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Research

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2023:12

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SSM perspective

Background

In Lund, the construction of the European Spallation Source (ESS) research facility is underway and the facility is also undergoing a stepwise licensing procedure in accordance with relevant legal requirements. At ESS, neutrons will be produced by spallation when high-energy protons from a linear accelerator hit a rotating tungsten beam target. The neutrons released from the radiation target will be used for various scientific experiments.

The Radiation Safety Authority (SSM) announced in 2021 funds for research to develop measurement methods for the specific radionuclides that may occur in the event of a release beyond expected operation from the ESS facility. The purpose of the call was to enable further development of useful measurement methods for these specific radionuclides and especially with regard to the specific radionuclides that have been shown to dominate the dose contribution to the public.

In the report Underlag till beredskapsplanering kring ESS (SSM 2018:22) it appears that Gd-148, W-187, Hf-172, Ta-182 and Hf-178n are the radionuclides that contribute the most to the effective dose to the public in the event that considered as dimensioning for emergency planning around the facility. Applicable measurement methods are missing for the majority of these nuclides today. Therefore, it is of crucial importance for radiation protection to have good measurement methods for exposure situations such as in a radiological emergency.

Investigations have already been conducted on the methods to assess releases of 148Gd from the ESS facility into the environment (Identifying radiologically important ESS-specific radionuclides and relevant detection methods 2020, and Region-specific radioecological evaluation of accidental releases of radionuclides from ESS, SSM2019-1010). The present report is a continuation of this work and extends it to the assessment of other radionuclides of concern. In this project, literature reviews and experimental studies were performed for two different techniques (ICP-MS and Gamma spectroscopy) in order to estimate their limits of detection for the ESS-specific radionuclides at trace levels in soil.

Results

This study provides information about the concentration of Tungsten (W), Hafnium (Hf) and Tantal (Ta) in the ESS soil and recommendations on the most appropriate sample preparation and measurement technique to assess contamination by these elements. The current levels of W, Hf and Ta measured in this study are in agreement with the estimated values from previous geological surveys. ICP-MS showed low limits of detection for W, Hf and Ta and is thus an appropriate technique for environmental monitoring. However, the three metals are difficult to extract from soil and require the use of specific sample preparation methods (based on hydrofluoric acid for example). The transfer of stable W, Hf and Ta from soil to plant is poorly known and only a handful of publications can be found that are relevant to the plants grown around the ESS. The transfer of the radioisotopes of W, Hf and Ta in particular to animals (and man) is even less studied. However, the existing articles indicate a fast excretion of radio-W and radio-Ta while the excretion is slow for radio-Hf.

The Minimum Detectable Activity (MDA) for gamma emitter released from the ESS facility will depend not only on the performances of the detection equipment but also on the composition of tungsten target at the time of the release.
The determination of limits of detection of ESS related gamma emitters was performed using a strategy based on simulation of spectra. Semi-synthetic gamma spectra were obtained by combining real soil measurements with simulated data for mixtures of ESS radionuclides using the software Nucleonica. The simulation of 187W spectra was used as a proof of concept for the method. With this approach, it is possible to estimate limits of detection by gamma spectroscopy for a given target composition. The limits of detection of four relevant radionuclides were successfully determined for two different compositions of the ESS target and at three different activity concentrations in soil.

Relevance

Knowledge of measurement methods and their application for the specific radionuclides produced at ESS is of vital interest as it increases the possibility of producing better data in the event beyond expected operation. This knowledge can also be useful for the operator and other similar activities in the world. This research is also a contribution to strengthening the national competence in radiation safety, which is in line with the needs identified in the government mission ”The basis for a long-term competence supply in the field of radiation safety” (SSM2017-134-23). SSM intends to use the results as much as possible within permit review and supervision and disseminate the information to authorities that regulate similar activities.

Need for further research

Additional research is needed to estimate transfer factors of W, Hf and Ta from soil to the plants cultivated around ESS that can enter the human food chain and to build transfer models based on these results. The existing data are scarce or incomplete. The existing knowledge regarding their transfer to animal and man is limited to the studies described in the publication 151 by ICRP but this type of research is difficult to perform, in particular when using radionuclides. A combination of additional experimental data and modelling of the transfer of these metals in the ESS environment would help to understand the risks caused to human health by the spread of radioactive target material in the environment.

Additional work may be needed to extend the work on limits of detection to more ESS-specific gamma emitting radionuclides including the metastable ones and to determine the most relevant accident scenarios where this method should be applied.

The MDAs for gamma emitter produced by the ESS will depend not only on the performances of the detection equipment but also on the composition of tungsten target at the time of the release and further studies taking this in consideration is needed.

Project information

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Investigation of the limits of detection for specific radionuclides in soil from the European Spallation Source (ESS) using radiometric and mass spectrometric methods

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Summary

The European Spallation Source (ESS) is a neutron research facility under construction and commissioning in Lund, Sweden. Through spallation reactions and activation of various materials in the facility, a unique range of radionuclides will be produced, in particular in its tungsten target. The Swedish Radiation Safety Authority (SSM), has established a list of the ESS-specific radionuclides that will have the highest impact on the absorbed dose in the first 7 days after a major accident [1]. This list includes ^{148}Gd, ^{187}W, ^{172}Hf, ^{182}Ta and ^{178n}Hf.

Investigations have already been conducted on the methods to assess releases of ^{148}Gd by the ESS in the environment [2], [3]. The present report continues this work and extends it to the assessment of the other radionuclides of concern. Literature reviews and experimental studies were performed for two different techniques in order to estimate their limits of detection for the ESS-specific radionuclides at trace level in soil.

These techniques are:

- ICP-MS, a non-radiometric technique used for elemental and isotopic analysis.
- Gamma spectroscopy, the most widespread technique for measurement of radioactivity in soil (*in situ* and in laboratories).

In the first chapter of this report, the scientific literature on environmental contamination by W, Hf and Ta is reviewed. The review includes the description of existing contamination sources, the transfer of these elements from soil to living organisms, and the methods to prepare and analyse soil samples containing these elements. The review is followed by an experimental study where ESS soil samples were chemically extracted and measured by ICP-MS. This study provides information about the concentration of W, Hf and Ta in the ESS soil and recommendations on the most appropriate sample preparation and measurement technique to assess contamination by these elements.

ICP-MS showed low limits of detection for W, Hf and Ta and is thus an appropriate technique for environmental monitoring. However, the three metals are difficult to extract from soil and require the use of specific sample preparation methods (based on hydrofluoric acid for example). Additional research is now needed to estimate transfer factors of these metals from soil to the plants cultivated around ESS that can enter the human food chain and to build transfer models based on these results.

In the second chapter, the determination of limits of detection of ESS related gamma emitters is performed using a strategy based on simulation of spectra. Semi-synthetic gamma spectra were obtained by combining real soil measurements with simulated data for mixtures of ESS radionuclides using the software Nucleonica. The simulation of ^{187}W spectra was used as a proof of concept for the method.

With this approach, it is possible to estimate limits of detection by gamma spectroscopy for a given target composition. The limits of detection of four relevant radionuclides were successfully determined for two different

compositions of the ESS target and at three different activity concentrations in soil. Additional work is now needed to extend this work on limits of detection to more ESS-specific radionuclides including the metastable ones and to determine the most relevant accident scenarios where this method should be applied.

The report ends with suggestions based on the conclusions of these two studies for future research on methods to assess contamination by ESS radionuclides in the environment.

Sammanfattning

Europeiska Spallationskällan(ESS) är en neutronforskningsanläggning under uppbyggnad och driftsättning i Lund. Genom spallationsreaktioner och aktivering av olika material i anläggningen kommer en unik serie av radionuklider att produceras, speciellt i anläggningens strålmål av volfram. Strålsäkerhetsmyndigheten (SSM) har upprättat en lista över de radionuklider som är specifika för ESS med avseende på de radionuklider som kommer att ha störst påverkan på stråldosen under de första sju dagarna efter en allvarlig olycka [1]. Denna lista inkluderar bl.a. ^{148}Gd, ^{187}W, ^{172}Hf, ^{182}Ta och ^{178n}Hf.

Metoder för att bedöma ESS-utsläpp av ^{148}Gd i miljön har redan undersökts [2], [3]. Den aktuella rapporten fortsätter detta arbete och utvidgar det till att även innefatta bedömning av andra ESS-radionuklider som är av strålskyddsbetydelse i samband med en allvarlig olycka. Litteraturgenomgångar och experimentella studier har genomförts för två olika tekniker i syfte att uppskatta deras detektionsgränser med avseende på spårnivåmängder av de ESS-specifika radionukliderna i jordprover.

De undersökta teknikerna inkluderar:

- ICP-MS, en icke-radiometrisk teknik som används för elementär- och isotopanalys,
- Gammaspektroskopi, den mest utbredda tekniken för mätning av radioaktivitet i jord (*in situ* och i laboratorier),

I rapportens första kapitel undersöks den vetenskapliga litteraturen gällande miljöföroreningar av W, Hf och Ta. Genomgången inkluderar beskrivningen av befintliga föroreningskällor, överföringen från jord till levande organismer, samt metoder för att förbereda och analysera jordprover som innehåller dessa ämnen. Granskningen följs av en experimentell studie där ESS-jordprover behandlas kemiskt, för separation av ämnena, vilka sedan mättes med ICP-MS. Resultaten från studien ger information om koncentrationerna av W, Hf och Ta i ESS-jorden samt rekommendationer för den lämpligaste provberedningen och mättekniken för att bedöma kontamination av dessa ämnen i jord.

I det andra kapitlet bestäms detektionsgränser för gammastrålande ESS-radionuklider med en strategi baserad på simulerade spektrum. Halvsyntetiska gammaspektra erhölls genom att kombinera verkliga *in situ* mätningar med simulerade data för olika blandningar av ESS-radionuklider med hjälp av programvaran Nucleonica. Simuleringen av ^{187}W-spektra användes som ett proof-of-concept för metoden. Med detta tillvägagångssätt är det möjligt att uppskatta detektionsgränser för gammaspektroskopi för en given strålmålssammansättning.

Avslutningsvis ges förslag på vidare studier av de två undersökta metoderna för noggranna bestämningar av ESS radionuklider i omgivningen.

Abbreviations and notations

BAC	Biological accumulation coefficient
BAF	Bioaccumulation factor
DTM	difficult to measure
EF	Enrichment factor
EMP	Environmental monitoring program
HPGe	High purity Germanium
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
LoD	Limit of detection
MDA	Minimum detectable activity
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
REE	Rare earth element
TF	Translocation factor
XRF	X-ray fluorescence

Contents

1. Introduction

This introduction chapter gives the background and goals of the project SSM:2021-787 financed by the Swedish Radiation Safety Authority (SSM). The present report covers the parts of the project related to soil analysis. The other part of the report related to aerosol analysis is published in another report: "Alpha spectrometry of radioactive aerosols from the European Spallation Source – an investigation of the possibilities of direct alpha spectrometry" by Stenström et al.

The present report is a continuation of previous work performed at Lund University on the methods for the detection and quantification of radioactive releases from the ESS during normal operation or after an accident [2] *and the transfer of such contamination to soil, plant and animals in the local environment* [3].

1.1. Background

Context of the ESS

The European Spallation Source (ESS) is categorized as a facility requiring a licence from Strålsäkerhetsmyndigeten, the Swedish Radiation Safety Authority (SSM). As a licenced source, ESS is obliged to optimize the radiation protection to limit the exposure to ionizing radiation for members of the public. The ESS must also carry out and report measurements of radioactive discharges from the facility as well as monitor these radionuclides in the environment, as stated by SSM in the special conditions for the ESS facility. Realistic dose assessments are required, and the integrated effective dose to members of the public resulting from 1 year of radioactive discharges and from external exposure from the ESS must not exceed 0.1 mSv. Furthermore, environmental consequence assessment of accidental releases has shown that effective doses to reference persons outside the ESS site may unlikely exceed the reference levels for evacuation (20 mSv/7 days), but may cause ground deposition requiring clean-up measures to decrease exposures below 1 mSv y^{-1}.

The radionuclides generated by the ESS will be different from those produced by nuclear reactors and other types of accelerator facilities. Simulations of the target composition [4], [5] present a list of radionuclides that are unique to the high-energy spallation reactions at the ESS, and that some of these are expected to give the highest dose contributions in case of an accident (see Table 1). The most important radionuclides for the first 7 days after a major accident are estimated to be ^{148}Gd, ^{187}W, ^{172}Hf, ^{182}Ta and ^{178n}Hf, with the first one having the highest dosimetric impact [1].

