

*B*IOPROTA

**Key Issues in Biosphere Aspects of Assessment of the
Long-term Impact of Contaminant Releases Associated
with Radioactive Waste Management**

Modelling the Abundance of Se-79 in Soils and Plants for Safety Assessments of the Underground Disposal of Radioactive Waste

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PREFACE

BIOPROTA is an international collaborative forum which seeks to address key uncertainties in the assessment of radiation doses in the long-term, arising from release of radionuclides as a result of radioactive waste management practices. It is understood that there are radio-ecological data and other information issues that are common to assessments required in many countries. The mutual support within a commonly focused project makes more efficient use of skills and resources, and provides a transparent and traceable basis for the choices of parameter values: it also provides a consistent interpretation of information used in assessments. A list of sponsors of BIOPROTA and other information is available at www.bioprot.com.

The general objectives of BIOPROTA are to make available the best sources of information to support modelling assumptions made within radiological assessments appropriate to radioactive waste management. Particular emphasis is placed on key data required for the assessment of long-lived radionuclide migration and accumulation in the biosphere, and the associated radiological impact, following discharge to the environment or release from solid waste disposal facilities. The programme of activities is driven by assessment needs identified from previous and on-going projects. Where common needs are identified across projects and countries, a common effort can be applied to finding solutions.

This report describes work undertaken to develop a better understanding of processes affecting Se-79 accumulation in soils and uptake into plants and, from that, either to develop better assessment models, or to provide a better basis for selection of parameters within existing models.

This particular study was supported financially by Posiva, NDA, NUMO, NWMO and ANDRA.

The report is presented as working material for information. It is intended to promote discussion and to form the basis for identifying gaps in current understanding. The content may not be taken to represent the official position of the organisations involved. The use of any material provided is entirely at the users' risk.

Report History

Version 0.1, Draft 21 April 2009 prepared on the basis of inputs from participants at a workshop held in Paris 19-20 March 2009, convened by Enviros Consulting Ltd and GMS Abingdon, for discussion with the International Union of Radioecology Waste and Radioecology Working Group and with participants at the BIOPROTA Forum, 4-8 May 2009.

Version 1.0, 27 August 2009 incorporates further inputs from participants, with feedback from the IUR and BIOPROTA meetings held in May 2009.

Version 2.0, 30 November 2009 is issued as a report for broader dissemination. It incorporates comments and clarification of areas outlined within version 1.0.

EXECUTIVE SUMMARY

This report describes work undertaken to develop a better understanding of the processes affecting Se-79 accumulation in soils and uptake into plants and, from that, either to develop better assessment models for radiation exposure, or to provide a better basis for selection of parameters within existing models.

This report includes reference to results from various new research studies carried out on the above topic, as well as material compiled previously. Information is based on the behaviour of stable selenium in the environment, as well as studies specific to Se-79.

An “assessment context” is set out, which provides background assumptions for determining doses to hypothetical critical groups arising in the long term due to releases to the terrestrial biosphere from a repository for radioactive waste disposal.

Consideration is also given to the Features, Events and Processes (FEPs) of potential relevance to the derivation of such doses. Particular consideration is given to those FEPs which relate to selenium specific behaviour in the environment.

An “interaction matrix” lays out a method to combine FEPs to create a conceptual assessment model. The intention is to provide a transparent and traceable record of how information has been included in (or excluded from) the assessment model, with recorded justification.

Suggestions are made for possible modifications to models and for the selection of data. A particularly relevant issue is the identification of data which need to be determined site specifically, as opposed to placing reliance upon site generic sources.

Further conclusions on model structure will continue to be developed as additional information becomes available. This report is therefore recognised to represent the best understanding based on current information.

The report is presented as working material for information. The content may not be taken to represent the official position of the organisations involved. The use of any material provided is entirely at the users’ risk.

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1. INTRODUCTION

Selenium (Se) is an essential micronutrient for organisms, characterised by a narrow range between deficient and toxic concentrations [Barceloux, 1999]. It is present in the terrestrial crust and in soil at a mean concentration of 0.05 mg kg^{-1} and 0.39 mg kg^{-1} , respectively [Sposito, 1989].

In a number of long-term safety assessments of underground radioactive waste disposal, Selenium-79 (Se-79) is one of the radionuclides contributing significantly to the assessed post-closure radiation exposure of members of hypothetical critical groups [Coppin et al., 2009; NEA, 2009; Zhang et al., 2002]. It is mobile and long-lived and therefore can potentially migrate into the biosphere following release from radioactive waste disposal facilities. However, data necessary for radiological assessment of Se-79 are scarce. This can lead to significant uncertainty, particularly in identifying parameter values relevant to different environmental conditions, or when selecting ranges around best estimate values to describe selenium behaviour in the terrestrial soil-plant system [BIOPROTA, 2008]. While a cautious approach to parameter selection can be used to avoid under-estimation of doses, it is important to avoid unnecessary pessimism in assessments, so as to achieve optimal allocation of resources in environmental and human health protection.

Selenium is an essential element with a complex chemistry. The different selenium species present in the environment show very different biogeochemical behaviour. In addition, volatilisation of selenium may result in a considerable loss of Se-79 from both soils and plants to the air. An added complexity is the chemical toxicity of selenium; with only a small concentration range between deficiency and toxicity. It is also notable that relatively new data suggest a half-life of Se-79 of the order of 350,000 years or longer [Bé and Chisté, 2006]¹, rather than the 65,000 years previously accepted [ICRP, 1983]. This revision does not affect the biosphere part of the overall assessment significantly, but it does change the estimates of releases of Se-79 to the biosphere from the geosphere, increasing the likelihood of release before decay.

Conventional dose assessment models include Features, Events and Processes (FEPs) which are largely radionuclide independent. Thus, they were not designed to take account of the particular behaviour of selenium in the environment. Speciation and volatilisation are neglected. Whilst the omission of volatilisation will generally be conservative, as this represents a loss mechanism from the soil-plant system, the effect of speciation may be more variable. This suggests that current assessment models for Se-79 may be unduly pessimistic and incomplete as mechanistic or process descriptions. As a result, different aspects of selenium behaviour in the soil/plant system and approaches to improving biosphere models were discussed in a workshop initiated by BIOPROTA in 2008 [BIOPROTA, 2008]. Some of the key findings were as follows.

¹ Bé and Chisté [2006] note a range of estimates of half-life from <65,000 years to >7,000,000 years – but with the range for all studies undertaken since 1990 falling in the region of 120,000 years to 1,100,000 years.

- ◆ Soil/plant models should consider the various selenium species and their specific properties (e.g. solid/liquid partitioning coefficients, plant transfer factors) rather than modelling “total selenium”.
- ◆ Soil/plant models should consider the properties and processes that may strongly affect the kinetics and partitioning of Se-79 in soils and plants, such as:
 - kinetics of the transformations between the different selenium species, taking into account geochemical conditions such as Eh and pH;
 - biogeochemical processes (e.g. microbially-enhanced transformation of selenium species); and,
 - different soil types (mineral content, organic matter, humic substances, etc.).
- ◆ The role of volatilisation of selenium from soils and plants to the air should be assessed as a potentially important loss mechanism of Se-79 in the soil/plant system.

These processes and properties, as relevant to selenium, are considered in the current report and recommendations made as to the mechanisms by which they may be incorporated into biosphere assessment models.

1.1 Objectives

The overall objective is to improve the basis for, and confidence in, long-term safety cases presented for the geological disposal of radioactive waste, through improved understanding of selenium behaviour: in particular the processes affecting Se-79 accumulation in soils and uptake into plants: and, from that, to improve on the modelling of environmental behaviour through new or improved parameter inputs.

1.2 Report structure

The output of the working group is detailed in the present report as follows.

Chapter 2 provides an overview of the current state of knowledge in relation to selenium in the soil/plant system, which largely draws from the results of specialist working groups on particular aspects of selenium behaviour, including behaviour in soils, uptake from soils into plants and volatilisation from both soils and plants. Output from specialist selenium workshops, run under the auspices of BIOPROTA, is also summarised.

