BIOPROTA

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

Report of an International Forum on Se-79 in the Biosphere

Wettingen, Switzerland
5-6 May 2008

Editor: K Smith

Hosted by NAGRA

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Preface

The forum and this report were produced within the international collaboration project BIOPROTA – www.bioprota.com

The report is presented as working material for information. The content may not be taken to represent the official position of the organisations involved.

Report History

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Contents

1. INTRODUCTION

Selenium-79 (Se-79) is an important radionuclide in some types of radioactive waste. It is mobile and long-lived and potentially could migrate into the biosphere following release from radioactive waste disposal facilities. Special attributes are its complex chemistry, notably the chemical form is dependent upon the redox state with some compounds being volatile. Selenium is an essential element, but can also be toxic with only a small concentration range between deficiency and toxicity.

The data necessary for radiological assessment of Se-79 are scarce and can be unreliable, particularly in relation to its behaviour in the terrestrial soil-plant system.

A workshop was therefore held to discuss those attributes of Se-79 of particular relevance to radiological assessments for geological waste repositories. The workshop was held on 5-6 May 2008 and was hosted by Nagra, Wettingen, Switzerland.

1.1 Objectives of the International Forum on Se-79 in the Biosphere

The objective of the workshop was to provide an open forum for presentation and discussion of the behaviour of selenium in the biosphere, with particular focus on the environmental processes involved in selenium migration and accumulation in the biosphere and how radioecological assessments of Se-79 could be improved.

The workshop involved both presentation and discussion of data requirements for dose assessment and knowledge and on-going research in the field of Se-79 behaviour in the biosphere.

1.2 Report structure

Chapter 2 provides an overview of each of the presentations made during the duration of the workshop. The main points arising from group discussions are outlined in Chapter 3 and conclusions and recommendations for further research are presented in Chapter 4.

1.3 Participation

There were 19 participants from 9 countries, representing a range of operators, researchers and technical support organisations. Participants are listed in Appendix A.

2. PRESENTATIONS

Presented below is an overview of each of the presentations given during the workshop. Points of discussion arising as a result of each presentation are also highlighted.

2.1 Introduction to and background of the workshop

The workshop opened with a presentation by Matthias Brennwald (Nagra), which gave an overview of the main drivers behind the workshop in relation to Se-79 dose assessment for geological waste repositories and provided some background in radiological dose assessment for non-experts.

The Nagra model for evaluating the transport of radionuclides to the biosphere as a result of releases from a geological waste repository consists of five compartments between which water and solids (both radiologically contaminated and uncontaminated) can be exchanged. The output of such models can then be used as input to exposure pathway models, which take account of food pathways leading to human exposure. Pathways include:

- direct exposure through external radiation from environmental media and internal exposure from the inhalation of volatilised Se-79 and contaminated dust particles ; and,

- indirect exposure resulting from the accumulation in, and ingestion of, foodstuffs (drinking water, plant and animal products).

In modelling dose over time, four radionuclides routinely dominate as dose contributors – carbon-14 (C-14); iodine-129 (I-129), chlorine-36 (Cl-36) and Se-79. Much work has been focused in the past on C-14, I-129 and Cl-36 and there is therefore a reasonable database on which models can be based. However, little attention has been directed at Se-79. Selenium is highly mobile in the geosphere and can therefore readily enter the biosphere through association with the migration of groundwaters.

A review of biosphere parameter values for Se-79 such as Kd and the soil-plant concentration ration (CR) has been conducted and it was evident from this that there is a large variation (of several orders of magnitude) in published data and much that is available is outdated and/or the original source, and thus robustness, is often unknown. The relationship between these two parameters is also unknown, but it is considered that there may be a strong correlation.

The presentation was concluded by the posing of three questions for which it was hoped that discussions and presentations during the workshop may assist in providing answers:

- are new (and robust) parameter values available?

- What processes govern the behaviour of selenium in the biosphere (with particular focus on soil behaviour and uptake into plants)?

- How can assessment models be improved (for example, are there additional processes that should be considered on a mechanistic level or should revised parameter values be employed etc.)?

Discussion

A number of discussion points were raised as a result of the opening presentation:

- Graham Smith (GMS Abingdon) questioned whether a simple box-model approach was the most appropriate tool for selenium biosphere model. It was considered that the available evidence suggests a more sophisticated model approach may be justified. For example, it was suggested that there may be an argument for considering Se-79 in 'soil water' separately from Se-79 associated with soil particles. This has not been the case in most models applied to dose assessment of long-term releases of Se-79 so far, though, of course, it can be implemented within a compartment model approach, and has been done in relation to I-129[1].

- The need for consideration of volatilisation of selenium from soils was raised by Steve Sheppard (ECOMatters) – up to 5% per annum of selenium in top soils could be lost as a result of this process. Volatilisation can result in exposure as a result of the inhalation pathway, but also results in dispersion.

- Frits van Dorp (Nagra) raised the question as to whether stable selenium soil concentrations should be taken into account when modelling Se-79 behaviour in soils? Soils can show a large variation in selenium concentrations with some exhibiting deficiency (e.g. those in Switzerland) and others containing concentrations that may result in toxic effects. These differences may affect the behaviour of Se-79 entering a system and there may therefore be a need to consider how selenium accumulates within areas of naturally high/low selenium content. However, this is further complicated by the fact that soil properties may change over the long time period for which performance assessments for geological waste repositories are conducted.