The main part of the effective dose during the first 7 days will be dominated by the inhalation dose, followed by cloudshine and groundshine [1]. Inhalation dose of ^{148}Gd (alpha emitter) is of highest importance as it may contribute more than 50% to the total effective dose whereas cloudshine and groundshine will be mainly caused by gamma emitters.

Table 1: Radionuclides that – in the worst case scenario **[1]**– will mainly contribute the most to the effective dose from ground deposition for time intervals during the first year after the accidental release

Nuclide	$T_{1/2}$	Decay mode	Daughter decay
^{148}Gd	74.6 y	Pure alpha, 3.183 MeV	None (^{144}Sm)
^{187}W	24 hours	Beta, gamma	^{187}Re, pure beta, $T_{1/2} = 4 \cdot 10^{10}$ y. Granddaughter stable (^{187}Os).
^{172}Hf	1.87 years	EC, gamma	^{172}Lu, beta+, gamma, $T_{1/2} = 6.7$ d. Granddaughter stable (^{172}Yb).
^{182}Ta	111.7 days	Beta, gamma	None (^{182}W)
^{178m}Hf	31 years	IT	None (^{178}Hf)
^{181}W	121.2 days	EC	None (^{181}W)
^{175}Hf	70 days	EC	None (^{175}Lu)
^{173}Lu	1.37 years	EC	None (^{173}Y)

To fulfil the obligations of environmental monitoring and maintain an emergency preparedness against accidental releases, it is crucial to use analytical methods that can quantify trace levels of the radionuclides that may result in this effective dose. Thus, to analyse ESS radionuclide emissions, the limits of detection achievable have to be determined for the most relevant radionuclides in environmental samples by the selected measurement techniques.

Methods

Simulation of gamma spectra

Indirect gamma spectrometry refers to a method to quantitatively determine the activity concentration of difficult-to-measure radionuclides by using a pre-established ratio (also called nuclide vector) between the nuclide of interest and a gamma emitter that is detectable by conventional gamma spectrometry. An example of a commonly used nuclide vector is the relation between the gamma emitters ^{60}Co or ^{152}Eu and the low-energy beta emitter ^{63}Ni, which are nuclides found in construction materials of nuclear reactor parts [6].

The gamma spectra of a define mixture of radionuclides can be simulated using codes such as MCNP or software such as Nucleonica. By combining the simulated data with experimental data, theoretical detection limits can be established.

Non-radiometric methods:

Mass spectrometric techniques do not rely on radiation detection but are instead based on atom-counting. They are widely used for the measurement of both radio and stable nuclides. One of the most common mass spectrometric technique in environmental measurements is inductively coupled plasma mass spectrometry (ICP-MS), which exhibit extremely low limits of detection (down to pg kg^{-1}) [2]. Inductively coupled plasma optical emission spectrometry (ICP-OES) is a spectroscopic technique also relying on a plasma torch for ionisation before detecting characteristic emissions from the de-excitation of the atoms in the sample [7].

The limits of detection obtained with these techniques for environmental samples are highly dependent on the samples preparation techniques (chemical extraction and separation).

1.2. Objectives

The project has been divided into tasks defined in agreement with SSM:

- **Task 1**: Analysis of ESS-relevant radionuclide in soil by non-radiometric techniques. *Sub task 1.1.* To review the literature on environmental contamination by some ESS-relevant elements, namely tungsten, hafnium and tantalum as well as the methods employed to extract, separate and analyse them in soil. *Sub-task 1.2.* To test methods selected from the literature on soil samples collected around the ESS to determine their efficiency and investigating current levels of these elements in local soils. *Sub-task 1.3.* To provide recommendations on the most suitable analytical methods for these elements in regards of the estimated detection limits.
- **Task 2**: Estimation of the Minimum Detectable Activities (MDA) for ESS gamma emitters in soil samples. *Subtask 2.1.* Simulation of semi-synthetic gamma spectra with Nucleonica. *Subtask 2.2.* Validation of the Nucleonica results. *Subtask 2.3.* Estimation of MDAs for ESS specific gamma emitters in soil samples based on the simulation results.

2. Analysis of Tungsten, Hafnium and Tantalum in soil samples

This chapter provides, firstly, a review of the scientific literature on three chemical elements, namely tungsten, the main component of the ESS target but also hafnium and tantalum that will be present in the ESS target material after irradiation. The chapter focuses on existing cases of environmental contamination by these elements and the analytical methods to extract and separate them from their sample matrix. The last section of the review focuses on the existing literature on environmental transfer of radio-W, radio-Hf and radio-Ta.

The second part of the chapter describes a series of experiments performed to estimate the current levels of W, Hf and Ta in soil samples collected around the ESS facility as well as the performance of different chemical extraction methods and analytical techniques.

2.1. W, Hf and Ta in the environment

Tungsten (W), hafnium (Hf) and tantalum (Ta) are classified as transition metals in the periodic table of elements. They are usually considered as non-toxic thus their spread in the environment is rarely controlled or regulated. This literature review includes general information about W, Hf and Ta in the environment, methods for their extraction, separation and analysis, examples of environmental contamination by these elements and finally studies of their transfer from soil to living organisms.

2.1.1. Introduction

Tungsten is a well-known metal compared to Hf and Ta. In a review, Koutsospysros *et al.* [8] described the applications of W (mostly metallurgy related) and the available data on its behaviour in the environment. The toxicity of W started to be investigated after the discovery of a cluster of leukaemia cases in the town of Fallon (Nevada, USA) [8]. Fallon hosts metallurgy facilities and elevated levels of cobalt and tungsten were observed in airborne dust [9]. The US Centers for Disease Control (CDC) also measured elevated levels of W in urine of the inhabitants [10]. The link between the tungsten contamination and the leukaemia cases could not be established but the event triggered more research showing the cell toxicity of W [10].

To our knowledge, only one review exists regarding Ta in the environment where Filella [11] summarised the properties of Ta and its spread in the environment from natural and human activities. Tantalum is now considered as a technology-critical element with applications in optics or electronics [12]. It is not playing a role in human biological processes and there is no known case of occupational poisoning with the substance that is actually used for very biocompatible prosthetics [11].

Publications regarding the behaviour of Hf in the environment or the fate of Hf contamination in soils are also extremely scarce. In nature, Hf is mostly found together with zirconium (Zr). Most of the existing literature treats the two metals jointly and their separation is a challenge [13]. Jones *et al.* [14] reported that the anthropogenic Hf emissions come as a byproduct of Zr mining and production. The authors also reported that the U.S. Environmental Protection Agency has not conducted any investigation on Hf toxicity [14].

Levels of W, Hf and Ta were estimated in Europe by the FOREGS survey (Salminen *et al.* [15]) after analysis of hundreds of topsoil and subsoil samples extracted with hydrofluoric acid (HF). In southern Sweden, topsoil concentrations are estimated to be around 5 mg kg^{-1} W, 8.8 and 11.7 mg kg^{-1} for Hf and between 0.21 and 0.68 mg kg^{-1} for Ta.

2.1.2. Extraction and separation of W, Hf, Ta

Extraction

Tungsten is resistant to pseudo-total extraction by aqua regia (mixture of hydrochloric acid and nitric acid) which is the most widely used method for environmental analysis [7]. However, it becomes soluble in presence of phosphoric acid allowing its extraction from soil matrices. Bednar *et al.* [7] reported improved extraction yields of W from reference materials with phosphoric and nitric acids compared to aqua regia or nitric acid alone. The achieved efficiencies are presented in Table 2. The extraction yield of the other analysed metals was not affected by the addition of the phosphoric acid however the Rare Earth Elements (REEs) which are particularly relevant in the case of ESS target material were not included in the study.

Table 2: Efficiency the extraction method on reference materials by Bednar *et al.* **[7]**

Type	Reference value (mg kg^{-1})	Measured concentration (mg kg^{-1})	Estimated efficiency (%)
W in solution	10	9.8	98
W extracted from agricultural soil	2	0.4	25
Soil contaminated with metal W particles (age 3y)	762 ± 44		98
Clay soil contaminated by W from military activities	483 ± 44		76

Hafnium and tantalum can also cause analytical issues. Reimann and de Caritat [16] analysed 59 elements extracted by aqua regia from Australian soils. The 60th element was Ta but all the values obtained were below their detection limit of 0.05 mg kg^{-1}. Regarding Hf, 50% of the values were below the limit of detection. These results are similar to our own observations (see section 2.2.6) and seems to indicate a poor solubility of natural Hf and Ta in aqua regia. The alternative to pseudo-total extraction with aqua regia is total dissolution using hydrofluoric acid (HF) or alkaline fusion.

Filella [11] also compiled various issues related to the analysis of tantalum. One important finding is that Ta does not stay in solution if HF is removed and it tends to adsorb on containers walls even if they are Teflon coated.

Tantalum was initially analysed by X-ray fluorescence (XRF) and neutron activation analysis (NAA) but these techniques have been largely replaced by inductively-coupled plasma mass spectrometry (ICP-MS) that offers low detection limits and few interferences [11].

Separation

A good separation of neighbouring elements is essential for the analysis of less abundant isotopes by ICP-MS. Indeed, one of the main interferences in ICP-MS comes from isobars, ions or molecular ions of the same mass as the isotope of interest. For example, the measurement of the minor very long-lived isotope of tantalum ^{180m}Ta (0.012% of natural abundance) will be affected by ^{180}Hf (30.08% abundance) and ^{180}W (0.12% abundance) [17]. This type of interference would also affect measurements of the isotopes produced in the ESS target like ^{182}Ta that has the same mass as stable ^{182}W (26.50% abundance).

Snow *et al.* [17] tested several ion exchange (AG1) and extraction chromatographic resins (TRU, TEVA, UTEVA) or combination of those resins to separate W, Hf and Ta. With a combination of TRU and TEVA, the separation of one metal from the others was >99% with most of REEs found in the Hf fraction.

Unfortunately, the literature on the separation of those three elements is quite scarce. Research studies usually focus on the separation of one of those elements from elements of the same column on the periodic table, e.g. W/Mo [18], Hf/Zr [13] and Ta/Nb [19]. Indeed, the measurement of these ratios can provide valuable information to geologists in their studies of rocks and meteorites [11] but is not particularly relevant in the context of the ESS.

2.1.3. Contamination of soils by W, Hf and Ta originating from human activities

The sources of environmental contamination by W, Hf and Ta that are investigated in the scientific literature are the following:

- Mining operations and its wastes (tailing)
- Smelting (transformation of the ore into metal and recycling of used metal)
- Other industrial sources (metallurgy, industries involving coal burning…)
- Military sources (W ammunitions)
- Agricultural sources (fertilisers)
- Road traffic

Examples from the literature covering these different sources are described in the following sections with comments on their similarities with the ESS situation.

Mining and smelting

Examples of contamination by W from mining and smelting can be found in the literature. Du *et al.* [20] investigated the migration of W in soil profiles near an abandoned tungsten smelter. Soil profiles were collected in undisturbed locations 1.4 and 3.1 km downstream from the smelter. Their analysis showed high values in the upper part of soil column (300 mg kg^{-1} and 180 mg kg^{-1} respectively at 20 cm). These values then decreased down to 60 mg kg^{-1} at 70 cm further below the ground. Tungsten levels in metalliferous areas in Australia were investigated by Pyatt and Pyatt [21]. The authors measured soil samples near the mining areas and tailing material deposits. They measured W concentrations from 25 to 78 mg kg^{-1} in the first 15 cm of soil that they later compared to the levels in the local wildlife (see section 2.1.4).

In the aquatic environments, contamination by W, Hf and Ta can be measured in sediments. As an example, we can cite Sutliff-Johansson *et al.* [19] that investigated contamination of marine sediments in Northern Sweden (Bothnian bay) originating from a smelting facility. The authors compared ICP-MS measurements in a sediment core collected close to the facility and one from open sea less affected by human activities. Their results showed an increase of the Ta/Nb ratio in the more recent sediment layers than could be attributed to a contamination by the smelting of Ta-rich technological materials by the facility.