Chapter 3 outlines the overall assessment context. It should be noted that the context will vary depending upon site specific features of an assessment, and upon broader assumptions for the biosphere and how to address environmental change. The assessment context discussed and developed here is needed in order to be able to understand how these wider context issues affect what is

appropriate to include in a Se-79 dose assessment model. This may vary from one assessment to another, because of site specific and other considerations. There is no assumption that one model will be the best for all situations.

Chapters 4 and 5 describe the main features, events and processes (FEPs) relating to selenium in the soil/plant system and their interactions, respectively. Recommendations on approaches to improving assessment models through mathematical representations of the important FEPs are given in **Chapter 6**.

Overall conclusions and recommendations for further research to address data gaps and outstanding uncertainties are provided in **Chapter 7**.

2. CURRENT STATE OF KNOWLEDGE IN THE BEHAVIOUR OF SELENIUM IN THE BIOSPHERE

The nature of the main selenium (Se) carrier phases in soil is in debate, with some authors emphasising the role of minerals, and others the role of organic material [Coppin et al., 2009].

The following information is summarised from the presentations and discussions during a specialist workshop on the behaviour of selenium in the environment, particularly focusing on the soil-plant system. The workshop was hosted by EdF at their offices in Chatou, Paris on 19-20 March 2009. A list of participants of the workshop, including presentation titles where applicable, is provided in Appendix A.

The availability of selenium in bedrock is a key feature governing the presence of stable selenium in soils, with soil deficiency occurring in regions where bedrock concentrations are low. Speciation of Se is a key factor controlling its behaviour in soil. This is influenced by a number of key factors (e.g. pH, redox and soil solution composition) and is controlled by biotic or abiotic soil properties. There are four oxidation states of Se, namely selenate (VI), selenite (IV), elemental Se (0) and selenide (-II), which form different mineral and organic compounds. The chemical form influences selenium behaviour, including partitioning between liquid and solid phases and bioavailability.

2.1 Soil-Water partition coefficient (Kd)

Models for Se-79 behaviour in soils largely make use of a selenium soil-water partition coefficient (Kd), applied as an instantaneous reversible equilibrium process. Kd data are largely derived from laboratory based batch experiments, and some column experiments. Typically, these reflect a short-term picture of the partitioning between liquid and solid phases. Such experiments may not represent adequately seasonal or longer term variability, such as occurs in field conditions. Without time series data it is also unclear whether they represent the long-term equilibrium partitioning between liquid and solid phases (if such an equilibrium exists). This does not mean that the current database is not valid, but does introduce a level of uncertainty in its interpretation and application. Consequently, there is a need to explore further the dynamics of sorption and desorption by more explicit consideration of those processes governing the distribution between liquid and solid phases.

Work is underway in France at IRSN to determine the sorption and desorption of selenium from various soils under field and laboratory conditions as a means of investigating whether the application of Kd values is appropriate in modelling studies or whether an alternative approach may be more suitable.

In situ results for Kd obtained through the separation of soil and soil moisture from field soils were high compared to reported laboratory Kd values (e.g. IAEA TRS-364 [IAEA, 1994]). However, laboratory batch experiments that measured sorption 48-hours after the addition of selenium to a selenium-free soil, and subsequent successive desorption steps, gave variable Kd estimates with time (range 122 l/kg for the sorption phase to 799 l/kg for the last desorption step),

with latter measurements being similar to field results. The range obtained for only one soil was similar to that reported by IAEA TRS-364 for all soil types. A similar K_d (GM – 110 l/kg, GSD – 5) was obtained by ECOMatters from stable element analysis of around 80 soil samples from across Canada, again providing independent validation to the IAEA TRS-364 recommended value.

Based on the results obtained from sorption and desorption experiments it was recommended that an alternative approach to K_d for modelling studies be investigated, which takes account of the different pools of selenium, including reversibly and non-reversibly bound selenium and that in solution. From these three selenium pools, parameters could be applied to determine a saturation index for chronic contamination. The approach would make use of K_d plus a kinetic parameter which takes account of irreversible binding of selenium to organic matter, producing better short and long term predictions of selenium sorption when compared with measurements obtained over 50 days of selenium sorption within a soil column. However, it was noted that a proportion of the non-exchangeable selenium may result from incorporation into plants. This pool of organically bound selenium may be cycled in the long-term. Knowledge of the timescales with which non-reversible selenium may become available once more would be beneficial for refining the approach.

2.2 Bioavailability

A greater understanding of selenium speciation and its influence on partitioning between solid and liquid phases is key to assessing the relative availability and uptake into plants from the total selenium pool within soils. K_d and transfer factors are generally assumed to be linked in a broadly inverse fashion. That is, elements which are tightly bound to soil are likely to be less bioavailable, and vice-versa. However, any such rule of thumb is subject to variability and may be influenced, for example, by chemical speciation and the presence of competing elements.

Selenium in soils can occur in a number of different forms, some of which are more biologically available than others. Selenate is regarded as the most bioavailable form. Where reducing conditions are present in soils (e.g. saturated soils), selenate can be reduced readily to less bioavailable forms.

Microbial activity can also have an influence on the form of selenium in soils. However, microbial activity is dependent on a number of factors, including nutrient availability. Thus nutrient deficient soils may have a slower rate of microbially-induced speciation than nutrient-rich soils.

Studies in Finland have investigated the different forms of selenium in different soil types [Keskinen et al., 2009]. In both mineral and organic soils, the majority of selenium was found to be associated with organic matter, with sequentially decreasing amounts of adsorbed selenite, metal selenides, elemental selenium and soluble selenate. The binding of selenium to organic matter renders selenium less bioavailable than that retained in solution. Soils varied greatly in the total selenium content, but showed a similar trend in the distribution of the different forms of selenium available.

It was concluded that to understand selenium behaviour in soils, one needs to understand speciation of selenium – different forms can be available within the same soils.

2.3 Plant uptake

Selenium is an essential element, but can also be toxic. It is possible that plants are able to discriminate against selenium uptake and it may also be possible for plants to access selenium from what would be considered biologically unavailable pools where necessary.

One factor governing uptake is the availability of ion uptake sites, which can be affected by the presence of competing anions such as phosphate and sulphate – a large reduction in selenium uptake (in the order of 60%) has been recorded as a result of the addition of sulphur to soils. The presence of competing anions is therefore an important factor to consider when modelling plant uptake of selenium from soils.

2.4 Distribution in plant tissues

The distribution of selenium within different plant components affects both uptake pathways relevant to dose assessment (e.g. accumulation or otherwise within edible components) and also affects cropping losses from the system. For example, should selenium be taken up into a leafy vegetable crop but effectively retained within root tissues, it is likely to be recycled to the soil system in an organic form following harvest.

Ongoing research in Finland is investigating the distribution of selenium in the tissues of different agricultural plants. Initial results indicate that the distribution varies considerably between plant types, with some accumulating selenium within roots and others within leaves. However, these differences may be partly explained by the form of selenium taken up from the soil. Selenite and organic selenium compounds tend to accumulate in the roots, whereas selenate is highly mobile in plants. Grain crops were found to accumulate the majority of selenium within grain, with translocation occurring in the final phase of the growth cycle.

The ongoing stable element analysis being conducted by ECOMatters has revealed similar plant distribution results for selenium in that seed crops were found to translocate the majority of plant selenium into grain. It is considered that this arises from the incorporation of selenium into proteins. For example, seed crops can allocate a large proportion (around 50%) of available resources into grain production.

2.5 Volatilisation

Volatilisation of selenium from soils occurs as a result of biomethylation of selenium by microbes and a number of factors may affect the rate of loss from soils:

- ◆ Selenium speciation (methyl selenium will volatilise to the greatest extent);

- ◆ Agricultural practices such as ploughing, which affect soil oxygenation levels;
- ◆ Temperature, both long-term and seasonal changes;
- ◆ Soil type, for example peat soils would be expected to have very different selenium chemistry to sand soils; and,
- ◆ Soil moisture content, affecting gas diffusion from the soil. Note that soils would have to be moist enough for the generation of volatile forms, but dry enough for release from the soil.