- Achim Albrecht (Andra) noted that in highly reduced systems, selenium will occur in a methylised form and it would therefore be of interest to understand the rate of change associated with changes in redox state as this will greatly affect uptake into plants. Annette Johnson (Eawag Duebendorf) explained that literature suggests this is a complex issue since soil conditions within the rhizosphere (root zone) – which is often used in experimental studies – will be very different to soils as a whole. There would therefore be a need for careful interpretation of results in light of the particular experimental conditions to determine just how applicable soil-plant CR values are for use in biosphere models.

2.2 Observations on the environmental behaviour of selenium relevant to dose estimation

Graham Smith provided a presentation on some of the key issues associated with dose assessments related to Se-79 release from geological waste repositories.

One of the key uncertainties is the degree of clarity over the half life of Se-79. ICRP 30 suggests the half life may be 6.5E+04 years, but data from the last ten years suggests the range is anywhere from 2.1E+05 to 1.1E+06 years and in 2006 the recommendation was made for a value of 3.56E+05 years to be adopted[2]. Irrespective of which particular value is selected from this range, the long half life suggests that Se-79 will reach the biosphere following release from a waste repository, prior to any significant radioactive decay occurring. However, the half life will have an effect on

1 White I F and Smith G M (1984). Management Modes for Iodine-129. CEC. Euratom Report EUR-9267.
2 A note prepared by M M Be and V Chiste reviewing Se-79 half-life experimental data.

the specific activity (Becquerel per gram) of Se-79, which is important if isotopic dilution is to be taken into account via a specific activity modelling assumption.

A cumulative distribution function was presented for Se-79 dose based on draft calculations made for EPRI. In this example the corresponding deterministic result was significantly higher than the mean of the distribution. The point was made that if distributions for parameter values, such as root uptake or accumulation in tissues, can be used as input then it may be possible to provide a better estimate of the more likely dose to a member of a critical group, rather than adopting a potentially overly pessimistic deterministic approach. In the draft EPRI calculations, irrigation using contaminated groundwater was assumed to result in contamination of soils and subsequent uptake into fodder and subsequent accumulation in animal produce. The consumption of contaminated meat and liver from cattle contributed the greatest to dose, but direct consumption of plants (e.g. root crops) was also a significant pathway, contributing a dose that was ten times that associated with drinking water consumption. Due to the importance of these pathways for human dose assessments, it was therefore considered that a better understanding of soil contamination processes and the relationship to uptake by crops would be warranted.

For predictive dose assessments, ICRP Publication 101 suggests that calculations should be for a ‘representative person’, a change in terminology from the previously used ‘critical group’. However, there is remaining uncertainty as to how parameter values for the ‘representative person’ should be selected. Achim Albrecht noted that both Andra and IRSN are looking at how best to continue this debate.

Prior to the workshop, a number of relevant papers were distributed to participants. However, some additional papers have since been identified from the most recent ICOBTE Proceedings[3]:

- Darcheville et al, which presents information from experiments on the how fungal activity can affect selenium volatilisation;
- Simon et al, on the phyto-extraction of selenium and how soil chemistry and form of selenium can affect uptake into plants; and,
- Upadhyaya et al, and Illinois, which both look at selenium volatilisation in relation to soil bacteria associated with Rabbitfoot grass.

In addition, a book has recently been published (by W T Frankenberger and Richard Enberg (Editors)) on the Environmental Chemistry of Selenium.

Discussion

The question of how much food should be assumed to come from outside the contaminated area was raised by Achim. In response it was explained that the approach would very much depend on whether or not it is assumed that radioactivity enters the biosphere from a point or diffuse source. This is a GBIZ (Geosphere-Biosphere Interface Zone) issue, which is difficult to address (e.g. taking into account the presence of fracture zones) and will largely affect the distribution within the biosphere.

3 Zhu Y, Lepp N and Naidu R (Eds) (2007). Biogeochemistry of Trace Metals: Environmental Protection, Remediation and Human Health. Proceedings of an International Conference, Tsinghua University Press, Beijing.

Matthias also noted that the pathways by which Se-79 is injected into and exchanged within the biosphere will also affect its mobility as a result of the potentially different oxidation states of the different environments. The oxidation state affects the ability of Se to accumulate in soils and, where accumulation close to the surface of soils occurs, release can occur (e.g. due to agricultural disturbance) and this can result in dose peaks occurring.

2.3 The oxidation-reduction potential in the near-field of a high level waste disposal site and the possible impact on Se speciation and migration

Achim Albrecht began by highlighting the importance of linking expertise between those working in the near field, the geosphere and the biosphere. For example, the biosphere is traditionally considered to be that area in which life can exist. However, bacteria are known to exist in deep groundwaters and may also occur in waste disposal cells and therefore it can be considered that there is a biological as well as hydrological link between the geosphere and biosphere.

Processes in the near field are largely defined from information gathered for the biosphere. However, rates of reactions (e.g. redox reactions) are unknown.

