Doctoral Thesis:

Radiactive particle biotic and abiotic processes

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A mis padres, siempre conmigo.

Estos agradecimientos, con toda seguridad, quedarán incompletos. Aun así, quiero tener unas breves palabras.

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A Pepe e Inma Diaz por tantas horas juntos en familia.

A Juan Mantero e Ignacio Vioque, por todo lo aprendido y compartido.

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A Ole Christian Lind y Brit Salbu. Su trabajo fue un pilar fundamental para esta tesis.

A mis amigos y compañeros Armando, Jose Antonio Lay, Miguel Cortes, Eloy, Pedro, Guille, Mayo, Víctor...

Y, por último, Elisa, mi compañera de vida. Ella sostiene y es la válvula de mi exceso de entusiasmo. Espero que mi energía te ‘consuma’ hasta que seamos muy, muy viejos. Lo siento, es una broma privada.

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Chapter 1

Radioactive particles: radiological and radioecological implications

Introduction and justification of the work

Since the Second World War until nowadays, huge amounts of anthropogenic radionuclides have been incorporated to the environment generating, according to the characteristics and dimension of the source term, environmental radioactive contamination either at local, regional or global scale. (UNSCEAR, 208)

Global radioactive contamination was generated mostly in the 50´s and the 60´s associated to the great number of atmospheric nuclear weapon tests carried out by the United States (Nevada, Marshall Islands) the former Soviet Union (Nova Zelmya, Semipalatinsk Test Site), Great Britain (Montebello and Maralinga in Australia), France (Argelia, Mururoa Atoll) and China (Lop Nor). In addition, in the nuclear tests site locations and their surroundings, enhanced levels of artificial radionuclides can be found due to local fallout.

Local radioactive contamination can be also found in places affected by non-critically accidents involving nuclear weapons (e.g., Thule, Greenland; Palomares, Spain), and in areas affected by military use of depleted uranium ammunition (e.g., Kuwait, Balkan countries), while environmental radioactive contamination at local or regional level, depending the magnitude of the source term, has been generated also due to nuclear reactor accidents (e.g., Windscale, UK; Chernobyl Nuclear Plant, Ukraine; Fukushima Daichi Nuclear Plant, Japan)

Finally, dispersion of artificial radionuclides in the environment has been also produced as discharges (generally, but not always, authorized) from nuclear installations either to rivers (e.g., Techa and Yenesei rivers, Russia) or to regional seas (e.g., Irish Sea, Sellafield, UK, English Channel) and also as nuclear waste dumped at sea (e.g., Kara Sea, Russia Federation).

The artificial radionuclides were initially dispersed in the environment in different physicochemical forms, i.e., as different radionuclide species. In particular, associated to the great majority of nuclear events described in the previous paragraph, it is possible to find radioactive particles which are defined as a localized aggregation of radioactive atoms that give rise to an inhomogeneous distribution of radionuclides significantly different from that of the matrix background. (Salbu, 2000)

In water, particles are defined as entities having diameters larger than 0.45 μm, i.e., entities that will settle in still water due to gravity. But in the environment, artificial radionuclide species can be also found within the size range 0.001 μm – 0.45 μm, being referred to as radioactive colloids, nanoparticles or pseudo-colloids, while species less than 0.001 μm (10^3 Da, 1 nm) are also possible, referred to as low molecular mass (LMM) species. These LMM species are believed to be mobile and potentially bioavailable (Salbu, 2000).

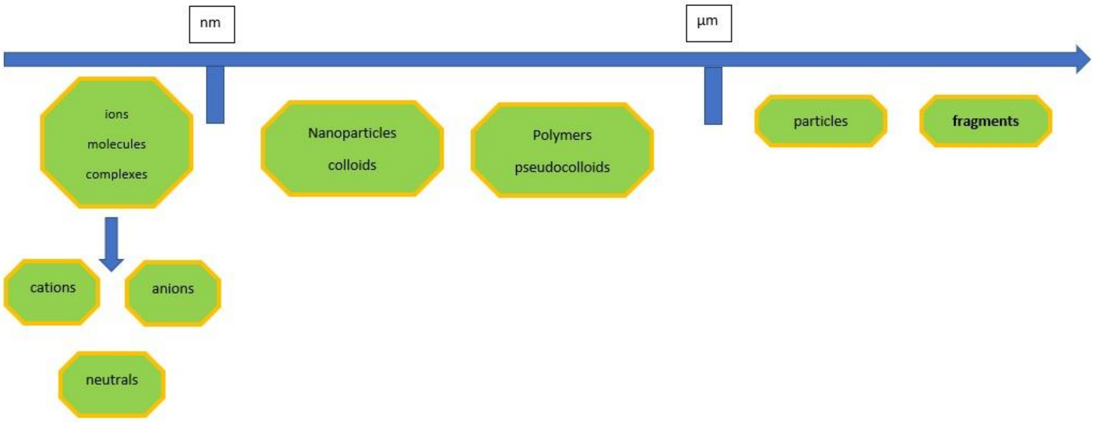

Figure 1.1.- Radionuclide species in water categorized according to size (nominal molecular mass). Left side figure: Low molecular mass species categorized according to charge properties from Salbu, 2000.

Radioactive environmental impact assessments are usually based on average bulk concentrations of radionuclides in various media, such as water (Bq/L), soil or sediment (Bq/kg or Bq/m^2) and tissues of animals and plants (Bq/kg) assuming homogeneous distribution of radionuclides, and without to have in consideration their distribution between species, i.e., their speciation. This fact can conduits in many cases to erroneous impact assessments for not consider properly the behaviour of the artificial radionuclides one released and incorporated to an environmental compartment. This behaviour will be clearly different depending of the dominant radionuclide specie: if the radionuclides are in the form of LMM species, in soils for example, it can be expected high mobility and transfer soil-to-plant, while if the radionuclides are present in the form of particles, in most cases a more inert behaviour will be observed, due to their refractory behaviour.

In addition, the different environmental compartments are dynamic, and due to interactions and transformation processes the original distribution of radionuclide species deposited is altered over time. As an example, in contaminated terrestrial ecosystems, the fraction of LMM species initially present can decrease, due to interactions with soil components. Simultaneously, the same LMM fraction can increase over time due to particle weathering if the particle specie coexists in the affected ecosystem. In the case of particles, their weathering and release of radionuclides in more available forms is generally also a time dependent process with an increment of this release over time. (Salbu et al., 2018).

In order to perform environment impact assessments, the radioecological conceptual models take into consideration the ecosystem transfer of deposited radionuclides by using different parameters such as soil-water distribution coefficients (Kd), transfer coefficients (TC), transfer factors (TF), concentration ratios (CR), etc… which until now have been generally based on measurements of the total activity concentration of individual radionuclides in bulk samples (Bq/kg, Bq/m^2) without any consideration about radionuclide speciation. Furthermore, Kd, TC, TF, CR… are usually present in the mentioned models as thermodynamic constants, assuming that the interactions between the different compartments are reversible and equilibrium conditions are valid along the time, The system dynamics and process kinetics is ignored, not considered.

Orders of magnitude of variations in Kds, TC, TF, CR and BCF can be found in the literature, with the additional problem that in the great majority of cases no information is given on the speciation of radionuclides such as LMM species, colloids/nanoparticles or particles. It is not taken into consideration, consequently, the fact that interactions and transfer between the different compartments of the ecosystem analyzed will vary according to radionuclide species and their time dependent interactions (Salbu et al., 2014).

Is not unusual to see in the literature the assignation to areas where the contamination can be found in particle form of Kd and TF parameters defined in terrestrial areas affected exclusively by weapon tests fallout. This can conduit to erroneous conclusions, with a general overestimation of the possible transfer to plants and animals and with associated overestimations of the population doses. The radionuclides disseminated as global fallout associated to the weapon tests are in general more bioavailable than the disseminated locally in some events associated to particles.

As a conclusion, we can indicate that in the past, inherent differences in transport, mobility and bioavailability of particle-bound radionuclides compared to simple ions have largely been ignored in radiochemistry, radioecology, radiation dosimetry and radiation protection. And this fact it is extremely important because although some scientists suggested that the release of radioactive particles was "a peculiarity of the Chernobyl accident" just after the reactor accident, radioactive particles containing refractory radionuclides have been released following a series of past nuclear events being more common that generally expected. In particular, whenever refractory radionuclides are released to the environment following nuclear events, radioactive particles should be expected (Salbu et al., 2018).

In areas affected by particle contamination, the radioactive contamination will be unevenly distributed, the inventories can be underestimated, and the assessment or impact and risk to human health and to the environment can be biased and suffer from unacceptability large uncertainties if radioactive particles are ignored.

The underestimation of the inventories is due to the refractory behaviour of the radioactive particles generated in a great number of nuclear events. It is not uncommon a partial dissolution of the radionuclides presents in the analysed aliquot if the presence of particles is not considered and the radiochemical procedure applied is not adapted to this reality.

The uneven distribution of the radioactive particles in the affected ecosystems generates also inherent difficulties related with the representativity of the aliquot collected to evaluate the degree of contamination of the affected ecosystem. In heavily contaminated ecosystems with the radionuclide contamination mostly present in particulate form, differences even of several orders of magnitude can be found between aliquots taken in the same area. Even more, these differences are found between sub-aliquots taken from a single aliquot in a defined sampling point (Jimenez-Ramos et al., 2008). The design of proper sampling strategies, taking into consideration the mentioned representativity problem should be defined.

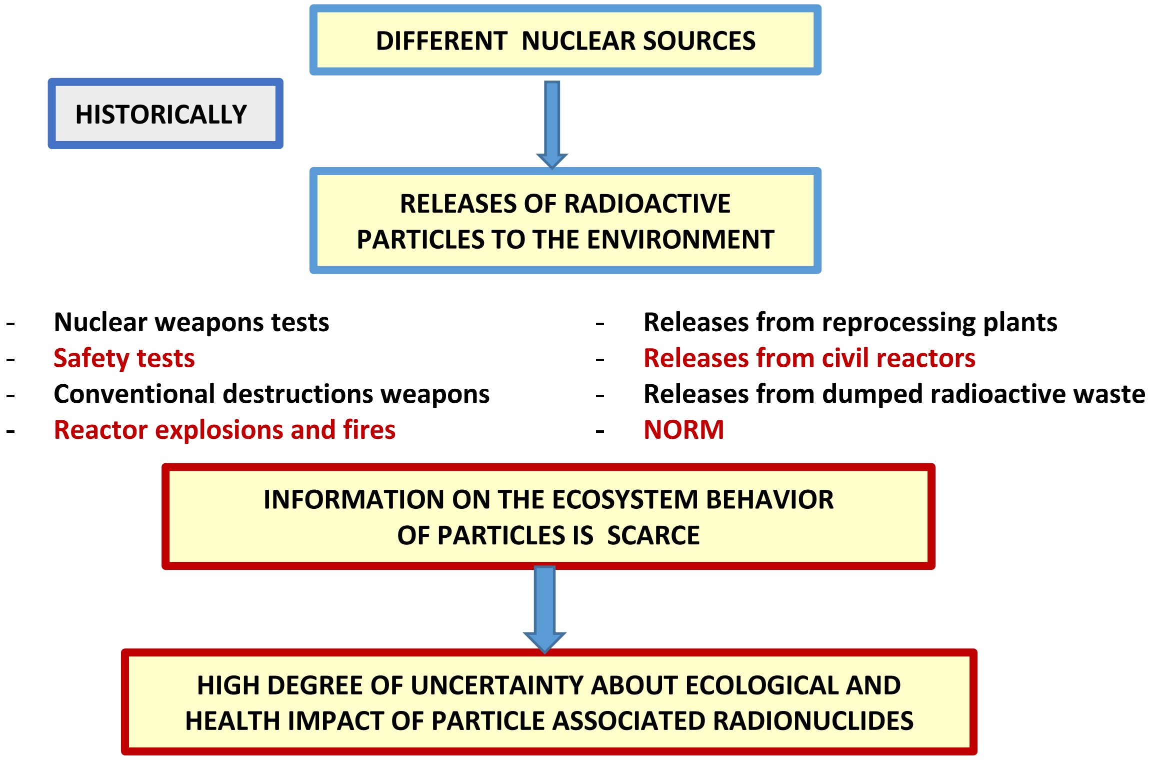

Figure 1.2.- Summary of the status associated to the radioecological research in ecosystems containing radioactive particles.

Associated to the radioactive particles generated in different nuclear events, on the other hand, it has been demonstrated that characteristics such as elemental composition depend on the source, while other characteristics such as particle size distribution, structure, and oxidation states, with high influence in the ecosystem transfer, depend also on the release scenarios, i.e., on the way that they were released to the environment and on the characteristics and particularities of the area contaminated. (Salbu et al., 2018)

The importance of the released scenario in the characteristics and behaviour of the generating radioactive particles was clearly evidenced in the radioactive particle contamination with origin in the nuclear reactor of Chernobyl. Without the aim to be exhaustive, it can be indicated that associated to the Chernobyl accident, two clear different episodes of radioactive particles releases occurs: the first one, associated to the initial explosions in the reactors, disseminated in particle form part of the nuclear fuel with the uranium present in reduced form (these particles were disseminated mostly at the north of the Chernobyl complex), while a second episode of radioactive particle releases occur associated to the fires that affected the reactor in the days following the initial explosion. In this last case, the uranium in the particles was present in high valence states, i.e., more oxidized, fact not unexpected due to the fire action, and the particles were disseminated due to the prevailing winds to the west of the reactor.

Radioecological studies performed during the last twenty years in the Chernobyl particulate contaminated areas have evidenced the clearly different behaviour of the radioactive particles depending of its temporal origin (and consequently of its geographical location) (Salbu et al., 2018). While the radioactive particles disseminated in the north associated to the initial explosions have shown a quite refractory behaviour in agreement with the presence of the uranium in reduced form (the particle weathering of these particles have been very limited), the radioactive particles disseminated in the west shown a different behaviour, with a non-negligible fraction of uranium leached from the particles in accordance with the presence of this uranium in oxidized form. A characteristic of the particles such as the oxidation state influence heavily their transfer behaviour in the ecosystem where are deposited.

It is then evident, that to assess appropriate environmental impact, and risks associated, in ecosystems contaminated with radioactive particles, links must be established between the source term, the deposition, and the ecosystem transfer.

Particle weathering rates and the subsequent remobilization and ecosystem transfer of particle-associated radionuclides will depend strongly on the particle characteristics (e.g., composition, structure, oxidation states). Soil and sediment will act initially as sinks for particles and will act as diffuse source of radioactivity if particle weathering occurs. Thus, information on particle weathering rates is essential for assessing long-term consequences.

Leaching experiments can provide important data on particle characteristics, the links to solubility particle weathering rates and remobilization potential for particle associated radionuclides (and metals). Usually until now, only bulk samples (soils, sediments) have been subject to leaching, while leaching experiments of single particles are quite rare. Leaching has been made in the past by single abiotic agents, such as simulated stomach juice (0.16 M HCl) and simulated lung fluids, but it is frequent also to apply sequential extraction procedures using reagents of increasing displacement and dissolution power (Kennedy et al., 1997; Skipperud and Salbu, 2015). Alternatively, biotic leaching experiments can be made utilizing biological fluids such as incubation with rumen liquids or, even, particles can be given to animals as part of their feed in order to study their in-vivo behaviour (Kozmin et al., 2020). In this last case, the proportion of the particle dissolved before to be excreted, the internal distribution of the dissolved radionuclides in the different organs of the animal, and even the effect that can be caused if the particle is stacked in a defined point of the digestive system, can be analysed.

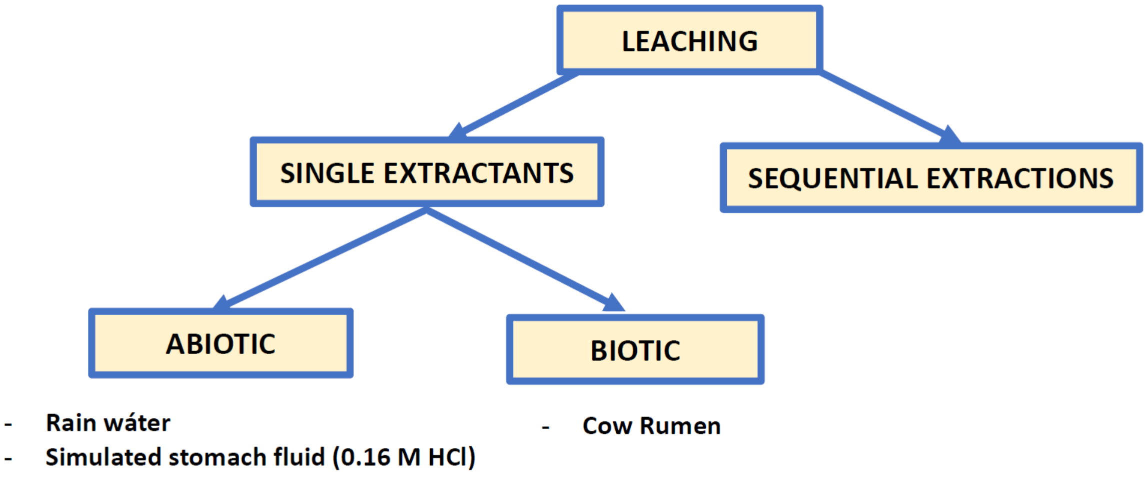

Figure 1.3.- Different types of leaching/extractions procedures applicable to isolated radioactive particles and radioactive particle contaminated soil aliquots.

Within the EU-funded RATE project, and in collaboration with the IAEA Coordinated Research project on Hot Particles, a leaching protocol has been established with the aim of identifying key parameters affecting properties of particles when exposed to a variety of different water qualities, temperatures and single abiotic leaching agents (COMET, 2017). This protocol will be presented and detailed in this thesis because we have been partners in both projects, and we have contributed actively in their construction (the first tests have been performed by us). When leaching experiments on single radioactive particles are performed, the same procedure should be applied on bulk samples from which the particle was isolated. This will aid the interpretation of results obtained on particle transformation processes, and also link new data to literature data.

Some data can be found in the open literature related to single abiotic leaching of soils and sediment samples heavily contaminated with radioactive particles. Lind et al., 2006, performed 0.16 M HCl leaching experiments with samples from a series of different sources trying to link information on site-specific particle characteristics to potential bioavailability and extraction kinetics. The cumulative extracted fraction (%) of ^{241}Am in soils collected in Semipalatinsk test site was very low, with 72-85% of the ^{241}Am remaining unextracted, even after 168 h of contact with the simulated stomach juices. The fraction of ^{241}Am dissolved at the end of these experiments were much lower than for the observed in contaminated Irish Sea sediments affected by releases from nuclear reprocessing at Sellafield (80-86 % dissolution after 168 h). These last results are consistent with reported plutonium sequential extraction data for samples collected in the same areas (Lucey et al., 2004), and confirm that a large proportion of the transuranics is associated with relatively mobile geochemical phases in sediments contaminated by releases from nuclear reprocessing at Sellafield, whereas most of the derived transuranium contamination in Semipalatinsk is in a highly refractory non-labile form (Conway et al., 2009; Jimenez-Napoles et al., 2004).

In areas affected for radioactive particle contamination, specific leaching studies should be performed to gain extremely important information for ecosystem transfer prediction and radiological impact assessments. Every nuclear event presented its own peculiarities, peculiarities that are fingerprinted in the associated radioactive particles generated. In other words, the peculiarities inherent to each nuclear event, provoke that the characteristics of the radioactive particles generated are also particular, and that consequently individual studies should be performed in order to evaluate properly their particle radioecological behaviour.

Following deposition, radioactive particles are retained in soils and sediments. Thus, the ecosystem transfer of particle associated radionuclides will be delayed compared to mobile species. But, due to particle weathering processes, particle associated radionuclides are with some delay remobilized and contaminated soils and sediments can act as diffuse sources of radioactivity in the future. A challenge is therefore to link particle characteristics to ecosystem behaviour, and to identify how environmental factors such as pH, redox, TOC and the presence of microbial activities can influence particle weathering processes.

Due to weathering of particles, associated radionuclides are remobilized and the ecosystem transfer increases with time. Thus, the distribution of radionuclides between solid and solution is a time depended process and the thermodynamic constant Kd should be replaced by a time function. Consequently, the leaching protocols stablished should have in consideration the time as a variable to be taken into account and the evolution of the amount of radionuclide transferred to the leaching agent with time should be studied.

Although recent projects have contributed with important knowledge on particle characteristics, weathering and leaching (essential for ecosystem transfer analyses), further research is clearly needed to address the challenges identified. As particle releases were seen following many kinds of historic nuclear events, particle releases should also be expected from events occurring in the future (Salbu et al., 2018). Therefore, existing radiological accidental and release sites should be utilized to improve the knowledge needed to link particle characteristics to sources, to transfer and to biological effects on which sound environmental assessments can be made. This is the objective of this thesis by performing leaching experiments with different abiotic and biotic leaching agents to isolated radioactive particles and associated radioactive contaminated soils collected in two areas affected in the past by non-critically accidents involving nuclear weapons (e.g., Thule, Greenland; Palomares, Spain), These two areas will be described in next chapter, together with a description of the nuclear events that provoked the dispersion of radioactive contamination in them and a summary of the main findings until now, concerning the characterization and radioecological behaviour of the remaining radioactive contamination.

In both nuclear events (Thule and Palomares) the source was the same (nuclear weapons with similar composition), the processes of dissemination of the radioactive content were also very similar, but the scenario where the radioactive particle contamination was deposited it is clearly different: a semi-dessertic terrestrial area affected by Mediterranean climate in the case of Palomares, and an artic area in the case of Thule. The similarities and differences found in the characterization of the radioactive particles and in the performed leaching experiments with isolated particles and with contaminated soils from the two areas, will allow evaluating the influence of the ecosystem affected by the radioactive contamination in their radioecological behaviour.

At this point, it is necessary to remark that the presence of radioactive particles in the environment is not a phenomenon associated in exclusivity to nuclear events and artificial radionuclides. Although historically the presence of radioactive particles has been associated to nuclear events, in a lot of high natural background radioactive areas distributed over the world, and in association to the mining and processing of some minerals and raw materials with elevated amount of natural radionuclides, the presence of the mentioned radionuclides as particles is frequent, containing the great majority of the radioactivity present in the associated soils (García-Tenorio et al., 2018). Particularly, in the high natural background radioactive areas with the presence of highly radioactive particles and aggregations, the performance of leaching experiments will have the same justification and will provide the same type of information that in the areas affected by nuclear events, being then possible to gain information about the ecosystem transfer of radionuclides, its magnitude and kinetics. This will allow decreasing the uncertainties in radioecological models adapted to these particular ecosystems, and a more proper evaluation of the radionuclide transfer between different compartments (soil-water, soil-plant, etc). For that reason, the leaching experimentation have been also extended and applied in a high natural background radioactive area located in Southern Norway, the Fen area, which will be described also in detail in the following chapter.

Our work in this thesis have been centred to perform leaching experiments in a great variety of ecosystems and samples, once a well stablished protocol was clearly defined between the specialists participating in the two coordinated (EC and IAEA) research projects previously mentioned. No radionuclide extraction or radionuclide sequential extraction procedures have been applied.

Extractions of radionuclides in soils and sediments have frequently been applied during the years to identify associated radionuclides. A major objective has been to obtain the bioavailable fraction mimicking plant uptake, but no extracting agent so far is able to predict plant uptake without large uncertainties. A compilation of different extractant reagents used to evaluate the bioavailable fraction in soils and sediments are cited and referenced in Jimenez-Ramos et al., 2008.

Extractions can be performed with individual reagents or sequentially using reagents with increasing displacement and dissolution power. Among sequential extraction procedures available, the one developed by Tessier et al., 1979 with modifications (Kennedy et al., 1997, Szabo et al., 1997, Skipperud et al., 2000) has proved to be the most useful. However, sequential extraction techniques have been subject to criticisms, especially due to the interpretation of analytical results. Instead of referring to the displacement or dissolution per the reagents (e.g., pH sensitive fraction, weakly reduced fraction, weakly oxidised fractions) several authors refer to a presumed mineral phase (e.g., bound to carbonates, bound to Fe and Mn oxides, bound to organics) without proving that the referred phases are present and are fully or partially responding to the specific chemical treatment. The results obtained from the application of sequential extractions are quite difficult to interpret, being in most cases only possible to obtain qualitative information that can be easily obtained with simpler leaching experiments.

Structure of the manuscript

This thesis is formed by a total of seven chapters including this Chapter 1.

Chapter 2 introduces the three analysed sites. Two of them correspond to sites affected by contamination provoked in nuclear weapon accidents (Palomares and Thule) while the third one is an area with the presence of radioactive particles of natural origin, The Fen area, which corresponds to a High Background Natural Radiation area where in some specific zones mining and other anthropogenic activities took place. In all the cases, the sites were described from a geographical, geological, and climatic point of view, and previous works describing the levels and distribution of the intended radionuclides, as well as, the ones analysing and characterising representative radioactive particles were summarized.

Chapter 3 compiles all the experimental techniques that were used and refined in this thesis. It describes, on the one hand, the different leaching protocols applied to radioactive particles and soils and the different adaptations of these protocols associated to the use of cow rumen or synthetic lung fluid as lixiviation agents, and on the other hand, it describes the two main experimental measurement techniques used : accelerator mass spectrometry (AMS) for ^{239}Pu, ^{240}Pu and ^{236}U determinations associated to the Palomares and Thule sites, and inductively couple plasma mass spectrometry (ICP-MS) for elemental U and Th determinations in the Fen area.

In Chapters 4 (Palomares), 5 (Thule) and 6 (Fen) the results of all the leaching tests performed in each site are presented and discussed, trying in all the cases to obtain some conclusions concerning the radioecological behaviour of the radionuclides present in particulate form. A special section in Chapter 5 was devoted to the comparison of the results obtained in Palomares and Thule, because both sites were affected by similar accidents, involving similar weapons, and the physicochemical characteristics of the formed particles were similar. Varying only the extremely different ecosystem characteristics (artic versus semi-desertic) of the sites that are storing the particles for more than 50 years.

All the conclusions obtained from the previous chapters are compiled and summarised in the chapter 7 as a final chapter. One key message will be highlighted: the importance to have in consideration the speciation aspects in any site affected by radionuclide contamination or by the presence of enhanced amounts of natural radionuclides. Any modelling work trying to describe the behaviour and transfer of radionuclides between the different compartments of the analysed ecosystem, should consider the possible presence of the radionuclides under analysis in particulate form, and their possible different behaviour in comparison with the reflected one in the models based in the use of default parameters.

Chapter 2

Sites and events analysed

The Palomares nuclear event

The site, the accident

Palomares is a small village sited at SE of Spain, close to the coastline. The area surrounding Palomares can be considered a semi-desertic plain. The temperature range is usually 12°C - 42°C in a year and the rainfall is scarce, although when occurs can generate flooding with transportation of matter to the sea, due to the low permeability of the terrain.

On 17th January 1966, two USAF aircrafts, a B-52 bomber and a KC-135 tanker crashed on the Palomares area after collision during a refuelling operation in air. The two aircrafts were destroyed, while a total of four thermonuclear weapons transported for the bomber dropped, after its immediate liberation following security protocols at the moment of the accident. Two of these weapons were recovered intact due to the correct action of their associated parachutes. The other two, due to the firing of the parachutes, impacted on land at high velocity, experimenting the detonation of their chemical explosives and the dissemination of the nuclear fuel in the form of Pu and U oxides.

The exact location where the thermonuclear bombs either safely landed or crashed are shown in the map of Figure 2.1. The two weapons that crashed were called weapon 2 and weapon 3. Weapon 2 crashed in a valley, 1.7 km west from the centre of the village, while weapon 3 crashed at the east of the village just in the limit with the urban nucleus.

Just after the accident, the US army identified the most affected zones and defines a line enclosing the area that can be considered contaminated, called “line Zero” (this line is also shown in Figure 2.1).

Immediately, the US army performed different actions in order to clean the contaminated affected area. In these operations, 1400 Tons of surface soils and vegetation were removed, introduced in barrels and transported to USA where they were stored in the Savannah River Depository Facility (South Caroline). (Sancho and García-Tenorio, 2019).

The decontamination of the affected area was not complete, due to the extension of the contamination, and in some cases due to the difficulties in the access to some areas. The superficial contaminated soil was only removed and transported to USA in the areas more contaminated. In most of the contaminated area the soil was simply ploughed, and the contamination distributed in the upper 20-30 cm.

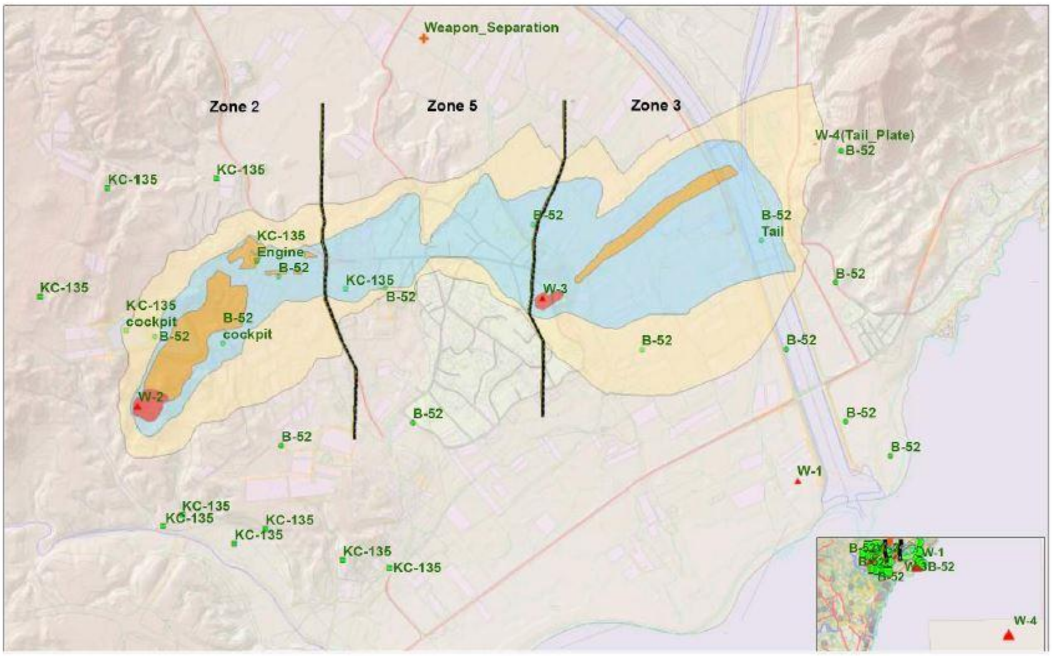

Figure 2.1. Map of the area affected by the Palomares accident. Impact points of the different weapons are marked. In addition, the so-called line-zero is marked, confining the area with non-negligible levels of radioactive contamination. The most contaminated areas were the marked in red, followed in the degree of contamination by the areas marked in orange and afterwards by the areas marked in blue (Sancho and Garcia-Tenorio, 2019).

Due to existence of this remaining contamination, several measurement programs started in order to survey the population, the animals, the food generated in the area and the different compartments of the ecosystem affected. In particular, and for the relation with this thesis, we should indicate that few months after the accident it started an Environmental Radiological Surveillance Program, that with some changes and adaptations to the socio-economical evolution of the Palomares area, has been maintained until now.

The Surveillance program was challenging due to the peculiarities of the contamination provoked by the accident. Due to the conventional explosion of the two weapons their nuclear fuel was dispersed, formed by a mixture of plutonium and enriched uranium. Plutonium isotopes, ^{235}U and ^{241}Am (as a daughter of ^{241}Pu) where the radionuclides dispersed, most of them pure alpha emitters. Then, the determination of the contamination levels in the samples included in the surveillance programs demanded of the application of radiochemical procedures and the conventional use of the alpha-particle spectrometric technique.

The fingerprint of the accident is reflected in characteristic isotopic ratios. The nuclear fuel dispersed in the Palomares accident are characterized by a quite low ^{238}Pu/$^{239+240}$Pu activity ratio and also by a low ^{240}Pu/^{239}Pu atom ratio (the so-called weapon grade plutonium). The nuclear fuel was formed by a mixture of the fissile radionuclides ^{239}Pu and ^{235}U, with low presence of ^{238}Pu and ^{240}Pu because they act as poisons in the weapons due to its tendency to absorb neutrons.

Environmental Radiological studies in Palomares

Initially, the surveillance program included radionuclide determinations in superficial soils, aerosols (using for that 4 sampling stations), vegetation (mostly edible vegetables produced in the contaminated area) and products of animal origin (as cow and sheep milk).

The results of these surveillance programs indicate that (sancho and García-Tenorio, 2019):

a) the terrestrial contamination did not experiment any appreciable mobility or migration along the years, being confined in the upper ploughed cm of the soils, or in the uppermost cm of the unaltered soils.

b) the transfer of radioactive contamination from soil to plant via uptake was negligible, (if radioactive contamination was detected in some vegetation samples, this contamination was superficial and associated to the deposition and attachment of contaminated soil dust).

c) the transfer to animals and associated products is negligible and with null radiological impact.

d) the main route of impact in the population was associated to inhalation of contaminated dust, because due to the semi-desertic conditions in the area, the resuspension of contaminated dust play a non-negligible role.

In any case, the dose to the population associated to the remaining contamination of the accident is clearly below the limits fixed by the Spanish Regulatory Body, limits that on the other hand, are simply transposition of the limits fixed in the European Union Directive.

In 1986, with the Nuclear Spanish Regulatory Body fully in operation, and due to important changes in the affected area (construction of two artificial dams in the zone, exponential growing of the intensive agriculture using greenhouses, the expansion of the Palomares village…) it was decided to perform a re-evaluation of the inventory of the remaining contamination with the information gained in the surveillance programs. This re-evaluation concluded that the remaining contamination in the area was higher than the initial estimation.