Whilst volatilisation rates have been reported in the scientific literature, few data are available from long-term studies and measurements are often made in soils with greatly enhanced selenium concentrations.

A review has recently been undertaken by ECOMatters [Sheppard & Sheppard, 2008] on behalf of NWMO, Canada, to establish the extent of this process in governing the loss of selenium from the soil-plant system. The review focused on volatilisation rates reported under field conditions for both sediments and soils. Analysis of results suggests that volatilisation will significantly reduce soil concentrations over time. Depending on the rate of annual input to the system (e.g. in fertiliser), equilibrium concentrations may be reached in around 10 years.

Results of volatilisation studies were found to be variable, which is largely attributable to variability in soil type, exposure time, soil conditions etc. Results suggest that volatilisation rates may be increased at higher pH, and reduced in the presence of organic matter, but no significant relationship was identified with soil clay content. The majority of available results were derived from short-term studies with results indicating that the length of study may be an important component. Rates reduce over time, suggesting that selenium may become incorporated into non-exchangeable forms.

Due to the variability in available results and the fact that studies where no volatilisation could be measured are unlikely to have been reported, the 25th percentile was used to determine overall volatilisation rates to account for potential bias. The resultant volatilisation rates recommended as a result of the review are:

- ◆ 3% per annum from soils; and,
- ◆ 6% per annum from sediments.

Ongoing research at IRSN in France is investigating volatilisation rates from soils with 'background' levels of selenium and how rates change over time and as a result of organic matter content and changes in soil selenium concentrations. Experiments were conducted within homogenous soil microcosms with constant air temperature and soil moisture content, but varying organic matter content. Soil contamination was achieved through the flooding of soils that were then allowed to dry.

The long-term study is focused on a grassland soil and volatilisation rates will be measured over a 1.5 year period. For this long-term study, emission of selenium during the drying period (first week) was not reported. Results indicate that only 0.2% of the added selenium was lost through volatilisation with the greatest volatilisation rate occurring in soils with added organic matter. For all soils the rate of volatilisation decreased with time. However the rate of decrease was soil dependent.

A shorter experiment, run over a 6 month period, looked at the effect of selenium concentration in combination with organic matter content and soil type. Two soil selenium concentrations were applied – 8 ppm and 8 ppb – and volatilisation rates measured. The greatest rates were reported in the first few days following addition of selenium with a subsequent gradual rate reduction. The reduction in rate was found to be dependent upon the selenium concentration in soil. Overall volatilisation rates varied with soil type, large differences being observed between sandy and silt-clay soils. A subsequent addition of organic matter to soils served to increase volatilisation rate. However, this increase in rate varied with soil type. In some cases, this increase persisted over a 3 month period after the addition of organic matter.

A good correlation was obtained between the amount of selenium volatilised normalised by the number of bacteria present within soils and the amount of selenium extractable from soils by CaCl_2 (considered as bioavailable Se) normalised by the number of bacteria present within soils. It is postulated that the bioavailability of selenium to bacteria controls the extent of its volatilisation.

3. ASSESSMENT CONTEXT

Post-closure safety cases for geological disposal facilities for radioactive waste are largely focused on the potential doses to humans arising from the release of radionuclides to the biosphere. Such release might occur because of entirely natural processes, or they might be modified by human activities. In the case of Se-79, one especially relevant assumption relates to whether humans modify the natural selenium levels because they are too low or too high. Regulatory requirements and guidance concerning how to address environmental change, and what to assume about human behaviour and exposure groups, varies from country to country.

There are a number of uncertainties relating to the state of the biosphere at the time release is likely to occur, and about human behaviour. There are also variations in regulatory requirements with respect to long-term dose assessments. Consequently, it is useful to set out the background assumptions to be made in a dose assessment. At the very least, agreement is required on:

- ◆ What you are trying to calculate, and
- ◆ Why you are trying to calculate it.

Most disagreements about models and data requirements etc. arise because people are arguing from different premises – they are not disagreeing about the science, but about how they are trying to use it. Therefore it is important for researchers and all others involved in an assessment to develop a common view of these premises, so that they can work consistently together. These background assumptions are called the “assessment context” and the components of the assessment context are justified and explained in IAEA [2003]. The following definitions for each component are offered here for the purpose of the current model review project.

Purpose: To make the best use of scientific information to improve confidence in the calculation of radiation doses to average members of hypothetical critical groups², due to long-term release of Se-79 into the terrestrial environment via groundwater.³

Assessment endpoint: Concentrations of Se-79 in plants which form part of the terrestrial foodchain relevant to assessment of radiation doses to hypothetical critical groups. In this review, we do not extend consideration as far as uptake by animals and assessment of radiation exposure. This is because the key uncertainties relate to Se-79 behaviour in soil and its uptake into plants.

Assessment philosophy (approach to addressing uncertainties): A cautious but realistic approach is taken to the inclusion of FEPs and consideration of choices of parameter values. The intention is to avoid under-estimating the

2 This is the most common form of words in use for this concept as applied to waste disposal, although ICRP Publication 101 [ICRP, 2006] introduces new terminology, referring to the ‘representative person’.

3 This means that, at this stage, this review will not consider issues specific to the assessment of doses to non-human biota.

assessment endpoint, but also to avoid grossly over-estimating it. Note that this implies taking different FEP decisions from those which might be appropriate if one wished to make a best estimate of the most likely dose, or, as would be required in relation to assessment of the proposed HLW repository at Yucca Mountain, for which regulators require an assessment of the expectation value of dose [Smith et al., 2008]. This illustrates how different regulatory requirements may affect the modelling assumptions.

Repository system: Not relevant for the current review.

Site context: The site is assumed to be inland, unaffected by the marine environment, in a currently temperate climate condition. A temperate climate is suggested because that is the first interest of participants. It may be necessary to distinguish model assumptions on a more specific basis, for instance to include local climate conditions, soil type, agricultural practices and other factors. With respect to a number of long-lived radionuclides of potential importance within disposal facilities, Leclerc-Cessac and Jaubert [2005] illustrate the extent to which site specific information may be used – but note that *“these specific data are useful only if main factors controlling mobility have been determined previously for each radionuclide”*. This implies that a good knowledge of the environmental behaviour of each radionuclide of relevance is available. The extent to which site specific descriptions are helpful, or even necessary, for modelling Se-79 behaviour is part of the matter to be investigated here – and it necessarily contains an element of iteration in that site descriptions and understanding of how local conditions affect behaviour must go hand in hand. In addition, post-closure assessments under-way within many relevant organisations take account of environmental change, potentially widening the issues of interest for Se-79 dose assessment. It is of interest to ask how inclusion of environmental change would affect the assumptions for Se-79 behaviour.

Source term and geosphere-biosphere interface: The source term to the biosphere is Se-79 contaminated groundwater. This is assumed to be able to reach the surface environment by:

- ◆ direct discharge to surface water bodies;
- ◆ direct discharge to near-surface sub-soils susceptible to phreatic surface variation over the seasons of the year and from which vertical capillary rise is possible (with subsequent sub-horizontal flow of water to surface water bodies); and,
- ◆ via well abstraction and addition to soil via irrigation.

Nothing is assumed in advance here about the stable Se content or other geochemical characteristics of the groundwater.

Time frames: Consistent with the modelling of release and transport of Se-79 from the repository in groundwater, the discharge to the surface is assumed to continue at near its peak rate for hundreds of years. The release may not begin until hundreds or thousands of years into the future. In that time before release starts, the site conditions will change, and such change may need to be

considered in the overall assessment, but not necessarily in the Se-79 assessment model. In addition, environmental change may occur while the release is taking place. Again, such changes may need to be considered, though not necessarily included in the model. (See discussion of FEPs management below and how they can either be included in the model, or excluded, with justification).