Redox reactions are simpler to model than to measure as equilibrium thermodynamics are assumed. However, in reality there will not be thermodynamic equilibrium since many reactions occur slowly and are microbially driven. The degree of microbial activity within the near field will therefore largely determine reaction rates.

Around 5% of cement (used for waste encapsulation and for engineered barriers) is comprised of organic matter. The near field system is therefore comprised of a diversity of components such as organic matter, nitrates, sulphates, radionuclides, stable metals, etc. Decalcification and hydrolysis can occur resulting in a reduction in pH and Kd values can be affected as a result of heat exchange and many of these processes cannot be decoupled. There is a also lot of uncertainty associated with the release of radioactivity from a repository, such as behaviour in relation to pH, corrosion, microbiology etc. and it is unlikely that equilibrium conditions will occur. All of these factors should therefore be taken into account when modelling the system.

Selenium is present in a number of forms, depending upon oxidation state:

- Selenate, which is weakly sorbed and is generally soluble and may therefore escape from the near field to enter the biosphere;
- Selenite, which is more strongly bound to mineral surfaces and will therefore migrate to a lesser degree;
- Elemental selenium, which occurs in colloidal form;
- Selenide, which co-precipitates with pyrite; and,
- Dimethyl selenide, which in not currently considered in near field.

Selenium is widely used in the manufacture of glass and ceramics and is therefore a component of the glass used for vitrification of radioactive waste. Each vitrified waste cell can contain 10^{13} to 10^{14} Bq of Se-79, but very little is known about the redox state in which it is present.

The presence of Nitrate has been shown to affect the form in which selenium occurs. Where nitrate is present at concentration then selenium will be in the Se(VI) form and will be mobile. The lower the nitrate concentration, the more likely that selenium will be in the colloidal form and will therefore remain in the near field.

Once selenium has exited the near field it can migrate through the geosphere to enter the biosphere.

Discussion

Discussions focused around the different forms in which selenium can occur, including the release of selenium in the gaseous form through methylation, which would occur as a result of bacterial activity. the release of gaseous selenium would be entirely different from that in the liquid form and has not been considered at Andra to date.

Whether there are key aspects that should be followed was questioned and in response it was recommended that greater focus should be on the redox reactions occurring in the near field and how these are then handled within the biosphere.

The point was also raised by Yongsoo Hwang (KAERI) that the importance of the form of selenium (e.g. colloidal selenium) will be dependant upon local conditions, particularly the geological media as for spent fuel disposal the near field environment will vary for each repository. In some instances (e.g. Andra), colloidal selenium would not have to be considered since the geosphere conditions would prevent its migration.

2.4 Se in soils: geochemistry and plant uptake...and human health

Annette Johnson (Eawag Duebendorf) gave a presentation on some of the biosphere characteristics of selenium that govern its behaviour in soils.

From review of available literature it is apparent that selenium concentrations are low within the earths crust, but are highly variable in sedimentary rocks (high concentrations have been recorded in shales). Similarly soil concentrations can be variable in seleniferous soils the concentrations recorded are generally low (< 1 mg/kg), but high concentrations (> 5,000 mg/kg) can be recorded. Concentrations within freshwaters are generally low, but can reach the mg/l range.

The mobility of selenium is dependant on both redox potential and pH – at low pH and in reducing conditions selenium is largely immobile. Redox conditions are also dependant upon organic matter concentration, clay content and the presence of iron oxides.

Selenate (an oxidised form) can leach from soils and can also be taken up strongly into plants whereas selenides (reduced form) are taken up more passively. Selenium can also become protein bound, particularly in cereals and these can then be transferred into animals. In the case of hyper-accumulating plants, selenium concentrations can reach 10,000 to 20,000 mg/kg dw and animals consuming such plants can receive short-term poisoning as a consequence. The presence of sulphate is an important factor governing uptake into plants.

A study conducted in Punjab (India) has also demonstrated that rice plants are capable of taking up colloidal selenium directly with the result that rice intake has to be diluted to prevent toxic effects from consumption. Groundwater concentrations of 30 µg/l were recorded in the area.

From the literature it appears that selenium can be taken up readily into plants where available, but is not essential. Selenate is taken up through an active sulphate-pathway whereas selenite is taken up by passive processes. In addition to plant uptake, volatilisation can be an important mechanism of loss from soils.

Human intake of selenium has been investigated and there appears to be only a narrow range of tolerance for uptake – from 40 to 200 µg/day. The average intake is about 60 µg/day from food and less than 10 µg/day from water.

A GIS database has been developed of concentrations of selenium in groundwaters. However, global data are sparce. Out of 6000 data points or more, only 36 had concentrations greater than 100 µg/l. The median value was 1.7 µg/l.

The database has been used to investigate reasons behind the high groundwater concentrations recorded and it was found that metamorphic intrusive rocks were generally associated with higher concentrations recorded. Groundwaters with a higher pH were also found to have higher selenium concentrations although there was not a strong correlation. However, in the case of soils, pH becomes more important due to its association with selenium mobility.