Industrial sources

As mentioned in section 2.1.1, contamination by airborne W dust originating from a metallurgic industry facility was observed in Nevada, USA [9]. Dust samples collected in the town of Fallon and its surroundings were analysed by NAA. The W levels in dust were found to be extremely elevated around the facility (up to 950 mg kg^{-1}) and rapidly decreased with increasing distance. The spread of the contamination over a populated area shares similarities with a possible accidental release scenario at the ESS.

In a recent article, Kumar *et al.* [22] investigated the contamination of agricultural soils by local brick production sites. The authors measured 53 elements including W, Hf and Ta in soils collected 250 and 500 m away from the brick kilns. They observed a moderate contamination by these three elements (among others) that they suspect to originate from ashes produced by the combustion of coal in the kilns. The authors based their estimations on several parameters such as the enrichment factor (EF, normalisation of metals content in soils with respect to a reference trace metal such as Fe), the geo-accumulation index, the contamination factor (ratio of concentration of a metal in the sample to the same metal in shale). The contamination factor is of particular interest since shale values are available for W, Hf and Ta but also for REEs [3].

Military sources

Tungsten has been used as material for military ammunitions in order to replace lead. Therefore, areas affected by military operations such as warzones or army training grounds can by contaminated by W [8].

The contamination of soil by W-based ammunitions has been heavily investigated in military training areas in the USA [23]. As an example, Clausen and Korte [24] analysed soil and water samples collected around a shooting range. The authors observed W concentrations of up to 2000 mg kg^{-1} in the most contaminated parts. Elevated W levels detected in ground waters could also be attributed to the W ammunitions.

Sadiq *et al.* [25] investigated the contamination of metal in soils from Saudi Arabia at the border to Kuwait just after the end of the first Gulf War (1990-

1991). The authors observed increasing W concentrations for the samples collected closer to the border (up to 126.5 mg kg^{-1}). They attributed the elevated metal concentrations to both the use of military explosive devices and the burning of Kuwaiti oil during the war.

Contaminations related to the agriculture

In 1988, Senesi *et al.* [26] analysed various inorganic fertilisers and found concentrations of W from 1.5 to 7 mg kg^{-1} in superphosphates. Other types of inorganic fertilisers ranges from below the detection limit to 4 mg kg^{-1}. These types of fertilisers may have been used in the agricultural lands surrounding the ESS making the analysis of local soils relevant to establish preoperational levels of metal contamination. The use of liming materials to correct the soil pH can also increase the levels of metal traces (including W) of agricultural soils [27].

Another potential source of contamination of agricultural soils by W, Hf and Ta is the spread of biosolids or sewage sludge, the final waste of wastewater treatment that are enriched in metals [28]. Yang *et al.* [28] assessed the contamination of soils amended with such biosolids in Texas, USA. The study includes measurements of W, Hf and Ta. The authors observed an enrichment of metals in the top soil after they were amended with biosolids but the migration of these transition metals deeper in the soil column was very slow. The concentration measured in these soils ranged between 1 and 10 mg kg^{-1} for these three metals.

Contamination from road traffic

Car traffic can also lead to contamination by transition metals in the vicinity of roads. Bäckström *et al.* [29] studied the seasonal variations of the elemental composition of road runoff (water) and total deposition (wet and dry) collected near two Swedish highways near Mariestad and Linköping. The W concentration in the collected water ranged from below the limit of detection in the summer months up to 15 µg L^{-1} during the winter months. This increase was not due to the use of de-icing salts that only contained 0.03 and 0.08 µg L^{-1} of W. The authors suggest that this increase could be due to the use of sturdier tires on constantly wet roads during the winter.

The same authors analysed soil profile samples and road dust samples from the same road sites by ICP-MS and X-ray fluorescence. On the site near Mariestad, the W concentration decreased through the soil profile with 31 mg kg^{-1} in the first 2 cm of soil to 4.5 mg kg^{-1} between 2 and 10 cm and 2.7 mg kg^{-1} between 10 and 30 cm for the sample collected 3 m from the road. For the samples collected 7 and 30 m from the road, the W concentration was only 4.5 mg kg^{-1} in the surface sample and below 1 mg kg^{-1} for samples collected deeper.

Possible sources of contamination present at the ESS site

The ESS facility is surrounded by land mainly used for agriculture and housing [3]. No existing contamination from mining, smelting or metallurgy industry is expected. The main difference between sites contaminated by these activities and a contamination originating from the ESS would be the elemental composition of the pollution. For example, in the case of mining wastes, there is a strong correlation between Hf and Zr since these elements, with similar physicochemical properties, are often found together in nature. The existing research on the analysis of such contaminants focuses on the separation of these elements. However, this would not be an issue for the analysis of contaminated ESS samples since their content in Hf would not be linked to Zr.

Since the ESS facility enclosed on two sides by roads, the E22 highway and Odarslövsvägen, the intense road traffic could have influenced the local environment. Taking into account the results from Bäckström *et al.* [29] described above, the contribution from road traffic would presumably be higher in samples collected close to the two roads. Thus, it seems relevant to determine the contribution from road traffic to the concentrations of W, Hf, and Ta in the local environment before the start of the beam on target operations at the ESS.

The records of agriculture practices around the ESS is not an easily accessible information. Metal rich fertilisers or sewage sludge could have been used on the nearby fields. It is thus relevant to check their pre-operational concentration in W, Hf and Ta.

The soils contaminated with sewage sludge investigated by Yang *et al.* [28] were amended for 1 to 20 years. The observed migration of metals through the soil could thus be used as model for long-term evolution of the trace-element composition of soils around the ESS after a contamination event.

2.1.4. Environmental transfer of stable W, Hf and Ta

Transfer from soil to plants and animals

Once soils (or water) are contaminated by W, Hf and Ta, the metals will eventually be transferred to biota. Since they are not considered as toxic to humans, these elements are usually overlooked in studies of transfer from soil to plants or animals. In most cases, the authors focus on essential elements and heavy metals known for their toxicity. One possibility to decontaminate soils is to use phytoremediation, which is the extraction of various elements from soil by uptake in plants that have the property to accumulate them. This technique can be applied to decontamination of heavy metals, REEs, transition metals or even radionuclides [3], [30]. The most valuable metals can later be extracted from the super-accumulating plant species.

Transfer of W

The toxicity of W has been studied for some plant species such as corn [31], oat and lettuce [32] or peas [33]. The authors of the studies focused on the seedling growth rather than on the accumulation in the plant. The explanation of this growth inhibition is that W is replacing molybdenum (Mo) in cells. The two elements share some physicochemical properties but the presence of W instead of Mo inhibits some essential biological processes. In the case of corn, W accumulated more in the roots than the shots and in the plants grown on the least acidic soil (pH = 7.4) selected for the study [31].

James and Wang [34] analysed soil and vegetable samples collected in China including potatoes (*Solanum tuberosum*), spinach (*Spinacia oleracea*), corn (*Zea mays*) and radishes (*Raphanus sativus*). The authors determined the total and available concentration in the soil, and the W concentration in the edible parts of the vegetable. They calculated the transfer factor (TF) from soil to plant, defined as TF = W concentration in edible parts (mg kg^{-1}, fresh weight) divided by the total or available W in soil (mg kg^{-1}, dry weight). Concentrations of W varied significantly between sampling locations (0.50–28.48 mg kg^{-1}). Spinach and radish samples were found to contain the highest concentration of W (> 1 mg kg^{-1}) and to have the highest transfer factor among the selected vegetables.

Wilson and Pyatt [35] collected samples close to an abandoned metal mine in the United-Kingdom. They analysed the content in W of spoil materials (wastes from mining operations) and in plant species such as heather (*Calunna vulgaris*) and mosses (*Sphagnum sp.*). The W levels in the spoil materials ranged between 944 and 1647 mg kg^{-1}. The levels of W in plants growing on these materials varied from around 100 mg kg^{-1} in moss and aerial parts of heather while the heather roots concentration reached 655 mg kg^{-1}. The authors calculated the accumulation factor (AF) from the soil to the heather parts and observed the highest value (56%) in the roots while only 10.6% and 4.2% were observed in the annual branches and the wood respectively.

The same authors also investigated abandoned mines areas in Queensland, Australia [21]. They measured W concentration in Eucalyptus trees (*Eucalyptus melanophloia*) and Australian perennial grass (*Triodia sp.*) growing on tailing materials, spoil materials and near a copper smelter. The Triodia species were accumulating W up to 10 times the concentration in soil while the levels in Eucalyptus were measurable but lower than in the soil. In another article, the same group analysed the W content in various Mediterranean shrub species growing on calcareous soils contaminated by former mining activities [36]. While the contaminated soils ranged from 20.5 to 78 mg kg^{-1}, the concentration in plant parts ranged from below detection limit to 10.5 mg kg^{-1}, with the lowest values found in berries.

Transfer of Ta and Hf

Tantalum is considered as a strategic resource (alongside with niobium since they share physicochemical properties) and is a candidate for phytoremediation in contaminated soils such as mining tailings (ore residues) [30]. Phytoremediation experiments by Lima e Cunha *et al.* [37] in a mining district of the Amazonian region (Brazil) indicated a low extraction of W and Ta by the tested species.

Similarly, Krasavtseva *et al.* [38] observed low transfer of Ta from soils contaminated with tailing material (Kola peninsula, Russia) to various plants of the boreal environment (*Salix sp.* and *Avenella flexuosa L.*).

Ray *et al.* [39] studied the bioaccumulation of Ta in various mangrove plant species (Sundarbans, India). The authors used three parameters to evaluate the bioaccumulation: the bioaccumulation factor (BAF) which they defined as the metal in the plant/metal in sediment ratio, translocation factor (TF), metal in leafs and wood/metal in roots ratio and enrichment factor (EF), which is similar to BAF but where the concentrations are normalised by the Hf concentration to evaluate the mobility of a metal compare to Hf. The Ta found in sediments (3 ± 0.8 mg kg^{-1}) originated from rock weathering and Ta concentrations in plants parts (roots, wood, leafs) varied greatly from species to species (on average 2 µg kg^{-1}). Once again the uptake of Ta by the plants seemed to be low.

The transfer of Ta through the food chain has also rarely been studied. Espero *et al.* [40] measured the bioaccumulation of Ta in marine species in various ecosystems in Chile. The concentration in the animal tissues increase along the food chain but to a lesser extent than mercury. However, in the studied environment that do not present high contamination, these concentrations are low (0.31-2.08 µg kg^{-1}).

In an article by Shtangeeva [41], oat (*Avena sativa L.*) and barley (*Hordeum vulgare*) were grown in greenhouses on Russian soils with known concentrations of Hf and Ta. The concentration of these elements was then measured in roots and leaves of the plant. Concentrations of Hf and Ta of about 0.5 mg kg^{-1} in roots and 0.2 mg kg^{-1} in leaves were measured while the soils contained 3-5.5 mg kg^{-1} of Hf and 0.7-1.5 mg kg^{-1} of Ta.

Jiménez-Ballesta *et al.* [42] also reported transfer of Hf in the environment from calcareous Spanish soils and grapevine leaves. They measured an average concentration of Hf of 4.8 mg kg^{-1} in the soil and 0.6 mg kg^{-1} in the leaves. They calculated the biological accumulation coefficient (BAC), the ratio of the element concentration in plant part to its concentration in the soil [37], of 0.11 which they consider as a low value. This value is in the same range as the REEs measured in the same study (Ce, Nd, La, Y, Sc).

Relevance of the existing data to the ESS environment

The available data on the transfer of W, Hf and Ta to foodstuffs are rather scarce since these metals were not considered toxic or relevant until the recent years. The list of foodstuffs currently produced in the vicinity of the ESS was established in a previous report (SSM 2021:21 [3]). Data on transfer of W, Hf and Ta to some of these species can be found in the articles mentioned above but no data is available for most species, as shown in Table 3.

Table 3: Literature data on W, Hf or Ta transfer or toxicity in foodstuff grow near the ESS (based on the list established in the SSM 2021:21 report [3])

Foodstuff grown near ESS	Element	Reference
Barley	Transfer of Hf, Ta	Shtangeeva [41]
Corn	Transfer of W	Petruzzelli *et al.* [31]
Green peas	Toxicity of W	Adamakis *et al.* [33]
Wheat, rapeseed, apple, sugar beet, honey	No data	

However, data exist for other species such as oat, potatoes, spinach or radishes that are grown as foodstuffs in Sweden by the farming industry or in private gardens. These results could be used as analogues of the locally grown species to develop models estimating the transfer of W, Hf and Ta in the ESS-specific environment.