The result of the re-evaluation conducted to the Nuclear Spanish Regulatory Body to (Sancho and García-Tenorio, 2019):

a) Define clear use restriction criteria in the area, defining limits for total of partial use restrictions of the land based in dose estimations.

b) Promote a very detailed (high-resolution) extensive radioactive characterization of the upper 15 cm of the soils in all the affected area.

This extensive characterization was performed in 2006 by CIEMAT and includes also as a novelty, the radiometric characterization of the hilly area located between the Palomares and the sea, not included initially inside the line zero due to the difficulties of access and the null use given to this area at the moment of the accident.

The results obtained in the mentioned extensive contamination are shown in Figure 2.2. In a total of 20 ha the levels of contamination overpass the limit criteria for total use-restriction and for that reason diverse zones were fenced (see Figure 2.2, where the red colour is associated to total use restriction and the yellow to partial use restriction).

One of the main peculiarities of the radioactive contamination in the Palomares area is its inhomogeneity, fact that made extremely difficult the construction of the extensive contamination map. This inhomogeneity is due to the fact that, most of the radioactive contamination at the moment of the accident, was dispersed as radioactive particles with a quite uneven distribution in the contaminated soils. Experiments performed by Jimenez-Ramos et al., 2008 collecting the upper 5 cm in a sampling point covering an area of 1 m^2. Distributing the material in 6-8 different aliquots indicated that the levels of ^{241}Am (used as a fingerprint of the radionuclide contamination due to the accident) varied between the aliquots even two orders of magnitude. The uneven distribution of fuel particles between the different aliquots is the reason behind the enormous differences found in the ^{241}Am concentrations of the different aliquots.

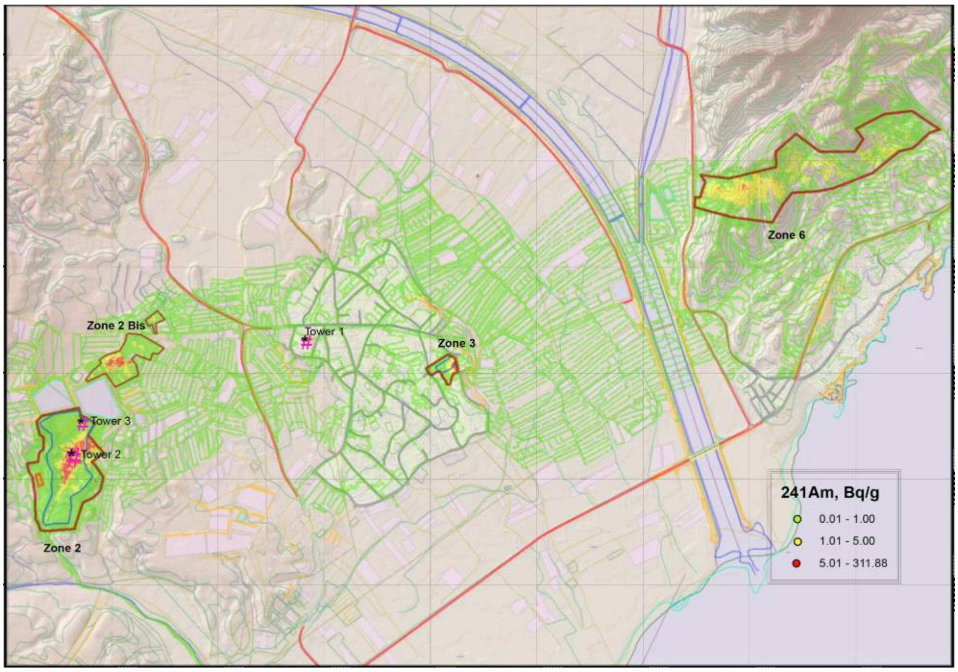

Figure 2.2.- This map shows the extensive radioactive characterization performed in Palomares. Zones 2 and 3 are the most contaminated areas (zone's number given by the contaminant weapon in each area) and zone 6, hilly area affected by the deposition of radioactive contamination in the interaction between the formed radioactive cloud and the terrain. (Taken from Sancho and Garcia-Tenorio, 2019)

In radioactive contaminated Palomares soils, some of the particles have been isolated for its posterior characterization. In some cases, isolation of radioactive particles has been performed applying simply the autoradiography technique. Clear "punctual" signals, due to their high radioactive content are generated by each radioactive particle. In this way, it can be localized and isolated. Alternatively, the isolation of particles has been performed by using gamma-ray spectrometry and applying the binary division technique.

In the binary division technique, each soil aliquot with high counting rate in the gamma-ray peak of ^{241}Am at 59,5 keV is divided in two halves, being both measured. The process continues rejecting the half aliquot with low signal of ^{241}Am and continuing with the half where the high ^{241}Am signal remains. This is an indication of the presence of radioactive particles (in general, in one of the two fractions remains more than 90% of the ^{241}Am counting rate). This binary division process continues applying the same protocol, until finish with a manageable amount of material (some micrograms) and apply of radioactive particles identification and characterization techniques.

The remaining material can be placed in a stainless steel planchette, adhered to a double side carbon film, one side with the remaining material and the other to the planchette. The identification process of the radioactive particle can start by applying for that non-radiometric, non-conventional techniques in the fields of radioecology and radiological protection.

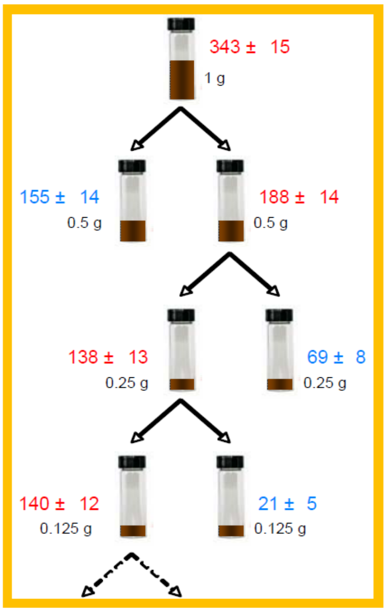

Figure 2.3.- Scheme of the binary division technique applied for isolation of radioactive particles

Scanning Electron Microscopy technique (SEM) have been used for the identification of radioactive particles originated in the Palomares accident, as the more typical technique. It has been applied between the different soil background particles adhered to a carbon film. This technique will be described in more detail in the chapter of materials and methods because it has been used in this thesis. As a summary, this technique can identificate Palomare's radioactive particles analysing the signals generated by the collection of the electrons impinged over the sample and experimenting back-scattering (Back-scattered Electron Image, BEI).

Isolated particles can be identified by the high bright that they generate due to the high rate of back-scattered electrons provoked in the collision of the electron beam with the material of the radioactive particles (plutonium and uranium, elements with very high Z) in comparison with the signal provoked by the back-scattered electrons generated in the collision of the electron beam with the soil background particles. In Figure 2.4 two typical BEI images obtained in the identification of Palomares radioactive particles are shown, where the discrimination and high resolution of this identification technique is clearly evidenced.

In combination with Scanning Electron Microscopy, the application of Energy dispersive X-ray analysis (EDX) allows the verification that the identified particle is a radioactive particle. In this technique, the characteristic X-rays generated by the excitation of the elements provoked by the collision of the electron beam are collected and the analysis of the obtained spectra allows to identify the elements present mostly in the surface of the impinged particles and even to perform their quantification (X-ray microanalysis, XRMA).

Once radioactive particles have been isolated, several solid-state speciation techniques can be used to characterize properties as their elemental composition, oxidation states, crystallographic structures, etc. In addition to the previously commented use of the combination SEM-EDX, alternative techniques such as secondary ionisation mass spectrometry (SIMS), particle induced X-ray emission (μ-PIXE) , X-ray fluorescence (μ-XRF) and laboratory based nano tomography can be utilized to obtain information on aspects such as distribution of elements below the particle surface, spatial distribution of densities, etc.

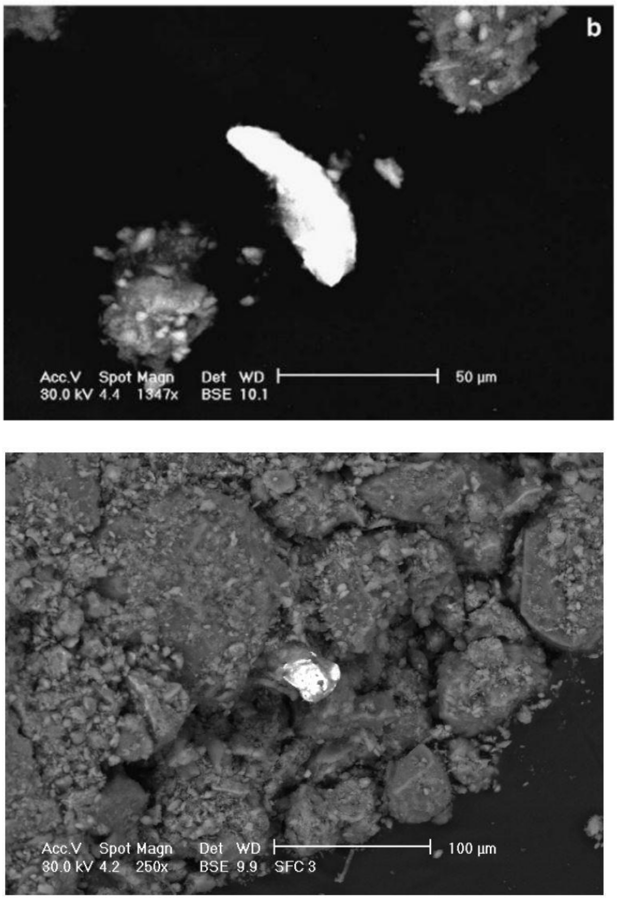

Figure 2.4.- Scanning Electron Microscopy (SEM) Images obtained by collecting the back-scattered electron signals (BEI mode) provoked by impinging the electron beam onto a carbon film containing Palomares soil. The radioactive particles are clearly identified with high resolution.

Special mention deserves the synchroton radiation (SR) nanoscopic and microscopic X-ray techniques because they represent state-of-the-art technologies in the characterization of radioactive particles. SR fluorescence analysis can give information on the 2-dimensional or 3-dimensional elemental distribution within individual particles, micro-X-ray diffraction (μ-XRD) gives information on the 2 dimensional or 3 dimensional crystallographic structures of the particles, and micro-X-ray absorption near edge structure spectrometry (μ-XANES) provides information on the oxidation state of the matrix elements at micrometre scale. A compilation of the analytical tools used for the identification, isolation and characterization of radioactive particles can be found in Table 2.1.

All the techniques mentioned until now are characterized by being non-destructive, and consequently can be applied sequentially or even in some cases in parallel to obtain the maximum possible information. However, no one of these techniques give information about isotopic composition.

In Palomares radioactive particles, the characterization of isotopic ratios such as ^{240}Pu/^{239}Pu ^{235}U/^{239}Pu and ^{238}Pu/$^{239+240}$Pu requires the application either of mass spectrometric techniques (accelerator mass-spectrometry, AMS, or high-resolution inductive couple plasma mass spectrometry, HR-ICPMS) for long-lived radionuclides, or radiometric techniques (alpha-particle spectrometry, gamma-ray spectrometric techniques) for radionuclides such as ^{238}Pu and ^{241}Am with shorter half-lives. The information gained determining these isotopic ratios is very rich because are evident fingerprints of the origin of the particles, but the most suitable isotopic determination techniques have the disadvantages that are destructive. i.e. needs the dissolution of the particle.

Identification and isolation
- *Digital autoradiography*
- *Repeated sample division with gamma-ray spectrometry*
- *Direct identification in SEM and confirmation by XRMA*
Characterization
- *SEM-XRMA (size, surface morphology, surface elemental composition)*
- μ*-PIXE (Elemental composition, 2D-distribution, depth information)*
- μ*–focused XRF (Elemental composition, 2D-distribution, depth information)*
- *Confocal* μ*-XRF (Elemental composition and 3D distribution)*
- μ*-XANES (oxidation states distribution)*
- *m-XRD (crystallographic information)*
- *nano-CT (spatial density distributions)*
- *Accelerator Mass Spectrometry (*^{240}*Pu,* ^{239}*Pu determinations)*
- *HR-ICPMS (*^{240}*Pu,* ^{239}*Pu,* ^{235}*U,* ^{238}*U,* ^{234}*U determinations)*
- *Alpha-particle spectrometry (*^{238}*Pu,* $^{239+240}$*Pu determinations)*
- *High-resolution Gamma-ray spectrometry (*^{241}*Am determinations)*

Table 2.1.- Analytical tools available in Palomares radioactive particle research (taken from Salbu et al., 2018)

Several studies have been performed in the past in relation with the characterization of radioactive particles collected in the Palomares area, all of them performed in this 21st century, at least 35 years after the accident. The size of these particles varies from submicron to fragments above 1 mm. The particles are a mixture of enriched U and weapon-grade Pu material (Jimenez-Ramos et al.,2007) in correspondence with the fact that the nuclear weapon fuel contain mostly 20% enriched U with an average Pu/U mass ratio of 0.8 (Sancho and Garcia-Tenorio, 2019). SEM-EDX and SR-based micro-XRF mapping indicated that the U and Pu were not homogeneously distributed in the particles with Pu/U mass ratios ranging between 0.5 and 1.5 (Lind et al., 2007).

Based on micro-XANES studies it was also concluded that the particle matrices are U and Pu mixtures, most probably in the form of oxides/hydroxides. The oxidation state of U seems to be predominantly +IV (UO_2) with a minor and variable contribution of higher oxidation states (U_30_8) while Pu seems to be as Pu(III)/Pu(IV), Pu(IV)/Pu(V) or a mixture of all the three oxidation states (Lind et al., 2007).

Radioactive particles from Palomares were used also for the comparison of two micro-beam X-ray emission techniques for the analysis of actinide elemental distribution in microscopic radioactive particles: particle induced X-ray emission with nuclear microprobe (μ-PIXE) and synchrotron radiation induced X-ray fluorescence in a confocal alignment (confocal SR μ-XRF). The results from both techniques showed a very good agreement being additionally proved the suitability of both techniques for the 3D analysis of the particles with good resolution (Jimenez-Ramos et al., 2010).

The morphology of particles is on the other hand generally granulated, some of them presenting well defined fractures and some of them having high porosity (as it is evidenced in the Figures 2.5 and 2.6).

In the most contaminated areas, a high proportion of the particles are adhered/coated with inert soil material, forming solid aggregates with several decens of micrometer size. The particles due to their fragility have first the tendency to be fractionated in smaller fractions, but at the same time tends to form aggregates with soils increasing their size. This combination is extremely important because the final evidence is the presence of aggregates that with the mentioned sizes cannot be resuspended by winds and consequently cannot be inhaled by the public and wildlife.

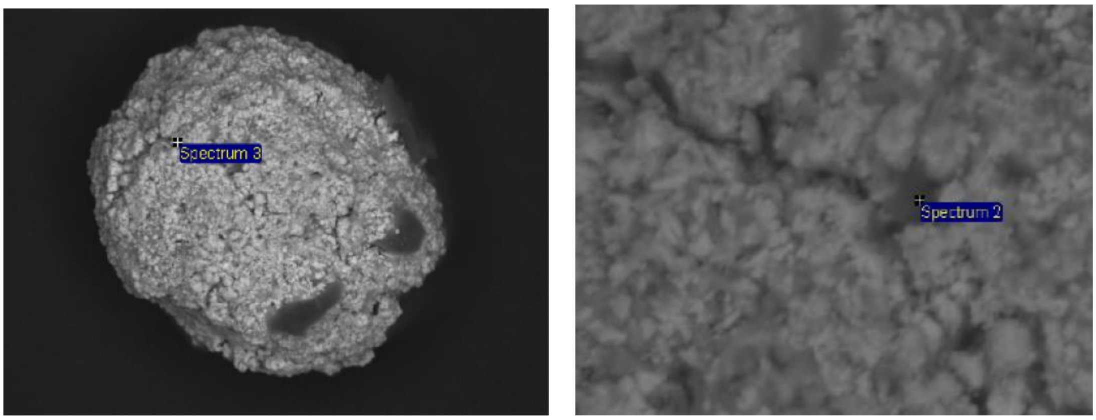

Figure 2.5.- Left: Spherical radioactive particle from Palomares (diameter of 100 micrometers). Right: High-resolution image of a small area of the particle where the granulated morphology is evidenced (COMET, 2017).

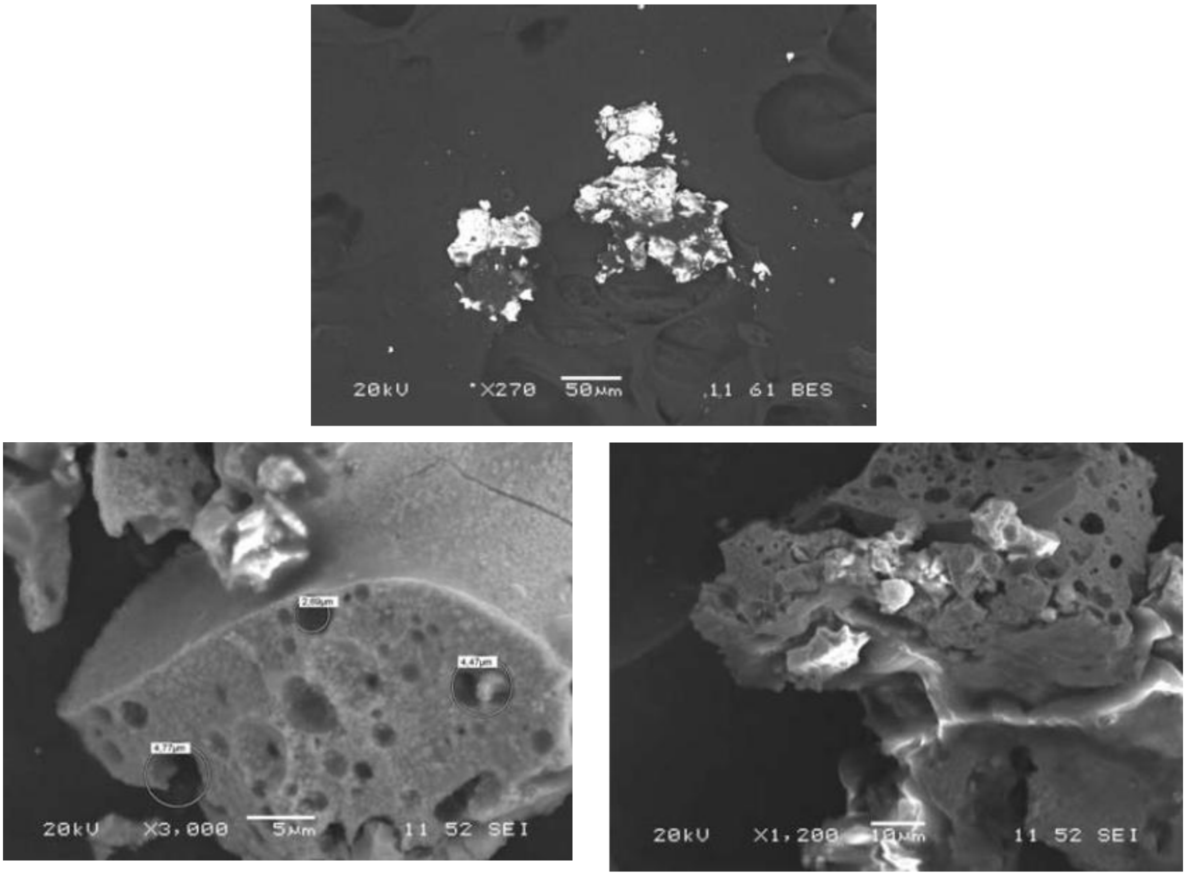

Figure 2.6.- Up: A very fragile particle of Palomares that experimented their fractionation during its mounting onto the carbon tape previous to SEM analysis. Down: High-resolution images showing how porous is this particle and giving additional evidences about their fragility. (Vioque, private communication).

In some Palomares particles the different isotopes values have been determined: ^{238}Pu/$^{239+240}$Pu activity ratios by alpha-particle spectrometry (Aragón et al., 2008), ^{240}Pu/^{239}Pu atom ratios either by AMS (Chamizo et al., 2006), by HR-ICP-MS (Lind et al., 2007; Pollanen et al., 2006), or even by high-resolution gamma-ray spectrometry (Jimenez-Ramos et al., 2010), ^{241}Am/^{239}Pu activity ratio by using LEPS and ^{241}Am/$^{239+240}$Pu by alpha-particle and gamma-ray spectrometry (COMET, 2017) between others have been determined. The values clearly indicate the fingerprint of weapon-grade plutonium with little massic presence of Pu isotopes different that the fissible ^{239}Pu. Typical values for the mentioned activity ratios in Palomares particles are compiled in Table 2.2

Ratio	Value
^{238}Pu/$^{239+240}$Pu activity ratio	**0.018 (2016)**
^{240}Pu/^{239}Pu atom ratio	**0.056 – 0.066**
^{241}Am/$^{239+240}$Pu activity ratio	**0.31 (2016)**
^{241}Pu/^{241}Am activity ratio	**3 (2008)**

Table 2.2.- Isotopic ratios determined in isolated Palomares radioactive particles. Between brackets the year to which the indicated results are referred.

Finally, it is interesting to comment that although the great majority of the radioactive particle remaining in the Palomares area are still present associated to the soils where they were deposited, some radioactive particles of small size has experimented resuspension at it has evidenced by their presence in the air-filters collected periodically in the contaminated area, and some radioactive particles have been incorporated by some species of the autochthonous biota.

The existence of small size radioactive particles have been detected in the faeces of snails collected in the contaminated areas, fact that should not be considered surprising because these gastropods eat soil as a fraction of their diet in order to extract the organic compounds associated as well as the essential elements that need for the growing of the shells: Even, as it shown in Figure 2.7, Palomares radioactive particles have been found embedded in the surfaces of some snail shells.

Radioactive particles have been identified, isolated and characterized also in faces of rabbits and hairs living freely in the area. These particles can be ingested directly because the particles are adhered to the vegetation consumed by these leporines or indirectly because the radioactive particles can be adhered to the faeces generated by these animals before to be consumed again (the rabbits and hares eat their own faeces in order to maximize the extraction of the nutrients from the vegetation eaten). These particles in most of the cases have been found inside the faeces indicating this fact that the particles have been ingested at least once time by the rabbit/hair going through all the digestive system.

It is not common to find radioactive particles in Palomares associated to vegetation. In the few cases that have been detected, they were found adhered generally to the leaves of surfaces of the fruit/vegetable after experiment its transportation together with resuspended soil material.

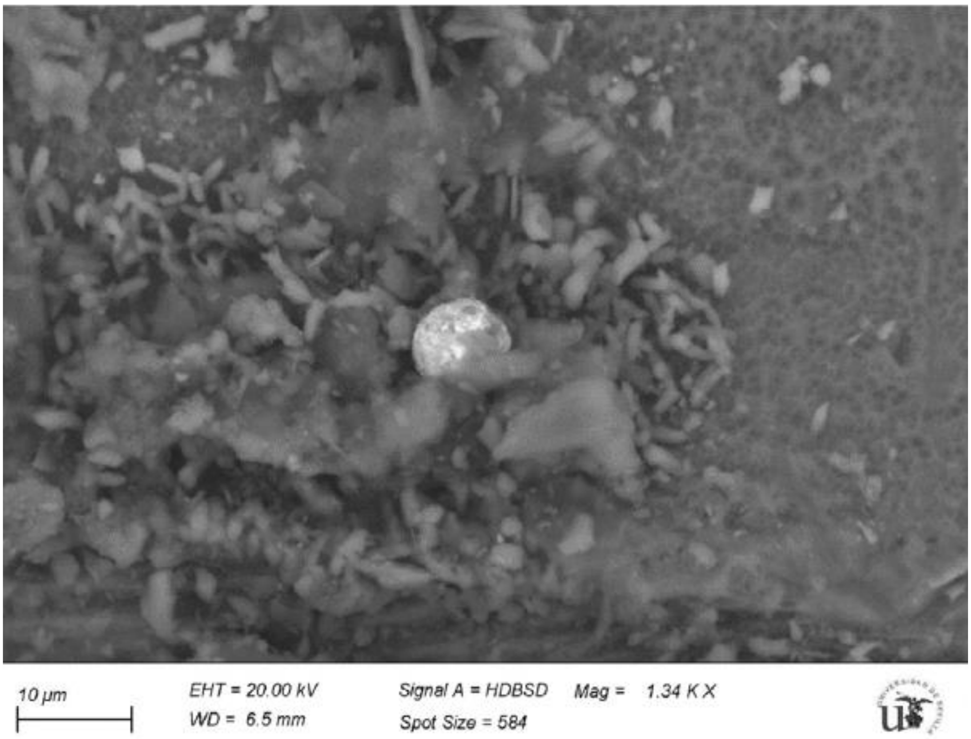

Figure 2.7.- SEM image of a radioactive Pu containing particle embedded in the shell structure of a free-living snail collected in the Pu contaminated terrestrial area of Palomares (Salbu et al., 2018).

Radioactive particles from Thule

The accident, the site

In January 1968, only two years after the Palomares accident, another B52 airplane crashed on the sea ice. It was about 12 km west of the Thule air base, NW of Greenland. The bomber was carrying four nuclear weapons. The impact triggered the conventional explosives within the weapons and the explosion pulverized and disseminated the fissile material (Eriksson et al., 2008).

The debris was scattered around the point of impact and some square kilometres of the ice were contaminated.

During most of the 20th century the accident was classified as “marine”. That’s because it was believed that the benthic marine environment received the fraction of the weapon material that was not recovered from the ice during the clean-up operation following the accident and, probably, also a fraction directly injected during the accident, as the impact caused part of the ice break up (Eriksson et al., 2008). However, at the beginning of this century it was confirmed the presence of radioactive contamination in some terrestrial areas at the south of the Thule base, being associated initially this fact to the possible transport of particles and aerosols by the smoke generated just after the accident that took this direction or by redistribution of contaminated snow during the first weeks or months, after the accident followed by snow melt.

However, the majority of the fissile material that was not recovered can be found within the sediments of Bylot Sound (Aarkrog, 1970), being estimated that the residual contamination in the bed sea is about 10 TBq of ^{239}Pu, i.e., about 3.8 kg (Eriksson, 2002). The Pu contamination is primarily found within a 6 km radius form the point of impact and Pu is to a certain extent present as radioactive particles, having a wide size distribution and a median diameter of 2 μm (Holm et al., 1987).

This residual fissile material shows relatively low solubility (Dahlgaard et al., 2001), because a clear signal from the accident in the water column (3-6 times higher than background) has only been identified in near bottom samples collected at the point of impact, being attributed mostly to resuspension of contaminated sediments. The plutonium found in brown algae collected 30 years after the accident in the contaminated area confirms that plutonium is not transported from contaminated sediments into the surface waters in significant quantities (Dalhgaard et al., 2001)

In the bay sediments, 30 years after the accident it was possible to determine plutonium even at 30 cm depth in part due to the sedimentation rates in the analyzed areas , but mostly due the biological activity that is quite dominant. The bethic population is enormous in these sediments.

The known terrestrial contaminated areas by the Thule accident are limited in extension, although due to the characteristics of the region it cannot be assured the existence of additional areas with the fingerprint of the accident (all the area has not been surveyed). The most contaminated zone is Narsaarurk at the south west of the Thule air base (see Figure 2.8) with some spots with clear lower contamination levels in Kap Atholl and Green walley (south of the Thule base). However, in the Thule air base area and also in places located at the west and north of the impact point (Moriusaq, Saunders and Wolsterhome) the level of Pu found in the soils correspond to weapon fallout levels (Nielsen and Roos, 2011)

Figure 2.8.- Map of the Thule zones indicating the different terrestrial areas analysed (taken from Nielsen and Roos, 2011).

Inventory estimations performed in the Narsaarurk area show that up to 100 grams of Pu are present in the contaminated area, mostly in the form of radioactive particles. The distribution of the Pu contamination in the Narsaaruk area is very inhomogeneous with Pu levels ranging from background values until 1 MBq/m^2 of $^{239+240}Pu$.

The inhomogeneity observed is on the other hand not consistent with a simple pattern of fallout from a radioactive plume extending from the accident site, being probably associated to the redistribution of heavily radioactive contaminated snow followed by ice melting. Individual radioactivity particles with Pu levels of even 1000 Bq have been found. The hot spots in the contaminated areas are found in places with high moisture and organic content supporting the last-mentioned theory.

In the terrestrial contaminated areas, the Pu is found nowadays mostly in the upper 2 cm (more than 90%), reinforcing the idea of the low solubility of the Pu present in the disseminated Thule radioactive particles. The activity concentrations determined in collected air filters from the Narsaaruk area, as well in rainwater samples corresponds to background levels indicating the no resuspension of radioactive particles in the area (this fact was confirmed by performing autoradiography of the collected air filters that indicates the no presence of punctual radioactive inhomogeneities). This lack of resuspension can be understood according to the main characteristics of the most contaminated soils (high moisture and organic content) and differentiates this contaminated area from the twin area of Palomares. The inhalation route is of no concern from the radiological point of view in the case of Thule.

There is not so much available information until now about wildlife radioactive contamination in the Thule terrestrial areas investigated. It could be the main route of dose increments for the population, because the wildlife in the area provides a local source for human food. Animals foraging on locations with high levels of radioactive pollution in soil are likely to ingest amounts of radioactivity that may afterwards be transferred to man. In this sense, it is interesting to mention that vegetation in the area is scarce but generally is found on moist and wet locations where, as was commented previously, is possible to find high levels of radioactivity (Nielsen and Roos, 2011).

Wildlife of relevance in this artic area includes the musk ox (Figure 2.9), artic hare and birds. Studies performed in faeces of musk ox collected in the area show the presence of radioactive contamination, and even in some cases the presence of radioactive particles ingested by this ruminant, as it has been evidenced by screening the low-energy gamma emission of ^{241}Am (COMET; 2017).

Figure 2.9- Musk ox inhabiting in the Thule area

The Bylot Sound (the marine area in front of Thule air base) has on the other hand a rich animal life with a food web that includes from plankton and benthic biota trough fish, seabirds, whales up to the top predator: the Inuits (autoctonous habitants in the area). Investigations performed in the 80´s and 90´s showed that there is no biomagnification of Pu, i.e., that transfer of plutonium to higher trophic levels was very small, and that no radiation hazard from food to native people exists.

With all the environmental research performed in the area, it has been possible to estimate the effective doses (order of magnitude) received by the local people in Thule though different routes: Inhalation, ingestion, through wounds with insertion of soil, and through wounds with insertion of a 20 μm radioactive particle, as a result of the terrestrial contamination in the Thule area (Table 2.3). The total dose rate is clearly lower than 1 mSv/y, value taken as fixed limit for the general public, limit that if it is overpassed implies the necessity to adopt regulatory actions.

<table>
<tr><th colspan="3">Indicative orders of magnitude for radiation dose as a result of terrestrial radioactive contamination in the Thule area</th></tr>
<tr><th>Exposure pathway</th><th>Dose rate mSv/year</th><th>Notes</th></tr>
<tr><td>Inhalation</td><td>10^{-6}</td><td><i>Based on measurements with filters</i></td></tr>
<tr><td>Ingestion</td><td>10^{-4}</td><td><i>Based on models</i></td></tr>
<tr><td>Through wounds 0.1g soil</td><td>10^{-3}</td><td><i>Probability significantly lower than 1%</i></td></tr>
<tr><td>Through wounds 20 μm particle</td><td>10^{-1}</td><td><i>Probability significantly lower than 1%</i></td></tr>
</table>

Table 2.3- Dose rate estimations for the autochthonous population living in the terrestrial contaminated area (Nielsen and Roos, 2011).

The source term in the Thule accident

The characterization of the source term is extremely important when dose assessments and environmental impact studies are going to be conducted in the area. In the case of the Thule accident and during the first 30 years, the fissile material in the destroyed weapons was assumed to be a plutonium device and not investigations concerning uranium can be found in the open literature. Later on, the first investigations about the ^{240}Pu/^{239}Pu atom ratio performed by ICP-MS suggested that the debris was formed by different Pu sources (Dahlgaard et al., 2001). From these studies it was also evident that the best way to identify the characteristics nuclear fingerprints of the accident is through the study of single isolated radioactive particles, which most probably are fragments of the weapon material and consist of nuclides from one single source (Eriksson et al., 2008)

Only in 1999 appeared the first publication indicating the presence of enriched uranium also in the fissile material. The enriched U in the radioactive particles until this moment was masked for the natural U associated to the bulk material analysed. Only when isolated particles started to be analysed, the presence of enriched uranium was evidenced.

The ^{240}Pu/^{239}Pu atomic ratio has been analysed by different authors in isolated radioactive particles. Eriksson et al. 2008 analysed a total of 5 particles observing that the results indicate only a single source with the ^{240}Pu/^{239}Pu atomic ratio of 0.055 (0.008). In 2005, Lind et al. analysed three Thule isolated particles, all with equal ^{240}Pu/^{239}Pu isotopic ratio as the particles investigated by Eriksson et al.

However, Ranebo et al., 2007 studied a total of 8 Thule radioactive particles by SIMS and found four different ^{240}Pu/^{239}Pu atom ratios. Five of these particles had a ^{240}Pu/^{239}Pu atom ratio similar to the previously indicated (0.058) and the other three have ratios of 0.042, 0.036 and 0.028. Also, Dahlgaard et al (2001) by analysing highly contaminated bulk sediments samples found that the Thule debris has at least two different Pu sources. About two-thirds of the debris originated from a source having a ^{240}Pu/^{239}Pu atom ratio of 0.056, whereas about one-third of the debris showed a lower ^{240}Pu/^{239}Pu atom ratio of 0.027. All the facts indicate that different weapon sources were involved in the accident, being possible to explain the dominance of particles with an atom ratio of 0.055 to the theory that the weapon characterized by this ratio generates in its disintegration larger radioactive particles that are easier to be found and isolated because they contain high levels of radioactivity.