The prediction of selenium deficiency in soils is more problematic, but is a more common problem that selenium excess. Soil pH, clay content, organic carbon and climate were all investigated to see if these helped predict areas of deficiency. A correlation was found between all categories and deficiency. However, even if it is possible to predict concentrations on the basis of soil type, it is difficult to then predict soil type over the tens of thousands of years of more that are of interest for performance assessments.

Discussion

In discussions, Achim questioned whether plant strategies for uptake in relation to soil concentrations are known; for example, whether plants have active mechanisms for enhanced uptake in deficient soils and vice versa.. Steve Sheppard volunteered that here is evidence for such strategies, but they may be very species dependant. For example, brassicas and garlic are known to accumulate selenium and this may be linked to their ability to accumulate sulphate.

Danyl Perez (CIEMAT) also suggested that the way in which soils are prepared for crops may have an effect on uptake, which will also have implications for assessments as models would be required to predict the way in which soils are worked.

It was also questioned whether deficiency in arid environments is largely a consequence of the presence of iron oxides or more as a result of greater irrigation rates. Irrigation was noted as being an important factor, but it is not yet certain what the dominant parameters are in such systems.

Further work is planned on selenium such as the factors governing bioavailability and a project is currently being defined for China. However, model calibration is proving to be a difficultly.

2.5 Occurrence of selenium at SKB sites

Two presentations were given on the occurrence of selenium at SKB sites. The first was presented by Ulrik Kautsky on the occurrence in the marine environment. The second focused on soils and freshwaters and was presented by Birgitta Kalinowski.

2.5.1 Occurrence of selenium in the marine environment of SKB sites

SKB have conducted dose predictions for their radioactive waste repository safety case. Dose calculations indicate that carbon-14 is the greatest dose contributor over the first 10,000 years, but following this Se-79 becomes one of the four major contributors to dose. Total dose remains below regulatory limits.

Work has also been conducted on fluxes (mass balance) of different radionuclides throughout the components of the biosphere. For uranium there is high flux to sea, with minor accumulation in fish when compared against that for phosphorous. Work in this field is ongoing and data for selenium are not yet available.

However, a study has been completed on the element composition of the marine foodchain. In total, 48 elements were investigated and Kd values, concentrations and transfer factors to biota in the Baltic sea were determined (A report will soon be published in the SKB report series, authored by Kumblad and Bradshaw). For selenium, a Kd in the order of 500 was calculated. For most organisms, concentrations of elements were generally around 0.5 mg/kg dw, although peaks were noted. In the case of selenium, zooplankton were found to contain high concentrations (>7 mg/kg dw).

Transfer factors, when calculated as fresh weight, were low for phytoplankton and highest in bivalves and fish. However, when calculated in relation to the carbon content of the biota a correlation was evident – the highest transfer factors were for phytoplankton and benthic microalgae followed by benthic snails that consume the diatoms. Those organisms with a more mixed diet had lower concentrations. The benefit of using carbon content as a means of standardising concentration data in order to determine patterns and trends was therefore highlighted.

2.5.2 Selenium at SKB sites – terrestrial and freshwater

Selenium is known to bind to iron oxide clay minerals with binding increasing as pH decreases.

Forest soils have been found to accumulate selenium, which is due to microbial activity causing a reduction of the selenium form and therefore reducing its mobility. In agricultural soils selenium occurs in a more oxidised form and is therefore more mobile. In Nordic countries, selenium concentrations are generally low in soils due to the underlying geology – in more than 90% of soil samples from around Sweden concentrations were below 0.45 mg/kg. This is below the concentration required within feed crops and therefore supplements are required to be added to animal feeds. Two sites are being investigated by SKB as potential areas for a geological waste repository – Laxemar and Forsmark. Till samples from these sites have been analysed and selenium concentrations of 0.13 +/- 0.07 and 0.18 +/- 0.07 mg/kg for Laxemar and Forsmark, respectively, have been recorded.

Concentrations in biota have also been investigated with the greatest concentrations being recorded in freshwater mussels. Much lower concentrations were recorded for all other higher organisms such as moose and small rodents.

In aquatic systems a reliance on modelling data was required. Selenium exists in the freshwater environment in three oxidation states with selenite being the dominant form in oxygenated surface waters.

A proposed biogeochemical cycle of selenium in a freshwater lake was presented. Selenium can enter lakes through direct inputs from rivers and streams, but also from power plant operations. Outputs from the lake can be by outflow to rivers/streams or by volatilisation processes or can be bound in the particulate organic phase as a result of photosynthesis. Similarly, biological respiration can result in particulate organic selenium being transformed back into the dissolved phase. Below the oxic zone (i.e. the hypolimnion), selenium can also be reduced to particulate elemental selenium (Se(VI)) where it may be deposited in lake sediments where biological activity can occur to release selenium into sediment pore waters where it is free to exchange with lake water or move to deeper sediments.

At the Forsmark and Laxemar sites, selenium surface water concentrations are low (average 0.11 µg/l) and have historically been below detection limits. However, due to developments in analysis methods there have been improvements in detection limits and it is therefore intended that samples will be re-analysed.