As mentioned above, W also prevents the growth of some plant species thus a contamination by W of the surrounding soils could be detrimental for agriculture in addition of the radiological risk.

2.1.5. Transfer of radioactive W, Hf and Ta

Transfer from soil to plants

Radioactive isotopes of W, Hf and Ta are not naturally present in soil (with the exception of very long lived ^{180}Hf, $t_{1/2} \approx 1.8\ 10^{18}$ y). Research of the topic is thus very limited. In one article from 1966, Wilson and Cline [43] grew barley (*Hordeum vulgare*, var. *Arivat L.*) for 18 days on soils spiked with ^{185}W in the form of potassium tungstate (3.7 MBq kg^{-1} of soil). They observed a significant transfer from soil to plant and an increase of the transfer with pH. The higher values were observed on slightly alkaline sandy loam with about 14.1 MBq kg^{-1} transferred into the plant against 0.26 MBq kg^{-1} in the acidic soil. By comparison, a similar experiment performed with 10 times higher activity of ^{239}Pu led to values of 0.02-0.08 MBq kg^{-1} in the plant tissues.

Transfer to animal and man

Information about radioactive W, Ta and Hf are summarised in ICRP publication 151 [44].

In a report from 1977 by Ekman *et al.* [45], Swedish goats received ^{181}W ($t_{1/2}$ = 121 d) in the form of sodium tungstate by ingestion or intra-venous injection. Up to 97.8% of the ingested ^{181}W and 93.4% of the injected ^{181}W were excreted in faeces and urine in the week following the contamination. Only 0.06% (ingested) and 2.6% (injected) of the ^{181}W were excreted in milk. Similar experiments were performed on cows by Mullen *et al.* [46] using ^{181}W and ^{187}W ($t_{1/2}$ = 23.7 h). After 4 days, 0.5% on the ingested W and 3% of the injected W were excreted in milk (while the rest was excreted in faeces and urine). Other studies were also performed from the 1950's to the 1970's by other authors on rats, dog and other farm animals [45].

Leggett *et al.* [47] provided an overview of the biokinetics data available for the elements of the group IVB that includes Hf. The review used in ICRP publication 151 [44] provides a summary of Taylor *et al.* works [48], [49] where the authors administered ^{181}Hf or $^{175+181}$Hf in the form of citrates to rats, hamsters and marmosets. They observed a very slow excretion rate of the radio-hafnium in the three species with around 30% excreted after 10 days but only around 40% after 50 d and around 50% after 100 d. The authors also analysed the spread of the radionuclides in the body of rats and hamster and found significant amounts in skin, muscles, bones and organs.

Regarding radio-tantalum, available data is almost limited to studies in rats [44]. Fleshman *et al.* [50] administered orally ^{182}Ta in solution to rats to study its excretion. After 2 d, about 9% of the Ta was excreted (mostly in faeces) and the value continued to decrease with only 0.1% of retention after 3 d and 0.01-0.02 after 100 d. Harrison and Quinn [51] analysed soft tissues and shells of freshwater clams (*Anodonta nuttaliana*) in water tanks contaminated with a series of radionuclides including ^{182}Ta. These edible fresh-water clams were selected as possible bio-indicators and food stuff. The authors faced difficulties with the experimental set-up due to the formation of insoluble tantalum hydroxides in the water. Only 9.6% of the total amount was recovered in the clams, the water and the tank's filters. In the animals themselves 1.6% of the total amount were found in the clam bodies and 2.3% in their shell.

Relevance of the existing data to the ESS environment

The available data on radioactive W, Hf and Ta is extremely scarce and covers only barley [43] from the established list of foodstuff currently grown near the ESS [3].

Cattle raise for meat is currently grazing ≈ 2 km from the ESS facility. Milk and meat are also produced in other locations near Lund. Regarding the relevant data on animals, the studies on goat and cows seems to indicate that W is poorly metabolised by cattle by digestion thus W from hot particles of ESS target material would not easily enter the human food chain via milk and dairies. However, these data are insufficient to dismiss the possibility for the W already absorbed by plants to be transferred to cattle through the food chain.

Radio-Hf in solution seems to have low excretion rates from mammals [47] while the radio-Ta in solution seems to be excreted fast [45], [50] but there is no information available on their intake from hot particles or transfer through the food chain.

2.1.6. Conclusions and perspectives for the ESS

In the case of the ESS, contamination by radioactive isotopes of W, Hf or Ta would originate from the accidental release of material from the irradiated tungsten target of the facility during operation, storage, dismantling or transport of the target materials. The SSM established a list of the most relevant radionuclides in terms of effective dose in the year following a release of target material [1]. The inventory of the nuclides from this list have been modelled by several authors. Barkauskas *et al.* estimated that the tungsten target irradiated for 5 years would contain immediately after shutdown $1.10 \cdot 10^{16}$ Bq of ^{181}W, $2.5 \cdot 10^{15}$ of ^{175}Hf, $8.07 \cdot 10^{14}$ of ^{172}Hf and $3.36 \cdot 10^{15}$ of ^{179}Ta [4], SSM also reports $7.4 \cdot 10^{12}$ of ^{172}Ta [1].

Prior to operation of the ESS, the site and its surroundings were presumably not subjected to mining, smelting, military operations or metallurgical activities that could have contaminated them with elevated levels of stable W, Hf and Ta. However, contamination from agricultural practices of samples collected on fields and from car traffic in the samples collected near the roads is a possibility.

Since the mass of stable W that could be released from the ESS is larger than the one of activated target material, it could be beneficial to evaluate the pre-operational levels of W around the ESS. These values could later be compared to samples collected for environmental monitoring purposes or samples collected after accidental releases.

The extraction of the three elements of interest is actually more difficult than for other ESS-relevant elements like the REEs [3]. Pseudo-total extraction that is commonly used for environmental monitoring will not be sufficient. W would require the use of phosphoric acid while Ta can only be extracted by total dissolution using hydrofluoric acid due to its poor solubility in other acids. The extraction difficulty of the three elements could turn into an advantage if one would need to limit interferences between isobars in ICP-MS or radionuclides with the same alpha/gamma energies.

If the separation of W, Hf and Ta would be necessary before analysis, Snow *et al.* [17] developed a method that fits this purpose. Its major limitation is once again the use of hydrofluoric acid, a chemical that cannot be used in all laboratories due to the associated risks.

There is a need of further research to study the transfer of these metals from soil to plants grown in the vicinity of the ESS since the existing data are scarce or incomplete. The existing knowledge regarding their transfer to animal and man is limited to the studies described in the publication 151 by ICRP [44] but this type of research is difficult to perform, in particular when using radionuclides. A combination of additional experimental data and modelling of the transfer of these metals in the ESS environment would help to understand the risks caused to human health by the spread of radioactive target material in the environment.

2.2. Experimental test on W, Hf and Ta extraction from ESS soil samples

This section contains the results of two series of experiments performed to investigate the potential of fast and easily accessible extraction methods to determine the W, Hf and Ta concentration in soil samples. The selectivity of the methods to these metals and gadolinium (Gd) are discussed as well as the detection limits obtained with two different analytical techniques, namely ICP-MS and ICP-OES.

2.2.1. Selection of samples

Five soil samples collected around the ESS site were selected among the ones archived from a previous study [52]. These samples are 7-centimeter-deep top soil samples collected in 2017 and 2018. The locations of the sample sites are presented in Figure 1.

Figure 1: Location of the sampling sites around the ESS facility

The sampling was performed in cultivated grounds or near roads including the E22 highway. Elevated levels of W, Hf or Ta may be present on these sites compared to undisturbed locations due to the car trafficking and the use of fertilisers as described in section 2.1.3. The REE levels, the chemical group that includes Gd, were previously measured in 4 of these sites and no elevated levels were observed compared to undisturbed forest soils from the region [3]. For comparison purpose and to validate the extraction methods used in this study, a reference sample of contaminated industrial soil with certified values for W, Hf, Ta and Gd (LGC, NCS DC73323A) was also analysed.

2.2.2. Extraction methods

In this study, two trace element extraction methods (also called soil digestion methods) were tested on ESS soil samples to determine what analytical strategy should be applied to measure contamination of soils by irradiated ESS target materials.

The first one is an aqua regia (mixture of hydrochloric and nitric acids) digestion of the sample which is a method commonly used in environmental monitoring studies of metals in soil. In the second one, the hydrochloric acid is replaced by phosphoric acid to enhance the extraction yield of W.

The two tested methods are called pseudo-total because they do not allow the dissolution of the silicates in the soil samples. Thus, the fraction of W, Hf and Ta contained in these silicates cannot be extracted. Total dissolution can be achieved using hydrofluoric acid or soil fusion but these methods could not be performed in our present laboratories.

Pseudo-total extraction with aqua regia:

- 0.5 g of soil sample was mixed with 20 mL of aqua regia (3:1 hydrochloric acid/nitric acid) and heated at 70°C for 4 h.
- Samples were evaporated to dryness and redissolved in 25 mL of 2% nitric acid.
- Samples were centrifuged for 20 min.
- The liquid fraction was collected and 2% nitric acid was added up to a 50 mL total before storage in a fridge at 5°C until analysis.

Phosphoric acid method:

The following procedure adapted from Bednar et al [7] was used:

- 0.5 g of soil sample was mixed with 2.5 mL of concentrated nitric acid (65%), 2.5 mL of water and 1 mL of phosphoric acid and heated at 95°C for 30 min.
- 10 mL of concentrated nitric acid were added and the mixture was headed at 95°C for 120 min.
- 3 mL of hydrogen peroxide were slowly added to the sample (15 min at 95°C)
- 2 mL more of hydrogen peroxide were added to the sample (120 min at 95°C)
- The samples were evaporated close to dryness
- After cooling, 25 mL of 2% nitric acid were added to the samples and they were centrifuged for 20 min
- The liquid fraction was collected and 2% nitric acid was added up to a 50 mL total before storage in a fridge at 5°C until analysis.

2.2.3. Extraction of ESS samples with a phosphoric acid-based method

The five soil samples and the reference soil sample were extracted two times using a mixture of nitric and phosphoric acid as described in the previous section based on the Bednar *et al.* [7] method.

Operating conditions

All samples were prepared using analytical grade reagents and ultrapure water (Millipore).

Sample preparation before analysis by ICP-MS was performed by diluting the samples 20 times in 2% HNO_3. The samples were then measured on a Bruker Aurora Elite ICP-MS instrument at the Geology Department (Lund University). The following list of nuclides were measured: ^{177}Hf, ^{178}Hf, ^{181}Ta, ^{182}W, ^{183}W. The calculation of the concentration for each element has been performed assuming that their respective isotopes were present in the sample at their natural abundance.

Quality assurance

A 2% nitric acid solution was used for blank measurements and standard solutions of W, Hf and Ta in 2% nitric acid (tracer solutions from, TraceCERT®, Supelco®) were prepared and used as a primary standard to calibrate the ICP-MS instrument. A calibration curve, using this solution diluted to 0.1; 1 and 10 ppb in the same 2% nitric acid solution was established. Solutions of ^{115}In, ^{159}Tb and ^{209}Bi were also used as additional internal standards.

In addition, a certified reference material (Industrial soil, NCS DC73323A) with certified concentrations of W (7.4 mg kg^{-1}), Hf (8.3 mg kg^{-1}) and Ta (1.6 mg kg^{-1}) was extracted and analysed using the same method to validate the results.

Results

The diluted solutions of extracted samples were measured by ICP-MS with each duplicate being measured twice. From the raw data in part per billion (ppb) obtained from dilutions of the extracted solutions, the actual concentrations in the soil samples can be calculated. The concentrations in the soil samples (in mg kg^{-1}) are presented in Table 4.

In all the soil samples collected near the ESS and the reference material, the values were above the limit of detection (LoD) of a few µg kg^{-1} for the elements analysed here.