In some hot particles the ^{238}Pu/$^{239+240}$Pu activity ratio was also analyzed, being obtained an average value of 0.016 in 2006, typical of weapon grade plutonium. This ratio is in concordance with the obtained ones in the analysis of the most contaminated sediment samples collected in Bylot sound, where the Pu with origin in the weapon tests performed in the 50´s and 60´s represent less than 1% of the total plutonium in the sample (Eriksson et al., 2008).

There are a lot of published data of the ^{241}Am/$^{239+240}$Pu activity ratios determined in bulk samples. Most of them should be taken with precaution because ^{241}Am and Pu-isotopes were determined in different aliquots and cannot be directly comparable. In many cases, ^{241}Am was determined by gamma-ray spectrometry measuring some grams of sediment, and afterwards only a small aliquot of this sample was used for Pu determination by alpha-particle spectrometry. On the other hand, it can be expected that the ^{241}Am/$^{239+240}$Pu activity ratio varied as the ^{240}Pu/^{239}Pu because ^{241}Am is a daughter of ^{241}Pu and can vary from weapon to weapon. In the case of the five isolated particles analyzed by Eriksson et al., 2008, all of them with the same ^{240}Pu/^{239}Pu atom ratio of 0.055, the mean ^{241}Am/$^{239+240}$Pu activity ratio was 0.169 (0.005) (reference date December 2001). This ratio will reach its maximum around the year 2030 and then start to decrease.

Very few data have been published about uranium in the Thule debris. Ranebo et al. (2007) show that all the particles analysed by them by SIMS have high enriched uranium mixed with plutonium. The $^{235}U/^{238}U$ atom ratio ranged from 0.959 to 1.437 in their study, in good agreement with the average value obtained for the same ratio by Eriksson et al., 2008 by analysing five radioactive particles that was 1.02 (0.06) (quite homogeneous, in correspondence with the homogeneous $^{240}Pu/^{239}Pu$ atom ratio found in these particles).

Characterization of Thule particles

In order to reduce the uncertainties of environmental impact assessments in particle contaminated ecosystems as Thule, information, as much as detailed as possible, is required on particle characteristics. Particle size, morphological structure and oxidation states of matrix elements such as U and Pu due to its influence in particle weathering rates and subsequent mobilization of radionuclides is needed (Salbu et al., 2004).

Lind et al. (2005) analysed different Thule radioactive particles that were isolated from contaminated sediments collected at Bylot Sound. The isolated single particles were characterised using scanning electron microscopy with X-ray microanalysis (SEM-XRMA) and synchrotron radiation (SR) microscopy techniques, in particular SR based micro-X-Ray absorption near edge spectroscopy (μ-XANES) to obtain information on oxidation states of U and Pu. Based on SEM, (an example in Figure 2.10). It was possible to conclude that the particle size distribution of the isolated particles ranged in the interval 20-40 μm, containing all the particles an apparently homogeneous mixture of uranium and plutonium in the particle surfaces.

The μ-XANES results on the other hand indicated that U was present as UO_2 while Pu is suspected to be a mixture of Pu(III) and Pu (IV).

In Jiménez-Ramos et al. (2010), a total of four isolated radioactive particles from Thule (see Figure 2.11) were analyzed by two different micro-beam X-ray emission techniques: particle induced X-ray emission with nuclear microprobe technique (μ-PIXE) and synchrotron radiation induced X-ray fluorescence in a confocal alignment (confocal SR μ-XRF). The results from both techniques show a very good agreement in the determination of the average Pu/U mass ratios, and in addition, indicate the suitability of both techniques for the analysis with good resolution (down to a few μm) of the Pu/U distribution within the particles.

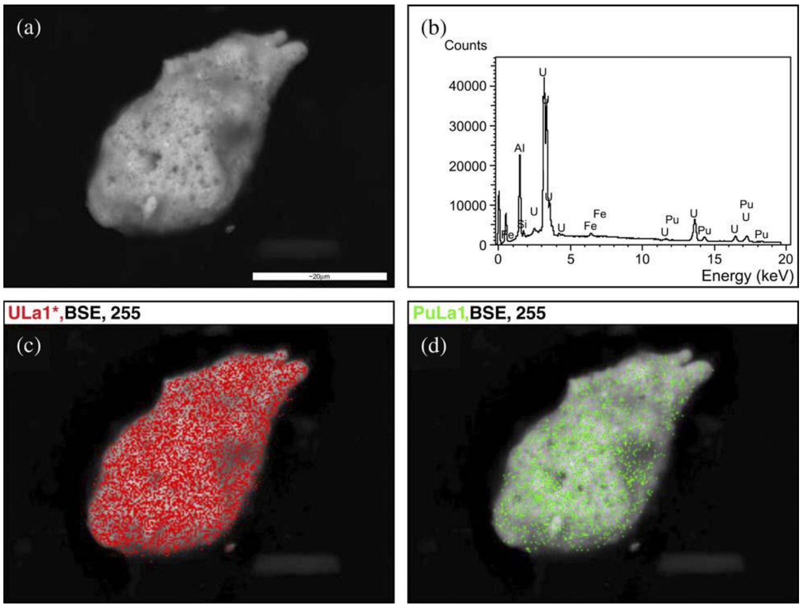

Figure 2.10.- Scanning electron microscopy of a Thule particle in BEI mode (a), elemental spot analysis by XRMA (b), and X-ray mapping of uranium (c) and plutonium (d) superimposed on the BEI mode image (Lind et al., 2005).

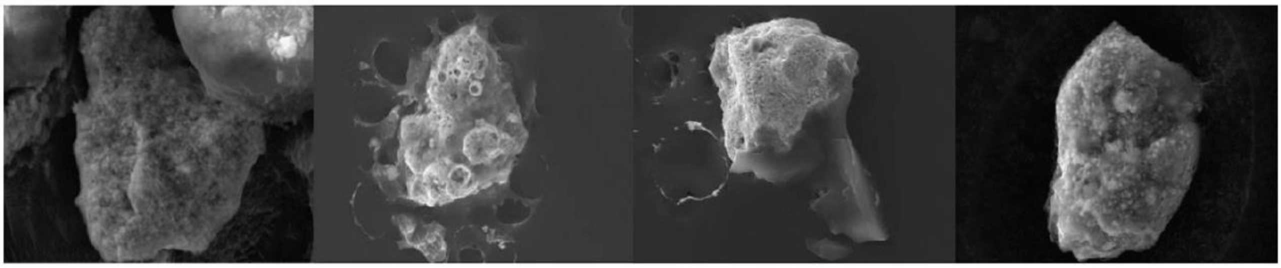

Figure 2.11.- SEM image of the four particles from Thule

In particular, the homogeneity of the Pu/U mixture in the particle matrix was studied by confocal μ-XRF. In this study it was observed that relative uncertainty of the voxel (small regions inside the particle) derived ratios in the Thule particles range from 10% to 87% indicating a heterogeneous mixture of the particle matrix. The relative uncertainty was especially high due to the surface values, being observed that if the data corresponding to the surface are removed the Pu/U mass distribution has a clearly lowers deviation. This fact indicates that the great majority of the heterogeneity in the Pu-U mixture is present at the surface of the particle. In the surface, the Pu/U are clearly higher than inside the particle, indicating the higher tendency of the U in relation to the Pu to be leached from the surface in its ecosystem interaction (it is important to remark that the four Thule particles analyzed have a marine origin as were isolated from marine sediments collected in Bylot Sound).

The preferential leaching of U in comparison with Pu it has been observed analyzing the ^{235}U$^{/239}$Pu mass ratio in isolated Thule particles versus time. As it can be observed in Figure 2.12, the ^{235}U/^{239}Pu mass ratio is decreasing with time, indicating that uranium is leaving the particle surface.

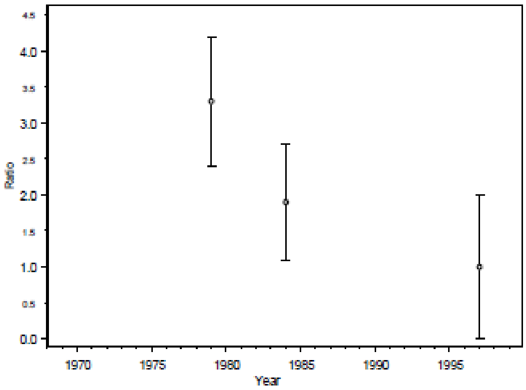

Figure 2.12.- The mean mass ratio ^{235}*U/*^{239}*Pu in particles collected during a specific year. There is a tendency that the uranium content is lower in the particles exposed to the sediment for a longer time, which would mean that there is preferential leaching of uranium from the particles in the sediments.*

We finish this section indicating that all the Thule radioactive particle characterizations that can be found until now in the open literature have a marine origin, i.e., were isolated from contaminated sediments collected in Bylot Sound. In this Thesis we will studied transformation processes of some terrestrial Thule particles. Their characterization will be shown in the chapter devoted to the results, being all the information given in this section.

The Fen Complex Area

In addition to the ecosystems affected by the release or dissemination of anthropogenic radioactive particles, there exists over the world different areas with the presence of “natural radioactive particles”. High Background Natural Radiation Areas (HBNR areas), located in several locations over the planet, are characterized by the presence of rocks containing extremely high levels of Uranium and Thorium. In these areas, the content of U and Th in the soils could be high mainly by the presence of particles broken off by weathering from the underlying bedrock.

Similar origin has the so-called placer deposits, depository areas where naturally heavy mineral particles, broken off by weathering from the rocks in which they are formed, are concentrated by the effect of gravity on moving particles. In some cases, these heavy minerals contain enhanced amounts of U and/or Th. There exist different types of placer deposits attending to their formation mechanisms (alluvial formed by streams transport, beach placers formed by wave action on the seashore, etc) and may be formed very near the bedrock from which are originated, or it could be located at great distance, being the heavy minerals mostly concentrated in different layers of strata in the depositary areas. HBNR areas in Ramsar (Iran) and Kerala (India) are paradigmatic well-known placer deposits.

The existence of NORM particle sites is challenging from a radioecological point of view, because in the past no proper radioecological evaluations were performed in the areas where are present. Inherent differences in transport, mobility and bioavailability of particulate-bound radionuclides compared to simple ions have been largely ignored. In most of the NORM particle sites it can be expected very low particle weathering rates and consequently extremely limited remobilization of the particle-associated radionuclides. No detectable transfer to plants and the food chain are normally observed.

In summary, to perform radioecological studies in HBNR areas and placer deposits is demanding because is not trivial as the natural radionuclides involved are present in the soils, mostly as particles of various sizes ranging from sizes at micrometre scale until several millimetres of diameter (fragments). The performance of abiotic leaching experiments to analyse transformation NORM particles processes is a demanding task that should be, and it is, included in this thesis to complement and complete the studies performed in sites affected by artificial anthropogenic radionuclide contamination due to nuclear events.

In this thesis, and to perform the commented NORM transformation radioactive particle studies, a high background natural radioactive area located in Scandinavia was elected: The Fen complex area.

The Fen complex area (county of Telemark, southern Norway) is an area rich in NORM, and particularly in radionuclides belonging to the thorium series. It contains significant levels of ^{232}Th, ^{238}U and progenies, as well as high levels of metals such as As, Cr, Pb and Zn. It is an intrusive complex of alkaline and carbonatite rocks of an apparent magmatic origin, with the presence of different ores at variable depths, and the presence of heterogeneous rocks, with mixtures of many minerals and a variety of elements. Thorium ore resources in the Fen Complex have been estimated to be among the world's largest, with an estimated volume of 170 000 tonnes (Popic at al., 2011),

In the Fen complex area, naturally occurring radioactive materials (NORM) are responsible for the major contribution to the total effective dose from ionizing radiation. A radiation map of the area is shown in Figure 2.13. Extremely high dose rates are observed in the central part of the site. In the Fen complex area, two legacy NORM (former mining sites) exist. They are marked in Figure 2.13, and are called Fen site and Sove site, respectively.

The former mining site Fen is located along the shores of a lake, called Lake Nordsjo, being the site formed by the rock type called rodbergite (red rock) rich in Fe and ^{232}Th. Mining for Fe was conducted during near three centuries: from 1652 until 1926. Ore exploitation was conducted in open pits and underground tunnels, many of which are still visible. (Popic, 2014)

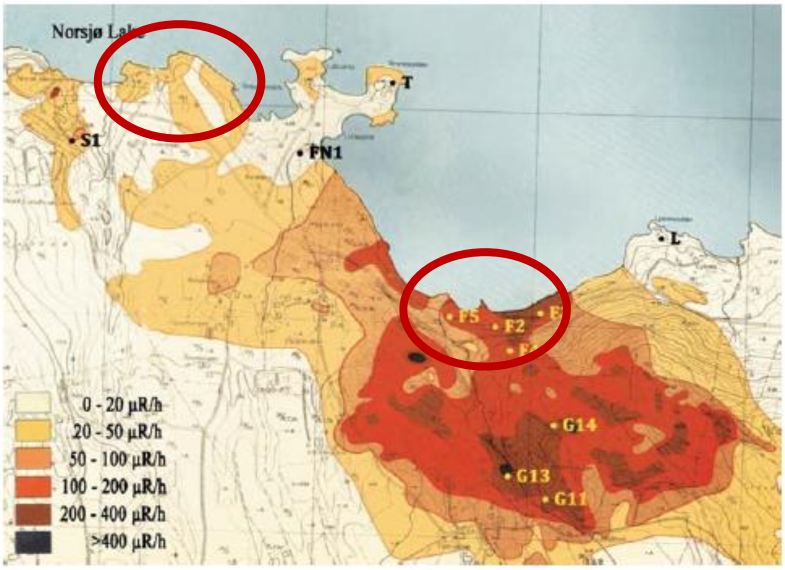

Figure 2.13.- Radiation map of the Fen complex area. Fen mining site (right) and Sove mining site (left) are marked. Taken from Popic et al., 2011.

The former mining site Sove is a decommissioned facility in the west part of the Fen complex with rock type sovite predominant in the bedrock. This sovite rock is mainly calcium carbonate with some minerals rich in niobium (until 0.4 % NbO_5) and, to a lesser degree, radionuclides ^{232}Th and ^{238}U. The ferro-niobium production was conducted at this site on commercial basis during only one decade (1953-1965), being documented that during this time about 1.2 million tons of sovite were extracted and submitted to Nb extraction. In the process production, two main types of waste were generated: a) some waste was produced in the initial steps of conditioning of the mineral by crushing the mineral material to necessary grain size, separation and centrifugation, being this waste released to the environment, and b) additional waste in the form of slag was generated in the process of ferro-niobium production by thermal exposure of the Nb-bearing minerals that were extracted in the previous phase. This slag was disposed in the rear of the site. (Popic,2014)

After decommissioning, the Sove mining site was covered with sand layers as a remediation measure. In this way, large amount amounts of waste, including slag and crushed rocks enriched with radioactive materials, were left in the area and only covered with a layer of sand of various thickness.

The radiation levels found in the different areas of the Fen complex is quite variable as it can be clearly observed in Figure 2.13, and it is clearly correlated with the type of the dominant bedrock in the different areas. While in the central part of the Fen complex and in the former Fen mining site, the rodbergite rock as dominant bedrock presents concentrations as higher as 3000 mg/kg, the Th concentrations in the sovite rocks, dominant in the former Sove mining site, are clearly lower (1 - 150 mg/kg). For comparison it is important to remark that the worldwide average concentrations of ^{232}Th in soils and rocks is 10 mg/kg.

The former mining sites only constitutes in extension a relatively small fraction of the Fen complex. Most of the complex corresponds to undisturbed zones were the rodbergite rock is the dominant. One of these undisturbed areas, is the so called Bollodalen area, a wooden zone in the central area of the Fen complex where only some few houses in the edge of the site breaks that natural undisturbed environment.

The annual radiation dose, received by the population in the Fen complex, is estimated to be among the highest in Europe. In the public areas of the complex the annual exposure dose due to terrestrial radiation is approximately 3 times higher than the world average value, but extremely high gamma radiation dose rates in the vicinity and around the former mining sites in the wooden zone of Fen can be found, up to 140 times higher than the world average.

Popic et al., 2011 performed a survey in the Fen complex determining the activity concentrations of ^{232}Th and ^{238}U in soils collected in the two former mining sites, as well as, in undisturbed areas located in the central part of the complex. The result of the soils analysed showed wide ranges, 69 – 6581 Bqkg^{-1} and 49 – 130 Bqkg^{-1}, for ^{232}Th and ^{238}U, respectively. In all the cases exceeding the world average values 45 Bqkg^{-1} for ^{232}Th and 33 Bqkg^{-1} for ^{238}U in soils. The highest concentrations were found in the central undisturbed areas of the complex, as well as, in some soils collected in the former mining Fen site, and the lowest in the former Sove mining site. Evidencing a clear connection with the abundance of the rock type rodbergite (with high ^{232}Th level as was commented previously) and with the abundance of the rock type sovite.

After a detailed and extensive literature survey, extremely limited information was found in the open literature analysing radioactive NORM particles. Quite recently, Garcia-Tenorio et al.,2018 published a study performed in a fluvial placer deposit located in the centre of Spain and containing monazite nodules enriched in Th with size at the mm level. Monazite nodules were isolated, and its elemental composition was analyzed by the application of two IBA techniques (μ-PIXE and μ-RBS), see Figure 2.14, and μ-XRF. Some leaching experiments performed with the nodules and using either groundwater or HCl 0.16M reflect the refractory behaviour of these nodules being not detected in the leachates Th and U by applying the alpha-particle spectrometry technique.

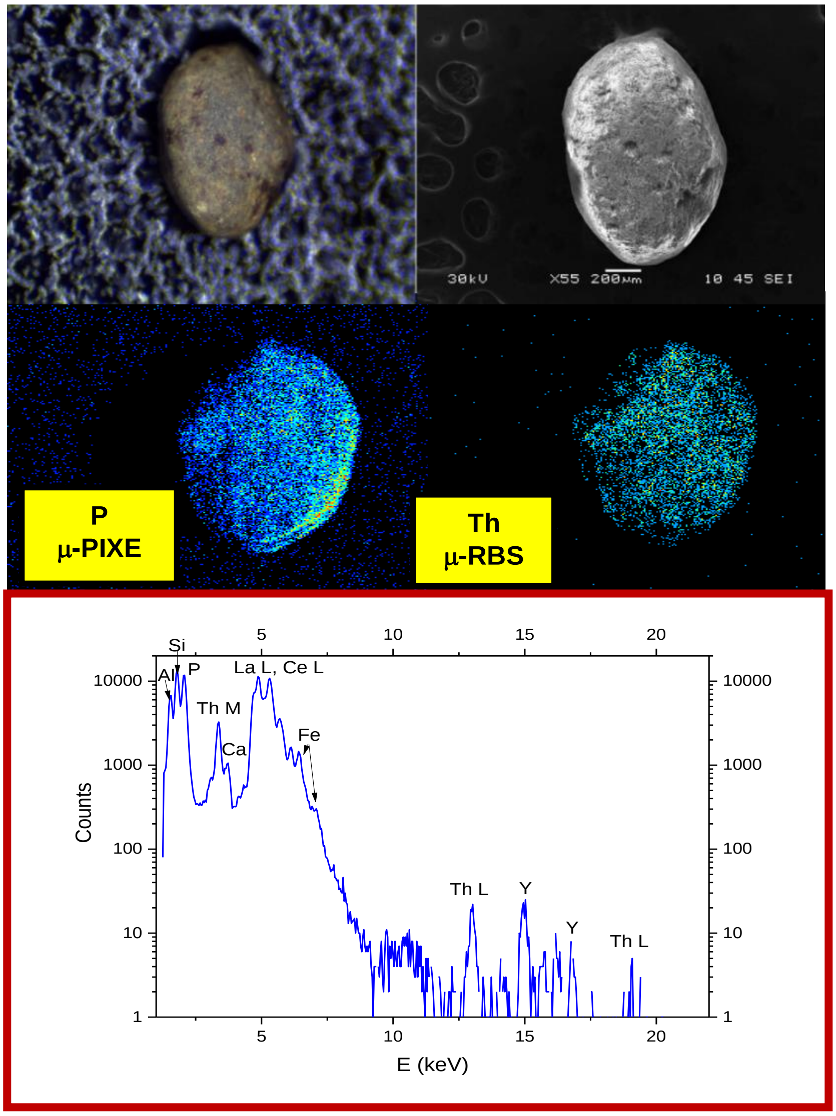

Figure 2.14.- Monazite nodule. Photo obtained with optic microscope (up left), SEM image in BEI mode (up right), P and Th mappings applying IBA techniques (centre) and typical PIXE spectra impinging 3 MeV protons (down).

The use of micro-analytical techniques for the characterization of particles and fragments with enhanced concentrations of natural radionuclides from the Uranium and Thorium series, are limited. In addition to the previous commented work, exists a pioneering study performed in former Soviet Union U-mining sites in Central Asia by Lind et al. (2013). With basis on digital autoradiography, it was observed in this study that the radionuclides were heterogeneously distributed in soil samples collected at the abandoned uranium mining sites Kurday, (Kazakhstan), Kadji Sai (Kyrgyzstan) and Taboshar (Tajikistan) (see Figure 2.15).

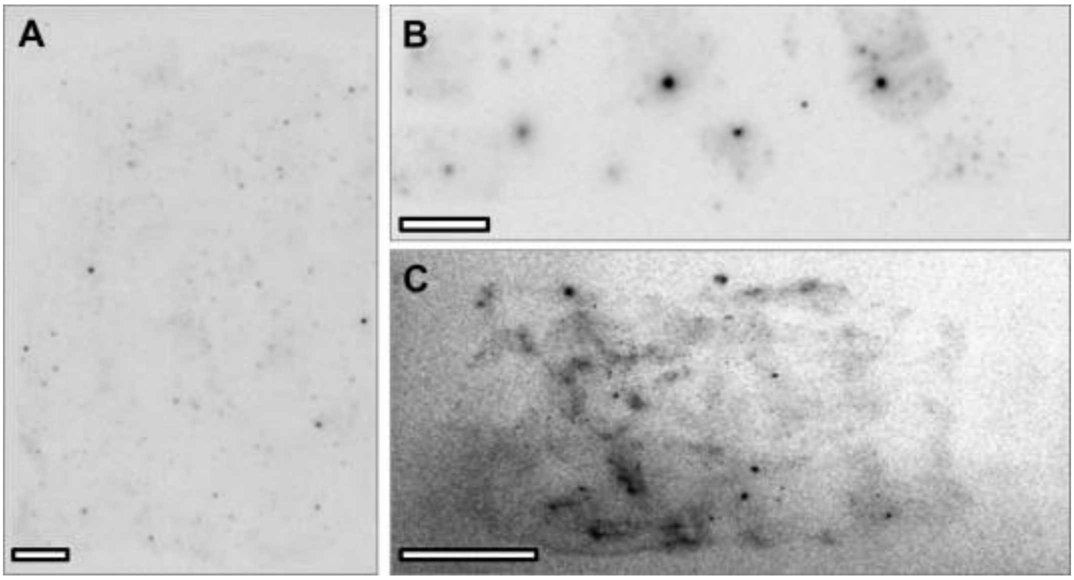

Fig. 2.15 Inhomogeneous distributions of radionuclides in TENORM samples demonstrated by digital autoradiograms of soil from the rim of the open pit lake in Kurday, Kazakhstan (A), soil from the Kadji Sai village located close to the mine, Kyrgyzstan (B) and soil collected from nearby the pit lake in Taboshar, Tajikistan (C). All bars 50 μm. (taken from Lind et al., 2013).

Afterwards, using electron microscopy interfaced with X-ray microanalysis (SEM-EDX), submicron - μm-sized radioactive particles and rock fragments with U, As, Se and toxic metals on the surfaces were identified in Kurday and Kadji Sai samples. Also, employing scanning and tomographic (3D) synchrotron radiation based micro-X-ray fluorescence (μ-SRXRF) and synchrotron radiation based micro-X-ray diffraction (μ-SRXRD) it was possible to observe the inner structure of the particles without physical sectioning. The distribution of elements in virtual cross-sections demonstrated that U and a series of toxic elements were rather heterogeneously distributed also within individual radioactive TENORM particles. Finally, by comparing with archived data, it was possible to conclude that U in Kadji Sai particles was present as uraninite (U_4O_{9+y} or UO_{2+x}) or Na-zippeite ($(Na_4(UO_2)_6[(OH)_{10}(SO_4)_3]\cdot 4H_2O)$, i.e., U minerals with very low solubility, information that have an enormous importance from a radioecological perspective. It is then evident that radioecological studies should benefit from the use of advanced methods such as synchrotron radiation-based techniques (Lind et al.,2013).

In this thesis abiotic leaching experiments has been performed on several particles (aggregates) isolated from soils collected in undisturbed zones from the Fen complex (an example shown in Figure 2.16) as well as in some soil aliquots collected in different parts of the complex for comparison purposes. Finally, knowing that the rodbergite bedrock is the main contributor to the Th levels in the area, samples formed by milled rodbergite rock were also submitted to the abiotic protocol.

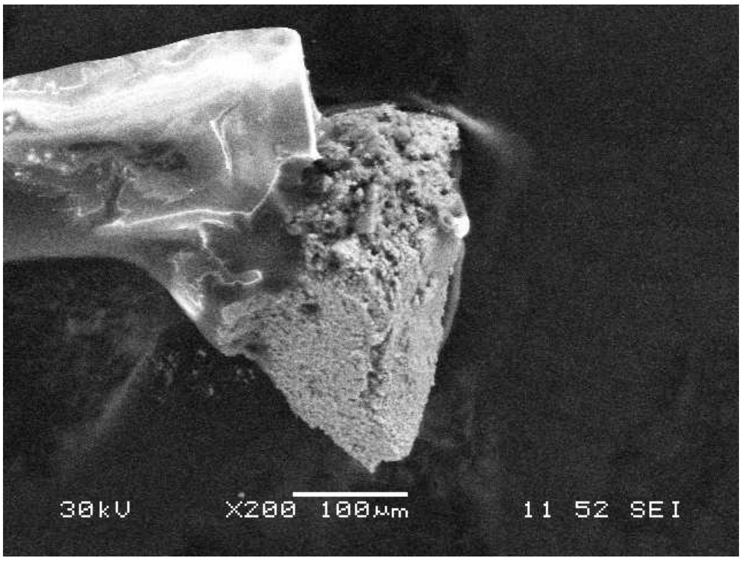

Figure 2.16.- SEM image of one of the Fen particles analyzed in this work. For easy handling is adhered to a capillary system. (Vioque, private communication).

The soils analyzed came from two different sites. A set of samples were collected from the former Sove mining site with moderate amounts of Th and sovite as the main contributing mineral, while a second set were collected in the undisturbed site of Bollodalen with clearly higher levels of Th, and with rodbergite as the main contributing mineral fraction. This combination will allow to perform comparison studies and to gain information about the radioecological behavior of different sites of the complex, including disturbed and undisturbed sites.

Recent studies about transfer factors and application of sequential extractions (Popic et al., 2020) complements and compare the obtained results with the protocol described in the next chapter and applied in chapter 6 to the Fen site.

Chapter 3

EXPERIMENTAL

As it has been stated in the introduction of this PhD thesis, all the work performed has been devoted to the construction, testing and application of different leaching experiments, to simulate possible transfers between different compartments in ecosystems affected by the presence of radioactive particles. The objective was to gain information about transformation processes. The importance of the experimental part in this PhD thesis is then evident, as it will be reflected in this chapter that compiles (Together with an annex) all the radiochemical methodologies developed/applied as well as the description and optimization of the measurement techniques used.

This chapter will start describing in detail the different leaching protocols developed, which were applied in our case to three different ecosystems: Palomares (Spain), Thule (Greenland) and Fen (Norway) (Section A). It will continue describing, due to their peculiarities, some specific radiochemical steps (digestions, chromatographic isolations) that the application of the leaching experiments demands (Section B).

The second part of the chapter will be devoted to all the experimental techniques used in this work. Section C will be devoted to describe the three measurement techniques forming the basis of the thesis: Accelerator Mass Spectrometry (AMS), Inductively-couple plasma Mass Spectrometry (ICP-MS) and alpha-particle spectrometry (AS), while section D will compile information about complementary techniques used in some specific cases for isolation, identification and characterization of radioactive particles (RP): gamma-ray spectrometry (GS) scanning-electron microscopy (SEM) and micro ion-beam analysis techniques (μ-IBA).

Section A: Leaching protocols

Isolated particles and soils aliquots have been submitted to the leaching protocols that will be described in detail in the following paragraphs. As stated previously, these protocols have been agreed by the partners of the RATE-COMET European Union funded project and by the participants in the IAEA Coordinated Research project on radioactive particles and are being disseminated to harmonize these procedures at global scale in order to provide to the scientific community information that can be directly comparable.

In these protocols, radioactive particles (RP) and soil aliquots are submitted to different leaching agents sequentially to evaluate the degree of particle transformation and soil solubilization over time. The agents used are either representative of the ones that can affect the particles and the soils in the affected ecosystem (rainwater, groundwater), compounds mimicking the acidity of the human stomach juices (0.16 M HCl) or directly cow rumen fluids in order to evaluate the possible incorporation of radionuclides by ingestion. In addition, a synthetic solution mimicking the lung fluids has been used in an independent leaching procedure to analyze the possible assimilation of radionuclides by the human body via the inhalation route.

A total of four different leaching protocols have been applied in this PhD thesis. They are the following:

a) *Radioactive particle protocol (rainwater, groundwater, 0.16 M HCl)*
b) *Abiotic soil protocol (rainwater, groundwater, 0.16 M HCl)*
c) *Biotic soil protocol (cow rumen)*
d) *Biotic soil protocol (lung fluid)*

a) Radioactive particle protocol (rainwater, groundwater, 0.16 M HCl)

The scheme of the procedure is shown in Figure 3.1. It starts adding 20 mL of the selected leaching solution (i.e., water, acidic solution, etc.) to the centrifuge tube containing the particle. The contact time RP-solution will be: 1h (hour) (T_1, S_1), 1d (day) (T_2, S_2) and 1w (week) (T_3, S_3), being generated consequently three leachates. From the 20 mL of each leachate, a total of 10 mL are separated and submitted to centrifugation, 10000 rpm. The upper 5 mL of this centrifugated solution are separated being considered as the Low Molecular Mass (LMM) fraction of the leachate (a fraction that could be associated roughly to the dissolved fraction of the leachate).

2 mL of each leachate are stored representing the leachate as it was formed (Total), while another ml was used to obtain filtrated fractions.

The different steps are the following:
1) Place the RP at the bottom of the selected container. A 50 mL polypropylene copolymer centrifuge tube with polypropylene screw closure is recommended.

2) Add 20 mL of the selected leaching solution (i.e., water, acidic solution, etc.) to the centrifuge tube containing the particle. The contact time RP-solution will be: 1h (hour) (T_1, S_1), 1d (day) (T_2, S_2) and 1w (week) (T_3, S_3).

3) After each contact time T_i (T_1,T_2,T_3), immediately transfer 10 ml of the solution to a clean centrifuge tube by using disposable plastic pipette and focusing on preserving the RP and its nearest surroundings as undisturbed as possible (S_{11} (1 hour), S_{21} (1 day), S_{31}(1 week)). Then transfer another 8 ml of the solution (S_{12}, S_{22}, S_{32}) to a pre-weighed 20 ml liquid scintillation (LSC) vial.

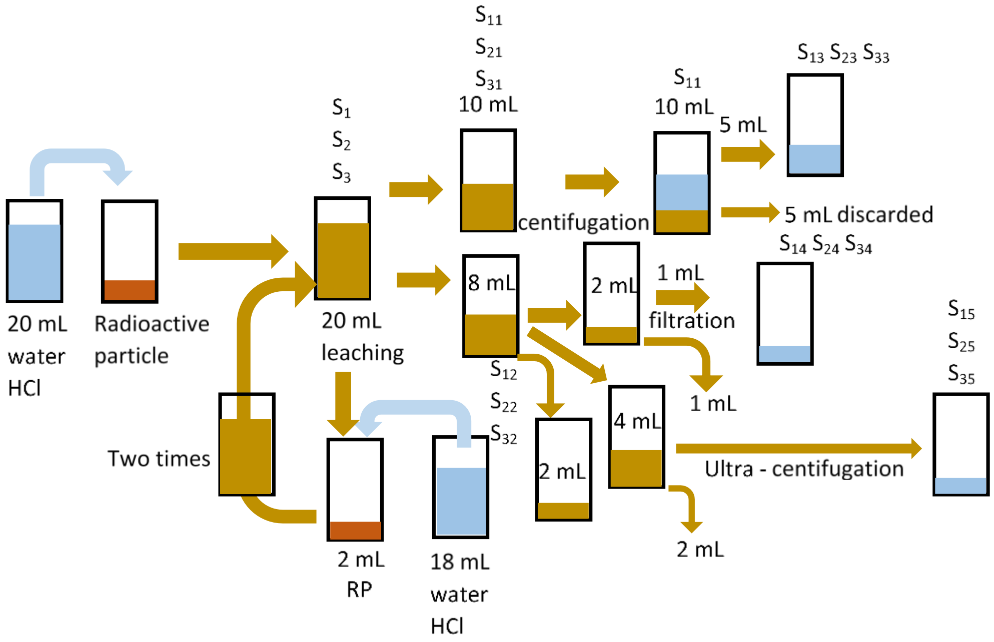

Figure 3.1.- Scheme of the Radioactive Particle (RP) protocol

a) The 10 ml aliquot of the solution (S_{11}, S_{21}, S_{31}) will be centrifuged at 10000 rpm, allowing the separation of the dissolved phase and the colloidal phase (mechanical disruption). Sample 5 ml of the supernatant into a sample vial and keep it until analysis (LMM fraction) (S_{13}, S_{23}, S_{33}).

b) From the 8 ml aliquot in the LSC vial (S_{12}, S_{22}, S_{32}), take 2 ml for 0.45 µm filtration using a syringe filter (Figure 3.2). The first ml is used for conditioning of the syringe filter (to be discarded) and the second 1 ml after being filtered is transferred to a vial for subsequent analysis (<0.45 µm faction) (S_{14}, S_{24}, S_{34}).