Societal assumptions: As there is little technical basis for predicting the nature or probability of future human activities, it is necessary to make assumptions about future human habits in order to calculate future doses and risks. For this study it is assumed that food is produced using modern agricultural practice, techniques and agronomic methods, consistent with the assumptions for the site context, e.g. climate and soil conditions. Consideration may also be given to plants contributing to the food chain outside of agricultural practice, such as wild berries and mushrooms.

4. FEATURES, EVENTS AND PROCESSES

Features, Events, and Processes (FEPs) are terms used to define the relevant scenarios for safety assessment studies, whereby:

- ◆ features include the components of the site, such as soil and water bodies;
- ◆ events include those incidents that may occur in the future, such as climatic changes; and,
- ◆ processes are those things that are ongoing, for example irrigation of agricultural land.

The FEPs relevant to the migration of Se-79 within soils and from soils to plants were identified during a specialist workshop held on 19-20 March 2009, hosted by EdF in Chatou, Paris. Many of those identified are currently considered in assessment models. All identified FEPs (both current and new) are listed in Table 4.1.

Table 4.1: FEPs relevant to Se-79 in the soil/plant system

FEP	New for Se-79 ^a	Potential for alteration of current FEP
Bioturbation		
Capillary rise		✓
Colloidal selenium	✓	
Cropping loss (plants & animals)	✓	
Decomposition	✓	
Degassing	✓	
Discharge from below		✓
Effect of plants on Se speciation	✓	
Environmental change	✓	
Erosion		
Fertiliser addition	✓	
Foliar uptake	✓	
Infiltration		
Ingestion		
Interception		✓
Isotopic dilution	✓	
Micro-organisms & fungi	✓	
Organics, complexes and binding mechanisms	✓	
Percolation		✓
pH	✓	
Precipitation	✓	
Recalcitrant Se	✓	
Redox potential	✓	
Root uptake		✓
Soil hydrology variation	✓	
Sorption		✓
Stable Se concentration	✓	
Translocation		✓
Volatilisation	✓	
Weathering		✓

A FEP is considered new if it is not routinely considered in available Se-79 models, although it is recognised that it may be taken into account in some models. Newly identified FEPs are largely phenomena that affect processes and pathways through the environment.

FEPs which are currently included within most, if not all, models for Se-79, but which may be amended on the basis of current understanding of behaviour are identified as 'potential for alteration' within current FEPs.

A brief description of new and existing FEPs, and their potential consequences for selenium behaviour in the environment, is provided below. In a number of instances, queries are identified where discussions to date have left areas unresolved.

Bioturbation

Not a Se-79 specific issue, but potentially relevant. It will be linked to soil type, climatic conditions and soil depth of interest. Bioturbation may involve recycling of sub-soil materials, incorporation of surface soil materials (e.g. detritus) and changes in chemical form (and hence availability for uptake).

Capillary rise

Capillary rise is important in the overall water and nutrient dynamics in soil-crop systems. Capillary rise with evapotranspiration may cause salt deposits to be formed at the soil surface. Whilst these general considerations may be important in modelling, is there evidence for Se behaviour being special in this respect?

Colloidal selenium

The colloid chemistry of selenium is generally similar to that of sulphur (S), although the hydrosol colloids of Se are less hydrophilic and therefore less stable than those of S. Since the discovery of the necessity for trace amounts of Se in animal diets, there has been interest in the availability of colloidal Se in the dynamics of soil-plant uptake (e.g. Peterson & Butler [1966]). There may be some size related impact on uptake, although the significance of this effect has not been explored.

Colloids may be formed biotically and abiotically. Colloidal selenium may thus form part of the 'soil solution' and the 'inorganic soil' components. Transport of colloids may occur with the soil solution into groundwater.

Cropping loss (plants & animals)

Potentially, cropping provides an important removal process, at least for the higher values of root uptake. Some models have conservatively ignored this process on the assumption that Se-79 taken up into crops would eventually be returned to the same soil through a variety of processes (including plant senescence and degradation or animal excretion).

Decomposition

During plant senescence and decomposition, changes in the location and chemical form of selenium may be identified (e.g. transfer from above ground to below ground storage organs during senescence or incorporation within detritivorous animals or decomposing micro-organisms).

Degassing

Water to air degassing can be a significant environmental transport pathway for PCBs. It is likely that this is also significant for sulphur and may represent a consideration of interest in Se dynamics, notably in the soil-solution to soil-atmosphere phase.

Discharge from below

What would be the chemical speciation response of selenium in groundwater reaching a near-surface redox front? What other GBIZ processes of accumulation and subsequent release under environmental change may be relevant?

Effect of plants on Se speciation

Changes in soil pH may be induced across the rhizosphere, influencing metal uptake. Is this likely to be of special interest for the uptake of Se? Is it of interest only in identifying processes, but unlikely to amend gross measured rates of uptake, or assumed equilibrium concentration ratios?

Environmental change

In the long term, climatic and associated environmental changes may alter plant uptake dynamics, through both physical changes (e.g. water regimes) and biological changes (e.g. vegetation species present). Is this likely to be of particular significance to Se or part of a broader consideration to be incorporated within modelling approaches?

Erosion

Not a Se-79 specific issue. Include if the site context suggests wind or water erosion is a process for removing soil from the area of interest.

Fertiliser addition

The addition of nitrate, through the application of nitrogenous or general NPK fertiliser, could affect the redox potential of soil and thus the chemical form (and bioavailability) of selenium.

Fertiliser may also influence selenium uptake through the availability of ion uptake sites, which can be affected by the presence of competing anions such as phosphate and sulphate. The addition of soil conditioners containing selenium, for instance in selenium deficient areas, may act to dilute uptake of Se-79 (see discussion on isotopic dilution, below).

Foliar uptake

Recent studies (e.g. Kapolna et al. [2009]) have demonstrated foliar uptake of selenium, when applied as sodium selenite or sodium selenate in a fine spray. Foliar application of solutions of selenite or selenate at $100 \mu\text{g Se ml}^{-1}$ to carrot leaves resulted in a selenium concentration of up to $2 \mu\text{g Se g}^{-1}$ (dry mass) in the carrot root. Within the leaves, application of the selenate resulted in up to $80 \mu\text{g Se g}^{-1}$ (dry mass), while the selenite-enriched leaves contained approximately $50 \mu\text{g Se g}^{-1}$ (dry mass). The predominant metabolised forms of selenium in the roots were selenomethionine and γ -glutamyl-selenomethyl-selenocysteine, regardless of which of the inorganic species were used for foliar application.

Whilst foliar uptake is likely to be a minor pathway for soil-plant systems, the possibility of absorption associated with volatilisation from the soil cannot be precluded.

Infiltration

This is the process by which Se-79 in irrigation water enters soil. The balance of infiltration, wash-off and evaporation will be determined by a number of factors including soil type, topography and rate of input. For most controlled systems, wash-off is likely to be negligible.

Ingestion

Not important given the current assessment context (i.e. soil-plant interactions).

Interception, translocation and weathering

Interception, translocation and weathering are processes largely considered in current models and no new aspects were identified that would assist in the refinement of assessment models. However, data for these processes for Se-79 could be improved. It was noted that sulphur may prove a useful analogue to address data gaps for particular scenarios.

Isotopic dilution and stable Se concentrations

Any activity which affects the stable selenium concentration (such as the addition of selenium to deficient soils) would serve to dilute Se-79 concentrations and potentially affect transfer factors from soils to plants.

Isotopic abundance data might be used to set an upper limit on concentrations of Se-79 in plants. This would need to rely on information about the dynamics of selenium migration and accumulation in various chemical forms within the soil-plant system.

Micro-organism activity

Micro-organisms play important roles in the environmental fate of many elements, with a multiplicity of physico-chemical and biological mechanisms effecting changes in mobility and speciation. Physico-chemical mechanisms of removal include adsorption, ion exchange and entrapment. Metabolism-dependent mechanisms of radionuclide immobilisation include metal precipitation as sulphides and sequestration by metal-binding proteins and peptides. Microbial processes involved in solubilisation include autotrophic and heterotrophic leaching, complexation by siderophores and other metabolites, and chemical transformations. Such mechanisms are important components of natural biogeochemical cycles and should be considered in any analyses of environmental radionuclide contamination.