Table 4: ICP-MS measurement result on five ESS soil samples and a reference material (uncertainty: standard deviation)

Sample ID	W concentration (mg kg^{-1} N = 4)	Hf concentration (mg kg^{-1} N = 4)	Ta concentration (mg kg^{-1} N = 4)
E3	0.29 ± 0.05	0.68 ± 0.14	0.03 ± 0.02
E52	0.38 ± 0.05	0.81 ± 0.19	0.04 ± 0.03
E258	0.22 ± 0.04	0.46 ± 0.14	0.04 ± 0.03
E331	0.32 ± 0.04	0.42 ± 0.07	0.03 ± 0.01
E344	0.64 ± 0.38	0.42 ± 0.11	0.03 ± 0.02
Ref	2.96 ± 0.44	0.71 ± 0.11	0.03 ± 0.02

2.2.4. Discussion of the results of the phosphoric acid-based method

Several valuable conclusions can be drawn from the ICP-MS measurements performed in the section 2.2.3.

Indeed, from this first set of experiments, both the efficiency of the extraction method using phosphoric acid and the concentration of W, Hf and Ta in soils collected near the ESS can be estimated. These values can then be used to estimate the LoD that would be possible to achieve for soils contaminated by ESS materials.

Efficiency of the phosphoric acid method

Based on the values from Table 4 and the certified values in W, Hf and Ta of the reference sample, the efficiency of the extraction method for the three elements was calculated. The results are presented in Table 5.

Table 5: Efficiency of the phosphoric acid extraction on industrial soil certified reference material determined by ICP-MS (uncertainty: standard deviation)

Element	Reference value (mg kg^{-1})	Mean value measured by ICP-MS (mg kg^{-1} N = 4)	Efficiency (%)
W	7.4	2.96 ± 0.44	40.0
Hf	8.3	0.71 ± 0.11	8.6
Ta	1.6	0.03 ± 0.02	1.9

The extraction efficiency is low for Hf and very low for Ta. The value measured for Ta was close to the LoD and had a large relative standard deviation value. It confirms the data found in the literature, in particular the fact that Ta is only soluble and stable in hydrofluoric acid solutions.

The efficiency of the W extraction is better but limited to 40%. This value is consistent with the ones obtained by the authors of the method for samples with low concentrations of W (25% for 2 mg kg^{-1}) but lower than the ones for more concentrated samples (79% for 1695 ± 203 mg kg^{-1}) [7]. The better results observed for this method for more concentrated samples as well as for samples containing metallic W (cf. Table 2, section 2.1.2) would be an asset in the analysis of samples contaminated by ESS materials.

Estimation of W, Hf and Ta levels in ESS soil samples by ICP-MS

The nature of the soil and the chemical form of the three elements in the reference material are unknown while the ESS soil samples are expected to be sandy loam with W, Hf and Ta in their natural form (see [3]).

In the hypothesis that the reference material and the ESS soil behave in a similar manner during the extraction procedure, the efficiencies determined in Table 5 can be used to normalise the concentrations of the three elements. These values can then be compared to their environment levels estimated by the geological survey FOREGS [53]. These values are presented in Table 6.

Table 6: Comparison between the calculated concentrations from the soil extractions and estimated data from geological surveys (uncertainty: standard deviation)

Element	Mean concentration normalised by the efficiency (N = 5, mg kg^{-1})	Range concentration normalised by the efficiency (mg kg-1)	Estimated levels from FOREGS survey maps (mg kg-1)
W	0.9 ± 0.3	0.6-1.6	< 5.0
Hf	6.5 ± 1.5	4.9-9.5	8.8-11.7
Ta	1.8 ± 1.2	1.7-2.1	0.21-0.69

After normalisation, all the concentrations of W and Hf in the soil samples are lower or within the expected range of concentration. The Ta values are above the expected values but the associated uncertainties are very high. Thus, the analysed soil samples collected around the ESS do not seem to present any current contamination of W, Hf or Ta.

Location of the samples

As shown in Figure 1, the five samples analysed in this study were collected around the ESS facility and represent the top 7 cm layer.

The literature mentions the risk of elevated W levels near roads [29]. In the present tests, the highest concentration of W was measured in the sample (E344) collected along the road Odarslövsvägen. However, the differences between the ESS samples are small (range of 1 mg kg^{-1} between the normalised concentrations).

Additional measurements could be performed in the future near the two main roads of the site to monitor the evolution of the W levels originating from car and cargo traffic, focusing on the ESS side towards Lund with the heavy trafficked E22 highway.

Estimation of the limits of detection for contaminated soils

The LoDs for the metals of interest measured by ICP-MS are ranging from 2 to 5 ppt [54] which means that concentrations in the µg kg^{-1} range could be measured in soil with this analytical technique. Since W, Hf and Ta are not routinely analysed with the instrument used in this study, no instrument-specific LoD were available for these elements and the LoD values from the literature were used.

In the case of W, the efficiency of extraction was satisfactory for the natural content of W in soils. This efficiency is expected to be even higher for contaminated soils according to the authors of the extraction method [7]. A contamination by ESS target material would mainly be composed of stable W regardless of the target irradiation duration and the section of target affected by the accident release. Thus, increases of the W concentration of soil in the range of a few mg kg^{-1} could be attributed to a contamination by ESS materials. An increase near the two roads could however be possible due to traffic but could be confirmed or discarded by additional measurement in other locations near these roads.

In the case of Hf and Ta, however, the poor efficiencies observed for the extraction are increasing this LoD and the associated uncertainties. In addition, the efficiency of the extraction method for these two elements in irradiated target material or stable analogues like mixtures of metal oxides is unknown. For these two elements, a total dissolution method (soil fusion or hydrofluoric acid) would be recommended to reach a LoD in the range of mg kg^{-1} measured by ICP-MS.

2.2.5. Comparison of the phosphoric acid method and pseudo-total extraction with aqua regia

Initially, the goal of this series of experiments was to compare the aqua regia pseudo-total extraction method commonly used for environmental monitoring with the method tested in section 2.2.3. We planned to give particular attention to the selectivity of these methods to W (main component of the ESS target) and Gd (most concerning alpha emitters produced by spallation of the target).

Unfortunately, due to technical issues with the ICP-MS instrument previously used, the study had to be performed with another analytical technique, inductively coupled plasma optical emission spectrometry (ICP-OES). This technique is also called ICP-AES for inductively coupled plasma optical emission spectrometry. The main difference with ICP-MS is that after the sample is ionised in the plasma torch, the detector registers the photons emitted by the de-excitation of the atoms from the sample. Each element has a characteristic emission spectrum, thus ICP-OES allows elemental analysis (but not isotopic analysis like ICP-MS).

The technique was used by Bednar *et al.* [7] to measure the W content of soil samples alongside with ICP-MS for sufficiently concentrated samples. ICP-OES was also a technique used for the analysis of rare earth elements (including Gd) thanks to its multi-element detection capabilities [55].

This change of circumstances gave us the opportunity to test the performances of ICP-OES and to compare them to ICP-MS.

Operating conditions

The measurements for this comparison study were performed by ICP-OES.

The samples were not diluted further after the extraction procedure described in section 2.2.2 due to the expected higher LoDs of ICP-OES compared to ICP-MS. The samples were measured on a Perkin Elmer Optima 8300 instrument at Instrumental Chemistry, Department of Biology, Lund University. W, Hf and Ta are not routinely analysed by the laboratory and no prior analysis method was set for these elements. The wavelength for analysis were selected according to recommendations in [54]. Ta, Hf, W and Gd were respectively analysed at 226.230 nm, 277.336 nm, 207.912 nm and 342.247 nm.

Quality assurance

A 2% nitric acid solution was used for blank measurements and standard solutions of W, Hf, Ta and Gd were prepared from tracer solutions (TraceCERT®, Supelco®) as primary standards.

In addition, a certified reference material (Industrial soil, NCS DC73323A) with certified concentrations of W (7.4 mg kg^{-1}), Hf (8.3 mg kg^{-1}), Ta (1.6 mg kg^{-1}) and Gd (4.5 mg kg^{-1}) was extracted and analysed using the same method to validate the results.

Results

The results obtained by ICP-MS after measurements of the five soil samples and the reference sample extracted by the two extraction methods are presented in Table 7.

Table 7: ICP-OES measurement result on five ESS soil samples and a reference material after extraction with nitric and phosphoric acid or aqua regia

Method	Sample	Ta (mg kg^{-1})	Hf (mg kg^{-1})	W (mg kg^{-1})	Gd (mg kg^{-1})
Extraction with phosphoric acid	E3	< LoD	< LoD	3.7	3.7
	E52	< LoD	< LoD	< LoD	3.8
	E258	< LoD	< LoD	< LoD	3.2
	E311	< LoD	< LoD	3.1	2.7
	E344	< LoD	< LoD	3.3	2.7
	Ref	5.0	< LoD	11.8	7.9
Pseudo-total extraction with aqua regia	E3	< LoD	< LoD	< LoD	2.9
	E52	< LoD	< LoD	< LoD	3.9
	E258	< LoD	< LoD	< LoD	4.4
	E311	< LoD	< LoD	< LoD	3.6
	E344	< LoD	< LoD	< LoD	2.6
	Ref	< LoD	< LoD	< LoD	< LoD (0.4)

Many of the obtained values were below the LoD estimated for measurements performed at the chosen wavelengths. These LoDs are presented in Table 8 and they are several orders of magnitude higher than the LoD for ICP-MS.

Table 8: ICP-OES estimated detection limits and interferences (from **[54]**)

Element	Wavelength (nm)	Estimated Detection limits (mg L^{-1})	Possible interferences
Ta	226.230	0.03	Sb, Nb
Hf	277.336	0.02	Nb, Cr, U
W	207.912	0.03	Ru, In
Gd	342.247	0.014	Th, U

The obtained results are discussed in the following section.

2.2.6. Discussion of the experimental results of the extraction method comparison

The results obtained by ICP-OES can be analysed and compared with the ICP-MS measurements previously performed on the same samples. Both the extraction efficiency and selectivity toward W and Gd of the two extraction methods can be compared. In addition, these results can provide insights on the detection limits for W, Hf and Ta but also for Gd that can be obtained by ICP-OES.

Estimation of W, Hf, Ta levels in ESS soil samples by ICP-OES

All the values measured for Hf were below the LoD for both extraction methods. It is thus not possible to determine the efficiency of the extraction methods nor to estimate the current levels in soils around the ESS by ICP-OES.

Regarding Ta, the only value above LoD is its concentration in the reference material extracted. The calculated efficiency based on the reference material concentration is over 312% (see Table 9). This overestimation could be due to the imprecision of the measurement since the value is above LoD but below the limit of quantification. The overestimation for W reaches 160% which could also be a sign of cross-contamination of the samples.

Table 9: Efficiency of the phosphoric acid extraction on industrial soil certified reference material determined by ICP-OES

Element	Reference value (mg kg^{-1})	Mean value measured by ICP-OES (mg kg^{-1})	Efficiency by phosphoric acid method (%)
W	7.4	11.9	160
Hf	8.3	Below LoD	-
Ta	1.6	5	312
Gd	4.5	7.9	176

No values were found above LoD for the pseudo-total extraction with aqua regia. This could be due to a combination of higher LoDs and low extraction efficiency for the three metals of interest.

Comparison of the ICPMS and ICP-OES results

Gadolinium was successfully extracted and analysed by ICP-OES. The results for the two series are in good agreement for the two extraction methods as presented in Table 10 even though the values obtained for the reference material are inconsistent for the two extraction methods with 176% with phosphoric acid and >10% with aqua regia (based on the value below LoD from Table 7).

Gadolinium was already extracted by aqua regia from a similar set of ESS soil samples and measured by ICP-MS and the obtained values were reported in a previous report [3]. This set of measurements is also in agreement with the ICP-OES method.

Table 10: Gadolinium concentration (ICP-MS values from **[3]**)

Analytical method	Extraction method	Concentration range (mg kg^{-1})
ICP-MS	Aqua regia	1.95-3.04
ICP-OES	Aqua regia	2.61-4.42
ICP-OES	Nitric/phosphoric acid	2.66-3.83

Thus, both extraction methods seem to be efficient for Gd and both measurement techniques are sensitive enough to detect natural levels of Gd in soils collected near the ESS.

Comparison between the two analytical techniques is not possible for the three other metals since all the values from ESS soils where below LoD.

Selectivity towards W and Gd of the two extraction methods

In the absence of W values for soils extracted with aqua regia, it is not possible to conclude on the selectivity of the methods. In the case of a soil sample contaminated by ESS target particles, a quantitative dissolution of their W matrix could be a necessity in order to analyse their Gd content.

We recommend performing additional extraction test on natural ESS soil but also on samples amended with tungsten oxides to get a better understanding of the behaviour of W and Gd in contaminated soils.