Discussion

The sampling programme for selenium at the SKB sites was questioned to determine whether or not a constant flux from bedrock to river was evident and whether there are signs that changes in precipitation can drastically change river concentrations. The sampling programme was conducted over a one week period for biota and simultaneous river flow measurements were made. This enables correlations to be noted between different biota species and in relation to water concentrations at the time of sampling.

2.6 Transport of selenium in a boreal stream network

Fredrik Lidman (Umeå University) presented some preliminary conclusions from a study of the Krycklan Catchment in northern Sweden. The catchment is subject to multidisciplinary study, and includes research on radionuclide transport that is being conducted in collaboration with SKB. The study area is large and includes some 18 sub-catchments, all of which are sampled regularly and there is a continuous record of hydrological and hydrochemical sampling stretching back to 1980.

Between 2004 and 2005 ten sub-catchments sampled and analysed for selenium. The landscape of the catchment is largely comprised of forest and wetland. There was a large spatial variation observed for selenium concentrations in the catchments studied, particularly between mire and forest systems. A large temporal variation was also observed with concentrations increasing dramatically over a matter of days in some instances.

Peat tends to dominate around forest streams and a riparian hypothesis has been stipulated that the peat controls much of the chemistry of the stream. During spring floods, groundwater rises, which results in an increase in dissolved organic carbon (DOC) within peat and this then increases DOC within the stream.

During the spring flood of 2005, high selenium concentrations coincided with rising run-off. Run-off is very closely correlated to groundwater in vicinity of stream. Only a small increase in groundwater level is required for a resultant large increase in stream flow.

Mobile species of selenium have been detected in groundwater and it is possible that redox reactions are occurring. However, no speciation data is, as yet, available. When spring flood data is removed, it appears that there is no limitation to the export of selenium from the forest, which may be due to soil conditions or due to the amount of water flowing through the riparian zone.

Mires and lakes exhibit less selenium than forests and export is therefore lower from these systems. For one mire, a selenium budget has been calculated from which 0.8 g of selenium enters the system from forest soils, but around 1 g is lost from the system. Atmospheric deposition may therefore be responsible for the additional input to the mire system.

The coverage of land area by mire has been shown to affect the export of a range of elements. For example, an increased export of antimony is noted where mire coverage is large (50% mire as opposed to 25%). However, in the case of selenium, export is slightly reduced where mire coverage increases. Selenium does not appear to accumulate to a high degree in mires and doesn't seem to have a high affinity for organic matter.

Discussion

It was noted by Achim Albrecht that the high DOC within mires would normally provide multiple sorption sites that would modify accumulation processes – e.g. see http://www.bgs.ac.uk/discoverymetadata/13480230.html for a discussion of natural analogue behaviour of uranium accumulation.

2.7 Study of the biogeochemical cycle of selenium in the environment

John Muller (SUBATECH) presented work in progress on a studentship on the biogeochemical cycle of selenium.

Selenium is known to occur in four oxidation states and three physical states (solid, liquid and gaseous). The study has investigated the sorption of selenium onto minerals (bentonite, goethite and calcite) using dialysis membranes in order to determine Kd.

The highest Kd was recorded for goethite and lowest for calcite. The pH remained constant for the duration of the experiment and equilibrium was reached. When a binary system was used (multiple mineral phases that are physically, but not chemically separated), the Kd was found to increase for goethite when in association with bentonite. It is intended that further studies will investigate the Kd of goethite when in association with silicon.

The sorption of natural organic matter in the form of humic acid has also been investigated. The greatest sorption (~90%) was observed for calcite with the lowest sorption (~30%) occurring on bentonite. No competition for binding sites was observed between selenium and humic acid on bentonite or calcite.

Rhizoplant experiments have also been undertaken using both clay-loam and sandy-loam soils (sterile and non-sterile) to investigate selenium volatilisation. Sandy soils were found to contain around 47% water soluble selenium, but in the clay-loam soil only around 36% was water soluble. No difference was noted for sterile and non-sterile conditions so sterilisation did not appear to affect the behaviour of selenium in soils. Ryegrass was found to have a large effect on selenium volatilisation however in both sterile and non-sterile soils. No reduction of selenium was evident from TEM analysis.

Although soil composition was found to affect selenium behaviour, no difference in the assimilation of plants was noted, irrespective of different soil compositions.

Discussion

Discussion focused around the experimental set up used for the rhizoplant experiments with Frits van Dorp (Nagra) questioning whether or not plant roots were capable of penetrating the soil (if not then uptake would be confined to soil water. However, small roots (microrhiza) were detected on the underside of the tissue used to separate the experimental compartments suggesting that soil contact was occurring. It was also suggested that transpiration rate may play a part in driving selenium uptake into plants. However, this was not measured in the experiments conducted to date.

Graham Smith questioned whether or not an experiment could be designed to determine the rates of exchange and sorption for different chemical forms of selenium in soils as knowledge of rates of exchange would potentially enable an assessment model to be developed that would take account of the different forms of selenium. It was suggested that this could be accomplished by running multiple extractions. The reduction rate of selenium in soils could also be measured by volatilisation rate.

2.8 Critical exposure pathways of selenium in Andra Safety Assessments

Elisabeth Leclerc (Andra) provided an overview of the behaviour of selenium in the environment and of the critical pathways of exposure from the Andra high level waste disposal safety assessment.