Microbial activity is dependent on a number of factors, including nutrient availability. Thus nutrient deficient soils may have a slower rate of microbially-induced speciation than nutrient-rich soils.

Microbial action may be an important factor in volatilisation of Se from soil.

Organics, complexes and binding mechanisms

In the environment, selenium combines with oxygen to form many different molecules; the main forms in soil being selenate (Se(VI)), selenite (Se(IV)) and selenide (Se(-II)). Their proportions in soil solution are governed by various physical-chemical properties including pH and oxidation potential, and biological processes (e.g. Kabata-Pendias & Mukherjee [2007]). Coppin et al. [2009] demonstrated that selenite binding to mineral or organic soils was nearly the same (at 99%) when applied at low concentrations. However, at high concentrations selenite sorption dropped to 44% in the mineral soil fractions, but remained at 93% in the organic fractions. This indicates that the sorption capacities of organic soils are likely to be higher than more mineralised soils. Binding within the organic fraction seems to be particularly associated with the 50-200 µm particle size fraction.

Binding sites within the soils, for both selenites and selenates, tend to be associated with clay particles, iron and manganese minerals, and organic matter. Organic matter has a strong tendency to form organo-metallic complexes which remove selenium as heavy metal selenides from soil solution [Kabata-Pendias & Mukherjee, 2007]. Metallic oxi-hydroxides (Fe, Al and Ti),

particularly, are known to sorb significant amounts of Se (IV) [Saeki & Matsumoto, 1994]. Hence speciation, as well as soil type, may influence binding characteristics.

The mechanism of selenate binding on iron oxides is not well understood. Some researchers have proposed that the bonding is electrostatic and weak, while others have proposed that covalent chemical bonds form between selenate and iron oxides. The nature of bonding can have a large effect on the transport and availability of selenate in the environment.

Percolation

This is the process by which Se-79 in soil water moves downwards into deeper horizons. This will depend on the proportion of Se-79 which is not bound to soil solids.

pH

Soil and soilwater pH is recognised to be important within most models of soil-plant interactions.

Selenates occur under oxidising conditions and are very weakly adsorbed to soils at alkaline pH. Due to their high solubility, selenates are very mobile in normal and alkaline soil conditions.

Selenites occur under mildly reducing conditions and are readily sorbed onto hydrous sesquioxides and organic matter, and/or precipitated as iron complexes. In acidic soils, selenium is usually found as selenite bound to these mineral components.

In poorly drained and acidic soils (i.e. very reducing conditions), immobile selenides are likely to form.

Precipitation

a) Water deposition

The rate of precipitation drives water flow from the soil surface to depth and acts as a source of (stable) selenium input to the system.

b) Chemical precipitates

Unsaturated vegetated soils are an important component in performance assessment models used to quantify risks associated with deep engineered repositories for underground radioactive waste disposal.

Within the saturated zone, sorption of selenium to hydrous oxides, organic matter and iron sulphides may result in precipitation and reduced availability. This mechanism is important in reducing Se levels in the ocean (with deposition to sediment). The relevance of precipitation to soil-plant studies may warrant further investigation.

Recalcitrant Se

The importance of recalcitrant Se may require further investigation. Materials which are poorly biodegraded are, by definition, likely to be poorly bioavailable and therefore of limited impact within transfer processes unless physico-chemical changes are effected.

Redox Potential

Recent column experiments, reported by Ashworth & Shaw [2006], using a sandy loam soil have indicated that the upwards migration of Se-75 (as a surrogate for Se-79) from a contaminated water table was dependent upon the redox status of the soil.

Low redox conditions within the water table strongly limited upwards Se-75 soil migration, presumably due to the immobilisation of reduced Se species.

It was suggested on this basis that upward transfer from a deep waste repository would be limited under 'natural' conditions.

Root uptake

Selenates tend to be taken up more readily than selenites, in part because selenites tend to adsorb more strongly to soils.

Currently Se uptake is typically modelled based on empirical data for the ratio between whole soil Se and plant Se. However, the data are highly variable. Should this be sub-divided into CRs for each soil component? Are the data available for this (for instance, selenium will be generally more available for plant uptake in alkaline soils)? If not could measurements or experiments be conveniently devised to provide that data?

Soil hydrology

This can include a number of processes, notably natural discharge or upwelling of groundwater to surface water bodies, with associated changes in oxygenation levels and nutrient status. What would be the chemical speciation response of selenium in groundwater reaching a surface water body?

Sorption

Currently, sorption is considered as an instant and reversible process through the application of K_d values. However, non-reversible sorption may also occur, or it may be necessary to consider the dynamic exchange between bound and unbound Se-79. The key issue is to distinguish the Se-79 which is available for uptake from plants from that which is not. Given the long-term nature of the release, it may be necessary to consider relatively slow processes which re-release bound/unavailable Se-79 back into the unbound/available form. Time series data on the effects of Se-doped fertiliser may be useful in this context. It may be necessary to consider separately the sorption onto different soil

fractions. However, such detail may not be useful if the data for root uptake into plants is empirically based on whole soil behaviour.

Volatilisation

Volatile selenium compounds can be formed by the methylation of elemental selenium and inorganic selenium compounds (such as sodium selenite). The transformation of inorganic selenium into volatile species is strongly dependent on a number of factors including pH, soil oxygenation, moisture content, temperature and on the concentration and chemical form of the selenium.

Methylated forms of selenium are unstable in water and are expected to be lost rapidly from soils.

A recent review of the literature [Sheppard & Sheppard, 2008] suggests that volatilisation may represent a significant loss term. It is suggested that a loss of 3% per annum from soils is a realistic estimate at the lower end of the observed range of volatilisation rates - although questions remain over long-term behaviour (see Section 2.5).

5. INTERACTION MATRIX

Because of the strongly-coupled nature of interactions at the temporal and spatial scales relevant to describing Se-79 in soil-plant systems, a practical approach is to use an interaction matrix to describe the dynamics of the system (see IAEA [2003] and IUR [2006]). The approach may be extended to allow for environmental changes. Modifications to the characteristics of leading diagonal elements of the interaction matrix, as a result of the action of regional-scale FEPs, may be propagated through the system by tracing pathways of influence via off-diagonal elements of the matrix.

Although a box-like matrix is used, it is not assumed that all the processes have to be represented by linear functions. The interaction matrix only provides the conceptual model, not its mathematical representation. Mathematical representation is described further in Agüero et al. [2005].

Figure 5.1 shows a provisional interaction matrix intended to provide a conceptual model addressing the assessment context given in Section 3. This matrix was developed in discussion with participants from the IUR Waste and Radioecology Working Group. The IUR matrices [IUR, 2006], including that drafted on Se-79, include a more analytical consideration of the science. Such an approach supports and complements the more descriptive approach used here to identify knowledge gaps.

Figure 5.1: Preliminary interaction matrix for a conceptual model of Se-79 in the soil plant system

	1	2	3	4	5	6	7	8
A	atmosphere	inhalation of dust and vapours	1) foliar uptake 2) interception	precipitation and infiltration		precipitation and infiltration	diffusion	wind driven loss from area of interest
B		animals	excretion	1) faeces 2) death & decomposition		urine		animals and animal products exported from area of interest
C	Volatilisation (translocation, retention, temperature)	Ingestion (translocation, retention)	vegetation	consumption and decomposition		Root exudation		export of crops from area of interest
D	1) volatilisation (mineral content, temperature), & methylation 2) erosion / weathering	ingestion	volatilisation, methylation and foliar uptake	soil organic matter, including soil fauna	1) speciation (pH, Eh, Fe hydroxides) 2) bioturbation 3) colloid formation	1) speciation, bioturbation, biological reduction 2) desorption (pH, Eh, Fe hydroxides) 3) colloid formation	1) respiration 2) volatilisation & methylation	Soil erosion
E	1) volatilisation & methylation 2) Erosion / weathering / other physical disturbance	ingestion	volatilisation, methylation and foliar uptake	speciation (pH, Eh, microbial activity)	soil inorganic matter	1) speciation 2) desorption (pH, Eh, Fe hydroxides)	volatilisation, and methylation	Soil erosion
F	degassing	ingestion	1) root uptake 2) metabolisation (fertiliser & stable Se)	sorption & speciation (pH, Eh, Fe hydroxides)	1) sorption & speciation (pH, Eh, Fe hydroxides) 2) colloid formation	soil solution	degassing	percolation to groundwater, run-off and sub-horizontal flow to surface water bodies (including colloid transport)
G	diffusion	inhalation (burrowing animals)				dissolution	soil atmosphere	
H								sink

Table 5.1 documents the definitions of the system components and processes included in the matrix. Note that the area of the soil which is of interest is the area directly affected by contamination from groundwater. Thickness (or depth) of the soil can be considered as the rooting zone of important vegetation; but this has not been defined quantitatively. The sub-division of the rooting zone into different layers has been discussed, but not decided upon. This issue is discussed further below.