Limits of detection by ICP-OES

ICP-OES LoDs were too high to measure the natural content of W, Hf and Ta extracted from 0.5 g of soil by aqua regia or a mixture of nitric and phosphoric acid.

Samples contaminated with ESS target material would need to be several times above the natural levels to be detected by ICP-OES with the tested operating conditions.

In order to detect lower amounts by ICP-OES, either a more efficient method or more concentrated solutions should be used. If such conditions are not achievable, ICP-MS would then be the recommended analytical technique.

2.2.7. Conclusions on the extraction experiments

In this experimental study, two extraction methods have been tested and compared on soil samples collected near the ESS: a pseudo-total method based on aqua regia commonly used for environmental monitoring and a method dedicated to the extraction of tungsten using phosphoric acid based on Bednar *et al.* [7].

Several conclusions can be drawn from the experimental study:

- Both extraction methods seem to have a limited effect on the extraction of Hf and Ta. However, the phosphoric acid method allowed a more satisfactory extraction of W and has the potential to be even more efficient on more concentrated samples according to its authors. One limit of the study is the use of ICP-OES for the second series of measurements. Further ICP-MS test should be performed in the future to fully dismiss the aqua regia method for the three metals of interest.

- The current levels of W, Hf and Ta measured in this study are in agreement with the estimated values from previous geological surveys. No detectable contamination from agriculture practices or road traffic was observed and the concentrations of the three metals seems to be homogenous at all the sampled locations.
- Regarding limits of detection (LoDs), ICP-MS offers better performances than ICP-OES. The detection of an increase by a few milligrams of W, Hf or Ta per kilogram of soil could be achieve by ICP-MS using only 0.5 g of sample.

2.3. Conclusions and recommendations

A review of the existing literature on W, Hf and Ta in the environment and in particular in soil was performed and an experimental study was conducted to assess extraction and analytical methods to measure those elements in soil samples.

The main conclusions of the literature review are the following:

- The behaviour of W, Hf and Ta in the environment and their effect on health have been relatively rarely studied in comparison to other ESS-relevant metals such as Gd.
- The three metals are resistant to aqua regia extraction and require specific extraction methods using for example, phosphoric acid for W or hydrofluoric acid for Ta.
- To our knowledge, only one method for the separation of W, Hf and Ta from each other has been published in the scientific literature.
- From the various sources of contamination of W, Hf and Ta, the most probable to happen around the ESS, besides an accident at the facility are the use of fertilisers rich in these metals or a local increase on the side of the surrounding roads due to road traffic.
- The transfer of stable W, Hf and Ta from soil to plant is poorly known and only a handful of publications are relevant to the plants grown around the ESS.
- The transfer of the radioisotopes of W, Hf and Ta in particular to animals (and man) is even less studied. However, the existing articles indicate a fast excretion of radio-W and radio-Ta while the excretion is slow for radio-Hf.

Our recommendation would be to perform additional experimental research on the transfer of W, Hf and Ta from soil to plants grown around the ESS facility and to attempt to design models of their transfer in the local environment-

The main conclusions regarding the experimental study are the following:

- No existing contamination by W, Hf and Ta was observed in the ESS soil samples analysed in this study.
- The experimental tests confirmed the efficiency of phosphoric acid to extract tungsten from soil samples.
- The limits of detection achieved by ICP-MS would allow the detection of low contamination levels in soils (down to several mg kg^{-1}) even if the efficiency of the extraction method is limited.

We recommend testing total extraction methods on ESS soil samples to get a better knowledge of the content of the soils surrounding the facility and to produce a better reference to compare the performance of various extraction methods.

Indeed, for samples containing actual target materials, a good dissolution of tungsten particles (in metal or oxide form) would be crucial for its measurement and the measurement of spallation products included in these particles.

The detection of low levels of contamination by W, Hf and Ta in soil samples with low natural levels of these elements requires a sensitive measurement technique and the studied metals are difficulty to extract from soil matrices. Thus, we recommend ICP-MS over ICP-OES as a non-radiometric analytical technique for the analysis of soil samples contaminated by ESS target material.

3. Simulation of gamma spectra of soil contaminated with target material

This chapter gives a summary of efforts made to replicate the possible gamma-ray spectra that would be produced by soil samples contaminated by ESS specific radio nuclides. Firstly, the relevance of gamma-ray spectrometry in the environmental monitoring program of the ESS is covered. The generation of semi-synthetic gamma-ray spectra, using measured matrix data and the Gamma Spectrum Generator within the Nucleonica web-portal, is described. An example of the extraction of the minimal detectable amounts, of radioisotopes of W, Ta and Hf is presented. The concluding section of this chapter includes a statement of how this work is set to progress in the near future.

3.1. Gamma spectrometry of accident releases from ESS in environmental samples

3.1.1. High-resolution gamma-ray spectrometry in environmental monitoring

Stationary high resolution gamma spectrometry is usually employed on environmental samples collected in connection to environmental monitoring programs (EMP) related to the operational releases from a nuclear installation. The typical sample matrices collected in an EMP are samples of soil, water, vegetation and sediment (e.g. Bernhardsson *et al.* [52]). More information on the advantages of gamma spectroscopy for important ESS-specific radionuclides can be found in a previous report (SSM 202:08) by Stenström *et al.* [2].

3.1.2. Challenges specific to the ESS

In addition to the naturally occurring terrestrial and cosmogenic radionuclides (e.g. ^{238}U-daughters ^{226}Ra, ^{214}Pb, ^{214}Bi; ^{232}Th-daughters ^{228}Ac, ^{212}Bi, ^{208}Tl; single primordial ^{40}K and cosmogenic ^{7}Be) and previous anthropogenic fallout (mainly ^{137}Cs from global fallout and Chernobyl accident in 1986) present in the environment, the EMPs currently designed for the operation of ESS includes a relatively limited amount of gamma emitters that are considered of main concern (See Table 11). This limited number of gamma lines enables quantitative evaluation of the radionuclide specific concentrations in the environmental samples using straightforward photo-peak assessment. Typical minimum detectable activity concentrations of these radionuclides using a 100% High purity Germanium (HPGe) detector range between 1.5 - 225 Bq kg^{-1} for a 24 h acquisition time (Table 11).

Table 11: Minimum detectable activity concentration, MDA, (Bq/kg) of gamma emitting radionuclides in 200 ml environmental samples (with densities ranging from 0.2 to 1.6 g cm^{-3}) for 24 h measurement by shielded stationary high resolution gamma spectrometry (Ortec p-type detector (GEM100210-S) with 100% rel. efficient @ 1332 keV). Values refer to normal conditions without presence of accidental releases from ESS.

Radionuclide	Principal gamma-line (keV)	MDA (Bq kg^{-1})
^{226}Ra	186.2	28 – 225
^{228}Ac	911.2	4.4 – 35
^{40}K	1460.8	26 – 210
^{137}Cs	661.7	1.5 – 13
^{7}Be	477.6	7.0 – 56
^{58}Co	810.8	1.0 – 8.0
^{54}Mn	834.8	1.0 – 8.0
^{172}Hf	122.9, 125.8, 127.9	To be investigated
^{185}W	125.3	To be investigated
^{60}Co	1173.2	1.9 – 15

However, in case of accidental releases from the ESS a vast number of target produced gamma-emitting radionuclides may be dispersed at the facility site and its vicinity. The listed radionuclides in Table 1 are the ones estimated to give the largest contribution to the long-term external gamma dose from the deposition following accidental releases. In addition, there are also other ESS target radionuclides that will potentially pose a greater radiological risk if entering the local food chain or if inhaled, such as the alpha emitters ^{148}Gd, ^{154}Dy and ^{146}Sm. These latter radionuclides are referred to as difficult-to-measure radionuclides (DTMs), as there are no standard methods for their extraction and subsequent radiometry or have only been developed recently [56]. For some of the DTMs, there are accompanying isotopes generated that could be detected by means of gamma spectrometry, such as ^{153}Gd and ^{146}Gd, that can be used to estimate the concentration of the alpha emitter ^{148}Gd in both environmental samples and for internal dosimetry assay [1], [57].

In an accident scenario, such as described in [1], *in-situ* gamma spectrometry combined with soil sampling will be carried out to enable projections of external dose to the people residing in the area. The spectra acquired from soil samples in connection with a recent atmospheric release of W-target particles from ESS will then be the result of a complex mixture of gamma lines:

- Primary gamma lines from the ESS fallout products and their daughters in the sample,
- Incompletely absorbed primary photons in the HPGe-detector,
- Compton scattered gammas from the radionuclides in the sample,
- Contributions of primary gamma lines from the naturally occurring radionuclides.

The complexity of the spectra will be dampened with time as the more short-lived radionuclides in the released mixture will decay. The aim of this part of the study is to obtain estimates of the MDA for the gamma-emitting radionuclides in Table 1 by using existing background spectra from environmental samples, containing typical concentrations of naturally occurring radionuclides, combined with a software for synthetic spectrum generation of various radionuclides. A

Gamma Spectrum Generator within the Nucleonica web-portal (Nucleonica GmbH[59]) was chosen for this purpose.

The end-goal of this study is to evaluate the time-window of detectability for these gamma-emitting nuclides and hence to define a methodology for assessing not only the gamma emitters of interest listed by SSM but also accompanying gamma emitting radionuclides of the DTM alpha emitters.

3.2. Simulation of gamma spectra

3.2.1. Method

Approached to simulation

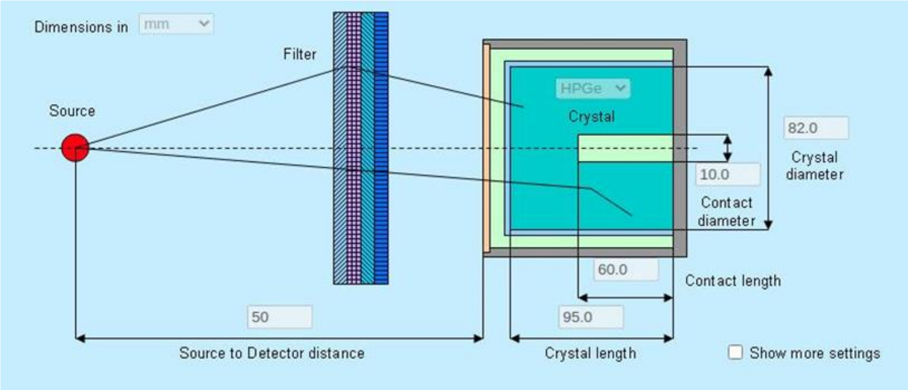
To enable estimates of the MDAs of the radionuclides generated in the ESS W-target in environmental samples in an accident situation, three things were needed:

1. specifications of the specific detector system to be used for measurement, including the measurement geometry;
2. a good knowledge of the background components that will be present in the measurement, including background from the sample matrix;
3. and a comprehensive list of all non-natural gamma-ray emitters that will be present in the sample measured.

Point-1 was reasonably straightforward to address by selecting an existing, and accessible, detector system that was fit for purpose. In this case a HPGe-detector (Ortec GEM 100, SN:S44-P41442A) at Medical Physics, ITM, Lund University was chosen. The relevant parameters for this detector system can be seen in Figure 2, which shows the setup window for the gamma-spectrum generator in Nucleonica.

Point-2 was addressed by using authentic, measured gamma-ray spectra from soil samples collected outside ESS in 2017 [52]. Spectra from five soil samples, contained in 200 ml plastic vials were pooled in the GammaVision software (Ortec) to yield a summed gamma spectrum (SummedSoil.spc) to represent the typical activity concentrations of naturally occurring radionuclides from ^{238}U-series, ^{232}Th-series and ^{40}K. The measurements for these soil samples were all made, in close geometry (represented by a distance of 50 mm between endcap of detector and the midpoint of a 200 ml vial, N.B the sample to the endcap detector distance is not to scale in Figure 2), on the same detector system chosen in Point-1. This would be the same conditions under which a soil sample collected *in-situ* after a W-particle fallout will be measured by the gamma spectrometry system.

Point-3 was more challenging to address than points 1 and 2, as it required not only a detailed knowledge of the radionuclide inventory in the ESS target, but also the release and migration mechanisms of these radionuclides. These factors are subject to a large set of variables and change over time. As it was not the goal of the study to investigate the specific release and transport phenomena associated with these radionuclides, the issue was tackled with the use of existing simulation data in combination with a few simplistic assumptions; as described below.