Figure 3.2.-. Syringe filters with Acrylic Housing 25 mm. Polyethersulfone with a pore size of 0.45 µm. Used to obtain the <0.45 µm size aliquots.

4) From the same vial as in 3b, for membrane ultracentrifugation, take 4 ml: the first 2 ml for conditioning of membrane (Figure 3.3) and subsequently 2 ml for obtaining the membrane ultracentrifuged aliquot (< 3 KDa fraction) (S_{15}, S_{25},S_{35}).

Figure 3.3.- Vial with the 3kDa filters embedded. Amicon Ultra-4 Centrifugal Filter Unit with Ultracel-3 membrane. We use this filter to separate between >3 kDa and <3kDa species.

5) From the same vial as in 3b and 4, and for a total sample analysis of the leachate, keep the 2 last ml (Total fraction).

6) The “removed solution” from the particle container will immediately be replaced by 18 mL of fresh solution and another leaching step is initiated with agitation until reaching next contact time.

7) After reaching each contact time, the process described in 3-5 should be applied

8) When the last contact time, T_3, is reached, (and after removing 10 + 8 ml as in 3) there will be 2 ml solution and the particle left in the extraction tube. This 2 ml can be filtered through a 0.45 μm filter in such a way that at the end of the experiment, we should have a RP on the 0.45 um filter to be measured by gamma-ray spectrometry.

All the leaching solutions should be prepared from 18 MΩ water and p.a. reagents. In addition, during the RP-solution contact time, gentle rolling agitation (ca 50-70 rpm) should be used. This agitation should be done in such a way that it would favor the interaction between the radioactive particle (RP) and solution but at the same time respecting the physical integrity of the RP, minimizing the chances of its mechanical disruption.

The different leachates obtained should be submitted to radionuclide analysis. The leachates should be treated and adapted for measurement. These adaptation processes will be detailed after the presentation of all the leaching protocols.

b) Abiotic soil protocol (rainwater, groundwater, 0.16 M HCl)

The scheme of the procedure is shown in Figure 3.4, and the different steps are the following:

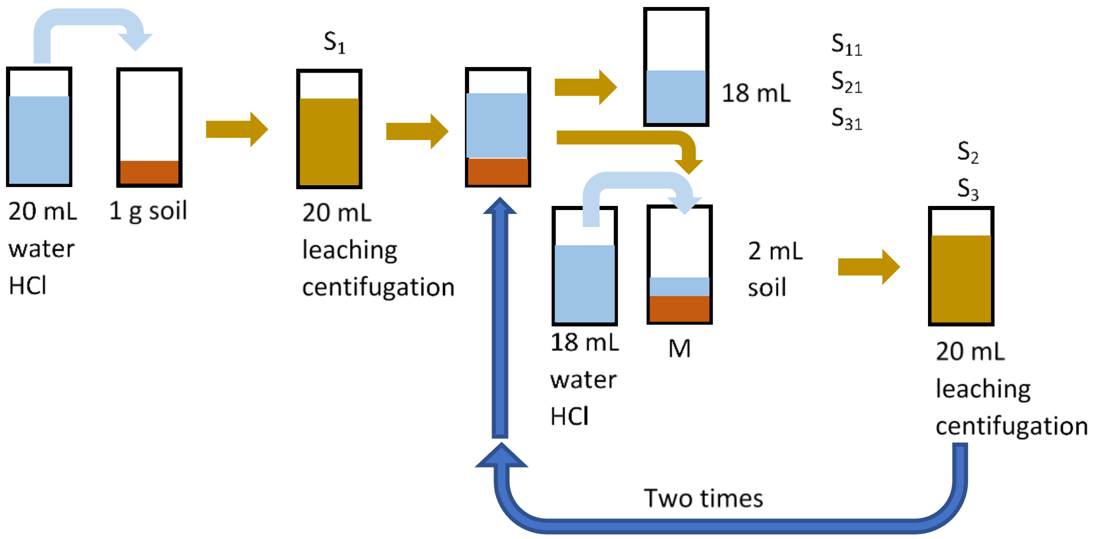

Figure 3.4.- Scheme of the abiotic soil protocol

1) Transfer 1 gram, dried in air at room temperature, of soil or sediment to a 50 mL polypropylene copolymer centrifuge tube with polypropylene screw closure.

2) Add 20 mL of the selected leaching solution (i.e., water, acidic solution, etc.) to the centrifuge tube containing the soil/sediment. The contact time soil-solution will be: 1h (hour), 1d (day) and 1w (week).

3) After a contact time T_1, centrifuge at 10000 rpm, and transfer 18 ml of the supernatant solution into a sample vial, using a disposable plastic pipette, focusing on preserving the soil/sediment and its nearest surroundings as undisturbed as possible. Keep the solution sample until analysis.

4) The “removed solution” will immediately be replaced by 18 mL of fresh solution and another leaching step is initiated.

5) When the last contact time, T_n, is reached, and after the 18 ml removal, 2 ml solution and the residual solid phase will left in the extraction tube. This remaining can be filtered through a 0.45 µm filter in order to have at the end of the experiment, a residual solid phase material on the 0.45 µm filter to be also analyzed.

All the leaching solutions should be prepared from 18 MΩ water and p.a. reagents, and during the leaching time, gentle rolling agitation (ca 50-70 rpm) should be used similarly to the RP leaching (Figure 3.5).

Figure 3.5.- Rolling/shake devices

The different leachates obtained as well as the remaining solid material should be submitted to radionuclide analysis. They should be treated and adapted for measurement. These adaptation processes will be detailed after the presentation of all leaching protocols.

c) Biotic soil protocol (cow rumen)

A scheme of the procedure is shown in figure 3.6, and the different steps are the following:

1) Transfer 1 gram soil, dried in air at room temperature, to a 50 mL centrifuge tube with polypropylene screw closure.

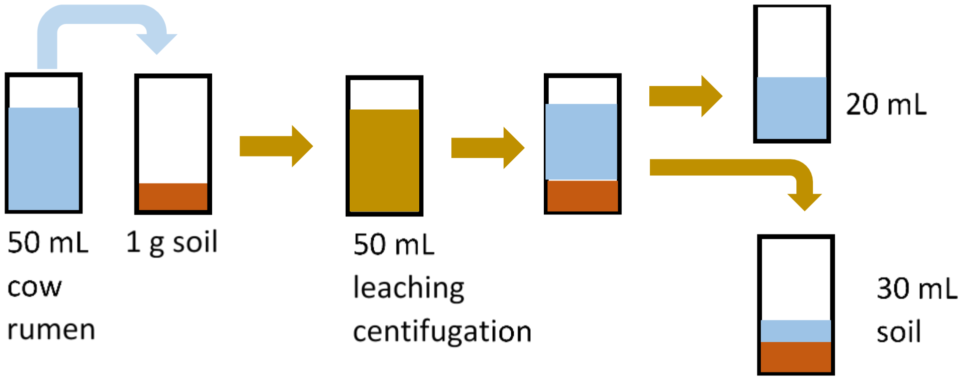

Figure 3.6.- Scheme of biotic soil protocol (cow rumen).

2) Add 50 mL of the cow rumen solution. This rumen should be collected the same day that the leaching experiment is going to be performed (Figure 3.7) and should be transported from the collection place to the lab maintaining its original temperature. In the laboratory, the temperature and the pH should be measured and recorded.

3) The amount of cow rumen added to the soil sample will fill completely the centrifuge tube, avoiding in this way the presence of air inside in the next steps.

4) The contact time between the sample and the rumen is restricted to 24 hours. The temperature at which the sample is leached must be on the other hand maintained at 39 ºC, and during the leaching time, gentle rolling agitation (ca 50-70 rpm) should be used similarly to the RP and soil abiotic leaching. In this way, the movements and temperature of the cow animal are simulated. For that reason, the centrifuge tube and the rolling agitator should be introduced in an incubator system.

Figure 3.7.- Collection of cow rumen juice at NMBU (Norway)

5) After 1h of leaching, the experiment should be interrupted in order to open the centrifuge tubes for removing any forming gases and avoid explosion accidents.

6) After 24 hours contact time, centrifugation is performed at 10000 rpm. The upper 20 mL of supernatant are taken for analysis.

It is necessary to remark that all the rumen gastric juice leaching experiments have been performed on soil aliquots. The turbidity of the rumen juice prevents for the moment its application to radioactive isolated particles due to the difficulties to follow and control their location and integrity during the leaching experiments.

d) Biotic soil protocol (lung fluid)

This protocol has the following steps:

1) An aliquot of the soil to be analyzed is introduced in a dialysis container which has the specifications given in Table 3.1. In this way, it is possible the interaction between the soil and the physiological solution that mimic the lung fluid, without provoking the dissemination of the material.

DYALISIS CONTAINER	
CHEMICAL PROPERTIES	*Cellulose tube containing water, glycerin and Sulphur compounds*.
PHYSICAL PROPERTIES	*Size of 25 mm x 16 mm and a diameter of 16 mm when is filled. It retains molecules with sizes higher than 12 kDa.*

Table 3.1.- Characteristics of the dialysis container used in this work

2) Once filled, the dialysis container is introduced in 250 ml of physiological solution. This solution is generated in the way that is indicated in Table 3.2 following the description given in Aragón, 2003. (Figure 3.8).

3) The interaction soil-solution is maintained during a week inside an incubator at 37ºC with occasional stirring. After passing this time, the dialysis container is taken out and introduced in a new fresh solution to repeat the procedure again in the incubator during the following week. The solution resulting of the first week of interaction is then ready to be analyzed.

Compound	Amount
Distilled water	1 litter
Concentrated Sulphuric acid	2.8 microliter
NH_4Cl	0.535 grams
NaCl	6.774 grams
$NaHCO_3$	2.268 grams
$Na_3PO4\ 12H_2O$	0.144 grams
Na_3-citrate	0.059 grams
Glycine	0.450 grams
$CaCl_2$	0.022 grams

Table 3.2.- Composition of the physiological solution used in the experiments. (Aragón, 2003)

4) The process of interaction soil-physiological solution is repeated 5 times, being obtained, at the end, a total of 5 different physiological solutions (one per week) to be analyzed. After finalization of the experiment, the remaining material inside the dialysis container is also stored for analysis.

Figure 3.8.- Dialysis container filled with soil (left), and process of interaction container-physiological solution during the leaching experiment.

The different leachates obtained the remaining solid material as well should be submitted to radionuclide analysis. They should be treated and adapted for measurement. These adaptation processes will be detailed after the presentation of all leaching protocols.

e) Conditioning of the samples for AMS measurements

Radioactive particles and contaminated soil samples associated to Palomares (Spain) and Thule (Greenland), has been submitted to abiotic and biotic leaching protocols. The leachates and associated remaining materials should be treated in order to proceed to their measurement.

For Palomares and Thule studies, the objective was the determination of ^{239}Pu, ^{240}Pu and ^{236}U associated to the application of the abiotic protocols and the biotic protocol with cow rumen, fact that was performed by applying the Accelerator Mass Spectrometric Technique (AMS). The procedures for conditioning the different aliquots to this technique will be described in the following paragraphs.

The aliquots to be treated have been classified in three different groups, needing each one some specific conditioning steps. The group 1 is formed for the soil leachates (either obtained with rainwater, 0.16 M HCl or cow rumen) and for the Total fraction obtained in the application of the RP abiotic protocol (2 ml remainings of S_{12}, S_{22} and S_{32}), the group 2 is formed by the LMM (S_{13}, S_{23}, S_{33}), <0.45 μm (S_{14}, S_{24}, S_{34}), and < 3 kDa (S_{15}, S_{25}, S_{35}) RP fractions, and Group 3 is formed by all the remaining soils materials.

Group 1: The conditioning protocol is the following (scheme shown in Figure 3.9)

1a.- The leachates are, immediately after being produced, totally dried in plastic vials and preserved in refrigerator before the application of the conditioning steps.

1b.- 10 mL of 65% HNO_3 are added to the solid residue in the plastic vial, which is introduced into a 250 mL glass beaker (“water bath”) with 100 mL of distilled water. The samples are warmed for one hour in order to dissolve the solid residue.

1c.- Once the solid residue was dissolved, the liquid solution is transferred into a 50 mL glass beaker. Then, the plastic vial is washed with 5 mL of 65% HNO_3 to avoid losses.

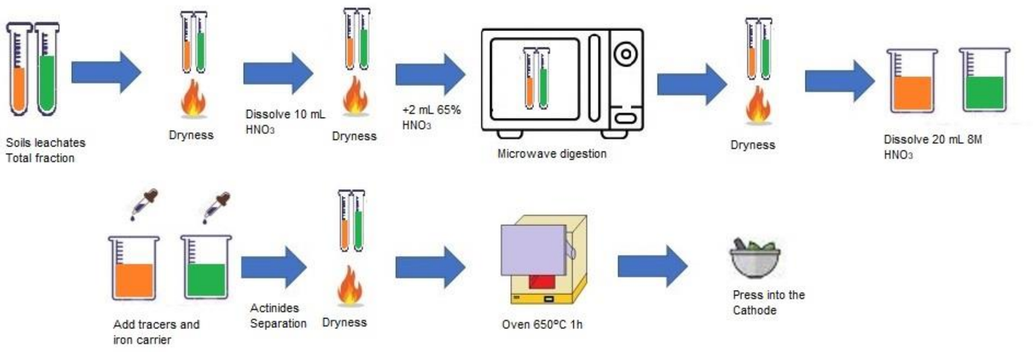

Figure 3.9.- Conditioning of aliquots from Group 1 (soils leachates, Total fraction) for AMS measurement.

1d.- The solution is evaporated near dryness.

1e.- 2 mL of 65% HNO_3 are then added into the beaker. And the solution is transferred to microwave vials.

1f.- The aliquots are submitted to a microwave digestion protocol that will be detailed in Section B of this chapter.

1g.- The final product of the microwave digestion is evaporated to near dryness, diluted until 20 mL with HNO_3 8M, and stored in 50 ml vials.

1h.- 10 mL of the sample in 8M HNO_3 solution are transferred to a 25 ml centrifugation tube and few pg of ^{233}U and ^{242}Pu are added as tracers.

1i.- 1 mL of Fe^{3+} from a carrier solution previously prepared is added to the solution which is afterwards evaporated to dryness.

1j.- 2 mL of concentrated HNO_3 and 3 ml of distilled water are added In order to dissolve the residue, with the help of gentle warming.

1k.- The pH of the formed solution is changed to basic, pH 8-9, by adding ammonia, provoking the precipitation of the iron in the form of hydroxides (and the co-precipitation of the actinides).

1l.- The sample is then centrifuged, and the supernate is removed.

1m.- 1 mL of ethanol is added to the precipitate, being the resulting material mixed and finally dried. This material is ready to be introduced into a muffle (Figure 3.10)

Figure 3.10.- Samples introduced at the muffle furnace (step 1n)

1n.- The dry material is introduced in an oven at 650ºC for 1 hour.

1o.-After cooling, some mg of Nb^{3+} are added to the ashes and mixed until a reddish colour is obtained. The sample is ready to be introduced in the AMS cathode.

1p.- The sample is introduced in the cathode and pressed using a pressing device.

1q.- The cathode is ready to be mounted in the sampling carrousel of the AMS system for its measurement.

Group 2.- The conditioning protocol is the following (scheme shown in Figure 3.11)

2a.- The leachates are immediately after being produced, totally dried in plastic vials and preserved in refrigerator before the application of the conditioning steps.

2b.- 5 mL of 65% HNO_3 are added to the solid residue in the plastic vial, which is introduced into a 250 mL glass beaker (“water bath”) with 100 mL of distilled water and warmed. The samples are warmed for one hour in order to dissolve the solid residue.

2c.- Once the solid residue was dissolved, the liquid solution is transferred into a 50 mL glass beaker. Then, the plastic vial is washed with 5 mL of 65% HNO_3 to avoid losses.

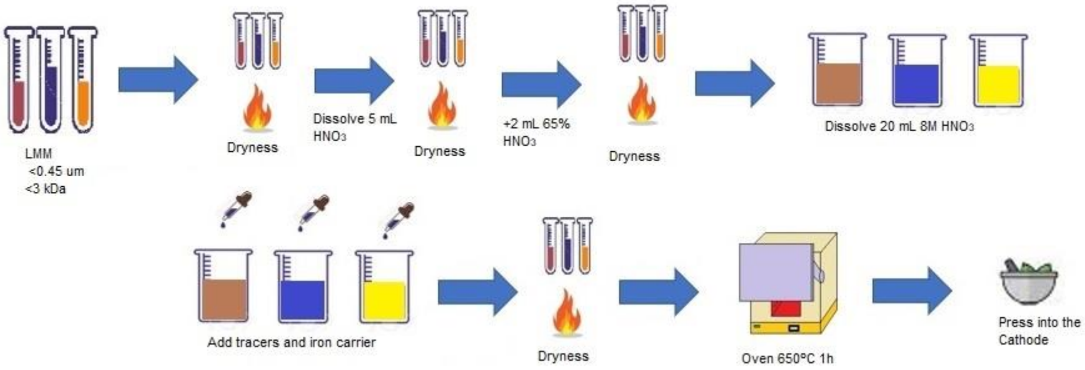

Figure 3.11.- Conditioning of aliquots from Group 1 (LMM, <0.45 mm, < 3 kDa) for AMS measurement

2d.- The solution is evaporated near dryness.

2e.- The residue is dissolved with 20 mL with HNO_3 8M and stored in 50 ml vials.

2f.- 10 mL of the sample in 8M HNO_3 solution are transferred to a 25 ml centrifugation tube and few pg of ^{233}U and ^{242}Pu are added as tracers.

2g.- 1 mL of Fe^{3+} from a carrier solution previously prepared is added to the solution which is evaporated to dryness. The resulting material (Figure 3.12) is ready to be introduced into a muffle.

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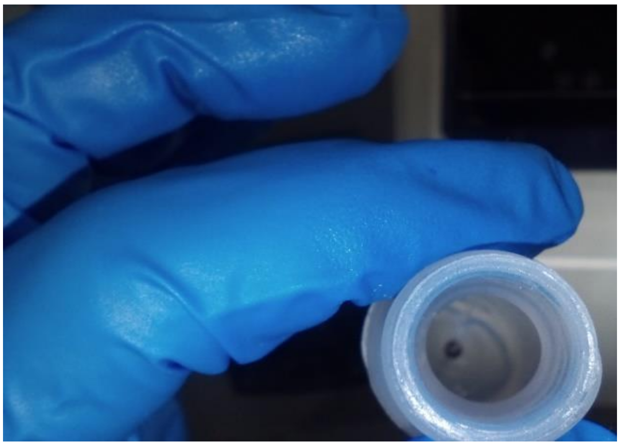


Figure 3.12.- Resulting material just before to be introduced in the oven (step 2g)

2h.- The dry material is introduced in an oven at 650ºC for 1 hour.

2i.-After cooling, some mg of Nb^{3+} are added to the ashes and mixed until a reddish colour is obtained. The sample is ready to be introduced in the AMS cathode.

2j.- The sample is introduced in the cathode and pressed using a pressing device.

2k.- The cathode is ready to be mounted in the sampling carrousel of the AMS system.

Group 3.- The conditioning protocol is the following (scheme shown in Figure 3.13)

3a.- The remaining material is evaporated to near dryness immediately after finishing the application of the leaching protocols until be conditioned for measurement.

3b.- The remaining liquid solution is removed by lyophilization. Using this procedure, losses are avoided, and the solid material (about 1 g) can be easily separated.

3c.-The solid material is then submitted to total dissolution by applying an alkali fusion method with $KHSO_4$. This alkali fusion method will be detailed in Section B of this chapter.

3d.- The final solution resulting from the alkali fusion is evaporated and the residue dissolved in 5 mL HNO_3

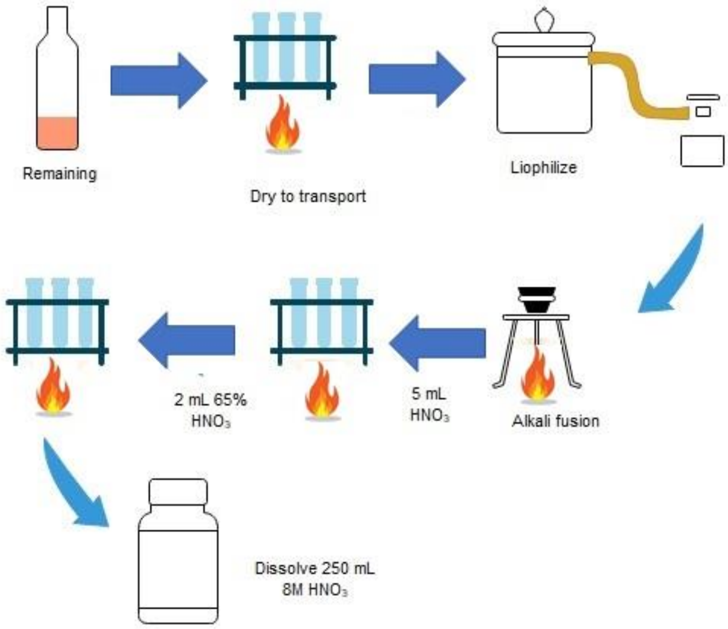


Figure 3.13.- Scheme of the conditioning procedure applied to Group 3 (remaining soil materials).

3e.- The solution is again dried and finally conditioned in 250 mL HNO_3. This high volume was selected in order to assure the total dissolution.

3f.- Then 10 mL of the solution are taken, and the same steps explained for Group 1, from 1h to 1q. are applied.

f) Conditioning of the samples for ICP-MS measurements

Radioactive particles and soil samples associated to the High Natural Background Area of Fen (Norway) has been submitted to abiotic and biotic leaching protocols. The leachates and associated remaining materials should be treated in order to proceed to their measurement.

For the Fen studies, the objective was the determination of the U and Th levels, fact that was performed by applying the Inductively Coupled Mass Spectrometric Technique. The procedures for conditioning the different aliquots to this technique will be described in the following paragraphs in summarized way, referring in most cases to the detailed conditioned procedures explained previously for AMS.

The aliquots to be treated have been classified in three different groups, needing each one some specific conditioning steps. The group 1 is formed for the soil leachates (either obtained with rainwater, 0.16 M HCl or cow rumen) and for the Total fraction obtained in the application of the RP abiotic protocol (2 ml remainings of S_{12}, S_{22} and S_{32}), Group 2 is formed by the LMM (S_{13}, S_{23}, S_{33}), <0.45 μm (S_{14}, S_{24}, S_{34}), and < 3 kDa (S_{15}, S_{25}, S_{35}) RP fractions, and the Group 3 is formed by all the remaining soils materials. Same as AMS cases.

Group 1: The following steps should be applied

1a.- The leachates are immediately after being produced, totally dried in plastic vials and preserved in refrigerator before the application of the conditioning steps.

1b.- 10 mL of 65% HNO_3 are added to the solid residue in the plastic vial, which is introduced into a 250 mL glass beaker ("water bath") with 100 mL of distilled water. The samples are warmed for one hour in order to dissolve the solid residue.

1c.- Once the solid residue was dissolved, the liquid solution is transferred into a 50 mL glass beaker. Then, the plastic vial is washed with 5 mL of 65% HNO_3 to avoid losses.

1d.- The solution is evaporated near dryness.

1e.- 2 mL of 65% HNO_3 are then added into the beaker. And the solution is transferred to microwave vials.

1f.- The aliquot is submitted to a microwave digestion protocol that will be detailed in Section B of this chapter.

1g.- The final product of the microvawe digestion is evaporated to near dryness, diluted until 20 mL with HNO_3 8M. and stored in 50 ml vials.

1h.- 10 ml of the final product is submitted to the ICP-MS service of CITIUS (University of Seville) where they are conditioned for ICP-MS measurement. In the final conditioning step, the 10 mL are evaporated to dryness and the residue diluted in HNO_3 1%.

Group 2: Quite similar procedure than for Group 1 is applied

2a.- The leachates are immediately after being produced, totally dried in plastic vials and preserved in refrigerator before the application of the conditioning steps.

2b.- 5 mL of 65% HNO_3 are added to the solid residue in the plastic vial, which is introduced into a 250 mL glass beaker ("water bath") with 100 mL of distilled water. The samples are warmed for one hour in order to dissolve the solid residue.

2c.- Once the solid residue was dissolved, the liquid solution is transferred into a 50 mL glass beaker. Then, the plastic vial is washed with 5 mL of 65% HNO_3 to avoid losses.

2d.- The solution is evaporated near dryness.

2e.- The residue is dissolved with 20 mL with HNO_3 8M and stored in 50 ml vials.

2f.- 10 ml of the final product is submitted to the ICP-MS service of CITIUS (University of Seville) where they are conditioned for ICP-MS measurement. In the final conditioning step, the 10 ml are evaporated to dryness and the reside diluted in HNO_3 1%.

<u>Group 3:</u> A more complicated conditioning procedure should be applied.

3a.- The remaining material is evaporated to near dryness immediately after finishing the application of the leaching protocols until be conditioned for measurement.

3b.- The remaining liquid solution is removed by lyophilization. Using this procedure, losses are avoided and the solid material (about 1 g) can be easily separated.

3c.-The solid material is then submitted to total dissolution by applying an alkali fusion method with $KHSO_4$. This alkali fusion method will be detailed in Section B of this chapter.

3d.- The final solution resulting from the alkali fusion is evaporated and the residue dissolved in 5 ml HNO_3.

3e.- The solution is again dried and finally conditioned in 250 ml HNO_3. This high volume was selected in order to assure the total dissolution.

3f.- 10 ml of the final product is submitted to the ICP-MS service of CITIUS (University of Seville) where they are conditioned for ICP-MS measurement. In the final conditioning step, the 10 ml are evaporated to dryness and the reside diluted in HNO_3 1%.

g) Conditioning of the samples for alpha-particle spectrometric measurements

Lung solubility tests were performed using Palomares soil aliquots, determining the plutonium content in the physiological solutions and in the remaining soil materials by alpha-particle spectrometry. The conditioning steps needed in this case are the following:

Physiological solutions

1) First of all, a known amount of an isotope alpha-emitter of Pu does not present in the sample (in our case ^{242}Pu) is added in order to control the radiochemical yield of the whole process. Afterwards, 4 mL of an iron carrier solution with a concentration of 5 mg/mL of Fe^{3+} are added to the 250 mL of the physiological solution.

2) The pH of the solution is changed to a basic value, between 8 and 9 by adding concentrated NH_3. This pH change provokes the formation and precipitation of iron-hydroxide and the co-precipitation of the actinides (including Pu).

3) After settling of the precipitate, most of the supernate is removed while the rest is submitted to centrifugation, and the precipitate isolated.

4) 15 mL of HNO_3 8M are added to the precipitate together with some mg of $NaNO_2$ in order to produce the oxidation of Pu to the state +IV. The resulting solution is then heated at 80ºC for ten minutes, while an anion exchange resin AG1-4x is prepared for plutonium isolation. The ion-exchange procedure applied is detailed separately in section B of this chapter.

5) The solution containing the Pu is finally evaporated and conditioned to proceed to the electrodeposition of Pu onto stainless-steel planchets following the procedure described in Vioque et al., 2002, which will be also detailed in the Section B of this chapter. Once the electrodeposited Pu source is ready, the

determination of its content is performed by applying high-resolution alpha-particle spectrometry.

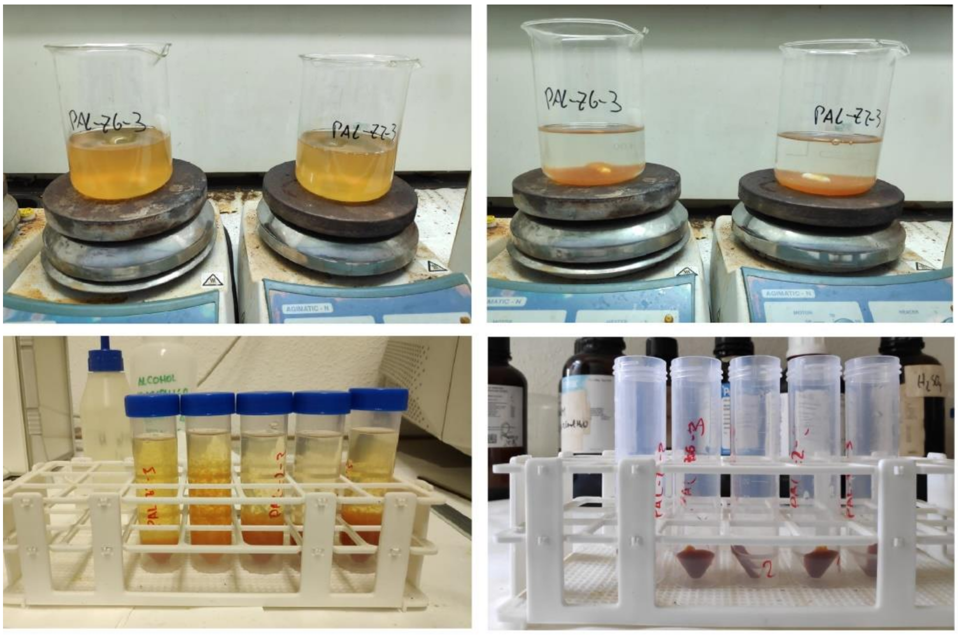


Figure 3.14.- Process of actinide co-precipitation with $Fe(OH)_3$

<u>Remaining soil material</u>

1) For the determination of the Pu remaining in the soils submitted to the leaching process, the material is first dried and then calcined at 550ºC overnight in order to remove the organic matter.

2) The resulting ashes are submitted to an acid attack with HNO_3 8M, heating and adding periodically H_2O_2 for oxidation of the Pu to the state +IV.

3) Finally, the sample is filtered by using a filter of 90 cm of diameter and 12 μm of pore size.

4) The obtained solution, containing the Pu original present in the soil, is then treated as the physiological solutions, following

a) the radiochemical procedure using ion-exchange resins,

b) the generation of the Pu source by electrodeposition and

c) the Pu measurement by alpha-particle spectrometry.

SECTION B: RADIOCHEMICAL PROCEDURES

In association to the application of the different leaching protocols described in the previous section, and mainly in association to the conditioning for measurement of the different products generated in the leaching experiments, some well-defined and specific radiochemical steps should be applied. In particular, the following radiochemical steps are needed and will be detailed in this section:

a) *Microwave digestion of leachates*
b) *Alkali fusion of remainings*
c) *Ion-exchange Pu isolation*
d) *Electrodeposition of Pu for alpha-particle measurement*

Microwave digestion

This radiochemical step is applied in the conditioning of soil leachates and total fractions of RP leachings. The following points describe its way of application:

a) 2 ml HNO_3 containing the radionuclides dissolved are introduced in a microwave cell, and 5 mL HCl and 1 ml HF are added.

b) The mixture HNO_3-HCL-HF is kept reacting with the material leached during 24 hours before introduction of the cell in the microwave.

c) The microwave digestion is then fulfilled at 1200 W during half hour with an initial ramp of 15 minutes of duration.

d) In order to remove the traces of HF, the digested solution is submitted to complexation with 6 ml H_3BO_3 5% in the Microwave during other half hour.

e) The solution after complexation is evaporated to dryness and conditioned in HNO_3 8 M as indicated in Section A.

Alkali Fusion

This radiochemical step is applied to the remaining soil materials after application of the different leaching protocols. The following points describe its way of application (schemes in Figures 3.15 and 3.16):

a) Melt 25 g of $KHSO_4$ (using a quartz crucible) over a Bunsen burner for 10-12 minutes.

b) Remove the crucible and wait until the smelted salt get colder. Then, add 0.25 g of the remaining material to be fused. Tracers should be added at this step.

c) Melt again the compound over the Bunsen burner until the mixing seems visibly smooth (this step can take 5-15 minor even more, depending of sample´s matrix).

d) Take the crucible from the Bunsen and introduce directly in a pre-heated oven to 800ºC for 20 minutes.

e) After that time, remove the crucible from the oven and wait until is cool. The fusion has been performed.

f) Pre-heat 150 ml HNO_3 8M at 90ºC and immerse the crucible in it to dissolve the content.

g) After some minutes, take the crucible out of the acid solution and rinse it with nitric 8M. A clear yellowish solution containing the sample totally digested is the final product.

h) The solution is conditioned to be fitted with the method used for adapting the samples to measuring conditions.

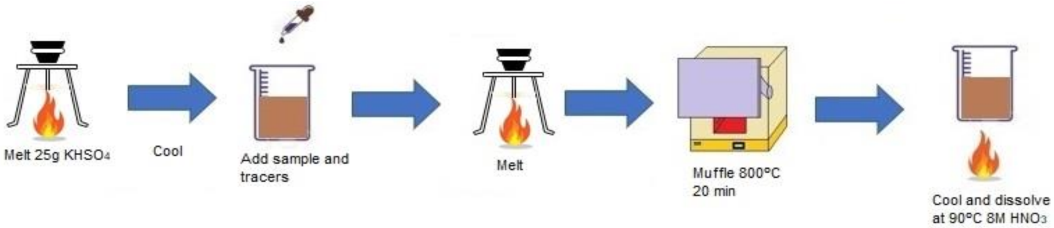


Figure 3.15.- Scheme of the alkali fusion method.

Figure 3.16.- Details of Alkali fusion. Left up is shown the melted salt dissolve impurities. Right up we show a sample properly dissolved. Down we can see the muffle furnace and the Bunsen burner, the two devices used to heat the samples.