Surface water bodies and sediments have not been included. They might need to be included if environmental change were thought likely to result in recycling and accumulation of Se-79 from waters and sediments to soils; however, this was thought unlikely to be significant in comparison to direct contamination of the soil-plant system, which in turn would provide the major source of Se-79 intake for humans.

Groundwater is not included in the matrix. The flux of radionuclides into various components of the modelled system needs to be taken into account but this does not require dynamic consideration of the groundwater system itself, since the Se-79 concentration in the groundwater is given as a constant value.

Table 5.1: Description of Elements in the Se-79 Interaction Matrix

Leading Diagonal Elements (LDE) defining the biosphere components of interest in the conceptual model				
	Name	Description	Includes	Comments
A1	Atmosphere	The air above contaminated soil and within which any evaporating Se from the soil can readily mix within seconds.	Dust and organisms in the air.	May subsequently need to be split between canopy atmosphere, air up to a specified height above the canopy atmosphere, and air above that.
B2	Animals	Living on the soil and in water bodies		Aquatic animals can be considered final consumers, but agreed to leave atmosphere at top of matrix.
C3	Vegetation	Vegetation which grows in the soil. May need to be divided into plant parts, such as seeds and rest, or above ground and below ground parts, according to contamination processes and translocation within the plants.	Agricultural products but also other vegetation	It was decided against changing vegetation to 'primary producer'. The group agreed that this was more relevant to the IUR matrix, but less to this matrix and that it is not feasible to deal with all organism levels.
D4	Soil organic matter, incl. soil fauna	Products from vegetation degradation, together with soil biota (micro and macro fauna and flora), exudates and detritus.	Soil in the area of interest, i.e. the area affected by contaminated groundwater	It was agreed that soil macro and micro fauna be integrated into soil organic matter, since the individual chemical processes associated with these receptors do not result in a change to the chemical form of Se.
E5	Soil inorganic matter	Broken rock altered from its parent rock, and other inorganic material	Soil in the area of interest, i.e. the area affected by contaminated groundwater	Not clear to what extent this includes residual soils.

Leading Diagonal Elements (LDE) defining the biosphere components of interest in the conceptual model				
	Name	Description	Includes	Comments
F6	Soil solution	Liquid content of soil.		Could be divided between connected and un-connected wet porosity
G7	Soil atmosphere	Gaseous content of soil.		
H8	Sink	Parts of the biosphere receiving losses from the area of interest, i.e. the area of soil receiving contaminated groundwater or irrigation water.	This could include a variety of media. The processes of transfer to each one from the area of interest are included in the matrix.	

Off-Diagonal Elements (ODEs) defining the Se-79 transfer processes of interest in the conceptual model				
	Name	LDE to LDE	Description	Comments from discussion
A2	Inhalation	Atmosphere to animals	Transfer via breathing into the respiratory tract	Low significance
A3	1) Foliar uptake 2) Interception	Atmosphere to vegetation	1) Transfer via stomata into leaves and branches. 2) Condensed atmospheric water vapour intercepted by leaves and branches	High significance. Group discussed but decided against amending cell A3 to include irrigation and precipitation in parentheses after interception.
A4	Precipitation & infiltration	Atmosphere to soil organic matter	Condensation of atmospheric water and associated particulate matter, deposited on soil surface	Negligible significance
A6	Precipitation & infiltration	Atmosphere to soil solution	Condensation of atmospheric water vapour then deposited on soil surface.	Low significance
A7	Diffusion	Atmosphere to soil atmosphere	Movement of atmospheric molecules along concentration gradient.	Low significance
A8	Wind	Atmosphere to sink	Advection to atmosphere not in the area of interest	Low significance
B3	Excretion	Animals to vegetation		Low significance
B4	1) Faeces, 2) Death and decomposition	Animals to soil organic matter	1) Elimination of faeces to soil surface 2) Decomposition of animal matter and release to soil	Low significance
B6	Urine	Animals to soil solution		Low significance
B8	1) Export of products 2) Migration	Animals to sink	Transfer to rest of the world by voluntary or non-voluntary movements of hosts.	Low significance
C1	Volatilisation (translocation, retention, temperature)	Vegetation to atmosphere	Transfer via vaporisation of plant moisture to atmosphere.	High significance

Off-Diagonal Elements (ODEs) defining the Se-79 transfer processes of interest in the conceptual model				
	Name	LDE to LDE	Description	Comments from discussion
C2	Ingestion (translocation, retention)	Vegetation to animals	Transfer via oral consumption of vegetation by animal.	High significance
C4	Consumption and decomposition	Vegetation to soil organic matter, including soil fauna	Transfer via oral or cellular ingestion by soil fauna/ breakdown of plant matter and release to soil surface	Medium significance.
C5		Vegetation to soil inorganic matter.		The group discussed burning but concluded that this is a tiny part of potential transfer to soil and thus should not be included.
C6	Root exudation	Vegetation to Soil Solution	Occurs within rhizosphere	Low significance
C8	Export of products	Vegetation to sink	Transfer to rest of the world	Medium significance. Changed from cropping to export.
D1	1) Volatilisation (mineral content, temperature), and methylation 2) Erosion/ weathering	Soil organic matter to atmosphere	Methylation and physical disturbance by animals, wind and farm machinery	High significance. Loss to atmosphere and transfer out of the system is important in reducing to local concentration of Se-79. Dust raising is probably less important.
D2	Ingestion	Soil organic matter to animals	Cows etc., consume soil with pasture	Soil ingestion could be important mechanism for uptake, depending on assumptions for crop uptake.
D3	Volatilisation, methylation and foliar uptake	Soil organic matter to vegetation	Foliar uptake following volatilisation at the soil surface	Minor pathway; assumed to be of low significance
D5	1) Speciation (pH, Eh, Fe hydroxides), bioturbation 2) Colloid formation	Soil organic matter to soil inorganic matter	Complex chemical and bio-degradation processes	Unclear significance but considered worth investigation
D6	1) Speciation, bioturbation, biological reduction 2) Desorption (pH, Eh, Fe hydroxides) 3) Colloid formation	Soil organic matter to soil solution	Complex chemical and bio-degradation processes	Unclear, but possibly high, significance over long timescales
D7	1) Respiration 2) Methylation	Soil organic matter to soil atmosphere	Complex chemical and bio-degradation processes	May represent a significant loss term from the system; considered to be worth further investigation
D8	Soil erosion	Soil organic matter lost to system	Any number of physical processes (wind or water scour)	Medium significance depending on site and climate characteristics
E1	Erosion/ weathering/other physical disturbance	Soil inorganic matter to atmosphere	Simple physical process, not Se specific. Generic data in IAEA [2003].	Low significance