Selenium is naturally present in the environment and can be present at concentrations that lead to both deficiency and toxicity. Under oxidising conditions the dominant species in soils are selenite and selenate ions, which are poorly sorbed by soil under the normal range of soil pH and can therefore be readily taken up by plants. Under reducing conditions the dominant species of selenium are less mobile. Due to the homogenous nature of soils, selenium in both reduced and oxidised forms can be present in relatively close proximity due to hotspots of anoxic conditions. Chemical speciation may affect Kd.

The Andra approach to estimating dose resulting from a HLW geological reposirtory involves the use of a dose conversion factor for water consumption. A simple model is employed that uses annual steps (i.e. seasonal variation is not taken into account) and environmental compartments are assumed to be in equilibrium.

The Andra HLW disposal site is located in north east France and the aim of the safety assessment models is to demonstrate that doses remain below the dose limit of 0.25 mSv per annum. The source term employed is a well located in an upper aquifer. It is assumed that this well provides water for human and livestock consumption and for irrigation. Assessments are conducted over a 1 million year timeframe, thus climate change and biosphere evolution are taken into account.

The environment around the repository site is largely agricultural, being comprised of open fields, grassland and forest ecosystems. Dose pathways considered therefore include open field crops plus garden produce and stock (cattle, pig and poultry) farming. The three main radionuclides of interest from the safety assessment are I-129, Cl-36 and Se-79.

For selenium, only ingestion exposure is taken into account (i.e. external exposure and inhalation are not considered).

Since Kd is very much a site specific parameter, representative soil samples have been taken from the site and Kd analysed. Concentration ratios have been derived from literature review.

A sensitivity analysis has been conducted to identify those parameters most important for defining dose. Translocation factors, soil-plant transfer factors for cereals and potatoes, and Kd were all sensitive factors. Transfer factors to poultry were high and this may therefore require further consideration.

The results of the assessment indicated that doses from Se-79 were greater for 10-year old children than for adults, with the difference being more pronounced than for other radionuclides. This may be a consequence of the dose coefficient and consumption assumptions employed. There is a high transfer of selenium to chickens and therefore egg consumption was found to be important for children.

In addition to the results of the safety assessment, a number of recent French references relating to selenium were highlighted:

- Février, L., Martin-Garin, A. & Leclerc-Cessac, E., 2007, Variation of the distribution coefficient Kd of selenium in soils under various microbial states, Journal of Environmental Radiaoctivity, 97, 189-205.

- Haudin C.S. Renault P., Hallaire V., Leclerc-Cessac E., Staunton S., 2007. Effect of aeration on mobility of selenium in columns of aggregated soil as influenced by straw amendment and tomato plant growth. Geoderma, 141, 98-110.

- Haudin C.S., Fardeau M.L., Amenc L., Renault P., Ollivier B., Leclerc-Cessac E., Staunton S., 2007, Responses of anaerobic bacteria to soil amendment with selenite, Soil Biology & Biochemistry, 39, 2408-2413.

- Haudin C.S., Renault P., Leclerc-Cessac E., Staunton S., 2007, Effect of selenite additions on microbial activity and dynamics in three soils incubated under aerobic conditions, Soil Biology & Biochemistry, 39, 2670-2674.

- Coppin F., Chabroullet C., Martin-Garin A., Balesdent J. and Gaudet J.P., 2006. Methodological approach to asses the effect of soil ageing on selenium behaviour: first results concerning mobility and solid partition of selenium. Biology and Fertility of Soils, 42, 379-386.

- Darcheville O., Février L., Haichar F.Z., O. Berge, Martin-Garin A., P. Renault., 2007. Aqueous, solid and gaseous partitioning of selenium in a sandy soil under different microbiological states. *J. Envir. Radioactivity*.

In addition to French studies, the recent international work was also briefly presented. The IAEA EMRAS programme has a working group for the revision of TRS-364, which contains data for selenium. The report has not yet been published, but will contain data on Kd and transfer parameters classified according to soil type. It was proposed that these could be added to the BIOPROTA database once the report becomes publicly available.

The IUR task force is currently focused on Ni and selenium has not yet been considered and it was therefore suggested that BIOPROTA may want to try to motivate this working group.

The presentation concluded with a number of questions in relation to modelling requirements:

- Use of Kd relevant for Se-79 biosphere modelling in long-term safety assessments?
- How to take into account selenium speciation?
- Need of kinetic models in order to consider ageing effect?
- Need to consider different soil compartments?
- Need to separate different plant groups in relation to selenium uptake (e.g. garlic and brassicas)?
- Whether experimental studies for transfer to plants and animals may be warranted?

Discussion

Steve Sheppard questioned whether or not Andra would be conducting work on volatilisation of selenium since this could be a key variable in modelling studies and may therefore warrant further consideration. Cloche studies conducted previously by Andra have suggested that volatilisation is low and therefore their model does not include this as a parameter at present.

The issue of quality factors for dose conversion factors was raised in relation to selenium as it was suggested that dose factors may be based on inorganic rather than organic selenium and a quality factor may therefore be warranted. Discussions are currently ongoing in relation to quality factors for tritium and this may result in such factors being considered for additional radionuclides, including selenium.