Ion-exchange plutonium isolation

This radiochemical step is used for Pu determination by alpha-particle spectrometry in the physiological solutions and in the remaining materials generated in the lung-solubility experiments. Pu-isotopes should be isolated from other interfering alpha emitters and from other stable interferences. The following points describe its way of application:

a) An amount of anion exchange AG1-4x resin is introduced in a column 5 cm height and 1 cm of diameter with the help of distilled water (Figure 3.17).

b) The ion-exchange resin is conditioned with 25 mL of HNO_3 8M, being then passed the previously prepared solution containing the Pu to be isolated (see section A). All the liquid effluents are discharged, being at this step the Pu originally present in the physiological solution attached to the resin.

c) The resin is washed then, first with 30 mL oh HNO_3 8M and afterwards with 30 mL of HCL 9M in order to remove possible interferences. The Pu still is attached to the ion-exchange column, and all the liquid effluents generated should be discarded.

d) Finally, the Pu is stripped by passing 30 mL of a solution of 1M NH_4I/9M HCl, solution that needs to be prepared just in the moment of use to avoid its oxidation (Figure 3.17). The effluent obtained in this last step contains the Pu isolated from other actinides (U, Th, Am…) as well from other interferences. This effluent is then heated until to assure the removal of the fumes generated by the volatilization of the iodine.

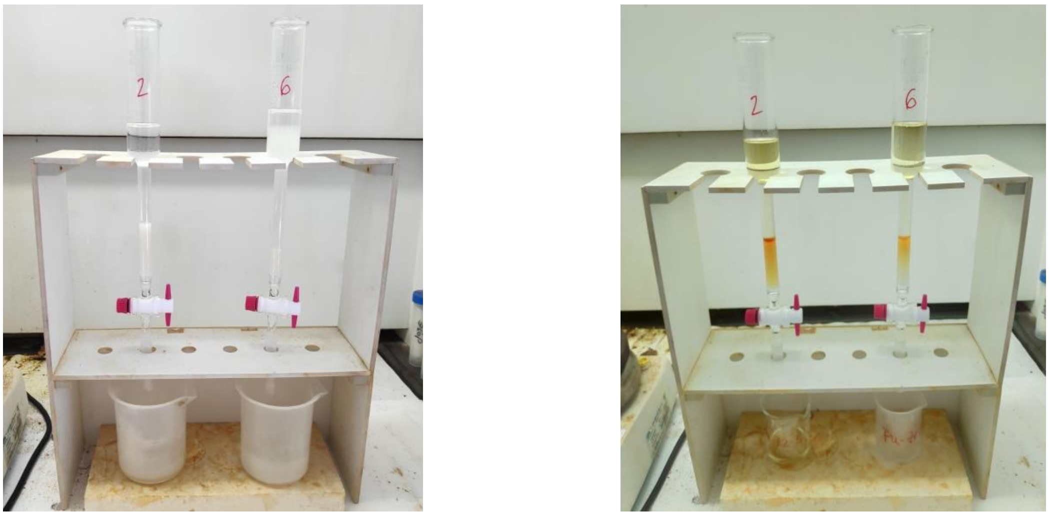


Figure 3.17.- a) Process of formation of the ion-exchange column (left), b) Process of stripping of Pu with the 1M NH_4I/9M HCl solution.

e) The solution containing the Pu is finally evaporated and conditioned to proceed to the electrodeposition of Pu onto stainless-steel planchets following the procedure described in the next paragraphs. Once the electrodeposited Pu source is ready, the determination of its content is performed by applying high-resolution alpha-particle spectrometry detectors.

Plutonium electrodeposition

The electrodeposition step (see Figure 3.18) consists in the deposition onto an stainless steel planchet of the actinides (in our case, Pu) present in an electrolyte (acid solution) submitted to a constant intensity current during a fixed time. In our case, this current intensity should be 1.2 A, acting for 2 hours.

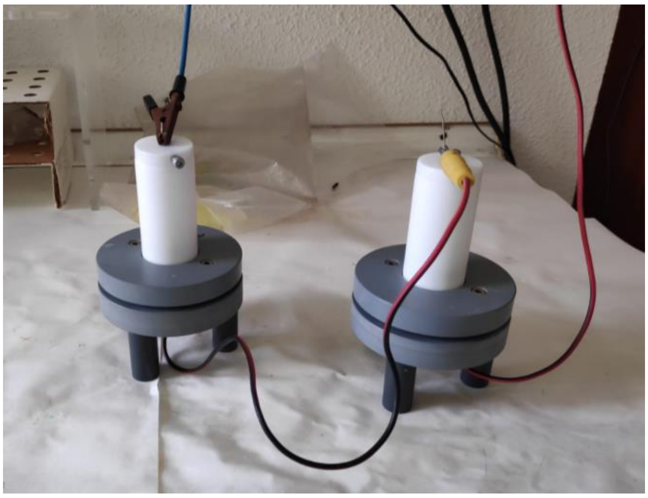


Figure 3.18: Electrodeposition set-up of two Pu samples in series

The electrolyte to perform the Pu electrodeposition is formed by following strictly the following points (Hallstadius, 1984):

a) The solution containing the Pu isolated stripped from the ion-exchange column is evaporated until reaching few mL. Then, 4 mL of concentrated HNO_3 and 1 mL of $NaSO_4$ 0.3 M are added, and the resulting solution is evaporated to dryness. The $NaSO_4$ is introduced in order to avoid the adsorption of the Pu in the walls of the beaker where the dryness is carried out. The final product is a dry salt containing the plutonium isotopes.

b) The electrolyte is then formed by dissolving the salt in 0.3 ml of conc. Sulphuric acid, and by adding 4 mL of distilled water and two drops of thymol blue to control the pH of the generated solution.

c) The pH of the solution should be adjusted to a value between 2.2 and 2.5 by adding ammonia vapours (the solution initially with a pink colour, turns to a clear yellow colour at the desired pH, see Figure 3.19).

d) The solution is then transferred to the electrodeposition cell (with the stainless steel planchet at the bottom), the beaker is cleaned with 5 ml of H_2SO_4 1% (which are also transferred to the cell), and the pH of the final solution in the cell is readjusted to the interval 2.2 – 2.5 with ammonia vapours. The electrodeposition can then be performed using a platinum wire as anode (the planchet acts as cathode) by applying an intensity current of 1.2 A for 2 hours.

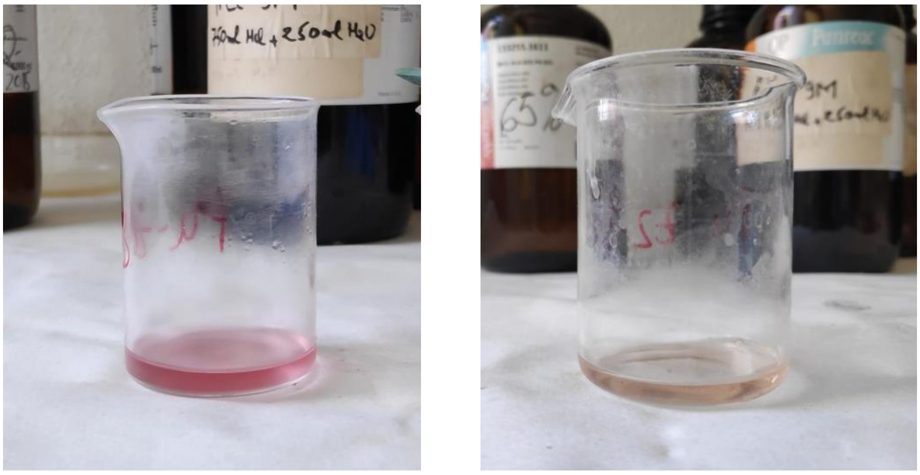


Figure 3.19: Change of the pH in the solution formed as electrolyte. The pH change provokes the change in colour of the thymol blue added as pH indicator.

e) One minute before the end of the electrodeposition, 2 mL of concentrated ammonia are added in the electrodeposition cell with the aid of a syringe. This addition avoids the possibility of the re-dissolution of the plutonium from the planchet when the electrodeposition is finished.

f) The electrodeposition is finished by cutting the current intensity suddenly.

g) The planchet is cleaned with distilled water and finally is dried at room temperature. The planchet contains now as a thin layer the Pu originally present in the solution stripped from the ion-exchange column and is ready for its measurement by alpha-particle spectrometry.

SECTION C

AMS determinations

The CNA, centro nacional de aceleradores, is an important ICTS (Singular scientific and technical infrastructure) in Spain. It’s facilities includes a set of accelerators are contributing to Spanish scientific research development nowadays.

Figure 3.20.- S.A.R.A. Device for mass spectrometry techniques with accelerators.

One of these accelerators is SARA (Spanish Accelerator for Radionuclides Analyses), which was installed in February 2006. This device is a 1 MV compact AMS system and it was designed and manufactured by High Voltage Engineering Europa B.V.

S.A.R.A. has been applied to plutonium (^{239}Pu, ^{240}Pu) measurements since 2008 (Chamizo et al., 2008) and it is being used for plutonium and other actinides today (López-Lora and Chamizo, 2019). Other use of SARA since 2016 is the determination of uranium (^{236}U). Later improvements of this technique have been recently published (Chamizo and López-Lora, 2018), contributing to consolidate the CNA facility as the second compact AMS facility in the world measuring actinides as a routine basis.

Overall, extremely low sensibilities, at the level of 10^6 atoms per samples (e.g., about 1 mBq of ^{239}Pu or 1 nBq of ^{236}U) can be obtained with no stringent constrains of the matrix components of the sample.

Nowadays, there are 12 AMS facilities measuring actinides in the world (see Table 3.3): 9 of them are based on accelerator terminal voltages of 3 MV and above (i.e., conventional AMS systems), the rests are based on accelerator terminal voltages of 1 MV and feature a compact design (i.e., low-energy or compact AMS systems) being the CNA among them. Because of the great capabilities, ease of operation and maintenance demonstrated by this kind of systems, the number of compact facilities has significantly increased in the last years.

AMS facilities	
ANU, Australia (15 MeV)	**CIRCE, Italy (3MeV)**
TU Munich, Germany (14 MeV)	**AEL-AMS, Canada (3 MeV)**
Wizman Institute, Israel (13 MeV)	**VERA, Austria (3 MeV)**
CIAE, China (13 MeV)	**Vega ANSTO, Australia (1 MeV)**
Antares, Australia (10 MeV)	**SARA CNA, Spain (1 MeV)**
LLNL, United States (6.5 MeV)	**Tandy ETH/PSI, Switzerland (0.6 MeV)**

Table 3.3.- AMS facilities measuring actinides at environmental levels. Conventional AMS are marked in red, Low-energy AMS are marked in green.

Although S.A.R.A. setup has been repeatedly described in the literature (Chamizo et al., 2008; Chamizo and López-Lora, 2018; López-Lora and Chamizo, 2019), a short description will be presented here for an easier comprehension of the text.

Negative ions (U^{16}O^{-}, Pu^{16}O^{-}) are extracted from a Cs-sputter ion source (model SO-110B). Next, the negative ions are analysed by a 90° magnet (LEM) according to their charge, mass and energy.

Then negative ions are accelerated to the terminal of accelerator. The terminal voltage is set to about 650 kV. Electrons of negative ions are captured by a stripper gas and ions are charged positive 3+ (Pu^{3+}, U^{3+}). Positive ions are accelerated again until the exit of accelerator.

Close to the exit of accelerator, positive ions are analysed according to their mass, charge and energy by other 90° magnet (HEM) and a 120° electrostatic deflector (ESA). A movable Faraday Cup (FC3) can be used to the deflection position of a not required isotope (e.g., ^{238}U) at the exit of HEM.

Once the mass, charge and energy of ions in the beam are accurate selected, the ions are detected and counted using a gas ionization chamber.

The count rates of the isotopes of interest, are normalized to the ones of their corresponding isotopic tracer. The resulting atomic ratios (i.e., ^{239}Pu/^{242}Pu, ^{240}Pu/^{242}Pu, ^{236}U/^{238}U) are corrected by: a) instrumental blanks (i.e., iron oxide mixed with Nb and pressed into the cathodes without further chemical treatment), that account for the spurious Pu and U events coming for either the ion source or introduced during the cathode preparation stage; and b) standards, to take into account the deviations of the output AMS atomic ratios due to machine-related effects.

The Pu-isotopes and the ^{236}U determinations have been benefited from several improvements performed in the S.A.R.A. facility, the most important being:

a) the off-axis Faraday cup at the exist of the HEM (FC3) used for the monitoring of the normalisation isotope as a current, was upgraded in 2012 with new Gated Charge Pump Digitizers (GCPD) supporting the measurement of pA,

b) the stripper gas changed from Ar to He motivated by the very promising ionization yields obtained at the lowest terminal voltages for the heaviest radionuclides in the 3+ charge state,

c) the original gas ionization chamber provided by HVEE, was replaced by a miniaturized one designed by ETH and featuring less electronic noise and a better charge collection efficiency in the active volume of the detector.

In fact, for ^{236}U, without the upgrade of FC3, it would not be possible to monitor the ^{236}U from small samples (the ^{238}U generates signals at pA level) and without the high ionisation yield achieved for actinides in 3+ charge states in He-based stripping process, getting good counting statistics for the minor actinides would have been an issue. With He, our system has the potential to offer the most efficient measurement conditions for actinides at low energies. However, in the case of ^{236}U, the abundance sensitivity that can be actually achieved is limited by the background caused by scattered ^{235,238}U molecular fragments.

In our specific applications, and due to the coexistence of U and Pu species in the same cathode, the interference of the naturally-occurring ^{238}U on ^{239}Pu and ^{240}Pu was systematically checked during the measurement to avoid wrong results. To this aim, a series of samples spiked with a few ng of natural U, were inserted into the measurement sequence, and the resulting ^{239}Pu and ^{240}Pu background effects calibrated and corrected, if necessary, for the samples of interest.

In contrast to the hot-particle-lixiviate samples, soil-lixiviate samples gave a U background slightly above the ones produced by the instrumental blanks, but not high enough to limit the sensibility of the technique. But in some cases, the limit of detection was compromised by other matrix components present in the cathode, limiting the efficiency of the formation of monoxide anions in the ion source. When necessary, those effects were kept at minimum by processing smaller lixiviated aliquots and measuring them once again by AMS. Note that any chemical purification of either the U or the Pu fractions was applied to perform these AMS analysis, which gives an added value to the work done. If such a treatment would have been necessary, the number of analyzed samples had been limited, which could have been detrimental to the conclusions of the study. In fact, one of the main advantages of the AMS technique is that not stringent radiochemical procedures should be applied.

ICP-MS Determination

The U and Th concentrations in the different leachates generated by applying the leaching protocols to soils and particles and in the remaining materials have been determined by applying the ICP-MS technique. The versatility of this technique, and its relatively low time demanding in comparison with radiometric techniques such as alpha-particle spectrometry, make it as the most appropriate one for these type of studies where low U and Th levels need to be determined in a high number of samples. In addition, the application of the ICP-MS technique allows the determination of the concentration of a good number of stable elements in the same leachates which can be useful in the discussion of the results obtained.

The low concentrations expected in some leachates for U and Th demands of the use of a quite sensitive ICP-MS system. For that reason, in this work we have used a Triple Quadrupole ICP-MS (Agilent 8800), placed in the Servicio de Radioisótopos in the University of Seville (General Research Services of the University).

The name “triple quadrupole” is used to describe a line of analysis formed by two quadrupole mass filters separated by an octuple reaction system ORS (or reaction/collision cell). Although the cell could contain different types of ion guide (quadrupole, hexapole or octupole) the common name “triple quadrupole” has been extensively used in the mass spectrometers field.

The first quadrupole, Q1, can operate as a filter with 1 amu of sensitivity. This quadrupole rejects the rest of ions different of target mass. Next, the polyatomic interferences are removed in the ORS. The second quadrupole, Q2, located just after the ORS, filters the ions not stopped in the cell and selects only the masses to be passed to detector: an electron multiplier detector.

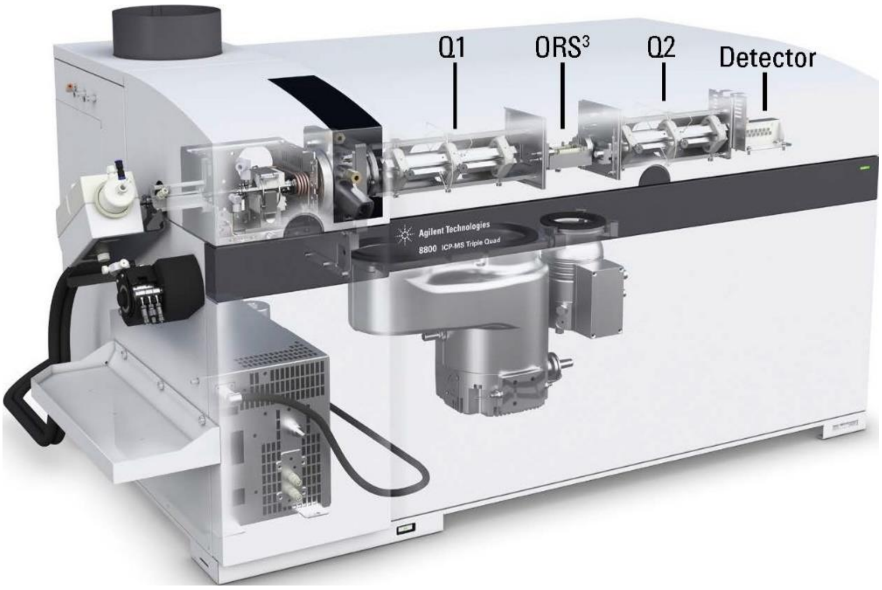


Figure 3.21.- Octopole Reaction System (ORS^3) (Agilent Technologies).

In our case, once the leachates were obtained, the measurement of the U, Th and several stable elements concentrations was done using the Method 200.8 (Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry) redacted by Environmental Monitoring Systems Laboratory of U. S. Environmental Protection Agency (USEPA).

The Method 200.8 is usually applied for determination of dissolved elements in underground waters, surface waters and drinking water. However, this method has been also successfully applied to determine element concentrations in liquid wastes, sludges and soil samples. In our case, it will be applied mainly to leachates of soils or radioactive particles and in the remaining materials after their dissolution.

The operating conditions of the ICP system should be reached before starting the sample measurements. With this end, a pre-calibration routine protocol should be followed. A period of several minutes is necessary to warm up the system and to proceed with the mass calibration and with the checking of resolution followed by the application of an instrument stability test, which is performed by running a tuning solution five times. Positive results will be considered if the standard deviation is lower than 5 % for all analytes present in the tuning solution.

For the ICP measurements, aliquots of the leachates and remaining materials were conditioned as it was detailed in the section B of this chapter with the addition of internal standards to make proper corrections for instrument drift and physical interferences during the measurements. In all the samples these internal standards (three) were added.

The samples, after being conditioned. were then analysed directly by pneumatic nebulisation. For quantitative analyses a minimum of three replicate determinations were required. The mean value of these measurements was used for data reporting. A rinse blank is used to flush the system between samples.

Quality check of results was done by measuring standard and blank samples after every 10 samples. In addition, the reagent used for conditioning of the samples was analysed in order to evaluate the background contribution to the sample measurements**.**

Alpha-particle spectrometry

Alpha-particle spectrometry is a radiometric technique that allows, if it is applied properly, the identification and quantification of the radionuclide alpha emitters that are present in the sample under analysis. This technique is based in the ionization provoked by the alpha particles emitted by the source when the alpha particles impinge in a medium. The ionizations provoked are used for the determination of the number of the particles emitted by the source, and of the associated energies of these particles. Through the determinations of these energies, the alpha-emitter can be identified because the alpha emissions of each alpha emitter radionuclide have characteristics energies.

An alpha-particle spectrometric system is formed by a material system that acts as detector, an electronic chain that process the ionizations produced in the detector and a system for the treatment and storage of all the information coming from the electronic chain. This information allows the quantification and energy identification of the detected emissions. The alpha-particle spectrometric system used in this work will be described later on.

The application of the alpha-particle spectrometric technique is far to be trivial. The high stopping power of the alpha particles do not possible the direct measurement of the samples, because the alpha particles will lose all or a considerable fraction of their energy before to leave the sample. On the other hand, although the energy of the alpha emissions is characteristic of the radionuclide emitting them, the simultaneous quantification and identification of all the alpha emitters present in the samples can be extremely complicated due to energy overlapping between different emissions.

For that reason, for the quantification of the alpha emitters of interest present in a sample, it is necessary to apply radiochemical procedures allowing a) the isolation of alpha emitter or emitters of interest from the matrix where are present, and b) the preparation of suitable sources for an appropriate measurement of the emissions. The radiochemical methods used in this thesis for Pu-isotopes determination in different matrixes have been previously explained in this chapter.

We have applied the alpha-particle spectrometric technique using semiconductor detectors. In the application of this technique with this detector type:

a) the detection efficiency only depends of geometric factors being for that reason easily quantifiable.

b) the detection efficiency is also independent of the energy, allowing the easy identification of the radionuclides present in the source through the energies of their alpha emission and the easy use of tracers which are essential to determine the radiochemical yield of the preparation and isolation process applied.

Our alpha-particle spectrometric system is equipped with ion implanted silicon detectors; PIPS detectors characterized with a very thin dead layer window that implies a good resolution in their energy response. These detectors are housed in chambers allowing vacuum to be performed in order to avoid the loss of energy of the alpha particles emitted by the sources in their way to the detector.

Each detection system requires in addition an electronic chain allowing the treatment of the signal generated in the detector. This electronic chain is formed by:

a) A preamplifier, which function is the formation of voltage pulse from the electric charge generated in the interaction of the alpha particle with the detector
b) A voltage source to produces the polarization of the detector.
c) An amplifier, to amplify the signal coming from the preamplifier, giving it a Gaussian form.
d) An analogic digital converter ADC, that transform the analogic signal generated in the amplifier in a digital signal according to its amplitude.
e) Multichannel Analyzer MCA that has the function of associate each digital signal with a channel which number will be proportional to the amplitude of the signal. The distribution of the number of pulses in the different channels of the MCA forms the alpha spectrum.

The spectrometric system used in this work for alpha spectrometric determinations is the model Alpha Analyst, from Canberra. This system is formed by a total of eight independent spectrometric units, each one equipped with a PIPS semiconductor detector of 450 mm^2 of active surface and a certified resolution of 18 keV for the alpha emission of 5.846 MEV of ^{241}Am, at a distance between the sample and the detector of 15 mm. The Alpha Analyst system is connected to a vacuum pump in order to reach the vacuum levels needed for optimum measurements in the eight chambers. All the system is feeded with a voltage source, each detector has its associated electronic chain, and the system as a whole is controlled though a personal computer that is connected to the equipment via Ethernet.

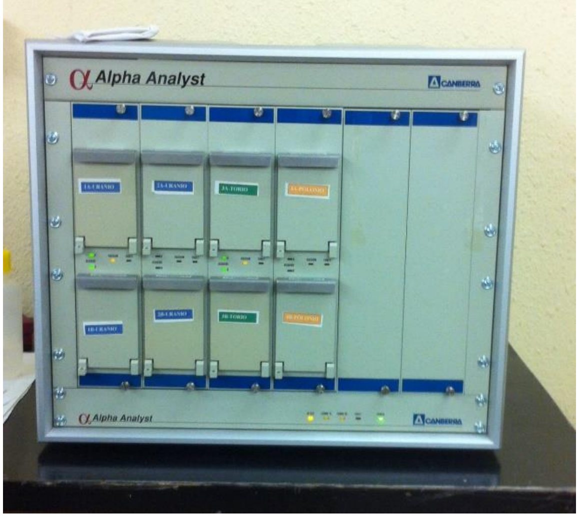


Figure 3.22.- Alpha-particle spectrometric system Alpha Analyst formed by eight chambers. Image from https://grupo.us.es, Universidad de Sevilla.

The Alpha Analyst program allows also the determination of the counting efficiency for each of the eight detectors once the distance source-detector is fixed, this counting efficiency is not generally used for the quantification of the radionuclides of interest in the samples analysed because we use for that the so-called isotope dilution technique. These counting efficiencies are used instead for the determination of the radiochemical yields.

The isotope dilution technique uses as data the activity added of the tracer, the number of counts in the alpha peak of the tracer and the number of counts in the alpha peak of the radionuclide of interest. The expression relating these factors can be obtained in the following way:

The equation reflecting the activity to be determined of the radionuclide of interest is:

$$A\ (Bq) = N\ /(t.\varepsilon.\ I.R) \qquad (1)$$

Where N is the number of net counts in the alpha peak corresponding to the radionuclide of interest, t is the measurement time, ε the counting efficiency, I the intensity associated to the alpha emission considered and R the radiochemical recovery yield.

In the same way, the expression allowing us the determination of the activity of the tracer from the information obtained from the alpha spectra is

$$A_0\ (\mathrm{Bq}) = N_0 / (t.\varepsilon.I_0.R) \qquad (2)$$

Where N_0 is the number of net counts in the alpha peak corresponding to the tracer and I_0 correspond to the intensity associated to the tracer alpha emission considered.

In both equations (1) and (2), ε and R have the same value, because the counting efficiency in alpha-spectrometry with semiconductor detectors is independent of the energy, and the tracer used correspond to one isotope of the radionuclide of interest and for that reason have the same radiochemical behaviour (same radiochemical recovery yield. Consequently, dividing (1) and (2) is obtained

$$A = A_0\ (I/I_0)\ (N/N_0) \qquad (3)$$

Where the activity A searched, is determined knowing the activity of the tracer added, the ratio between the intensities of the alpha emissions and the ratio between the number of net counts in the alpha peaks considered (the radionuclide of interest and the tracer).

Once the Activity A is determined though (3), the equation (1) could be used for the determination of the radiochemical recovery yield R, once the counting efficiency is known.

The counting efficiencies have been determined for the eight detectors of our alpha-spectrometric system in a non-automatized way by using a planchet of the same diameter that the used ones in our determinations, containing a known activity of an alpha emitter, and placing this planchet at the same distance of the detector that the used one in the conventional measurements.

SECTION D

Finally, in this last section we will describe the peculiarities of one radiometric and two microscopic techniques applied for the identification, isolation and characterization of some of the radioactive particles submitted to lixiviation experiments in this work.

SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron microscopy (SEM) is a non-destructive technique that allows to obtain information about the morphology and superficial composition of the sample analysed at microscale level. The basis of this technique is the interaction of an electron beam with the sample and the detection of some of the products of such interaction.

Between all the signals which are generated in the interactions of one electron beam with matter, we are going only to describe briefly (our relationship with this technique has been mainly as user) the ones that have been used in our work or in literature works described in the introduction section.

The first signal considered by us is the signal generated by the backscattered electrons. It is possible that the impinging electrons after multiple collisions with nucleus and electrons of the matter under analysis are “reflected” (backscattered) escaping from the sample. These backscattered electrons are detected with a suitable detector located near the incident axis of the beam.

The backscattered electrons offer a qualitative but extremely interesting information about the composition of the sample, because the intensity of the signal generated by the backscattered electrons depends of the atomic number Z of the element impinged. The backscattered coefficient varies as a function of Z (higher Z, higher backscattered coefficient) although at high Z the variation is quite small. As a consequence, the intensity of the signal generated by U and Pu cannot be differentiated, but on the contrary exists a clear difference of intensities between the signals produced by the mentioned actinides and light elements such as C, Si, Al, etc. The image obtained from the scanning of the sample by analysing the backscattered electrons shows clearer (white) colours in the zones with higher Z and darker in the zones with lower Z.

The second interaction product generated by the electron beam considered in our work are the secondary electrons which are generated when an electron of the incident beam excites one electron of the sample acquiring enough energy to escape it. The signal generated by these electrons after their detection does not offer information about the composition of the sample because the number of secondary electrons does not depend of the atomic number. The number of secondary electrons is very much dependent of the incident angle between sample and electron beam, and for that reason with the secondary electron signal it is possible to obtain information about the morphology/topography of the sample.

The last interaction product of interest in our study are the generated X-rays. The electrons from the beam excite the electrons of the atoms of the sample, escaping some of them generating holes that are covered by electrons of higher layers, being generated in this process X-rays with energies that are characteristics of each element excited. By using an appropriate detector, the signal generated by the different X-rays generated can be collected and processed being obtained an X-ray spectra that allow the identification of the elements present in the sample and even a semi-quantification.

The experimental system to generate and detect these signals should be formed by:

a) an electron beam column containing a simple electron canyon (a filament) with a combination of lens to reduce and focalize the beam, and a scanning system allowing the displacement of the beam along the sample,

b) three different types of detectors with their corresponding electronic chains to collect the three different interaction products previously commented (backscattered electrons, secondary electrons and characteristics X-rays),

c) a refrigeration system to avoid the formation of spurious signals due to the thermionic effect, and

d) a vacuum chamber to avoid the loss of the electron signals before their arrival to the detectors. In addition, the sample needs to be placed over a conducting surface to allow the proper interaction of the electron beam.

The scanning electron system used in this work was the JEOL 6460LV system located in the Microscopy Service of the University of Seville (CITIUS). In this system, the filament of the electron column is of tungsten and the three detectors are the following: the used for the secondary electrons is a scintillator with the configuration Everhart-Thomley, the used for the backscatter electrons is a semiconductor detector with the same configuration Everhart-Thomley and the X-ray detector is a semiconductor detector of silicon doped with lithium, Si (Li).

ION BEAM ANALYSIS TECHNIQUES (μ-PIXE and μ-RBS)

For the elemental characterization of some of the radioactive particles analysed along this work and for obtaining the maps distribution of some elements along the particle, some analyses have been performed by applying ion beam techniques. These techniques have been used as a simple user in collaboration with some members of the Applied Nuclear Research Group of the University of Seville, and for that reason its description in this section will be quite general without to entry in technical details. The main emphasis will be given to explain the information that could be gained with its application, their advantages in comparison with another alternative techniques and also their limitations.

Both techniques (μ-PIXE and μ-RBS) are based in the interaction of an ion beam (protons, He ions,...) with the sample under analysis. In these interactions, the charged particles interact either with the atomic nuclei or with the electrons of these nuclei, being both interactions important for the study of the sample although the interaction between the nuclei of the incident beam and the sample nuclei are clearly less probable.

Due to this low probability, the interaction between the incident nuclei and the nuclei of the sample contributes in a quite reduced way to the loss of energy of the ion beam in its path along the sample. However, the products of these interactions are the basis of two analytical techniques with ion beam, two IBA (ion beam analysis) techniques quite used. One of these products are the backscattered ions, which constitute the basis of the Rutherford Backscattering Spectrometry technique (RBS), and other products are the nuclei resulting of nuclear reactions, which form the basis of the Nuclear Reaction Analysis Technique (NRA).

On the other hand, the interaction of the incident nuclei from the beam with the electrons of the sample is produced in two different ways: a) though elastic collisions that provokes the ejection of secondary electrons, basis of the Secondary Electron Imaging (SEI) technique, and b) through inelastic collisions that provokes that the blank atom absorb the energy of the incident nuclei, passing to an excited state, from which return to the fundamental state though different alternative energy emission processes.

One of the last-mentioned emission processes, is the basis of the so called Particle Induced X-ray Emission (PIXE) technique, which is a non-destructive analytical technique based in the spectroscopy of the X-rays emitted by the excited atoms of the sample after the interaction of the ion beam. Each X-ray has an energy characteristic of the atom emitting it, and in each individual case its rate of production it will be dependent of the concentration of the element generating in the sample under study. The analysis of the X-ray spectra generated by the excitation of the atoms of the particles will allow then to identify the different elements forming part of its matrix and even to perform some quantification.

The Particle Induced X-ray technique has similar basis that other techniques fundamented in the same principle such as the X-ray fluorescence technique (XRF), with the difference being found in the beam type used (ions in the case of PIXE, high energy photons in the cases of XRF). The advantage to use ions such as protons or helium nuclei is related with the limit of detection of the technique. The background radiation generated by the ionization provoked with ions is clearly lower that the generated one using energetic photons, being for that reason the limits of detection lower with PIXE.

The RBS technique, as PIXE, allows the analysis of materials in a non-destructive way. Determining the energy lost by the backscattered ions in their interaction with the sample it is possible to determine the composition of the sample as well as the depth distribution of the elements constituting it. The advantage of this technique is that no requires the use of a reference sample in order to obtain quantitative information, is non-destructive and has a good resolution in depth. However, this technique has the drawback of its low sensibility to detect light elements, requiring in many cases the use of simultaneous IBA techniques such as Nuclear Reaction Analysis (NRA) or Elastic Recoil Detection Analysis (ERDA) to cover the mentioned deficiency.

The energy of the ion beam (generally protons or He) can range from 500 keV to several MeV, being the angle of scattering fixed in the interval 150º-170º.

In relation to the application of the two mentioned IBA techniques in this work, we can indicate that PIXE and RBS determinations have been performed in some isolated particles using the 3MV tandem accelerator of Centro Nacional de Aceleradores (CNA) using as an ion beam proton of 3 MeV, and as a beam line the equipped one with a nuclear microprobe. This nuclear microprobe is essential because is a system that allows to direct the beam and to reduce its size until obtaining lateral resolutions of approximately 1 μm, allowing the performance of microanalysis and particularly the performance of μ-PIXE and μ-RBS.

The nuclear microprobe is formed by a triplet of magnetic quadrupoles in charge to reduce the beam size, a scanning magnetic system, a collimation system formed by four stainless steel cylinders and a chamber of analysis where are located the different detectors and an optic microscope to observe and locate the sample under analysis (in our case micrometre radioactive particles). A photo of the nuclear microprobe line is shown in Figure 3.23.

For 3 MV protons the magnetic scanning system allows to scan the sample with a maximum amplitude of 3mm x 3 mm. The synchronization of the scanning system with the data acquisition system allows obtaining elemental maps by PIXE and RBS (by selecting a determined energy for PIXE or a channel spectra in RBS corresponding to element under analysis).