Off-Diagonal Elements (ODEs) defining the Se-79 transfer processes of interest in the conceptual model				
	Name	LDE to LDE	Description	Comments from discussion
E2	Ingestion	Soil inorganic matter to animals	Cows etc., consume soil with pasture	Soil ingestion could be important mechanism for uptake, depending on assumptions for crop uptake.
E3	Volatilisation, methylation and foliar uptake	Soil inorganic matter to vegetation	Foliar uptake following volatilisation at the soil surface	Minor pathway; assumed to be of low significance
E4	Speciation (pH, Eh, microbial activity)	Soil inorganic matter to organic matter	Complex geo-chemical and decomposition processes	Unclear significance but considered worth investigation
E6	1) Speciation 2) Desorption (pH, Eh, Fe hydroxides)	Soil inorganic matter to soil solution	Complex geo-chemical processes	Unclear, but possibly high, significance over long timescales
E7	Volatilisation and methylation	Soil inorganic matter to soil atmosphere	Complex chemical processes	May represent a significant loss term from the system; considered to be worth further investigation
E8	Soil erosion	Soil inorganic matter lost to system	Any number of physical processes (wind or water scour)	Medium significance depending on site and climate characteristics
F1	Degassing	Soil solution to atmosphere		Low significance compared to via degassing to soil atmosphere and diffusion to atmosphere.
F2	Ingestion	Soil solution to animals	Cows etc., consume soil with pasture.	Soil ingestion could be important mechanism for uptake, depending on assumptions for crop uptake.
F3	1) Root uptake 2) Metabolisation (fertiliser & stable Se)	Soil solution to vegetation	Complex bio- chemical processes, moderated by microbiology and local chemical conditions	High significance
F4	Sorption and speciation (pH, eh, iron hydroxides)	Soil solution to soil organic matter	Complex geo-chemical and decomposition processes	Uncertain but potentially high significance; considered worth investigation
F5	1) Sorption and speciation (pH, Eh, iron hydroxides) 2) Colloid formation	Soil solution to soil inorganic matter	Complex geo-chemical processes	Uncertain but potentially high significance; considered worth investigation
F7	Degassing	Soil solution to soil atmosphere	Volatilisation and methylation	High significance
F8	Infiltration to groundwater and run-off and sub-horizontal flow to surface water bodies (including transport of colloids in soil solution)	Soil solution to sink	Advection, slope and subsystem hydrology dependent	High significance

Off-Diagonal Elements (ODEs) defining the Se-79 transfer processes of interest in the conceptual model				
	Name	LDE to LDE	Description	Comments from discussion
G1	Diffusion	Soil atmosphere to atmosphere	May be pressure effects dominating transfer rather than simple diffusion. See discussion of radon release from soils (e.g. Sharman [1992]).	High significance
G2	Inhalation (burrowing animals)	Soil atmosphere to animals	Transfer via breathing into the respiratory tract	Low significance
G6	Dissolution	Soil atmosphere to soil solution	Water chemistry dependent	Unclear significance but considered worth investigation

The Figure 5.1 interaction matrix has been reviewed against the FEP list to check that all the FEPs in the FEP list identified as of potential interest have either been included, or excluded, with appropriate reasoning and justification. The importance of traceability and transparency in how information has been included, or excluded, in the assessment models is reflected in the conclusions of SSI [2004].

The result of the review is presented as Table 5.2.

Table 5.2: Review of Interaction Matrix Contents against FEP list

FEP	Included at	Excluded because
Bioturbation	D5, D6	
Capillary rise		Note a
Colloidal selenium	D5, D6, E6, F5, F8	
Cropping loss (plants & animals)	C8	
Decomposition	B4, C4, E4, F4	
Degassing	F1, F6	
Discharge from below		Fixed source term
Effect of plants on Se speciation	D6, E6, F3	
Environmental change	Still to be considered	Still to be considered
Erosion	D8, E1, E8	
Fertiliser addition	F3	
Foliar uptake	D3, E3	
Infiltration	F6	
Ingestion	D2, E2, F2	
Interception	A3	
Isotopic dilution	F3 (see note b)	
Micro-organisms & fungi	D4, E4	
Organics, complexes and binding mechanisms	D6, E6, F4, F5	
Percolation	F8	
pH	D5, D6, E4, E6, F4, F5	
Precipitation	A4, A6	
Recalcitrant Se	F3, F4, F5 (note c)	
Redox potential	D5, D6, E4, E6, F4, F5	
Root uptake	E6 (note d), F3	
Soil hydrology variation	Note e	
Sorption	Note f	

FEP	Included at	Excluded because
Stable Se concentration	F3	
Translocation	C2, C3	
Volatilisation	D1, D3, E3	
Weathering	E1	

Notes to Table 5.2

- a. Horizontal discretization not yet considered. See discussion in section 6.
- b. Isotopic dilution could result in an entirely different model basis.
- c. Recalcitrant Se will be poorly biodegraded and, by definition, poorly bioavailable. It is not included as an explicit term but will be included implicitly within the availability of Se in soil solution for root uptake, or for transfer to the organic and inorganic soil fractions.
- d. Root exudation is included as well as root uptake.
- e. Consideration may need to be given to seasonal variation and to year on year variation, as well as changes due to environmental change.
- f. This is taken into account by consideration of organic and inorganic soil interactions with soil solution. While some factors have been identified which affect the effective sorption, the details processes which control those factors have not been identified here.

The review shows that all the FEPs have been included in the interaction matrix; however, some further explanation of the FEPs is necessary in order to have a clear definition of the conceptual model. In part, this may be best resolved within a particular, rather than the generic, assessment context considered for this review in Section 3. This is discussed further in Section 6.

6. IMPLICATIONS FOR MODELLING SELENIUM-79 IN THE SOIL/PLANT SYSTEM

Figure 5.1 provides the basis for a conceptual model description, identifying biosphere components of relevance and processes by which Se-79 would be dynamically transferred between them. Many of the important but non-selenium dependent processes could be represented mathematically according to suggestions in IAEA [2003] and Agüero et al [2005]. These references in turn rely substantially on previous work.

It can be argued that the description of the biosphere components and the selenium specific processes are not sufficiently defined to allow ready mathematical representation. In particular, the vertical discretization of the soil has not been defined. The root zone of the soil may need to be subdivided into several layers to take account of bio-geochemical factors which affect the vertical profile of selenium sorption and volatilisation. This may be especially important if the source of Se-79 is from below. However, it may be argued further that such discretization may better be performed according to site specific information about the soil type and hydrology.

The interaction matrix suggests that separate consideration should be given to the solid inorganic and organic components of each soil layer, and to soil solution and soil gas. The need to do this arises because the data for sorption of Se in soils and for its uptake into crops is hard to interpret at a gross level. By accounting for the soil characteristics and soil processes in greater detail, it may be possible to obtain a more precise understanding Se-79 behaviour, how it is retained in soils and how it then may be available for root uptake. The conceptual structure has been outlined, but it remains to be shown if relevant data are available to support such a model.

If data are not available to allow for soil compartmentalisation as indicated, it may be necessary to re-iterate the previous steps to simplify the model, and/or lead to recommendations for new experiments, field measurements and other research.

The process of loss of Se-79 from soil by volatilisation has been clearly demonstrated and data made available to allow at least a cautious estimate to be made for the loss rate.

7. CONCLUSIONS AND RECOMMENDATIONS

The soil-plant system FEPs relevant to long-term dose assessment for Se-79 have been identified and incorporated within a preliminary interaction matrix which provides the basis for an appropriate, transparent and traceable conceptual model.

Selenium has a relatively complex chemistry and a number of recommendations are drawn for further investigation and associated model developments.

7.1 General data requirements

The identification and resolution of soil-water partition coefficients (Kd values) relative to specific soil types and water regimes would improve understanding of Se behaviour, and permit greater differentiation between specific disposal sites.

Volatilisation of selenium from the soil surface has been shown to be of potential consequence as a loss term from the soil-plant system. Data currently available are insufficient to draw long term conclusions. It is possible that volatilisation rates will vary over time. It is also suggested that volatilisation is correlated with total soil microbial activity. Given the potential significance of this parameter, clarification of rates of loss over time, and influencing factors, can be seen as a high priority.

Speciation of selenium, and factors affecting binding to soil (and hence bioavailability), requires further investigation in order to better define uptake to biota and pathways back to local populations.