Dimensions in: mm
HPGe
Crystal diameter: 82.0
Contact diameter: 10.0
Contact length: 60.0
Crystal length: 95.0
Source to Detector distance: 50
☐ Show more settings

Figure 2: Detector model from Nucleonica, using a simplified geometry a 100% relative efficiency P-type HPGe-detector situated at Medical Physics, ITM, Lund University. N.B: the source-endcap distance is not to scale with the detector crystal length.

Radionuclide inventory data

FLUKA simulation results, of radionuclide inventory in the ESS target, from Barkauskas and Stenström [4], was used as the basis for this study. These data give the activities of radionuclides at 1-year intervals over the 5-year operation of a W-target wheel, and at 50-day intervals after operation has ceased, up to 350 days. Two specific points in time were considered: the end of the 5-year operational period (t_0), when activity in the target is at its highest; and 350 days after operation has ceased (t_{350}). The t_0 data set represents 225 radionuclides, constituting 71 chemical elements, with a total activity of 6.9 10^{16} Bq and a total mass of 247.1 g (value calculated from the simulation from [4]). Within the t_0 data, 26 of the radionuclides were found to produce no gamma radiation. Four of these are pure alpha-emitters, five decay via either beta+ or electron capture and the remainder by beta-decay. Consequently, none of these may be detected directly by gamma spectroscopy. Six of these nuclides however, decay to nuclei which further decay producing gamma rays that will therefore contribute to the count of gamma pulses, even though presence of the parent nuclide will remain obscure in the acquired gamma spectrum. At t_{350}, only 133 radionuclides remain across 60 chemical elements, with a total activity of 6.0 10^{15} Bq and a total mass of 142.7 g. Of these 133 radionuclides, 23 remain with activities over 1 Bq, which produce no gamma-ray emission; of which four have daughters which do produce gamma-rays. It should be noted that due to limitations of FLUKA, nuclides with isomeric states were not included in the inventory; the true inventory is therefore expected to be somewhat larger.

Building semi-synthetic spectra

It was assumed that, in the event of a release, the relative amounts of the target inventory components, would be dispersed equally in the environment. Three cases for the concentration of target material in soil samples were then defined:

- **n_1:** 30 mg of target material per m^2 of soil, equivalent to evenly dispersing 1% of the target over 1 km^2;
- **n_2:** 300 µg of target material per m^2 of soil, equivalent to evenly dispersing 1% of the target over 100 km^2, or 0.01% of the target over 1 km^2;
- **n_3:** 3 µg of target material per m^2 of soil.

It should be made clear that the three cases above are not supposed to replicate any particular release scenarios. The intention is simply to provide a broad range (four orders of magnitude) of soil contamination scenarios; the points chosen for which can be easily, and reproducibly, related to measurable physical parameters i.e. target mass, land area and activity.

From the two time points t_0 and t_{350}, and the three cases of soil contamination n_1, n_2 and n_3, six hypothetical soil samples can be defined. As soil samples are taken from a circular core, with diameter 5 cm (experimental procedure described in [52]), total masses and activities of all radionuclides can be easily defined for each set of t and dispersion scenario (n_1 to n_3). For the purposes of reducing the input data required for simulating in Nucleonica, radionuclides with activities of less than 0.01 Bq in each sample composition were removed. The six samples are summarised in Table 12. For reference, the total mass of target material used for n_3 would correspond to a single particle approximately 4 µm in diameter.

Due to limitations on the number of nuclides that can be run in a single simulation in Nucleonica, the nuclide lists for each sample were divided into batches of 25. A measurement time of 24 hours was simulated for each batch. The resulting spectra were exported from Nucleonica in .spe format (Ortec^{TM}) and summed. Finally, the summed experimental soil spectrum was normalised to the same measurement time of 24 hours used in the simulations, before being summed with the simulated spectra.

Table 12: Summary of the ESS radionuclide contamination in each of the simulated soil samples.

Sample	Total mass of target material (µg)	Total mass of radionuclides (ng)	Num. of gamma-ray emitters > 0.01 Bq	Total activity of ESS radionuclides (Bq)
$t_0\_n_1$	58.905	4.04	192	1.37×10^6
$t_0\_n_2$	0.589	3.97×10^{-2}	176	1.37×10^4
$t_0\_n_3$	0.006	3.96×10^{-4}	84	136.6
$t_{350}\_n_1$	58.905	1.96	86	1.12×10^5
$t_{350}\_n_2$	0.589	1.88×10^{-2}	61	1.12×10^3
$t_{350}\_n_3$	0.006	1.88×10^{-4}	21	11.13

3.2.2. Results

Obtaining spectra

The semi-synthetic gamma-ray spectra, for each of the six samples summarised in Table 12, are presented in Figure 3. It is immediately evident that these are highly complex spectra which presents challenges for peak identification. Regardless of the assumptions on the radionuclide inventory used to generate these spectra, it can be reasonably assumed that this level of complexity is representative of a potential real-world situation.

Both the number of lines, and the total activity of the samples can be seen to be higher in the t_0 spectra; as would be expected from the decay of the shorter-lived radionuclides by t_{350}. Significantly, it is the higher energy lines in the t_0 spectra which disappear preferentially. This means that for longer-lived nuclides with lines in this high energy region (> 2000 keV), the minimum detectable activity concentration, MDA (Bq kg^{-1}), in a soil sample may decrease the further in time a measurement is made from a release.

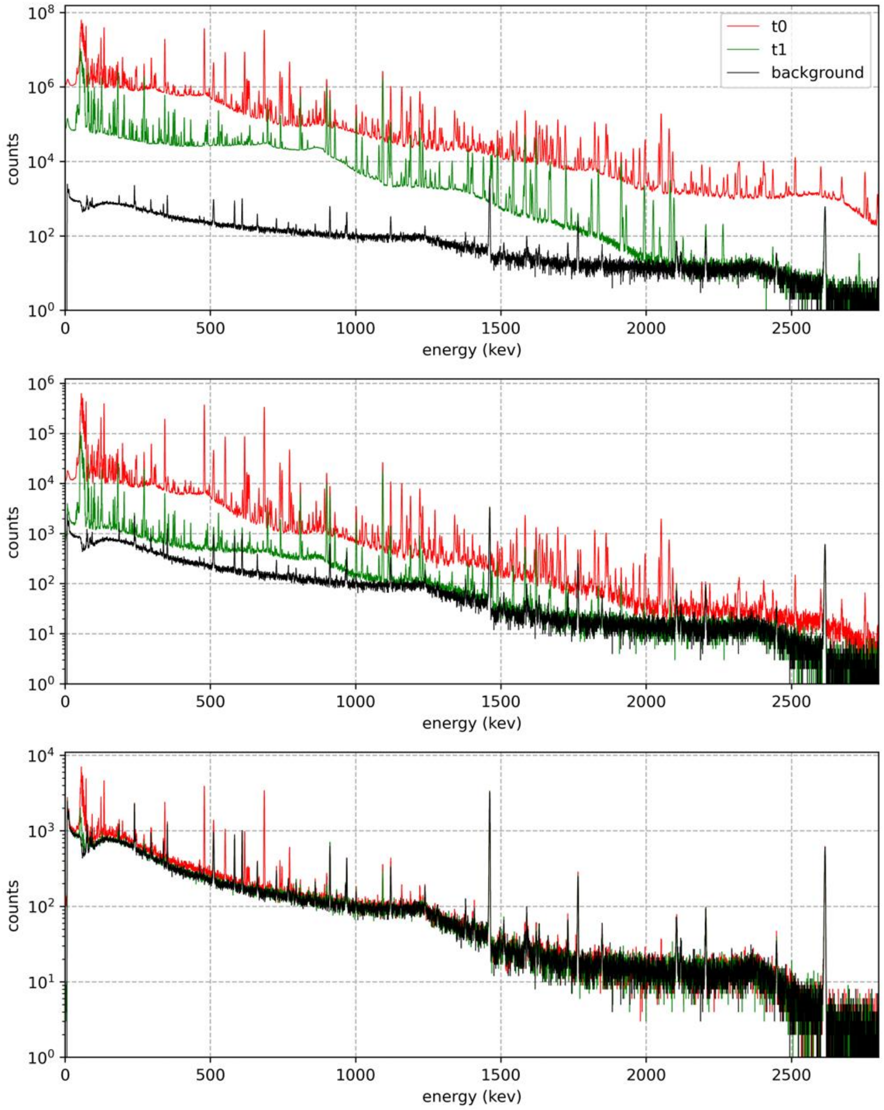


Figure 3: Semi-synthetic gamma-ray spectra, generated by combining Nucleonica simulations with real background data. The three plots represent different fractions of target material in the simulated samples; from top to bottom: n1, n2 and n3. Spectra at two points in time were considered: the end of the 5-year operational period (t_0), and 350 days after operation has ceased (t_1). The background spectrum is repeated in each plot for comparison.

Some gamma lines are still visible at the low-energy end of the t0_n3 spectra, despite this representing very low amounts of target material in the sample and sub-ppb concentrations of the actual radio nuclides. The strongest of these lines originate from ^{187}W, which has a relatively short half-life of around 24 hours and is hence no longer present in the t_{350} spectra. Despite this short half-life, ^{187}W has a very high production rate in the target and is therefore of particular importance with regards to gamma-ray dose immediately following release during operation. Indeed, this radioisotope has the highest activity of all gamma-ray emitters in the t_{350} data used, with an activity of around 44 Bq in the n_3 sets. It also presents a number of well separated lines which could be used for quantification, at 134 keV, 479 keV, 551 keV, 618 keV, 685 keV and 773 keV. These data show the possibility of using the peaks at 1188 keV, 1221 keV, 1230 keV in the t_{350} spectra to quantify ^{182}Ta, and the peak at 343 keV to quantify ^{175}Hf.

Obtaining MDAs

As the spectra presented here are semi-synthetic, with the lines of interest being the synthetic part, it is easy to decompose the spectra and identify the origin of the peaks precisely. In a real-world measurement, this will not be the case, and peak identification must be made using a gamma assessment software, such as GammaVision^{TM} (Ortec, 2022). This work is ongoing, but for the purposes of demonstration, attempts were made to manually extract estimates of the MDAs for ^{181}W, ^{187}W, ^{182}Ta and ^{175}Hf.

For each of the four nuclides, a specific peak was selected, that was observable in all semi-synthetic spectra generated. For each peak, a ROI (region of interest) in terms of energy was defined around it; and within this ROI, the peak was fitted with the sum of a linear function, to account for background, and a Gaussian function to account for the peak. In cases where the selected peak was barely separated from adjacent peaks, Gaussian functions were also fitted to the adjacent peaks, to make the linear function fit the background more accurately. Whatever the ROI selected for a particular peak, and number of Gaussian functions used, this was kept consistent in all spectra. From the area of the Gaussian function covering the peak of interest, the counts-above-background for this peak was obtained, with associated fit uncertainties. As the activity of each radionuclide was an input variable to the simulations used to generate the spectra, they were known for all spectra. It was then trivial to fit a linear function to the three points of counts vs activity, resulting in a calibration that was independent of the agreement between the efficiency calibration simulated in Nucleonica and the real HPGe detector set-up (Ortec GEM 100, SN:S44-P41442A), for each nuclide in each set of t_0 and t_{350} spectra. The MDA of a 24 h pulse acquisition was then the activity this function gives for a sensibly defined lower count limit. A lower count limit of 100 was defined in this case; which would give a statistical uncertainty of 10% in a real-world-measurement, assuming a background free spectrum. The process was also repeated, for semi-synthetic spectra containing only the nuclide of interest, combined with the soil spectrum. An example of the final linear fitting step of the procedure is presented graphically in Figure 4, for ^{187}W. The resulting MDAs for all nuclides studied are presented in Table 13; with the condition of ‘contamination’ defined for MDAs obtained from spectra containing the full ESS radionuclide inventory, and the condition ‘normal’ defined for MDAs obtained from spectra with only the nuclide of interest

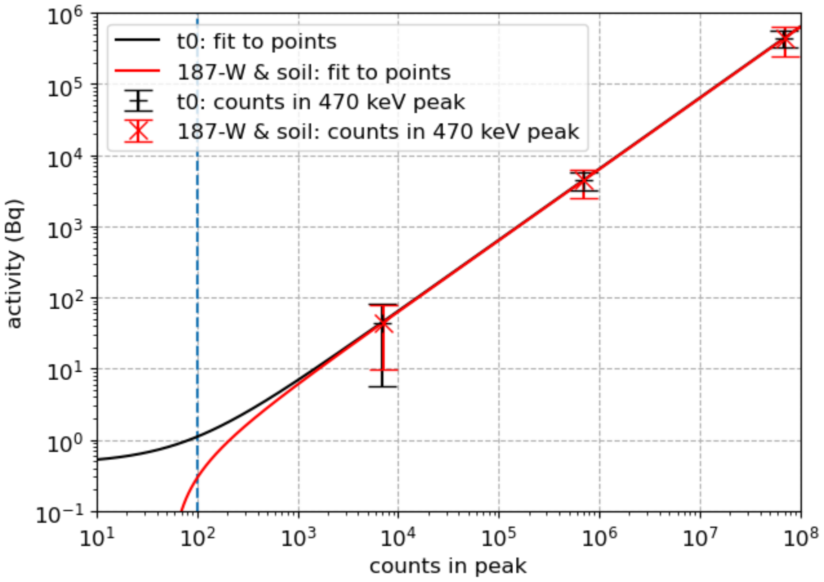


Figure 4: Determination of detection limits for ^{187}W. Marker show counts-above-background, for the 479 keV peak, obtained by Gaussian fitting to spectra for different activities of ^{187}W. The detection limit is defined as the activity at which the linear fit to the markers crosses 100 counts (marked with blue dashes) (NB: ‘W-187 & soil’ refers to a situation with only this particular radionuclide being present in the soil i.e. the ‘normal’ condition).