Uncertainties relating to dose coefficients were also discussed and the fact that much of the skill in this field will be lost in future years through retirement. It was therefore suggested that a workshop could be considered at which information could be distilled to those more recently entering the field.

Finally, selenium speciation was discussed. This was raised as a potentially important aspect as it may affect bioavailability and thus uptake into foodstuffs. Stable selenium in the natural environment was suggested as being of particular use in deriving data on speciation. However, the point was raised that irrigation would add Se-79 into a system that may be in a different form from that occurring naturally and would be applied during the main cropping period. The use of stable selenium, which is in equilibrium may not therefore be directly applicable for the model scenarios.

2.9 New selenium data

Steve Sheppard briefly presented some new data on selenium from central Canada obtained from measurements of stable natural selenium.

The soil Kd value obtained (110 L/kg) from the measurements were very similar to those included in the draft revision of IAEA TRS-364. Revised data for transfer to fish were an order of magnitude lower than previous at 10 L/kg. However, the soil to plant concentration ratio derived (0.24) was an order of magnitude greater than that from that used previously. A similar finding was obtained for animal transfer (0.16 d/kg compared to 0.015 d/kg). The revised data were obtained from measurements of selenium in gut contents and muscle of wild deer, whereas previous data were obtained from cattle measurements for which selenium additives may have been added to feed. Should the deer in the present study have been sampled from a selenium deficient area, this would account for the larger transfer factor obtained.

Discussion

The importance of considering ranges in data was raised by Frits van Dorp. Since soil conditions today may be very different from those in the future due to evolving ecosystems there should not be too much reliance placed on site specific data. Such data should therefore be considered in the context of other available data.

2.10 Developing a sustainable plant integrated farm management system for utilising poor quality waters (New data from Gary Banuelos)

Annette Johnson presented some new data on selenium from Gary Banuelos, a plant/soil scientist, who has been researching the bioremediation of selenium contaminated soils and has also looked at volatilisation rates for selenium using brassicas. Experiments have all been conducted on selenium rich soils (soil bulk density 13 g/cm) under field conditions. A soil depth of 0-30cm was used which contained 100 µg/l selenium.

Daily volatilisation rates have been found to be greater for vegetated plots compared to bare soil plots where both receive irrigation. Selenium removal from soils was found to be greatest for canola (with 71% removed). Broccoli removed 33% of selenium, alfalfa 32% and poplar trees removed 24%.

2.11 Summary of main issues raised

Following the presentations, Graham Smith summarised the main issues that had been raised in relation to release from the geosphere, i.e. the source term to the biosphere; migration and accumulation within the biosphere; and consequent exposure modes for Se-79.

- **Release to the biosphere:**
  - The half life of Se-79 has not been accurately defined and this will affect the specific activity and doses estimated using an SA approach.
  - The release rate will be dependent upon chemical form and there is uncertainty associated with this.
  - The mechanisms for release to biosphere, specifically in relation to selenium, are not fully known. In general the release will be related to groundwater, but volatilisation from subsoil to surface soil may also be important.
  - In general release to groundwater and wells is considered. However, for some (e.g. Sweden), the evolution of rivers and lakes is an important factor.

- **Migration.** Once in biosphere, most assessments do not include volatilisation of selenium in models, but data suggest this may be an important process [4], particularly in arid zones where evaporation rates may be high. Where this is combined with contamination of a surface aquifer, high accumulation could result.

- **Accumulation.** Within soils and sediments, selenium sorption is affected by pH and Eh. Accumulation in the near surface environment (e.g. in acidic reducing conditions) could be followed by environmental change resulting in oxidation and mobilisation of selenium and thus potential acute bioavailability and associated higher doses for a short period. For example, acid soils in which selenium accumulates such as peat bogs could be drained and subsequently used for agriculture. A further uncertainty is associated with how Se-79 will transfer in the environment in relation to areas that are naturally high or deficient in selenium.

- **Exposure.** Exposure pathways tend to be standard, but how these are dealt with (e.g. consumption rates) can differ to a large extent. Selenium is known to accumulate in liver and it may therefore be prudent to consider this separately from other meat products. Similarly, both eggs and poultry are assumed to accumulate selenium and further consideration could be given to the accuracy of the concentration factors currently employed.

- **Dose estimation.** A question was raised about the quality factor for dose estimation from Se-79. Because Se is incorporated into biological molecules and is a low-energy emitted, it may be analogous to tritium, and for tritium the quality factor has been revised upward. The concept is that if the ionization is highly localized and is in biologically essential molecules, the impact is greater than would be predicted from standard ionizing radiation exposure. The point in this workshop is that, if true, dose conversion factors for Se may be revised upward in future.

4 The reader is referred to the following paper, made available by Steve Sheppard following the workshop – Sheppard (2008). Perspective: Critical loads changing with time. Human and Ecological Risk Assessment 14: 439-454.

3. HOW CAN RESEARCH ON SELENIUM CONTRIBUTE TO IMPROVED CONFIDENCE IN LONG-TERM RADIOLOGICAL ASSESSMENTS?

A number of possible research topics that may be helpful for improving confidence in long-term radiological assessments of Se-79 releases and related model improvements were raised for discussion.