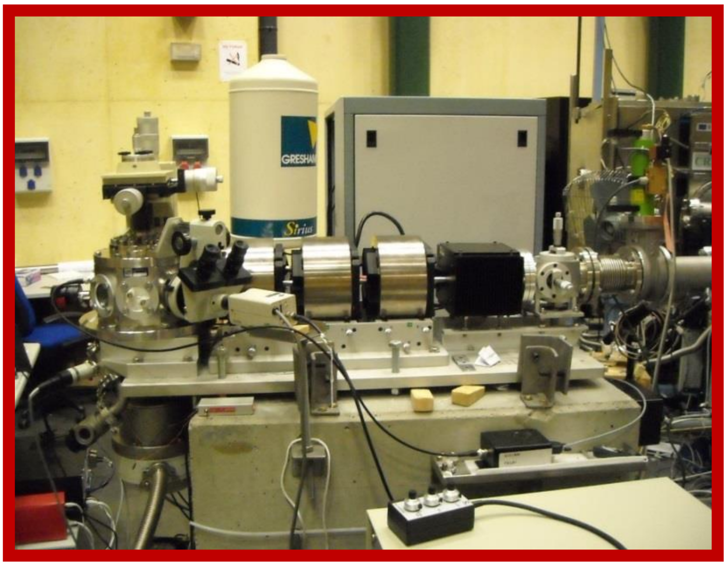


Figure 3.23.- Nuclear microprobe line at CNA.

The detectors used are of big solid angle, because the intensity of the beam ranges in the different experiments in the interval 100 pA – 1 nA being consequently the number of counts generated small. The detectors used are: a) Si(Li) detector from Gremsham of 80 mm^2 of active surface, with a 8 μm Be window and a resolution of 145 eV located at 135º for the study of the PIXE spectra, and b) A silicon detector for RBS from Ametek with a size of 300 mm^2 and 15 keV of resolution located at 143º in geometry Cornell (in a plane under the beam). A photo of the chamber with the different components is shown in Figure 3.24.

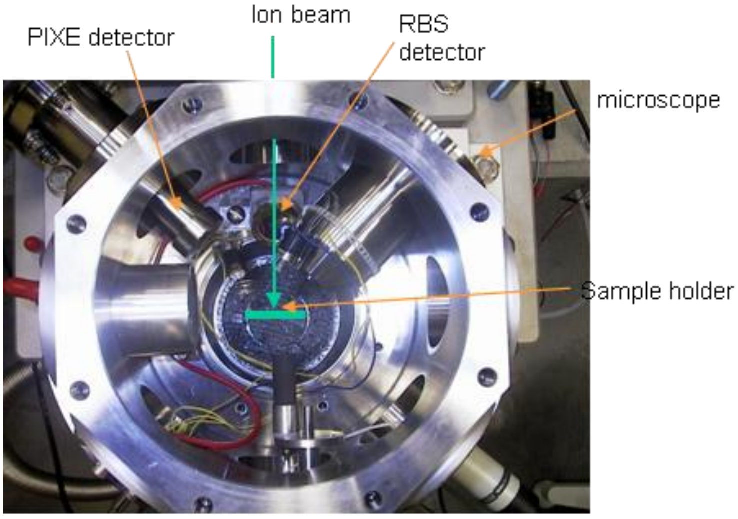
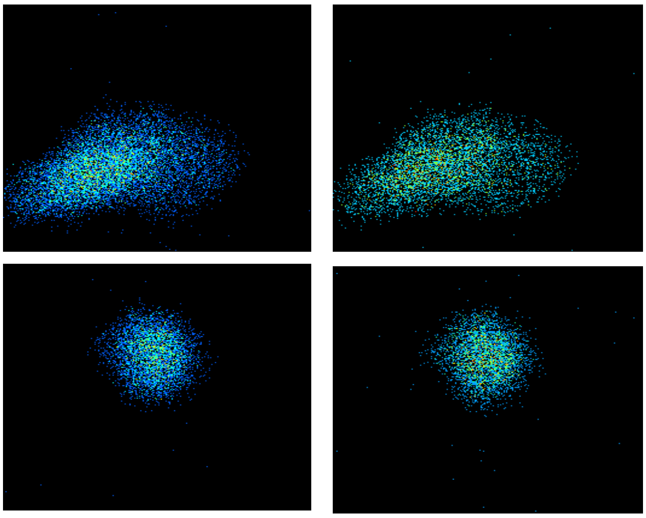


Figure 3.24.- Chamber associated to the nuclear microprobe line.

The analysis of the PIXE spectra is performed by using the GUPIX program which has a library that contain all the necessary data for the identification and quantification of the elements present in the sample. The RBS spectra are analysed by using the SIMNRA program giving information about the surface of the particle. With both techniques, it is possible to perform elemental mappings with a lateral resolution of 4 μm. The maps are performed with dimensions of 236 x 236 pixels. The maps of U and Pu in two Palomares particles are shown in Figure 3.25.



Pu (left) and U (right) maps in hot particles with origin in the Palomares nuclear accident.

Figure 3.25- U and Pu elemental maps of two particles from Palomares obtained by μ-PIXE

HIGH-RESOLUTION GAMMA SPECTROMETRY

In the process of identification and isolation of radioactive particles originated in the Palomares and Thule accident, the gamma-ray spectrometric technique has been used. The radioactive particles in both accidents contain a mixture of Pu and U, and consequently it contains ^{241}Am as a daughter of the ^{241}Pu originally present in the composition of the particles. The radionuclide ^{241}Am is an alpha emitter, that in some cases decay to an excited state of its daughter. This daughter, decays to its fundamental state by emitting a gamma-ray emission of 59.5 keV. The presence of ^{241}Am in one sample can be identified then through the mentioned low-energy gamma-ray emission.

The levels of ^{241}Am in the radioactive particles of both accidents (Thule and Palomares) are several orders of magnitude higher than the found as background in soils. Consequently, the gamma-ray signal provoked by the ^{241}Am gamma-emissions can be used in the process of radioactive particle isolation by binary division, until the practical isolation of the particle from the matrix where is embedded. In addition, once isolated, the ^{241}Am, ^{239}Pu and ^{240}Pu levels in the particle can be easily determined because through the net counting rate in the 59.5 keV ^{241}Am photopeak, the activity of ^{241}Am in the particle can be evaluated, and consequently the ^{239}Pu and ^{240}Pu, because the ^{241}Am/^{239}Pu and the ^{240}Pu/^{239}Pu activity ratios have a well-known and defined ratio in both accidents.

The conversion of the net ^{241}Am photopeak counting in activities require the determination of the detection efficiency at the mentioned energy, parameter that in this case is trivial to determine because the particle can be considered as a punctual source (the activity determination searched is for the posterior use in the estimation of the leaching percentages and do not require high precision).

As a gamma-ray spectrometer we have used a Low Energy Germanium detector (LeGe) shielded with 10 cm of old lead to protect the detector from the cosmic rays. These types of detectors are specially designed for the measurement of low-energy gamma emitters such as ^{241}Am and presents a very good resolution which allows to find the 59.5 keV gamma-ray peak isolated from interferences.

Chapter 4

Kinetics and Transformation of radioactive particles in the terrestrial zone affected by the Palomares accident

Introduction

As it was indicated in Chapter 2, since early 1960s leaching experiments have been performed to simulate possible transfers between different compartments in ecosystems affected by radioactive particle releases, in order to gain information about transformation processes. In the case of Palomares, these leaching experiments have been applied in the past only to soil aliquots. Results shows that the degree of solubility of Palomares particles seems to be in general quite low and dependent on several factors such as pH, temperature, presence of oxidants and/or reducing agents and the surface area of the particles (Baeza et al., 2005; Espinosa, 2003; Iranzo et al., 1991; Lind et al., 2005).

A first study was conducted in the 80`s simply using water as extractant, indicating an extremely low percentage of the Pu dissolved, although significant increase in the aqueous solubility of Pu oxide present in soils was observed with time. The average value of the Pu solubility in water determined in five samples was 0.0082 % (σ = 0.006) in 1986, while determinations carried out in samples taken in 1999 and 2000 indicated an increase of the Pu solubility of two orders of magnitude (Espinosa et al., 2005), fact that the authors associated to the oxidation of Pu on the surface particles and to the increase of the specific surface of the Pu oxide particles due to the fragmentation of the nuclear material. The results obtained by Lind et al., 2007 indicating the existence of a small fraction of the U and Pu in oxidation states that may differ from +4, and the existence of Pu/U heterogeneities on particle surfaces support the fact that the particles could represent a higher remobilization potential than previously observed and is an indication that radionuclide ecosystem transfer is time dependent.

In an independent study performed in order to make an empirical assessment of the Palomares Pu availability by plant uptake, leaching experiments using 1 M

Cl_2Mg at pH=7 as the most suitable extractant were performed (Jimenez-Ramos et al., 2008), being applied to soils with different degree of contamination. The obtained results indicated that the bioavailable fraction was relatively variable but low and ranges from 0.4 to 6 %, with the great majority of values being lower than 1 %.

Another study performed more than 30 years after the accident (Espinosa et al., 2005) shows that the possible presence of organic fertilizers in soils such as cow urine mixed with solid excrements could increase Pu solubility, as demonstrated in contaminated soil samples treated with cow urine; a Pu ($^{239+240}$Pu and ^{238}Pu) solubility value up to 18 % was observed. The authors indicated that the solubilization was probably due to the oxidation of the actinides by the presence of HNO_3, due to decomposition of the urea. The percentage of plutonium dissolved with the cow urine is similar to the one obtained with sodium pyrophosphate acting as extracting solution and should be considered as a clear warning of what might happen if organic fertilizers are used in the contaminated area.

Another type of leaching studies was performed by using 0.16 M HCl as extracting reagent. In this case the objective was to simulate with this extractant human gastrointestinal tract fluids to know the possible solubilization of Pu if some uncontrolled digestion of contaminated soil is produced. The results obtained in these experiments show the low availability of Pu through this extractant (10 %) in soil samples collected in Palomares (Lind et al., 2005, Jiménez-Ramos et al., 2008), in part due to the buffering effects of the Palomares soils (the acidity of the 0.16 M HCl extractant is considerably neutralized in its reaction with the soils).

All the leaching experiments performed historically with Palomares soils, although informative, were quite scattered and were carried out applying different procedures with difficulties to obtain from them useful/comparable information.

If they are properly established/justified and validated, leaching experiments can provide important data on particle characteristics and the links to solubility, particle weathering rates and remobilization potential for particle associated radionuclides (Lind, 2006). With this objective, and as it was indicated previously, the abiotic protocol described in the previous chapter and established with the aim of identifying key parameters affecting properties of particles, when exposed to a variety of different water qualities and abiotic leaching agents has been applied.

The applied leaching experiments have been performed on single radioactive particles, but also on bulk samples from where the particles were isolated because it will help in the interpretation of results obtained on particle transformation processes, including re-adsorption processes and also link new data with literature data. The applied protocols were detailed in Chapter 3. In the abiotic protocol, isolated and well characterized radioactive particles or small bulk samples known to be contaminated with particles are transferred to centrifuge tubes and extracted with 20 ml of the leaching medium for 1 hours (representative of a residence time in the stomach), 24 hours (transit time through the intestine) and 168 hours (long term potential mobility of radionuclides). As abiotic reagents rainwater and HCl 0.16 M have been used (in this last case mimicking the acidity and strength of gastric fluids).

Similar experiments have been also performed on small bulk soil samples using cow rumen as in vivo biotic reagent for 24 hours following the work of Cooke and co-workers (1995).

In the case of the leaching experiments performed with isolated particles the different leachates obtained were submitted to size fractionation. In each leachate, information about the radionuclide concentration in four fractions (total, dissolved (<0.45 mm), low molecular mass (LMM), and < 3 kDa fractions) was obtained by taking advantage of the extremely low limits of detection that can be obtained by accelerator mass spectrometry (AMS). This would allow to gain information about the different transformation process affecting the particles in the leaching experiments. In the case of soil samples the radionuclide determinations have been performed only in representative aliquots of the leachates (total fraction) although in addition another aliquots will be analyzed by ICP-MS in order to obtain elemental information that can be of importance in order to explain possible processes of incorporation of radionuclides to the leachates.

The samples from the contaminated site

As it was detailed in Chapter 2, some remaining contamination still exists in the area affected by the accident. In fact, recent studies performed in the area have allowed evaluating the magnitude of this remaining contamination, as an initial step for its cleaning. The resulting remaining contamination map (Figure 2.2) shows that the highest levels of contamination can be found in the two zones, Zone 2 and zone 3, where the weapons crushed, but also relatively high levels were found in a hilly area located near the coast, at the east of the denotation points (zone 6), where the radionuclide deposition was produced due to the impact of the generated radioactive clouds travelling to the sea following the direction of the dominant winds at the time of the accident. The zone 2 was the area used immediately after the accident for the disposal of all the contaminated material picked-up during the clean-up operations, and to fill all the drums sent to USA; being for that reason more extended than in zone 3 the area affected by high remaining contamination.

In this chapter will be analyzed the transformation processes of a couple of isolated hot-particles: one from zone 2 and one from zone 6. In addition, and in the surroundings (less than 10 meters) of the places from where the particles were isolated, several soil samples were collected to be submitted to the bulk sample leaching protocol. Photographs characteristics of both zones, zone 2 and zone 6 are shown in Figure 4.1.

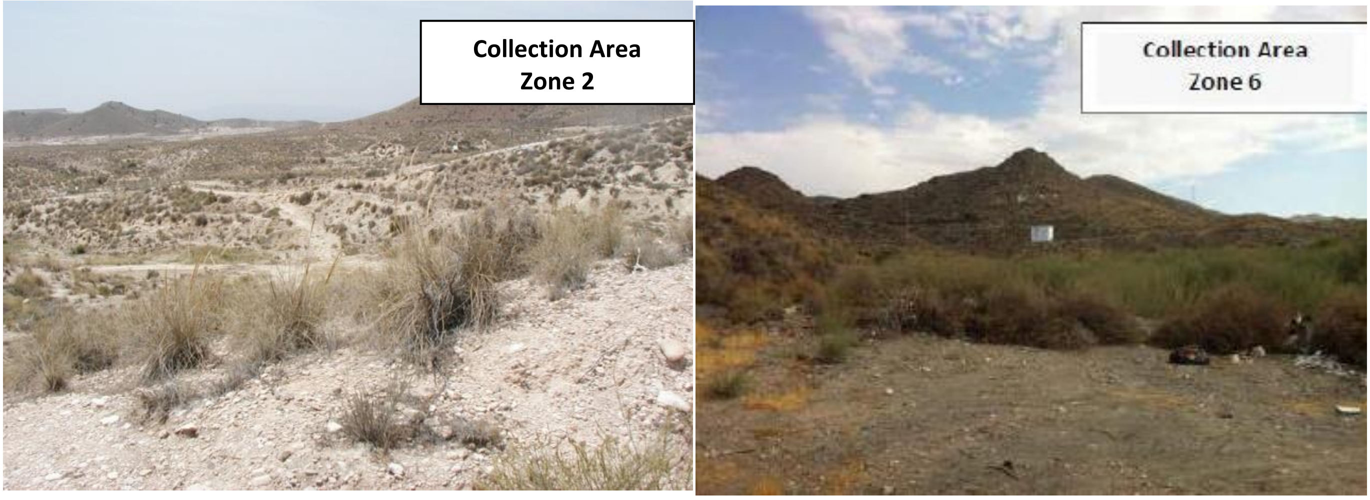


Figure 4.1.- Photographs of the two areas where Palomares soil samples were collected, and from where radioactive particles were isolated

Results in isolated particles

As it was indicated below, a couple of isolated particles were submitted sequentially to two sequential leaching protocols. The first one was performed using rainwater collected in the Palomares area as a leaching agent (trying to mimic possible dissolution processes after heavy rainfalls), and the second one using 0.16 M HCl as a leaching agent (trying to mimic the possible dissolution by the action of gastric juices in case of ingestion).

The particle called 2-2 was isolated from a soil aliquot collected in zone 2, the zone most affected nowadays for the presence of remaining Pu contamination, in an area anthropogenically altered after the accident in order to do agriculturally productive the terrain (the terrain was flattening, distributing the soil material from some hills). It was a relatively small particle, less than 100 μm in diameter and its ^{239}Pu content was estimated in 3.5 Bq, with basis in the determination of the ^{241}Am content, performed by high-resolution gamma ray spectrometry, and in the application of a well-defined ^{239}Pu/^{241}Am activity ratio in the contaminated area.

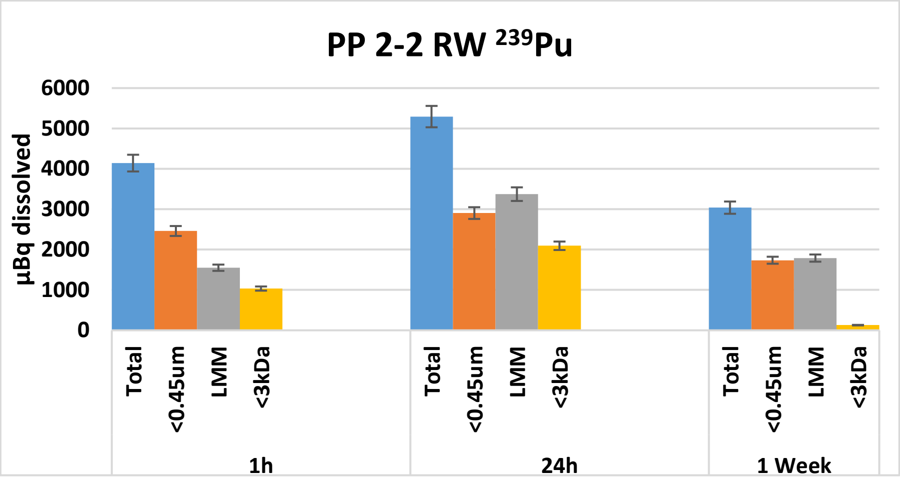
The particle called 421 was on the other hand isolated in zone 6 from an area where soil material is deposited after runoff transport, located at the basis of the hilly affected area, in the east region nearest to the village of Villaricos. It was a quite small particle (around 25 μm diameter), with a spherical shape and an estimated ^{239}Pu activity of 13.5 Bq. In addition, and through submicro-XRF analysis it was possible to observe that the Pu/U atomic ratio inside the particle is not uniform (average Pu/U value = 2) (Lind et al., 2018).

The set of ^{239}Pu activities found in the different fractions (total, <0.45 μm, LMM and < 3 kDa) of the different leachates (1h, 24h, 168 h) obtained from the particles 2-2 and 421, using Palomares rainwater as leaching agent are shown in Figure 4.2.

The parametrization of the evolution over time of the cumulative percentages associated to each fraction, or in other words, the parametrization of the cumulative desorption curve obtained for the Palomares particles has been performed by fitting in each case the experimental data to the so-called Rosin-Rammler, which takes the following form:

$$Y=1-\exp\{-(t/t_o)^m\}$$

where **Y** is the cumulative fraction (from 0 to 1) that pass to solution, **t** is the time since the beginning (the accumulated after each extraction), t_o is a characteristic time (the time needed for the dissolution of 1-1/e, because for $t=t_o$ $Y=1-(1/e)$) and **m** is a homogeneity factor. It allows easy comparisons between the different leachates. With the experimental data the fitting can be easily done by linearizing and solving by minimum squares the values of t_o and m. The use of the Rosin-Rammler is supported by the fact that, $dY/dt= R(t)$ has a clear physical meaning: it corresponds to the temporal evolution of the desorption rate as a function of time.



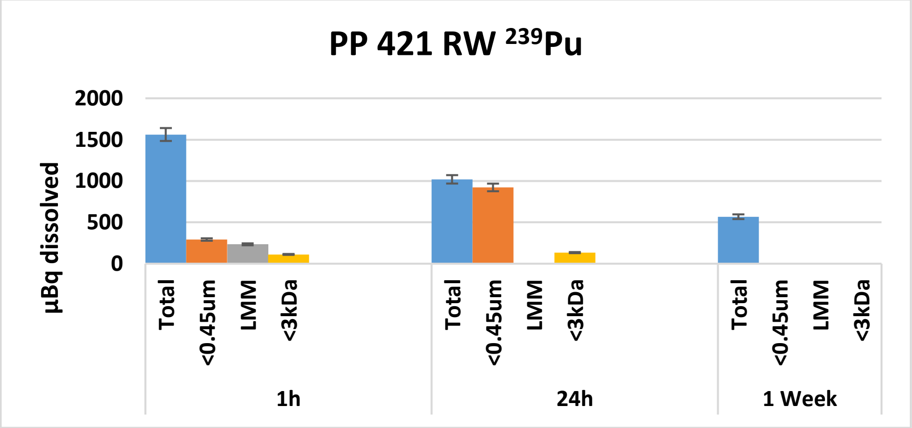
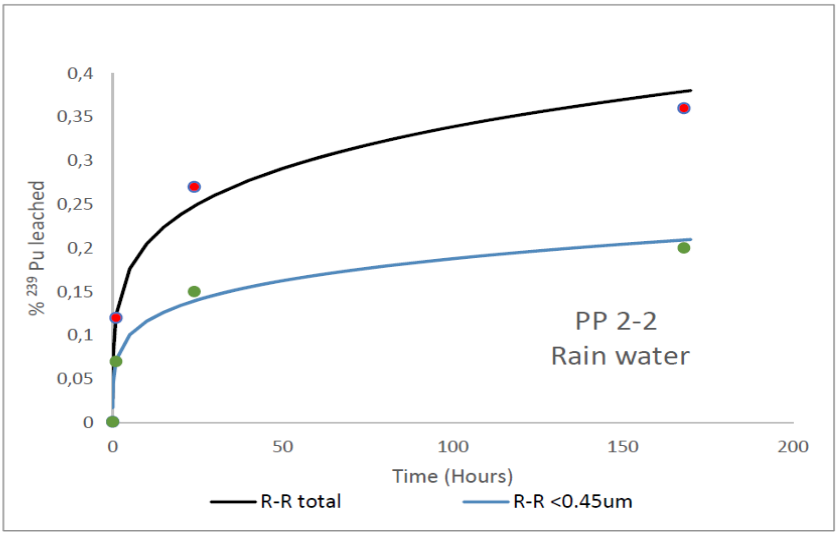


Figure 4.2.- Activities of ^{239}Pu found in the different fractions of the leachates obtained for the isolated particles 2-2 (up) and 421 (down) from Palomares using the leaching protocol described in this paper and using local rainwater as a leaching agent.



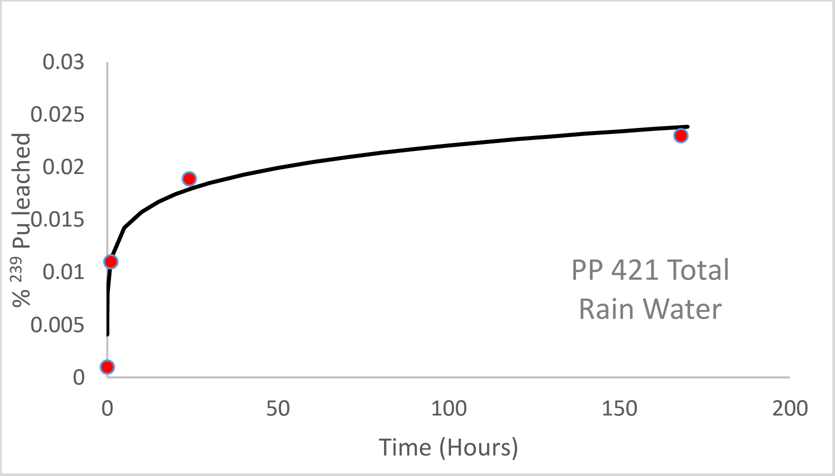


Figure 4.3.- Cumulative percentage (%) of ^{239}Pu in the total leachate fraction of particle 421 (up) and in the total and 0.45 µm leachates fractions of particle 2-2 (down) after application of the leaching protocol using rainwater.

As it can be observed in Figure 4.3, the fittings of the experimental data to the Rosin-Rammler function describe properly the temporal evolution of the Pu desorbed associated to each fraction, allowing extrapolations and comparisons between different fractions of the same aliquot or between equal fractions corresponding to different particles through the analysis of the fitted parameters t_o and m.

The analysis of the results compiled in Figures 4.2 and 4.3, first of all, clearly indicates that in both cases the total amount of ^{239}Pu incorporated to the rainwater solution along the leaching experiment is very small: in the order of 10^{-2} to 10^{-1} % after a week of interaction. This evidence is not surprising, according to the results obtained in the past by submitting soil samples heavily affected by the Palomares accident to leaching using irrigation water that were quite similar (Espinosa et al., 2005) and clearly indicates that the transformation processes affecting to the particles disseminated in the terrestrial area under the action of dissolution agents (rainwater, irrigation water) are quite slow.

Additional information can be obtained by analyzing the data obtained from the size fractionation studies performed: in fact, if we take into account that the percentage of cumulative ^{239}Pu incorporated to the rainwater in particulate form (> 0.45 μm) can be determined through the expression

$$\mathbf{^{239}Pu_{\text{(particulate fraction)}} = {}^{239}Pu_{\text{(total fraction)}} - {}^{239}Pu_{\text{(< 0.45 mm fraction)}}}$$

and that the colloidal fraction can be evaluated by considering that

$$\mathbf{^{239}Pu_{\text{(colloidal fraction)}} = {}^{239}Pu_{\text{(< 0.45 mm fraction)}} - {}^{239}Pu_{\text{(< 3 kDa fraction)}}}$$

It can be deduced from the data readapted now in Figure 4.4, that a considerable proportion of the Pu incorporated to the rainwater during the application of the abiotic leaching with rainwater is in particulate form. A considerable fraction of the Pu present in the rainwater is not really dissolved, being possible to hypothesize that is incorporated as particles by mechanical disruption effects.

In support of this last conclusion, it is important to indicate that studies performed characterizing different Palomares particles on the frame of the previously commented COMET-RATE European Union project, shows that these particles have a quite fragile behavior with a clear tendency to suffer fragmentations under different actions, see Figure 4.5 (COMET, 2017). The average size of the particles has clearly diminished since the time of the accident, especially in areas like zone 2 where anthropogenic actions (land movements) were performed (Sancho and García-Tenorio, 2019).

The presence of colloids in the different leachates is also in some cases not negligible and its importance or weight in the <0.45 μm fraction should not be neglected. These colloids could be interpreted mainly as nanoparticles, according to the theory expressed in the previous paragraph.

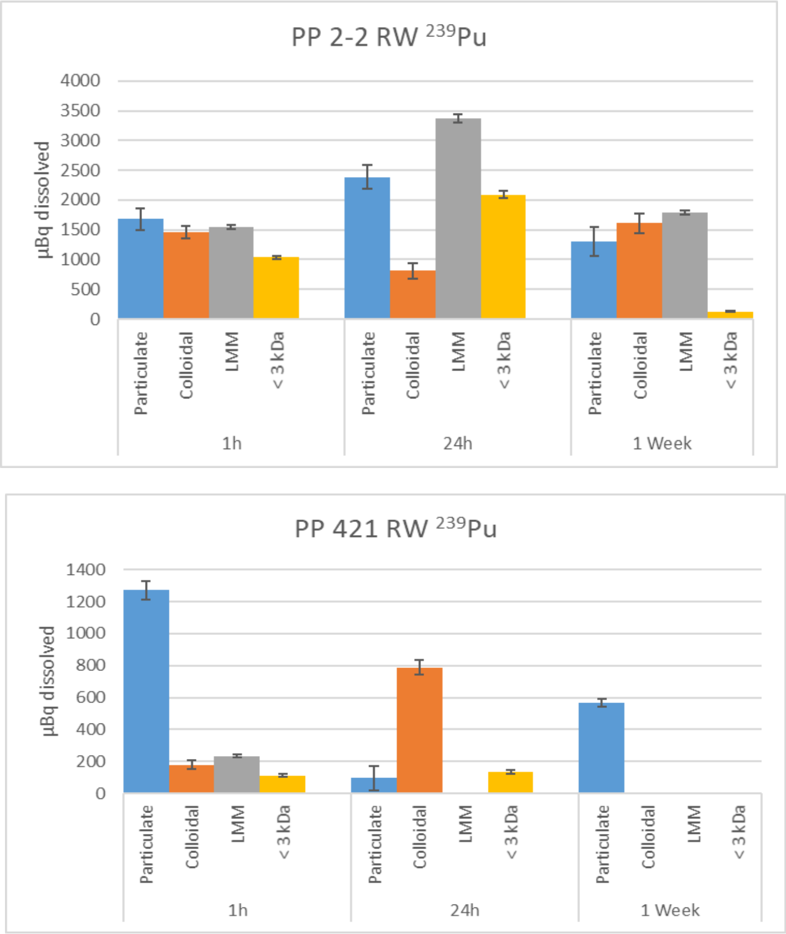


Figure 4.4.- Activities of ^{239}Pu associated to the different fractions of the leachates obtained for the isolated particles 2-2 (up) and 421 (down) from Palomares using the leaching protocol described in this paper and using local rainwater as a leaching agent. (Calculated particulate and colloidal fractions are shown)

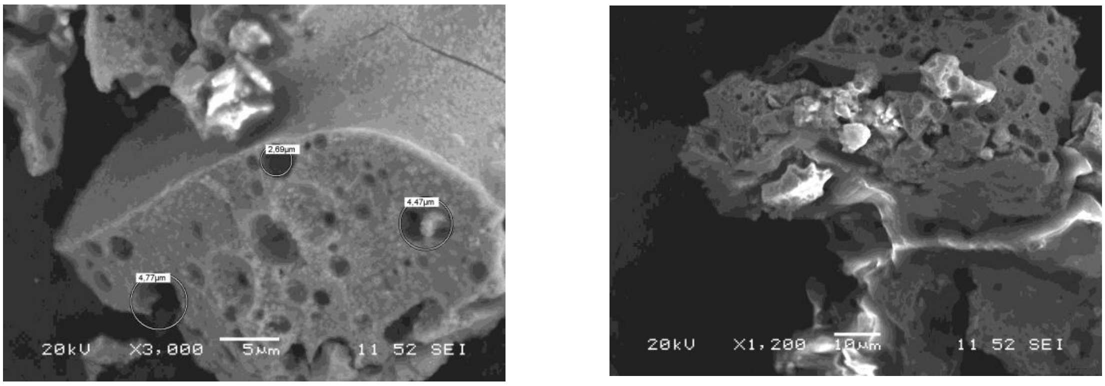


Figure 4.5.- High resolution images of a Palomares particle with secondary electrons, demonstrating the porosity and fragility of the particle.

Finally, it is interesting to mention that in the great majority of the leachate fractions, it was possible to measure in addition to ^{239}Pu, the content of ^{240}Pu, in spite of their low plutonium content. In Figure 4.6, and as example are shown the

$^{240}Pu/^{239}Pu$ atom ratios determined in leachates from the particle 2-2. These ratios were measured with a good precision, are quite uniform and its average value 0.06 is clearly an indicative that the analyzed particles are formed by weapon grade plutonium. No isotopic fractionation is observed in the leaching processes with rainwater, with atom ratios in the leachates totally concordant with the obtained ones in soils heavily contaminated by the Palomares accident where the Pu contribution due to the weapon test fallout is negligible (Chamizo et al., 2006).

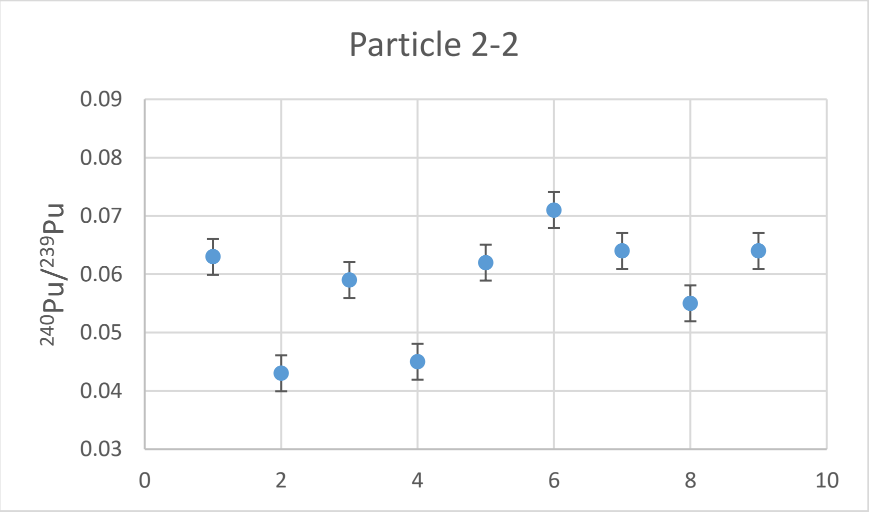


Figure 4.6.- $^{240}Pu/^{239}Pu$ atom ratios determined in different leachate fractions obtained by treating the particle 2-2 with rainwater.

Quite different results were obtained by applying to the two previously mentioned particles the same leaching protocol but in this case using 0.16 M HCl as extracting agent. Obviously in the interpretation of the results should be considered that this 0.16 M HCl study was performed after the previous leaching/washing with rainwater. In Figures 4.7, 4.8 and 4.9 the results obtained for the particle 421 are presented. A separation between the results obtained for both particles is done because the behavior observed was totally different.