Table 13: Estimates of the Minimum detectable activity (MDA), of gamma-ray emitting radionuclides, that could be detectable in a volume of 200 ml of soil. Estimates are based on a 24h measurement by a shielded, stationary, HPGe gamma-ray spectrometer. Values for both accidental release to normal conditions, and under the hypothetical conditions presented by an accidental release from the ESS. Uncertainties on MDAs are propagated from the fit uncertainties only.

Nuclide	**T½ (days)**	**fitted gamma-ray peak**	**MDA (Bq) at:**			
			0 days		**350 days**	
			Under condition:			
			normal	**release**	**normal**	**release**
^{175}Hf	70.0	1221 keV	-	2.19 ± 0.00	2.01 ± 0.03	2.28 ± 0.43
^{182}Ta	111.7	343 keV	-	-	-	-
^{181}W	121.2	65 keV	1.23 ± 0.02	-	0.89 ± 0.00	0.90 ± 0.0
^{187}W	1.0	479 keV	1.04 ± 0.00	0.64 ± 0.39	Not present	Not present

It should be emphasised, that the values presented in Table 13 are only preliminary estimates and should be used with caution. The uncertainties stated, take into account only statistical uncertainties from the fitting algorithms used, and do not account for systematic uncertainties that could originate from the choice of ROI, the treatment of the measured soil spectra, or for the accuracy of the synthetic spectra generated in Nucleonica (see Section 3.2.3). The six table entries which contain no data, all had uncertainties exceeding 100% of the corresponding MDA value and greatly higher than 100% in some cases. These results emphasise the challenge presented by the complex spectra which result from such measurements; for ^{182}Ta, it was not possible to obtain reliable MDA estimates for any of the time points or conditions examined. A ROI, ideal for a particular peak of a radionuclide, in a spectrum collected at one point in time, will not necessarily be ideal for other points in time. Great care will therefore be required when attempting to extract quantitative information in a reproducible manner from an authentic real-world-measurement.

3.2.3. Comparison of Nucleonica with MCNP

The end goal of the semi-synthetic spectra simulation is to obtain spectra as representative as possible of a soil contaminated with ESS target material. These data could then be used to determine the MDAs of the main gamma emitters contributing to the dose, as well as the Gd isotopes that could be used to recalculate the concentration of alpha emitting ^{148}Gd.

In order to validate the results obtained with Nucleonica, a pilot study was thus conducted using detectors, sources and spectra simulated with MCNP (Monte Carlo N-Particle Transport), which is another code that is regularly used for such purposes [59], [60].

A HPGe detector was modelled, using the same parameters as the Nucleonica simulation, given in Figure 5. The source simulated was a radioactive water solution ~200 ml (reference material from IAEA), containing: tritium and strontium-90 (beta emitters); and barium-133 and europium-152 (gamma emitters). A real, 200 ml, reference solution was also measured with the physical gamma-ray detector mentioned previously (100% p-type HPGe-crystal). Pilot spectra calculations for a water solution containing this list of radionuclides measured by the HPGe detector previously described were performed with both Nucleonica and MCNP. The obtained spectra are presented in Figure 5.

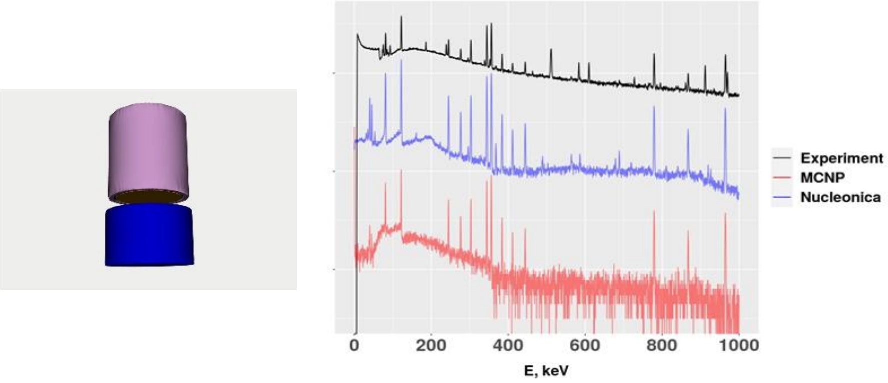


Figure 5: Validation of Nucleonica simulations using MCNP and experimental data. Left: Rendering of the detector (pink) and source (blue) modelled in MCNP. Right: Comparison of the gamma-ray spectra of the reference water solution containing ^{3}H, ^{90}Sr, ^{133}Ba and ^{152}Eu; obtained experimentally and simulated by Nucleonica and MCNP up to 1000 keV (the spectra were shifter on the y axis for better visual comparison)

From visual inspection, a good agreement with experimental data from IAEA standard solution is obtained for both Nucleonica and MCNP up to 1000 keV, but the count rates of the peaks in the simulated spectra exceed the ones in the measured spectra at higher energies.

One should be aware, that all spectra obtained from MCNP are normalized per radioactive decay of the source. The MCNP spectra given here, are therefore multiplied by a freely chosen factor to achieve a similar trend in the continuum part of the simulated spectrum to the one in the experimentally obtained spectrum. MCNP is a validated and much more flexible tool for such calculations in comparison with Nucleonica. However, MCNP requires additional coding competence and time to create models and perform calculations. One possibility to improve the MCNP simulation obtained in this pilot study would be to increase the simulation times to have less noisy spectra and to identify the reasons of differences compared with the measured spectrum in the lower energies. A single MCNP simulation on ordinary laptop took not more than 2 hours, but this is lengthy in comparison to Nucleonica, which generates such spectra in a matter of seconds.

3.3. Conclusions and recommendations

A procedure for the generation of semi-synthetic gamma-ray spectra has been developed, which can be used to predict minimum detectable activities of W-target specific radionuclides in environmental samples. This procedure relies on the availability of: i) a background spectrum specific to the sample matrix, the detector system and the geometry that will be used in real measurements, and ii) the parameters of the detector system. The generation of the synthetic part of the spectra was validated using MCNP and experimental data. Estimated MDAs have been obtained for a limited number of key radionuclides.

The detection limit for a given radionuclide was found to be highly dependent on the presence, and quantity of, other radionuclides in the sample. The estimation of a given MDA is therefore limited by the accuracy of the estimation of the complete composition of the radioactive contamination in a sample. A number of gamma-ray lines have been identified for measuring ^{187}W, ^{181}W, ^{182}Ta and ^{175}Hf, which are amongst the most prolific gamma-ray emitting nuclides produced in the ESS target. With the ability to generate and view synthetic spectra for any individual radionuclide, the identification of gamma lines and corresponding ROIs for the fitting of peaks is a relatively straightforward process. What is less straightforward, is using the information obtained to reproducibly quantify small activity concentrations of these radionuclides in environmental samples.

A more detailed validation between experiment, Nucleonica and MCNP, will also be undertaken, including a quantitative analysis of variation of the two simulation approaches as a function of gamma-ray energy. More detailed analysis of the semi-synthetic spectra presented in this report, will be conducted, using the GammaVision software package for sample acquisition and peak identification. Using this method, a comprehensive list of MDAs will be obtained that will also include metastable radionuclides such as ^{178m}Hf that were not included in the current work. An additional task will be to perform blind peak-fitting of selected spectra, representing a real-world environmental measurement situation, where the person analysing a spectrum has limited pre-knowledge of the sample composition. Additional semi-synthetic spectra will be generated, for other time steps and other normalisation coefficients. These data will also include semi-synthetic spectra corresponding to contamination that would result from a radionuclide release from the target, prior to it completing its life cycle. The result of this work will be published in the near future.

4. Summary and conclusions

The present report is a continuation of the work done in SSM reports 2020:08 and 2021:21. It provides additional recommendations on the analytical techniques to be used to assess potential environmental contaminations by radionuclides produced by the ESS. It also provides additional data on the local environment around the facility, in particular on its soil composition.

The calculation of the absorbed dose from releases of radionuclides by the ESS during normal operation or after an accident is a very complex issue due to the uniqueness of the facility and its potential releases.

The present report confirms this complexity in the case of soil contamination. The measurement of the main radionuclides contributing to the dose, which includes ^{148}Gd, ^{187}W, ^{172}Hf, ^{182}Ta and ^{178n}Hf, will be made difficult by the presence of a long list of other radionuclides but also by stable isotopes. These interferences will affect the limits of detection (LoDs) for the radionuclides of most interest and have to be taken into account.

ICP-MS and alpha spectroscopy provide excellent LoDs for traces of metals and alpha emitters respectively. In the case of ICP-MS, LoDs of mg kg^{-1} could be reached in soil. However, these techniques require sample preparation steps such as chemical extraction and separation. The analysis of the soil samples content in radioactive and stable isotopes of W, Hf and Ta will be made difficult by their resistance to usual chemical extraction methods. Indeed, the use of extractants such as phosphoric or hydrofluoric acid is necessary to dissolve them and keep them stable in solution. A good extraction yield of W will be critical since it will be the main component of the target particles that could be released in the environment by the ESS. The extraction of the other radionuclides of interest such as the alpha emitter ^{148}Gd may be conditioned by the quantitative dissolution of the W matrix.

The MDAs for gamma emitter produced by the ESS will depend not only on the performances of the detection equipment but also on the composition of tungsten target at the time of the release. Indeed, the target composition will vary with the duration of its irradiation (up to 5 years) and the decay of the produced radionuclides. Simulation is a great tool to estimate the target composition at any given time of its operation or storage. As demonstrated in this report, gamma spectra of contaminated soil can be simulated from a given composition. The method was applied to the list of ESS radionuclides established by SSM and the MDAs of ^{187}W, ^{175}Hf and ^{181}W were estimated in soil contaminated with target materials at 0 and 350 days after the end of 5 years of irradiation of the target. This method could then be used to estimate the MDAs of other radionuclides of interest and target compositions including metastable ones. Additional research is actually already ongoing in our group to provide estimates of the such MDAs.

5. Outlooks

The present report highlight the need for future research in several directions:

- The study performed on ESS soils by ICP-MS regarding their content in stable Gd, W, Hf and Ta now needs to be extended to the plants already known to be representative of the local environment and agricultural practices. It is indeed important to identify risks of accumulation of these elements in plants that will enter the human food chain. The most relevant plants grown around the ESS facility have already been identified in previous studies. With the knowledge of the levels of Gd, W, Hf and Ta in local soil and these relevant plants, transfer parameters could be calculated.
- Using these transfer values and data from the literature, models could eventually be built to anticipate the fate of these elements and their radio-isotopes of interest once released in the environment.
- The simulation of gamma spectra has proven to be a successful strategy to determine the limits of detection of ESS produced radionuclides. This strategy now needs to be applied to relevant operational and accidental release scenarios to improve the environmental monitoring programs and emergency preparedness plans for the facility. This work has already started in our research group.

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