3.1 Research topics

Possible ideas presented and discussed include:

- **Review of available selenium data in light of requirements for waste management assessments** to identify particular research that is still required.

- **The ability to predict selenium deficient soils (or those with excess concentrations) based on certain soil characteristics**. It may also be possible to predict the form in which selenium may occur according to soil type.

- Consideration could also be given to the **effects of differing soil conditions on the bioavailability of selenium**, such as the presence of iron and also on those factors that affect accumulation such as irrigation in arid environments.

- **Exploring the relevance of sulphur as an analogue for selenium**.

- **The effect of different agricultural practises on selenium mobilisation**. For example, the depth of soil ploughed will affect oxygenation and, where ploughing is not a common practise, reducing conditions may occur leading to the accumulation of selenium.

- **Measurement of volatilisation in relation to varying soil-plant conditions**. In relation to this, it was suggested that evapotranspiration should also be considered as this will have a significant effect on the transport of mobile elements such as selenium.

- **Determining selenium availability in relation to total selenium soil concentrations**. Selenate and selanite are considered to be the dominant forms of interest for agricultural soils, but other forms may also be of interest (e.g. organoselenides). Papers are available on selenium uptake into plants and it was therefore suggested that these should be reviewed to determine the main forms that should be further considered.

- **Consideration of the importance of interception as a means of plant uptake** – what percentage of selenium is taken up from interception and uptake by leaves in relation to root uptake? This was considered to be a potentially important pathway for plant uptake in regions where sprinkler irrigation is used in agriculture.

- In relation to the above, consideration could also be given to **the chemical form in which selenium occurs within irrigation water**. Selenium added via irrigation water will likely be in a different form from that in soils and this will potentially affect uptake (depending upon equilibrium time). In addition to providing information relevant to plant uptake scenarios, this information would be important for feeding into experimental programmes to ensure that results are directly applicable to model studies (and may assist in interpreting previous research).

- **Conversion rates for selenite and selenate and what drives these conversions**.

- **Consideration of important plants (e.g. rice) for selenium uptake**. Rice is of particular importance in relation to iodine uptake due to redox conditions during field flooding and drainage and similar may be the case for selenium (although, unlike iodine, selenium becomes more mobile under oxidising conditions).

- Consideration could also be given to the **accumulation of selenium in animals in different tissues.** Such information could be used to link meat concentrations to blood concentrations, which would make available a much larger data set from the published literature.

- **Variability in the dose coefficient for selenium**. Questions to consider include whether selenium is controlled homostatically within the body and whether the body can act to rid itself of selenium (considered unlikely due to toxic effects)?

3.2 Model improvements

Suggestions for possible modelling improvements, particularly in relation to additional pathways, were raised for consideration:

- **Volatilisation as mechanism for removing selenium from soil** could be included within models.

- **Consideration of the form in which Se-79 arrives in soil and how this interacts with stable selenium** in its various forms.

- **Consideration of soil type and its affect on oxidation state** (i.e. whether selenium will bind to soils, be available for plant uptake etc). To incorporate such data into models would also require information on **uptake rates into plants for the different forms of selenium** that could occur in soils. It may also be worth considering non-agricultural pathways such as game animals, which may result in high consumption pathways, but these would not be influenced by irrigation as a source of selenium to soils. In relation to the above, it was suggested that a review of databases on selenium in soils in different countries could be undertaken to identify particular data gaps that could then be subject to focused research.

- Consideration of the **implications on dose (human and non-human biota) of selenium hyper-accumulators**.

- Consideration of **isotopic dilution of Se-79** with stable selenium.

- The **effect in arid climates of capillary rise resulting in salt pans**.

3.3 Conclusions and way forward

A number of research areas were suggested during discussions that would initially involve literature review to determine current knowledge in relation to selenium processes in the biosphere – the basic science and identification of the critical assessment factors to reduce unnecessary pessimism. The aim would be to identify aspects of selenium transfer in the biosphere that would have direct implications for assessment models, through highlighting areas for improvement or to enable validation that current approaches are accurate. It was therefore suggested that a working group should be formed to undertaken this review (either directly or by appointment of sub-contractors). The working group should include both researchers and those from the model assessment field.

It was agreed that the initial stage would involve a kick-off meeting in order to prioritise the literature review and ensure the necessary focus upon those issues of most importance for long-term assessments. This should include consideration of the research areas listed in this workshop report, but should also include direct consideration of requirements for performance assessments and research currently underway (and its likely output). In addition to the prioritisation of review areas, the meeting would also provide opportunity for the allocation of tasks (to either working group members or sub-contractors, as appropriate).

Matthias Brennwald agreed to champion the selenium working group and will make contact with all those that have expressed an interest to take this forward.

Anyone interested in the selenium working group who has not yet expressed an interest should contact Matthias directly at Matthias.Brennwald@nagra.ch. Alternatively, contact can be made through the BIOPROTA Technical Secretariat (Karen.smith@enviros.com and GMSAbingdon@btinternet.com).

APPENDIX A: LIST OF PARTICIPANTS

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