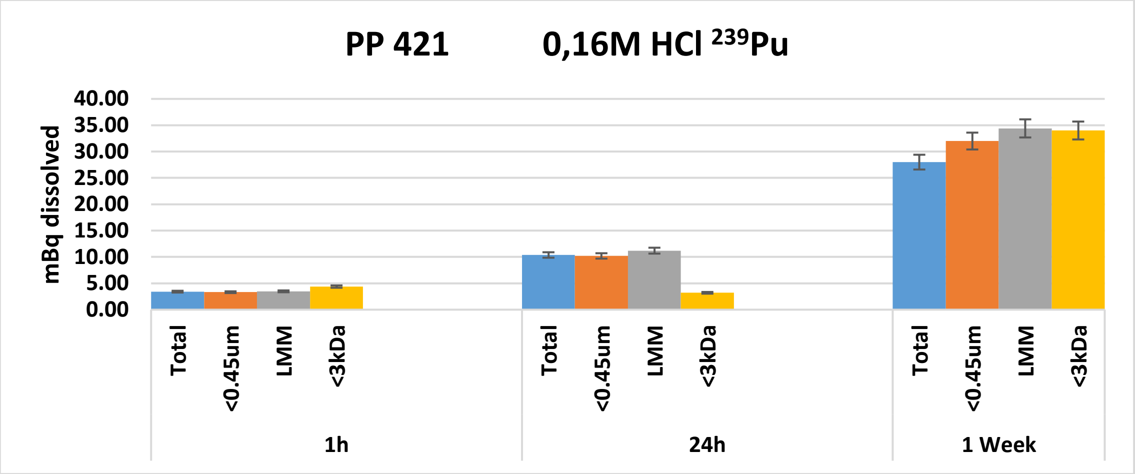


Figure 4.7.- Activities of ^{239}Pu found in the different fractions of the leachates obtained for the isolated particle 421 from Palomares using the leaching protocol described in this paper and using 0.16 M HCl as a leaching agent.

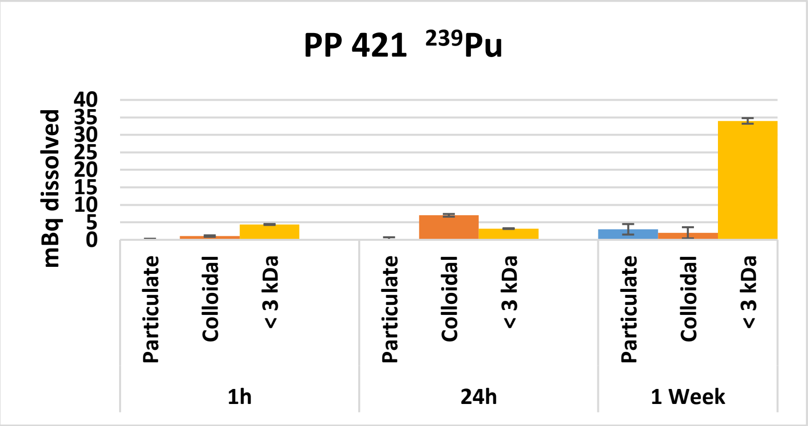


Figure 4.8.- Activities of ^{239}Pu found/determined in different fractions of the leachates obtained for the isolated particle 421 from Palomares using the leaching protocol described in this paper and using 0.16 M HCl as a leaching agent (calculated particulate and colloidal fractions are shown).

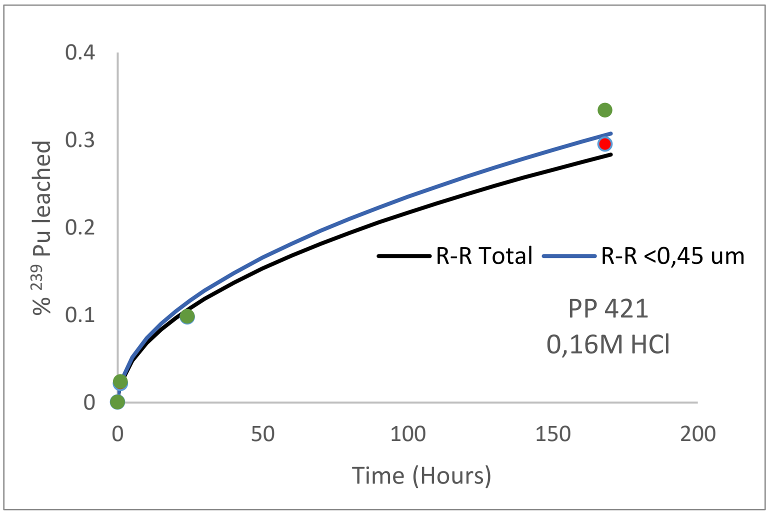


Figure 4.9.- Cumulative percentages (%) of ^{239}Pu in the total and 0.45 m leachates fractions of particle 421 after application of the leaching protocol using 0.16 M HCl as a leaching agent.

The incorporation of ^{239}Pu to the leachates in the case of the particle 421 has increased, due to the 0.16M HCl action, one order of magnitude in relation with the previously observed with rainwater, but still continues being extremely low its total amount. A ^{239}Pu leaching percentage not reaching after a week of interaction even 1% evidence that the weapon material disseminated in the Palomares area remains in a quite refractory form, mostly as Pu oxide.

The ^{239}Pu leaching behavior with 0.16 M HCl on the other hand, shows a remarkable difference with the observed one with rainwater. While in the washing/leaching process with rainwater, the particulate fractions in the leachates played a considerable role, with the 0.16 M HCl it is observed that the ^{239}Pu incorporated to the leachates is mostly in dissolution as is reflected in the fact that the ^{239}Pu activities in all the fractions (total, <0.45 μm, LMM and < 3 kDa) are in general homogeneous. The particulate and colloidal phases play a minor/marginal role in this case. With independence on the way and the form in which the ^{239}Pu is incorporated to the liquid fraction (it cannot be discarded the initial incorporation of a fraction in particulate form as in the treatment with rainwater), this ^{239}Pu experiments its total dissolution and homogenization in the different fractions before the collection of the leachates. This fact is especially relevant in the case of the leachate with high contact time (one week).

In two of the leachates (24h, 168h) with higher activities, it was also possible to determine the ^{236}U in their different fractions. The results obtained, which are compiled in Figure 4.10 by representing the ^{236}U/^{239}Pu, together with the ^{240}Pu/^{239}Pu, atom ratios confirm the fact that all the actinides incorporated to the leachates are found in dissolution. Although the ^{236}U/^{239}Pu atom ratios were higher in the different fractions of the leachate collected after a week of interaction, in comparison with the obtained ones in the 24h leachate evidencing a possible preferential leaching of U in relation to Pu from the particles, for each leachate, the ^{236}U/^{239}Pu atom ratios in the four fractions were very uniform indicating the same behavior (in terms of distribution between the different fractions) of both elements. In addition, and as in the case of rainwater the ^{240}Pu/^{239}Pu atom ratios found are indicative of weapon-grade plutonium (6%) and of the no existence of Pu isotopic fractionation in the leaching process in acidic conditions.

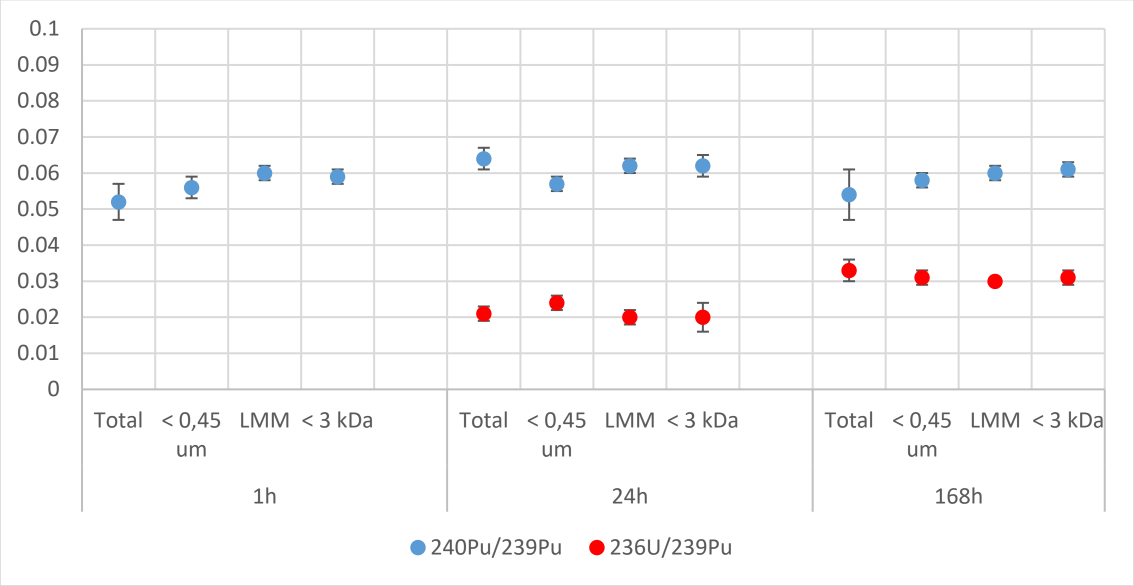


Figure 4.10.- ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu atom ratios determined in the different fractions of the leachates obtained in the treatment of particle 421 with 0.16M HCl. The ^{236}U was not detectable in the fractions corresponding to the 1 h leachate.

The results obtained in the application of the leaching protocol with 0.16 M HCl to the particle 2-2 were totally different as it can be deduced by observing the Figures 4.11, 4.12 and 4.13. After a week of leaching treatment practically 100% of the Pu present in the particle has been incorporated to the different leachates, reflecting the practical disintegration of the particle.

These results should not be interpreted as contradictory with the conclusions obtained in the analysis of the previous particle. The data suggests that the fragility and physical unstable behavior of these particles is behind the results obtained in this case, and that along the leaching processes, very small fragments were initially incorporated in particulate form to experiment after that and under the action of the acidic agent its dissolution.

In support of the previous comment are the size fractionated data obtained in the analysis of the leachate obtained only after 1 hour of treatment. Near 40% of the ^{239}Pu activity initially associated to the particle is found in the leachate, being a considerable proportion of this 40% present in particulate form. The interaction time was enough to physically fractionate the particle but not for the posterior dissolution of the small fragments generated.

Similar processes as the described for the first leachate could affected to the leachates collected after 1 day and 1 week but with the difference that the time of the 0.16 M HCl interaction was enough to provoke the total dissolution of the material fragmented, being no detected in these fractions the presence of particulate material (>0.45 μm).

We can conclude indicating that the obtained data suggest that is the fragile behavior of the particles the main factor which can affect the possible incorporation of actinides to the acid leaching solution. In the particle where its integrity remained, the percentage of Pu and U incorporated to the leached fraction was minimum, while, on the opposite, high actinide incorporation was observed in the particle that experimented its fragmentation/disintegration during the application of the leaching protocol.

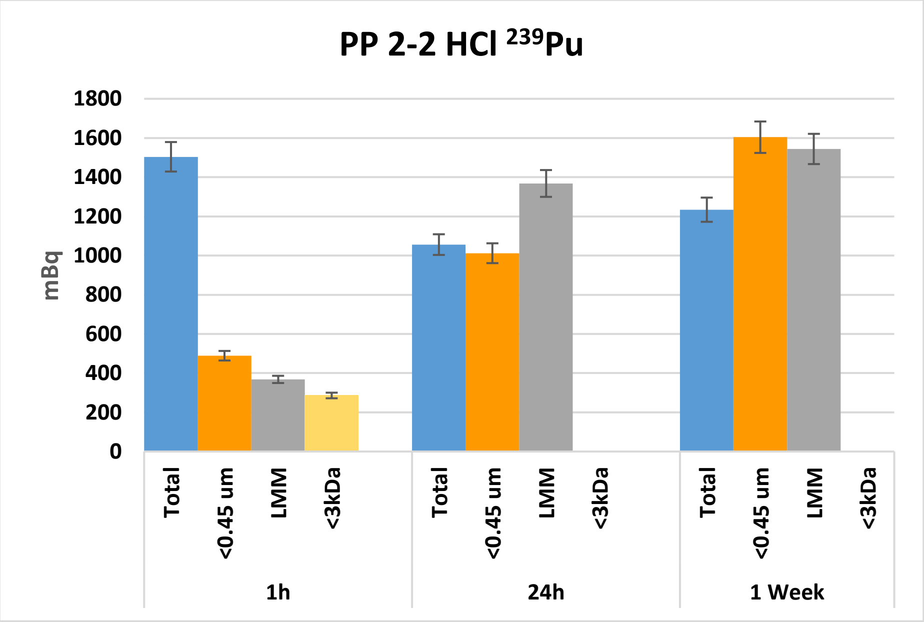


Figure 4.11.- Activities of ^{239}Pu found in the different fractions of the leachates obtained for the isolated particle 2-2 from Palomares using the leaching protocol described in this paper and using 0.16 M HCl as a leaching agent.

The observed particle behavior under the action of 0.16 M HCl as leaching agent has obviously clear implications from the radiological point of view. The use of 0.16M HCl mimicking the strength of the acid gastric juices in potential ingestion cases and the obtained results indicate that in not all the cases the particles are going to maintain its integrity releasing in dissolved form a minimum percentage of its plutonium content. The fragility of these particles can provoke their fragmentation and even disintegration and the incorporation of a no negligible amount of Pu into the body.

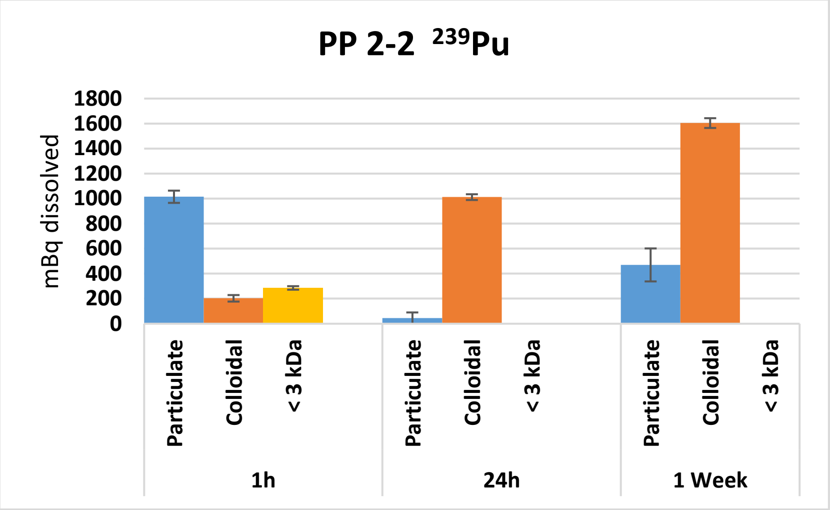


Figure 4.12.- Activities of ^{239}Pu found/determined in the different fractions of the leachates obtained for the isolated particle 2-2 from Palomares using the leaching protocol described in this paper and using 0.16 M HCl as a leaching agent (calculated particulate and colloidal fractions are shown).

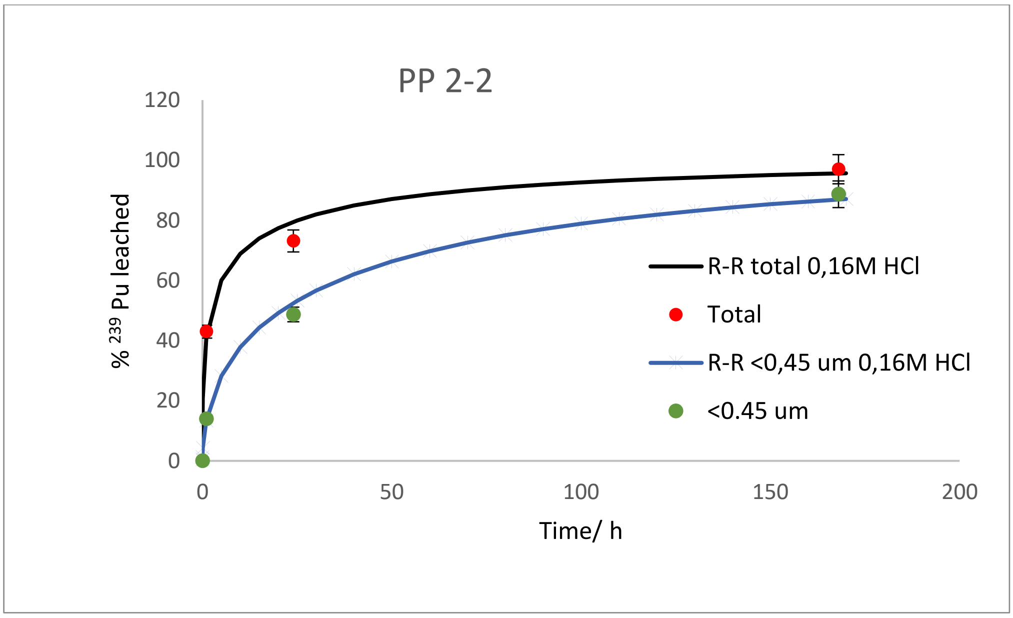


Figure 4.13.- Cumulative percentages (%) of ^{239}Pu in the total and 0.45 µm leachates fractions of particle 2-2 after application of the leaching protocol using 0.16 M HCl as a leaching agent.

In contrast to leaching of particle contaminated soil or sediment samples, leaching of individual particles are quite scarce in the literature and for that reason the study shown in this work represents important progress in particle science (Salbu et al., 2018). The only studies available correspond to leachings applied to particles isolated from former weapon tests sites by using different extracting agents. No size fractionation studies of the particle leachates as shown in this paper can be found until now in the open literature.

Results in soils

The leaching experiments performed with isolated particles has allowed to evaluate their direct response to the action of the extracting agents, which are clearly dependent of its formation origin (is source dependent) and also is dependent of the possible physico-chemical changes experimented over time by the particles, due to its interaction in the ecosystem where initially are deposited (is ecosystem-scenario dependent). But in order to complement the information obtained, and to evaluate also the role that can play the soil/sediment material where these particles are embedded in the possible incorporation or inhibition of the contamination to the extracting agents, leaching experiments have been carried on a set of soil aliquots heavily contaminated with Pu originated in the Palomares accident.

The leaching protocols, described in chapter 3, have been applied as appropriate to a total of 5 soil aliquots collected in zone 6, in the area where the particle 421 was collected, and to a total of 4 soils collected in zone 2, in the area where the particle 2-2 was found. As extracting agents have been used rainwater, 0.16 M HCl and cow rumen. The level of transuranic contamination of the soil aliquots is high, with for example ^{239}Pu activity concentrations in the range 300-400 Bq/kg d.w. in the aliquots from zone 6 (activity concentrations 2 to 3 orders of magnitude higher than the expected values if the only origin of the Pu is the weapon fallout).

In Figure 4.14, are shown the cumulative percentages of ^{239}Pu determined by treating over time 3 soil aliquots from zone 6 with rainwater, together with their fits to a Rossin-Rammler distribution. The Pu leached with rainwater from these soils can be evaluated in principle as quite low, ranging in the interval 0.8 – 2.5% after a week of interaction, but if these values are compared with the results published in similar experiments performed in the past and summarized in the introduction of this thesis, they are relatively higher. In experiments performed in the 80´s and 90´s the incorporation of Pu to water were in all cases clearly lower than 1%. In addition, the percentage of Pu leached from the soil aliquots is clearly higher than the percentage of Pu leached using the same leaching agent from the particle isolated from this site.

Several are the reasons that can be argued in order to understand the percentage of Pu leached in these experiments. First of all, it is necessary to remark the origin of the aliquots analyzed. They were collected from a sedimentary place at the basis of the hills located in the zone and where material is deposited/accumulated after their transport (mostly by runoff from the hills). A fraction of the contamination, due to the transport processes experimented by the material analyzed could be more available and can be incorporated to the leached fraction, either in dissolved or in particulate form. The Pu particles in the soils analyzed are expected to have quite small dimensions due to physical fragmentations, presenting high surface to volume ratios.

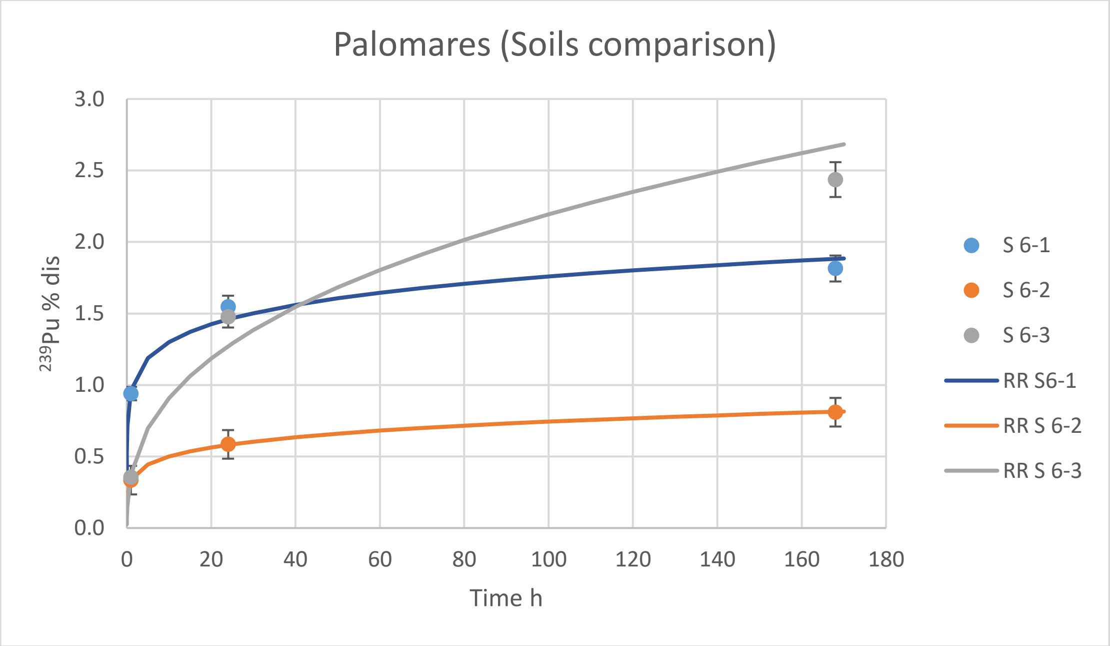


Figure 4.11.- Cumulative percentages (%) of ^{239}Pu determined after application of the leaching protocol using rainwater as a leaching agent in three different soil aliquots from zone 6.

Other factors that should be taken in consideration to explain the obtained results are: a) the possible oxidation over time of a proportion of the PuO_2 forming originally the particles, as it has evidenced in microanalytical analysis carried out in isolated particles (Lind et al., 2007), and b) the characteristics of the extractant used, because the ionic composition of the rainwater used in these experiments and its potential interaction is a peculiarity not present in the aqueous fractions used in the experiments taken for comparison.

Despite the low actinide percentages leached in these experiments, the high sensitivity of the accelerator mass spectrometric technique has also allowed to determine in the different leachates the activities of ^{240}Pu and ^{236}U in addition to ^{239}Pu. In Figure 4.15, the corresponding ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu activity ratios are shown.

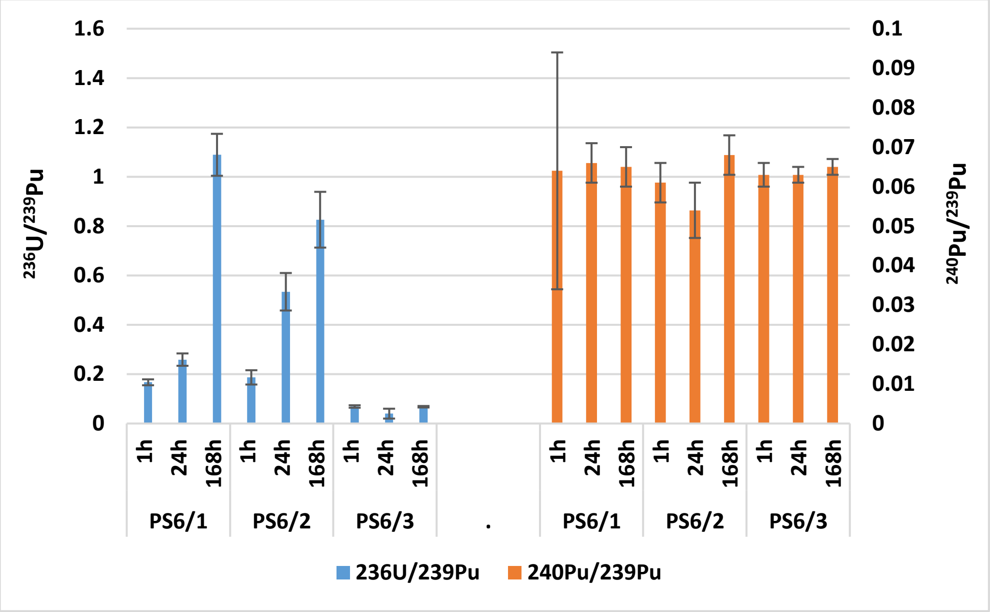


Figure 4.15.- ^{236}U/^{239}Pu and ^{240}Pu/^{239}Pu activity ratios determined in the different leachates obtained by treating three soil aliquots of zone 6 with rainwater.

The ^{240}Pu/^{239}Pu activity ratios obtained in the different leachates were quite uniform, as in the case observed previously for the isolated particles, with an average value of 0.06 typical of the weapon-grade fallouts forming the bombs involved in the Palomares accident (no Pu isotopic fractionation is found). On the contrary, quite different ^{236}U/^{239}Pu activity ratios were found with clear differences between the values obtained for the different soil aliquots, and also with clear differences between the leachates obtained over time in the same aliquot. The ^{236}U and the ^{239}Pu present in the contaminated soils does not follow the same behavior with a tendency of an increase in the solubilization of the U in comparison with the Pu over time (see evolution over time of the $^{236}U/^{239}Pu$ activity ratio in soil aliquots PS6/1 and PS6/2).

Finally, in the 9 rainwater leachates corresponding to the three soil aliquots analyzed from zone 6, elemental determination was performed by ICP-MS. The amount of As, Ba, Ca, Cd, Ce, Cu, Cr, Fe, Mn, Nb, Nd, Sr, Ti, Th, U and V was determined in these leachates, being this set of data together with the ^{239}Pu activities determined by AMS submitted to a Principal Components Analysis (PCA). A PCA is a method for reducing a large number of variables, finding new variables (principal components), which make the data easier to understand. The PCA is used to study the relationship between variables and identify how groups of variables change with respect to each other. The Graph corresponding to the PCA results is shown in Fig 4.16 (variable loadings),

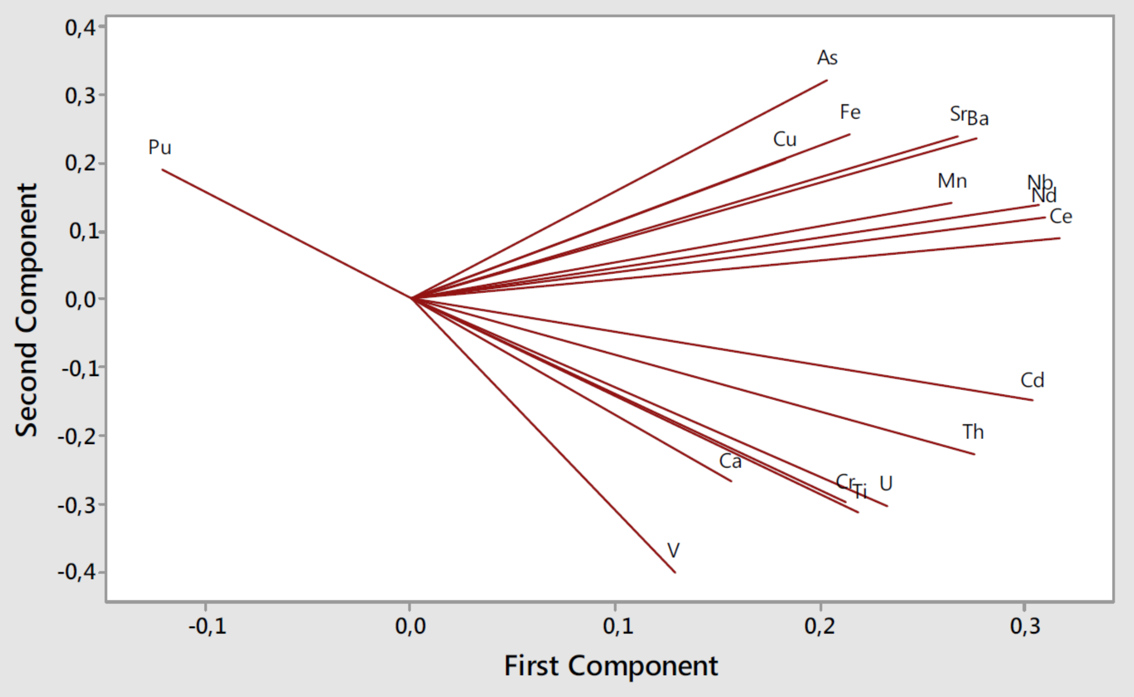


Figure 4.16.- PCA results (loading plot of variables) associated to the rainwater leachates obtained from 3 soil aliquots of zone 6 (17 elements).

The PCA shows that 83.6% of the data set total variance is accounted by the two first components (F1: 54.4%, and F2: 29.2%), and with independence that the majority of elements can be classified in two big groups both positively correlated with component 1, but each one with opposite correlation with component 2, the most important observation is the different pattern and behavior observed for the

Pu, isolated from the rest of the elements. This fact is an indicative of the presence of Pu in the soil aliquots in a peculiar form, i.e., in anthropogenic particulate form with a different behavior that many of the leached elements from the treated soils.

The conclusions obtained from the previous PCA analysis are clearly reinforced if with from the same set of data corresponding to the 9 leachates obtained with rainwater, we perform a new PCA analysis but restricting it to 7 elements: Cu, As, Fe, Cr, U, and Th determined by ICP-MS and Pu determined by AMS. The new graph corresponding to the PCA results is shown in Fig. 4.17 (variable loadings),

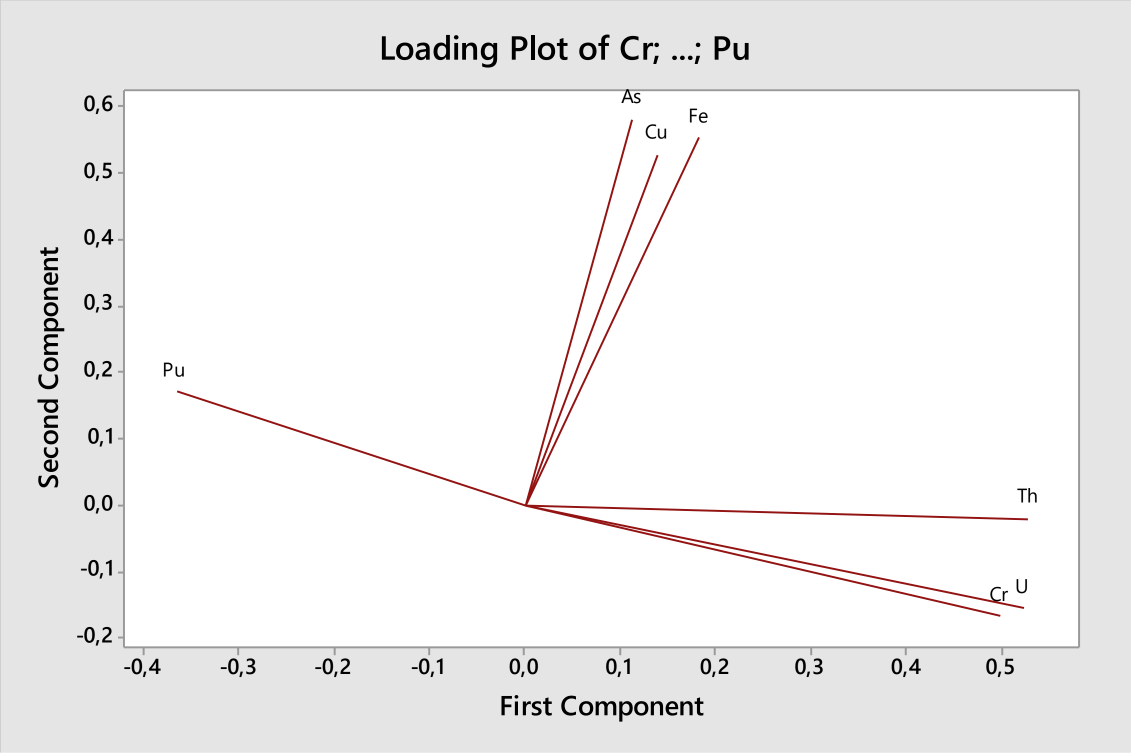


Figure 4.17.- PCA results (loading plot of variables) associated to the rainwater leachates obtained from 3 soil aliquots of zone 6 (restricted to 7 elements).

The new PCA shows that 77.5% of the data set total variance is accounted by the two first components (F1: 46.0%, and F2: 31.5%), and the loading variable plot evidences, in addition to the previously observed totally uncorrelated behavior of the Pu with the rest of elements, that the elements included in the analysis are distributed in two groups: one group positively correlated with component F1 (U, Th and Cr) and the other positively correlated with component

F2 (As, Cu, Fe). This difference between the groups and the elements associated to each one should reflect the different association of the elements involved in the analysis to the soils analyzed. All the heavy metals are clearly correlated between them and show different behavior that elements that can be more associated to the matrix of the analyzed soils.

The soils from zone 6 previously treated with rainwater were afterwards submitted to the biotic protocol using cow rumen as a leaching agent. As it was indicated in section 4, the cow rumen was in interaction with the soil for 24 hours and incubated at 39ºC to mimic as much as possible the possible action in the digestive system of the ruminants due to the inadvertent ingestion of contaminated Palomares soils.