Distribution within the soil column appears to have received relatively little attention. This affects quite fundamentally bioavailability as linked to rooting depths of different plants species.

The half-life of Se-79 is currently subject to debate. Previous estimates of 65,000 years have been challenged and a median estimate around 350,000 years has been proposed, whilst noting a range in recent estimates from 120,000 years to 1, 100,000 years. Whilst this does not affect bioavailability, it does impact significantly on the time course of source terms to the biosphere.

7.2 Modelling

Modelling approaches may be refined to incorporate a number of specific features. These include:

- ◆ Incorporation of pH and redox potential within soils to determine Se behaviour;
- ◆ Inclusion of organic, inorganic and soil particle size within the soil compartment;
- ◆ Vertical differentiation of soil layers; and,

- ♦ Consideration of the chemical form of Se and background concentrations of Se – this may be expanded to consider specifically an isotopic dilution approach to modelling.

In general, modelling should be linked with experimental and field-based programmes determining behaviour across a range of environmental conditions and time profiles.

7.3 Site specific characteristics

At this stage, it remains too early to identify with certainty characteristics to be determined on a site specific basis to improve predictive capabilities for selenium behaviour in the long-term. Nonetheless, it appears that soil type and particle size density are primary characteristics to quantify. Likewise, the presence of competing ionic species, or binding facilitators, will influence the bioavailability of selenium.

Given the potential importance of volatilisation, and the indication that this is linked to total soil microbial activity, the determination and unification of suitable measures of microbial activity would appear to be a priority task.

7.4 Additional consideration of Se-79 impacts on non-human biota

The present report has focused on bioavailability as a pathway to impacts on man. In recent years, there has been increasing emphasis on protection of non-human biota. The extension of current studies to include assessment of impacts of Se-79 on non-human biota is recommended on the basis that determination of this aspect is a new and developing aspect of international recommendations and regulatory requirements.

8. REFERENCES

Agüero A, Moraleda M, Perez-Sanchez D and Trueba C (2005). Mathematical Representation of Features, Events and Processes and Associated Parameters for Biosphere Assessments. CIEMAT. ISBN 84-7834-507-8.

Ashworth DJ and Shaw G (2006). Soil migration, plant uptake and volatilisation of radio-selenium from a contaminated water table. *Science of the Total Environment* 370: 506–514.

Barceloux DG (1999). Selenium. *Journal of Toxicology – Clinical Toxicology*, 37, 145–172.

Bé M and Chisté V (2006). Se-79: Comments on Evaluation of Decay Data. LNE-LNHB/CEA, January 2006.

BIOPROTA (2008). Report of an International Forum on Se-79 in the Biosphere, version 2.0, June 2008. Ed. K R Smith. Available from www.bioprota.com.

Coppin F, Chabroullet C and Martin-Garin A (2009). Selenite interactions with some particulate organic and mineral fractions isolated from a natural grassland soil. *European Journal of Soil Science*: 60, 369–376.

IAEA (2003). Reference Biospheres for Solid Radioactive Waste Disposal. Report of BIOMASS Theme 1 of the BIOSphere Modelling and ASSessment (BIOMASS) Programme IAEA-BIOMASS-6. International Atomic Energy Agency Safety, Vienna.

IAEA (1994). Handbook of parameter values for the prediction of radionuclide transfer in temperate environments. IAEA Technical Report Series 364, International Atomic Energy Agency, Vienna.

ICRP (2006). Assessing Dose of the Representative Person for the Purpose of Radiation Protection of the Public, and the Optimisation of Radiological Protection: Broadening the Process. ICRP Publication 101. *Annals of the International Commission on Radiological Protection*, Volume 37 (2-4). Elsevier.

IUR (2006). Recommendations for Improving Predictions of the Long-term Environmental Behaviour of C-14, Cl-36, Tc-99, Np-237 and U-238. Findings of the IUR Waste and Radioecology Task Force. International Union of Radioecology Report 6.

ICRP (1983). Radionuclide Transformations: Energy and Intensity of Emissions. ICRP Publication 38. *Annals of the International Commission on Radiological Protection*, Volume 11 - 13. Pergamon.

Kabata-Pendias A and Mukherjee AB (2007). Trace Elements from Soil to Human. Berlin: Springer-Verlag.

Kapolna E, Hillestrom PR, Laursen KH, Husted S and Larsen EH (2009). Effect of foliar application of selenium on its uptake and speciation in carrot. *Food chemistry*: 115, 1357-1363.

Keskinen R, Ekholm P, Yli-Halla M and Hartikainen H (2009). Efficiency of different methods in extracting selenium from agricultural soils of Finland. *Geoderma* 153: 87-93.

Leclerc-Cessac E and Jaubert N (2005). Selection of biosphere transfer parameter values for radioactive waste disposal impact assessments, a site specific approach. *Radioprotection* 40 (Suppl. 1): S359-S365. DOI: 10.1051/radiopro.

NEA (2009). Mobile Fission and Activation Products in Nuclear Waste Disposal. Workshop proceedings, la Baule, France, 16–19 January 2007. Nuclear Energy Agency, NEA No. 6310. ISBN 978-92-64-99072-2.

Peterson PJ & Butler GW (1966). Colloidal selenium availability to three pasture species in pot culture. *Nature* 212: 961-962.

Saeki K & Matsumoto S (1994). Selenite adsorption by a variety of oxides. *Communications in Soil Science & Plant Analysis* 25: 2147–2158.

Sheppard MI, Sheppard SC (2008). Volatilization of Selenium: Factors Affecting the Rate of Volatilization. Nuclear Waste Management Organisation, NWMO Nuclear Research and development Program, Technical Memorandum, version R0.

Sharman G (1992). Seasonal and spatial variations in Rn-222 and Rn-220 in soil gas, and implications for indoor radon levels. *Environmental Geochemistry and Health*, 14(4), 113–120.

Sposito G (1989). *The Chemistry of Soils*. Oxford University Press, New York.

SSI (2004). SSI and SKB's Review of SKB's Updated Final Safety Report for SFR-1. SSI Report 2204:6. Swedish Radiation Protection Authority, Stockholm.

Smith GM, Merino J and Kozak M (2008). Uncertainty and variability in biosphere dose conversion factors for the groundwater release scenario for Yucca Mountain. In Proc 2008 International High-Level Radioactive Waste Conference, Las Vegas, 7–11 September. American Nuclear Society.

Zhang P-C, Krumhansl JL & Brady PV (2002). Introduction to properties, sources and characteristics of soil radionuclides. In: *Geochemistry of Soil Radionuclides* (eds P-C Zhang & PV Brady), pp. 1–20. Soil Science Society of America, Madison, WI.

APPENDIX A: PARTICIPANTS AT A WORKSHOP ON SE-79 BEHAVIOUR IN THE ENVIRONMENT: 19-20 MARCH 2009

Participant	Affiliation	Presentation / Role
Laureline Fevrier	French Institute for Radiological Protection and Nuclear Safety (IRSN), France	Microbial volatilisation of selenium from soils
Frédéric Coppin	French Institute for Radiological Protection and Nuclear Safety (IRSN), France	Non reversibility of selenium sorption in soils - Alternative model to Kd for selenite migration in soils
Steve Sheppard	ECOMatters, Canada	1) Se volatilisation from soils and sediments 2) Se concentration ratios based on stable element data
Danyl Perez-Sanchez	CIEMAT, Spain	Technical advice
Yves Thiry	ANDRA, France	Technical advice
Anne-Maj Lahdenperä	Poyry Environment, Finland	Technical advice
Rikka Keskinen	MTT Agrifood Research Finland	Soil selenium fractions and plant selenium uptake efficiency in Finnish field soils
Achim Albrecht	ANDRA, France	Technical advice
Mike Thorne	MTA, UK	Technical advice
Karen Smith	Enviros, UK	Technical advice and BIOPROTA Technical Secretariat
Graham Smith	GMS Abingdon, UK	Technical advice and BIOPROTA Technical Secretariat