solid phase of deep rock	DeepRock
Flowing porosity and fractures	Flowing phase of shallow rock in area of recharge	FracPorosity_SR

Feature of system	Description	Amber compartment
Flowing porosity and fractures	Flowing phase of deep rock in area of recharge	FracPorosity_DR
Flowing porosity and fractures	Flowing phase of shallow rock in area of discharge	FracPorosity_SD
Flowing porosity and fractures	Flowing phase of shallow rock in area of discharge	FracPorosity_DD
Soil	Surface sediments	Soil
Rivers	Rivers flowing from lakes and within valleys	River

AMBER parameters and nomenclature

The user defined parameters that 'set' the model are described in Section 6. Here, the other fixed parameters and brief descriptions, and the AMBER nomenclature systems used in the equations are listed in Tables A2 to A4.

Table A2: AMBER parameters used in the modelling of the crystalline rock environment.

AMBER parameter	Description	
	Transfer rate between compartments [yr^{-1}]	λ
Amount	Amount in a compartment [mol]	I
AmountInSolution	Amount of an element in solution [mol]	
AmountPpt	Amount of an element precipitated [mol]	
AmountSorbed	Amount of an element sorbed [mol]	
AqueousConc	Aqueous concentration of an element [mol/m^3]	C
AqueousConc_mgl	Aqueous concentration of an element [mg/l]	
AqueousConc_mgkg	Aqueous concentration of an element [mg/kg]	
AreaOfIntersection	Area of intersection between compartments [m^2]	χ
AreaOfLandsurface	Area of intersection of compartment with landsurface [m^2]	A
Dm3Tom3	Conversion factor from cu dm to cu m [-]	
EffectiveCapacity	Capacity of compartments, related to volume	
ErosionSoil	Erosion rate of soil [m/yr]	e
ErosionSoil1..6	Erosion rate of soil in each of the climate states (needed to avoid recursion error)	
EquilibrationTime	Time taken for element to reach geochemical equilibrium [yr]	τ
EquilibrationTimeZone	As EquilibrationTime, for each zone in model	
FastRate	A high flux rate used to model dissolution	
FlowVelocity	Flow velocity [m/yr]	v_i
FractureDensity	Density of fractures in basement rocks as a proportion of volume [-]	
GrainDensity	Grain density [kg/m^3]	ρ_g
H	Vertical thickness of a compartment [m]	H
InitialAbundance	Initial elemental abundance in compartment [mol]	
InitialSoilH	Initial soil thickness	
InitialH	Initial vertical thickness of compartment [m]	H_0
Kd	Sorption coefficient [m^3/kg]	K_{di}
L	Length of a compartment parallel to flow direction [m]	L
MaterialDensity	Density of compartment [kg/m3]	ρ

AMBER parameter	Description	
mgToKg	Conversion of mg to kKg [-]	
MinH	Minimum vertical thickness of a compartment [m]	H_{min}
Porosity	Total porosity in each compartment [-]	θ_i
PropHToVFlow	Proportion of horizontal to vertical flow in shallow rocks	ψ
PropInfiltration	Proportion of rainfall infiltrating the lithosphere	ϕ
Q	Water Flux [m^3 y^{-1}]	Q
Qin	Total Flux of water into system	Q_{in}
R	Retardation coefficient [-]	R_i
RainFall	Annual Rainfall [m/yr]	r
SoilThickness	Thickness of soil [m]	
SoilThickness1..6	Thickness of soil [m], avoids recursive error	
SolLimit	Solubility Limit of a transfer	SL_i
SolLimitZone	Solubility Limit of a transfer by Zone	
W	Width of a compartment [m]	
Weathering	Weathering rate of lithosphere [m/yr]	w
Weathering1..6	As weathering, avoids recursive error	
V	Total volume of compartment [m^3]	V_i

Table A2: AMBER namesets and mappings used in the modelling of the crystalline rock environment.

Nameset	Original feature	Mapping	Description
CompartmentToLithology	Amber Compartment	lithology	Links each compartment to a rock type.
FlowDirection	N/A	N/A	Direction of groundwater flow
Zone	compartment	Zone	Links compartments to a zone in model

Table A2: AMBER parameter type and multiplicity used in the modelling of the crystalline rock environment.

Parameter	Parameter type	Multiplicity dimension	Multiplicity Definition
AmountInSolution	Observer	2	[Contaminant][compartment]
AmountPpt	Observer	2	[Contaminant][compartment]
AmountSorbed	Observer	2	[Contaminant][compartment]
AqueousConc	Observer	2	[Contaminant][compartment]
AqueousConc_mgl	Observer	2	[Contaminant][compartment]
AqueousConc_mgkg	Observer	2	[Contaminant][compartment]
AreaOf Intersection	Standard	1	[transfers]
AreaOfLandsurface	Standard	1	[compartment]
Dm3Tom3	Standard	0	N/A
EffectiveCapacity	Standard	2	[Contaminant][compartment]
ErosionSoil	Time dependeant	0	N/A
ErosionSoil1..6	Standard	0	N/A
EquilibrationTime	Standard	0	[compartment]

Parameter	Parameter type	Multiplicity dimension	Multiplicity Definition
EquilibrationTimeZone	Standard	0	[Zone]
FastRate	Standard	0	N/A
FlowVelocity	Standard	2	[transfers]
FractureDensity	Standard	0	N/A
GrainDensity	Standard	1	[compartment]
H	Standard	1	[compartment]
InitialAbundance	Standard	2	[Contaminant][compartment]
InitialSoilH	Standard	0	N/A
InitialH	Standard	1	[compartment]
Kd	Standard	2	[Contaminant][lithology]
L	Standard	1	[compartment]
MinH	Standard	1	[compartment]
Porosity	Standard	1	[lithology]
PropHToVFlow	Standard	0	N/A
Porosity	Standard	0	N/A
PropInfiltration	Standard	0	N/A
Q	Standard	1	[compartment]
Qin	Standard		N/A
R	Standard	2	[Contaminant][compartment]
RainFall	Time dependant	0	N/A
SoilThickness	Time dependant	0	N/A
SoilThickness1..6	Standard	0	N/A
SolLimit	Standard	2	[Contaminant][compartment]
SolLimitZone	Standard	2	[Contaminant][Zone]
W	Standard	1	[compartment]
Weathering	Time dependant	0	N/A
Weathering1..6	Standard	0	N/A
V	Standard	1	[compartment]