The ^{239}Pu results obtained in the 24h treatment with cow rumen is shown in Figure 4.18 together with the cumulative ^{239}Pu leached previously in the leaching with rainwater for comparison purposes,

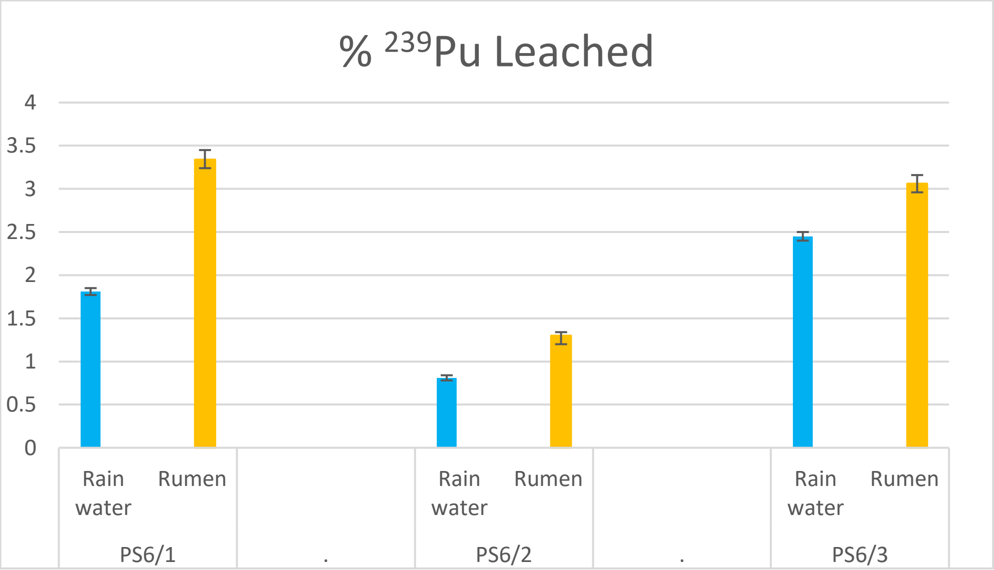


Figure 4.18.- % of ^{239}Pu leached in cow rumen after 24 h of interaction compared with the cumulative % of ^{239}Pu leached previously in the same soil aliquots with rainwater during one week.

The percentage of Pu leached with the cow rumen is an all the cases higher than the percentage previously leached with rainwater (in three different sequential aliquots acting during a week), but with quite moderate values that ranges from 1.5 to 3.5%. The quite refractory behavior of the Pu is dominant even under the action of these juices, fact that is in concordance with some studies analyzing the peroral intake by cows of radioactive particles and contaminated soils with origin in the Chenobyl accident which concludes that the bioavailability of the Cs and Sr in particulate form was two orders of magnitude higher that in the water-soluble form (Yorshenko et al., 2007).

In order to go more in depth in the analysis of the potential bioavailability of the Pu contaminating the Palomares soils, the leaching protocol was applied to two additional soil aliquots collected in Zone 6, but in this case using 0.16 M HCl as extracting agent in order to mimic the action of the human stomach juices in the case of inadvertent ingestion of some Palomares soil. The obtained results are compiled in the Figure 4.19. Although the refractory behavior of the contamination minimizes the transfer through the roots of actinides from the contaminated soil to the plants (very low TFs), a peculiar characteristic of a semi-desertic area like Palomares is the high resuspension of soil material that could finish deposited on the vegetables leaves or on the fruit skins growing in the area. (Palomares zone is nowadays an area devoted to the intensive production of agricultural products) and ingested by population.

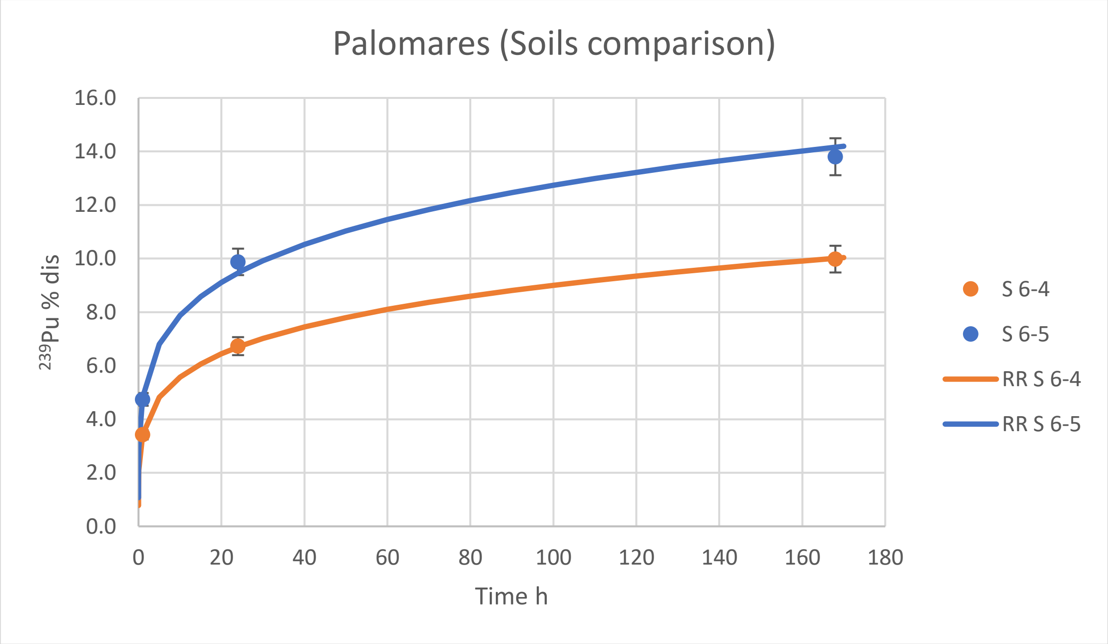


Figure 4.19.- Cumulative percentages (%) of ^{239}Pu determined after application of the leaching protocol using 0.16 M HCl as a leaching agent in two different soil aliquots from zone 6.

The percentage of the Pu leached with the 0.16 M HCl extractant is clearly higher than the obtained ones with rainwater and also higher than the obtained with cow rumen. However, the cumulative percentages leached after a week (from 10% to 15%) continues being a relative minor fraction of the total amount of Pu contaminating the aliquots analyzed.

The obtained results are in good agreement with the obtained ones applying similar procedures in Lind, 2006 (results summarized in Salbu et al., 2018). In the mentioned works low leaching percentages (in all the cases lower than 15%) were obtained treating also Palomares soil aliquots with 0.16M HCl.

The refractory behavior of the Pu contamination present in the contaminated soils, as it has been evidenced previously in this work can explain these low percentages, although a peculiarity of the Palomares soils can also have a high influence: their high carbonates content. The soils provoke a buffering effect neutralizing the strength of the acidic solutions used as a leaching extractrants as it has been experimentally proven by controlling the pH of the solution after the addition of 20 ml of 0.16 M HCl to 1 gram of Palomares dry soil. pH values of 4 just 10 minutes after the addition, pH values of 5 after passing 1 hour and pH values of 6 after 24-48 hours were obtained by treating 6 different aliquots (the evolution of the pH can be considered quite reproducible). This neutralization diminishes the strength of the solution and its transuranic extracting impact.

In the leachates of these soil's aliquots the content of ^{240}Pu and ^{236}U have been also determined. The evolution of the extracted ^{236}U over time follows the same trend as the observed for the ^{239}Pu, as it can easily be deduced observing the data and the good fitting of the experimental values to Rosin-Rammler distributions in the Figure 4.20.

As in the case of ^{239}Pu, the amount of ^{236}U leached was clearly higher with 0.16 M HCl than with rainwater, although the percentage leached continues being a relative minor fraction of the total amount of the ^{236}U contaminating the aliquots analyzed.

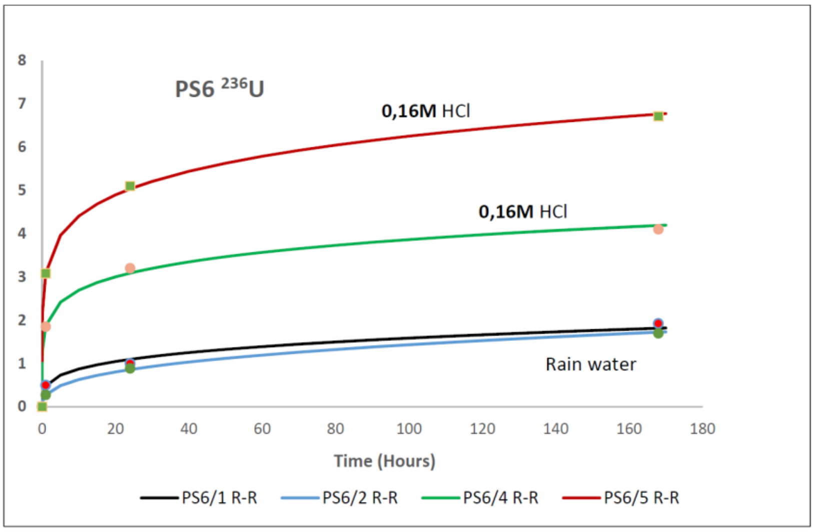


Figure 4.20.- Cumulative percentages (%) of ^{236}U *determined after application of the leaching protocol using rainwater and 0.16 M HCl as a leaching agent in different soil aliquots from zone 6.*

Finally, in Figure 4.21 are compiled the $^{236}U/^{239}Pu$ and the $^{240}Pu/^{239}Pu$ activity ratios determined in the 0.16M HCl leachates from the two zone 6 soil aliquots treated. The $^{240}Pu/^{239}Pu$ activity ratios are similar to the obtained ones when the aliquots were treated with rainwater, indicating the no existence of isotopic fractionation, while the $^{236}U/^{239}Pu$ activity fractions were found to be quite uniform and clearly lower than the observed ones in the rainwater leachates, indicating that the processes affecting the incorporation of the actinides to the solution are different depending the extracting agent used. Similar differences were observed in the leaching experiments performed with Palomares isolated particles: while in the case of the leaching with rainwater the particulate (>0.45 μm) fraction was dominant, in the leaching with 0.16 M HCl the great majority of the leached Pu was in dissolved form.

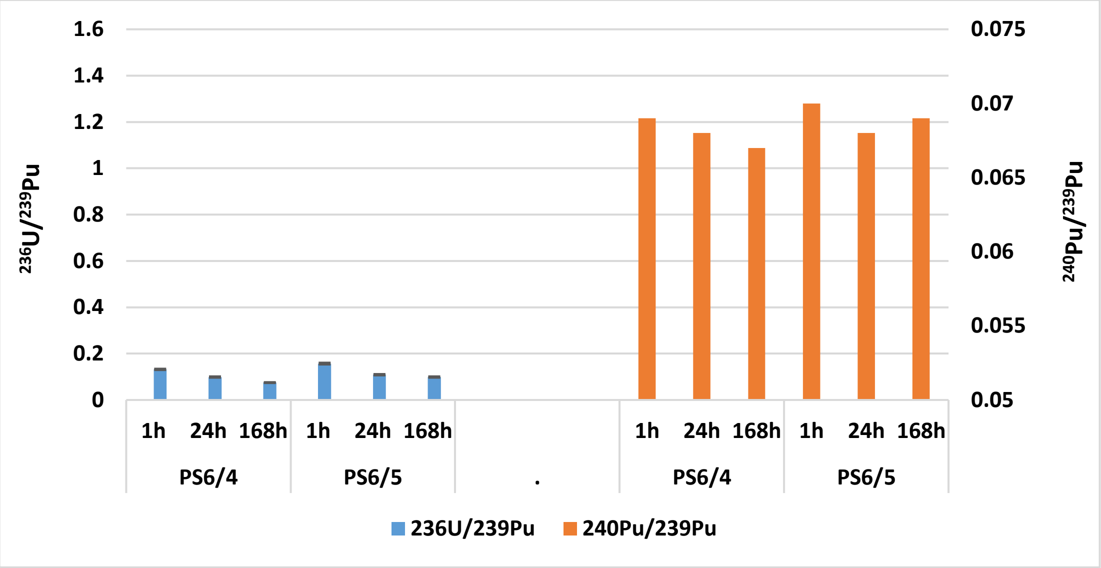


Figure 4.21.- ^{236}U/^{239}Pu and ^{240}Pu/^{239}Pu activity ratios determined in the different leachates obtained by treating two soil aliquots of zone 6 with 0.16 M HCl.

The leaching studies in Palomares soils have finally included analysis of different soil aliquots collected in the zone 2, for comparison purposes. A total of five different soil aliquots from zone 2 were submitted to the soil leaching protocol, three of them with rainwater, and the two remaining with 0.16 M HCl. The interest of this comparison is mainly related with fact that while the samples collected in zone 6 were taken from an area where the material was deposited by run-off from the hilly area contaminated in the accident. Material of zone 2, although probably altered due to movements of land with agricultural purpose, have not experimented the natural transportation and weathering processes suffered for the material of zone 6. In addition, the levels of contamination in the samples with clearly higher ^{239}Pu levels in some aliquots of zone 2.

In Figure 4.22, are first compiled the results obtained applying the leaching protocol with rainwater. It can be observed that the cumulative percentage of leached ^{239}Pu in the three cases is quite low and any case after one week of leaching the value of 1% is approached.

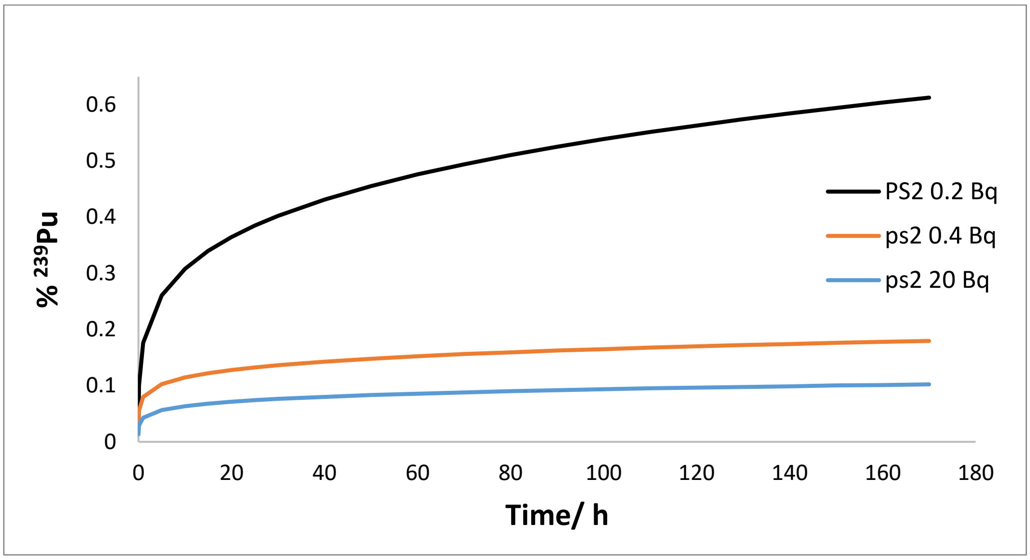


Figure 4.22.- Cumulative percentages (%) of ^{239}Pu determined after application of the leaching protocol using rainwater as a leaching agent in three different soil aliquots from zone 2.

Two main comments deserve the obtained results: first, it is possible to observe an inverse relationship between the cumulative percentage of ^{239}Pu leached from the soils and the total ^{239}Pu in them: less percentage leached from the soils the most contaminated aliquots. The presence of the contamination in the form of hot particles and possible differences in its behavior associated to their size and their fragile structure can give the reason. The second interesting point is that although in both cases the proportion was quite low, the percentage of ^{239}Pu leached with rainwater from the soils collected in zone 6 were higher than the obtained with the soil's aliquots treated in soil 2, even having in some of the aliquots comparable Pu contamination. The previous run-off and weathering history of the material collected from zone 6, could be the reason of the difference observed with the particulate contamination more fractionated and relatively more available that in the samples from zone 2.

In the 9 leachates obtained from the three soil aliquots, it was also determined the ^{240}Pu/^{239}Pu atom ratios. The obtained values were again quite uniform, average of 0.06, and not differentiable from the results obtained in the soils of zone 6.

The results obtained by applying the leaching protocol with 0.16 M HCl to two soil aliquots (not previously submitted to the rainwater leaching) are summarized in Figure 4.23.

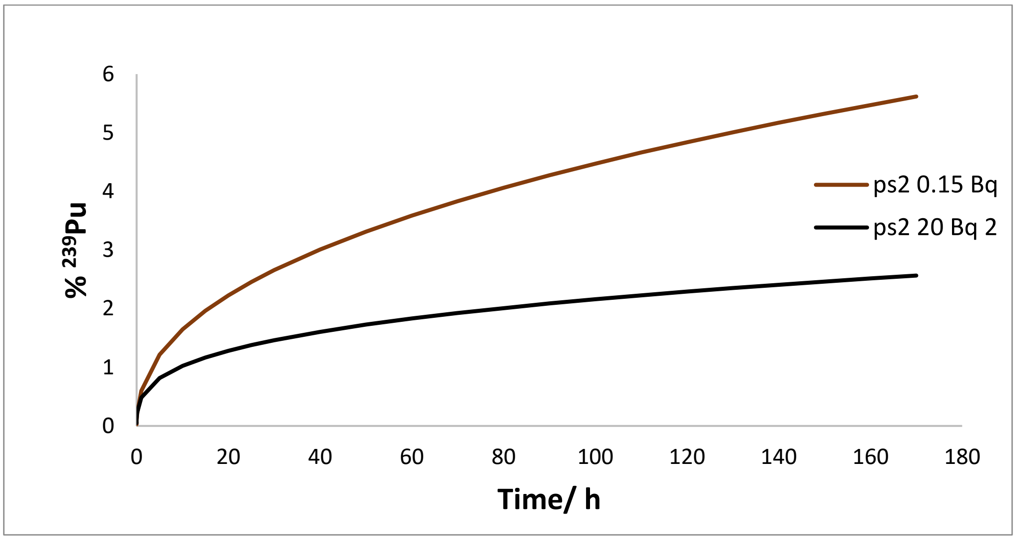


Figure 4.23.- Cumulative percentages (%) of ^{239}*Pu determined after application of the leaching protocol using rainwater as a leaching agent in three different soil aliquots from zone 2.*

The percentage of ^{239}Pu leached from these soils with the 0.16 M HCl as extractant is clearly higher than the leached with rainwater but at the same time it is necessary to remark than even these acidic conditions the leached Pu represent a quite minor fraction of the total Pu present in the soils in good agreement with the observations performed by other authors treating also soil aliquots with HCl (Lind, 2006, Salbu et al., 2018).

The percentage of ^{239}Pu leached with 0.16M HCl from the soils of zone 2 is on the other hand, lower than the percentage leached from the soils of zone 6 following the same tendency that the observed previously with the soils treated with rainwater. Reinforcing previous comments about different availability from the soils collected in the two zones due to their different history.

Additional studies

a) Long-term abiotic leaching experiments with rainwater and 0.16 M HCl

A detailed analysis of the Rosin-Rammler fittings of the data obtained applying the stablished leaching protocol to Palomares soils treated either with rainwater or 0.16M HCl indicates that the maximum leachability is not obtained in most cases after one week of treatment. It is possible to see how the fits show a tendency to higher values of Pu leached if the leaching experiments continues after one week of treatment.

In order to evaluate the long-term behavior of Palomares soils under the action of different leaching agents, a new set of experiments were designed. Soil aliquots corresponding to the zone 2 of Palomares, where submitted to the leaching protocol defined in this work, with the modification that the leachates were collected after one week (168 h) and three months (2160 h) of interaction. A total of six aliquots were treated: three of them with rainwater (W1, W2 and W3) and 3 with 0.16M HCl (HCl-1, HCl-2 and HCl-3). Obviously, the protocol developed for soil aliquots was applied and only total fractions (no fractionation) were analyzed for Pu content by Accelerator Mass Spectrometry. The results obtained with the three aliquots treated with rainwater, and graphically represented in Figure 4.24.

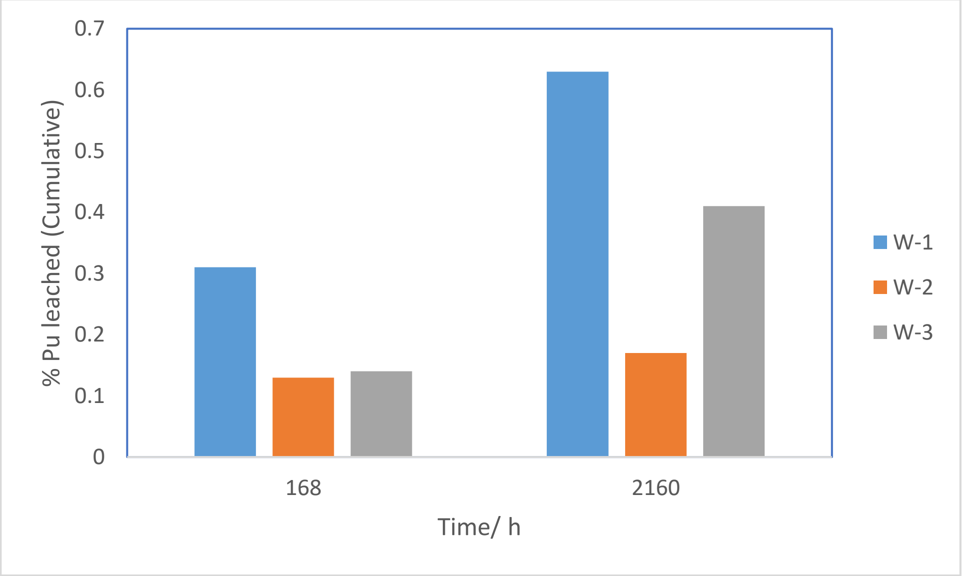


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Figure 4.24.- Percentage of cumulative ^{239}Pu (%) leached from soils in a long-term experiment using rainwater as a leaching agent.

The obtained results confirm that the leaching of plutonium continues with time after one of week of treatment, with increments in the time interval 1 week - 3 months that cannot be considered negligible and are comparable with the amounts of Pu leached during the first week of treatment.

In any case, the Pu leached with rainwater is quite low, even after three months of treatment, not overpassing in the three experiments the value of 1%. This fact is in agreement with the observations carried out in the contaminated zone of Palomares which indicates that in soils not altered since the accident, the Pu initially deposited in 1966 has not suffered any appreciable migration. And is also in agreement with the extremely low soil-to-plant transfer factors determined in the area (Sancho and Garcia-Tenorio, 2019). Most of the Pu that can be found in plants and fruits growing in the area, is deposited on the available surfaces due to resuspension of contaminated dust and not incorporated solubilized through the plant roots.

Quite different values, as expected were obtained when contaminated soils were leached with 0.16 M HCl. The results obtained with the three aliquots treated with 0.16 M HCl are graphically represented in Figure 4.25.

The results indicate that while the proportion of Pu leached in the first week is in agreement with the values obtained in the leaching experiments shown previously in the main text, the proportion of Pu leached with HCl in the time interval 1 week – 3 months is comparable or even higher that the amount of Pu leached during the first week, reaching cumulative values in the interval between 30 and 40%. The continuous action of the acid medium with the treated soil during 2000 additional hours provoke the release of Pu to the liquid medium in a considerable fraction.

However, these new results should be placed in its proper context. The 0.16 M HCl solution is used as a leaching agent mainly because it mimics the strength and action of the gastric juices. Consequently, the results generally are used to evaluate the proportion of Pu that can be solubilized and distributed in the body after inadvertent ingestion of contaminated soil. In this sense, and as the typical time residence of ingested soils in the body before excretion can be evaluated between 1 and 3 days, the results obtained in the leaching experiment shown here and with a duration of three months are not applicable.

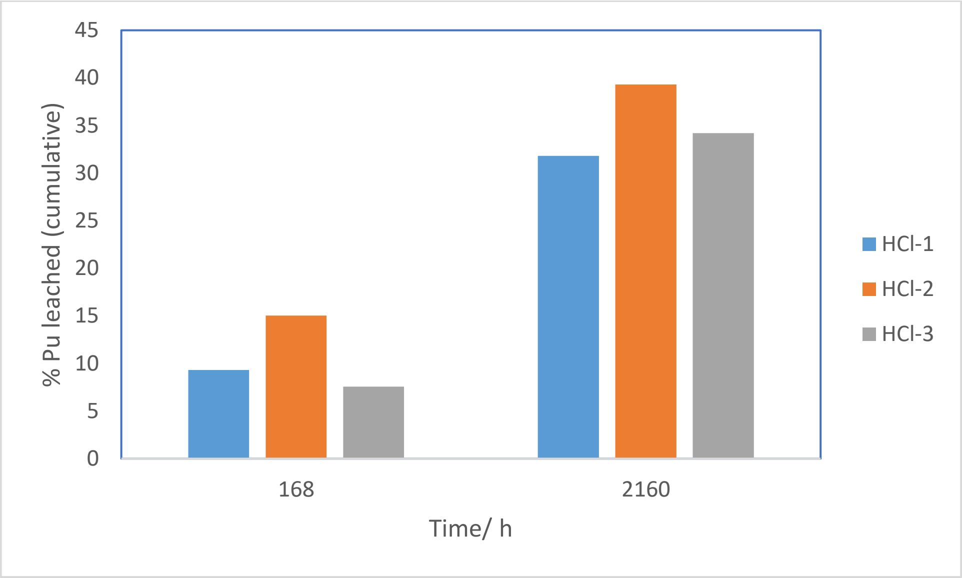


Figure 4.25.- Percentage of cumulative ^{239}Pu (%) leached from soils in a long-term experiment using 0.16 M HCl as a leaching agent.

But, on the other hand, the leaching action of the 0.16 M HCl can be also used as a good indicative of the actions of acidic fertilizers in Palomares contaminated soils (as cow urine, urea and others) (Espinosa et al., 2005). In this case, the Pu leaching percentages obtained after three months of treatment have sense, and due to their relative high values (30-40%) open some concerns about the increase of the available Pu in Palomares contaminated soils treated with the mentioned fertilizers.

b) *Solubility of Pu associated to inhaled contaminated soil material: In vitro experiments*

The leaching experiments that have been applied until now, although being laboratory experiments, gives important and rich information about the behavior of the Pu particulate contamination in Palomares. Leaching experiments using rainwater were used to have some insights about the potential transfer of Pu from soils to other compartments of the environment, while leaching experiments using 0.16 M HCl gives information about the possible incorporation of solubilized Pu by the human body after inadvertent ingestion and about the possible liberation of Pu in the soils treated with acidic fertilizers.

Another in vitro leaching/solubilization studies can be independently designed to study one of the main concerns from the radiological point of view associated to the Palomares accident. The possible incorporation by the public of Pu via inhalation of resuspended material. This route of Pu incorporation can be evaluated as the most important one in Palomares, particularly after analyzing the results shown previously in this paper reflecting indirectly the very limited transfer of Palomares Pu via the food chain, and also after considering that due to anthropogenic radionuclides involved (only alpha (Pu isotopes and ^{241}Am) or low-energy gamma-emitters (^{241}Am)) the contribution to the effective doses of external radiation is negligible.

The arid and semi-desertic conditions dominating in Palomares favors the resuspension of contaminated soils, its possible inhalation by the farmers and people living in the surroundings, and the possible incorporation of Pu to the human body though it solubilization in the pulmonary system.

The magnitude of the material resuspended, and the consequent Pu contamination of the breathable air, can be clearly deduced from historical data determined in aerosols filters collected in the zone 2 and in the village of Palomares, which are compiled in Table 4.1. In this Table, and with comparison purposes the activity concentrations determined in two well-known cities no affected by local anthropogenic inputs of plutonium are also shown.

Having all these facts in consideration and in order to cover all the possible cases where the performance of in vitro leaching experiments with Palomares material could be useful, a final set of experiments have been carried to study the possibility of solubilization of some of the Pu present in Palomares contaminated soil aliquots. It’s made by physiological solutions mimicking the composition and action of the fluids of the human respiratory system. In this way, the potential Pu that can be distributed in the body via the inhalation route can be evaluated.

Year	New York USA	Triestre Italy	Palomares Village	Zona 2-(Palomares)
1966	3.1	2.6	14.8	44.8
1967	1.3	1.6	4.1	441.8
1968	2.0	2.7	2.6	21.8
1969	1.5	1.8	2.6	142.1
1970	1.8	1.8	2.2	5.9
1971	1.5	1.7	1.8	2.2
1972	0.7	0.8	1.8	10.4
1973	0.3	0.5	2.2	3.0
1974	1.1	1.4	4.1	8.1

Table 4.1: Average activity concentrations of $^{239+240}$*Pu from 1966 until 1974 in several locations, including zone 2 and the village of Palomares, expressed in µBq/m*^{3}*. (Iranzo & Richmond, 1998).*

The protocol followed in these physiological experiments have been detailed in Chapter 3. This in vitro protocol using physiological solutions, has been applied to a couple of soil Palomares aliquots: one aliquot corresponding to the zone 2, and the other corresponding to the zone 6. A total amount of 1.5 grams in each case were filled in the dialysis tubes and a total of five physiological solutions were obtained in each case.

The $^{239+240}$Pu activities in the remaining soil aliquots were the following: 30.5 + 1.2 mBq for the aliquot of zone 2, and 15.3 + 0.6 mBq for the aliquot of zone 6. These results clearly show the contamination of the treated aliquots, because the obtained values are 2-3 orders of magnitude higher that the activity concentrations in similar aliquots affected only by the presence of Pu with an origin in the nuclear weapon tests performed in the 1950-60s. The fingerprint of the contamination, indicating that correspond to weapon grade Pu, was reflected in the ^{238}Pu/$^{239+240}$Pu activity ratios found for the mentioned aliquots (García-Tenorio et al., 2015): these values were 0.019 + 0.001 and 0.023 + 0.002, respectively.

The activity concentrations of $^{239+240}$Pu determined in the different physiological solutions are compiled in Table 4.2. Due to the low levels expected, these samples were measured for more than 3 days and using new PIPS detectors with extremely low background. The obtained values were in all the cases lower than

0.17 mBq, even in some of them below the limit of detection, and for that reason are not unexpected the high values of the associated uncertainties. The radiochemical yields for the different physiological solutions corresponding to the aliquot of zone 2 ranged between 25 and 77%, while for the solutions corresponding to the aliquot of zone 6 ranged between 20 and 87%.

The data in both experiments indicate that some solubilization of Pu in the physiological solutions occurs, although the magnitude of the solubilization is extremely low. As it can be observed in Table 4.3 and in Figure 4.23, the percentage of plutonium dissolved in each solution never overpass 1.2%, while the cumulative percentage of Pu dissolved after one month of interaction soil-solution was 0.72% for the aliquot of zone 2 and 2.9% for the aliquot of zone 6.

Sample	**$^{239+240}$Pu, mBq**
Zone 2	
Z2-1 week	N.D.
Z2-2 week	0.036 ± 0.014
Z2-3 week	0.08 ± 0.03
Z2-4 week	0.03 ± 0.02
Z2-5 week	0.08 ± 0.03
Zone 6	
Z6-1 week	N.D.
Z6-2 week	0.095 ± 0.018
Z6-3 week	0.17 ± 0.07
Z6-4 week	0.09 ± 0.02
Z6-5 week	0.08 ± 0.03

Table 4.2.- Activities of $^{239+240}$Pu, in mBq, found in the different physiological solutions after interaction with the treated soil aliquots. (N.D. not detected, below the limit of detection).

Sample	**Absorbed fraction (%)**	**Cumulative absorbed fraction (%)**
Zone 2		
Z2-1	-	-
Z2-2	0.12 ± 0.04	0.12 ± 0.04
Z2-3	0.25 ± 0.11	0.37 ± 0.12
Z2-4	0.09 ± 0.07	0.46 ± 0.14
Z2-5	0.26 ± 0.10	0.72 ± 0.17
Zone 6		
Z6-1		-
Z6-2	0.63 ± 0.12	0.62 ± 0.12
Z6-3	1.2 ± 0.5	1.8 ± 0.5
Z6-4	0.57 ± 0.15	2.4 ± 0.5
Z6-5	0.5 ± 0.2	2.9 ± 0.6

Table 4.3.- % and cumulative percentages of $^{239+240}$Pu incorporated to the physiological solutions during the one-month in vitro experiment.

Similar results to the obtained in the in vitro experiments, were found by Aragón et al., 2003, applying to three Palomares aliquots of zone 2 a quite similar protocol and using a physiological solution with the same chemical composition. Exchanging every week, the physiological solution and determining in them their Pu content, it was concluded that after one month of interaction (5 physiological solutions) the cumulative percentage of Pu solubilized ranges in the interval 0.2 -0.5 %. Additionally, the authors analyzed the solubilization of ^{241}Am, being concluded that the magnitude of the solubilization observed for this radionuclide is similar to the observed one for Pu.

As an additional step, the temporal evolution of the cumulative Pu solubilized in the two parallel experiments performed, are represented in the Figure 4.27. The cumulative Pu versus time data have been also fitted to Rosin-Rammler functions with success.

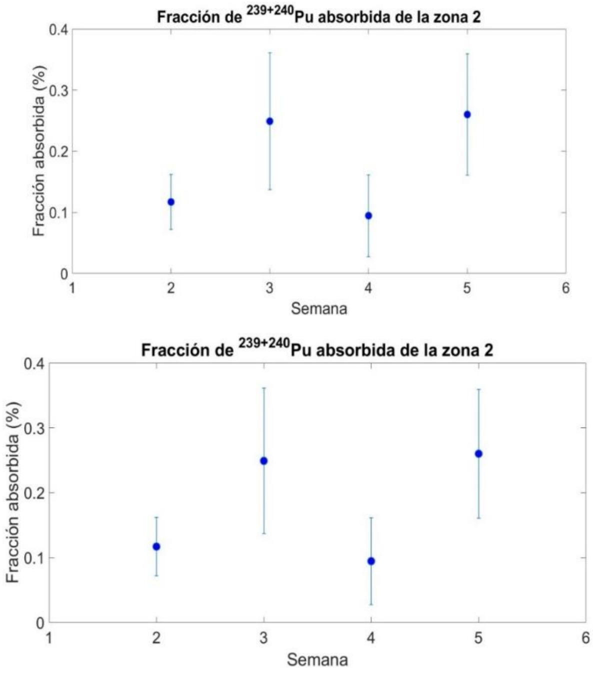


Figure 4.26: Temporal evolution of $^{239+240}$Pu absorbed fraction by the physiological solutions in interaction with aliquots collected in zones 2 and 6.

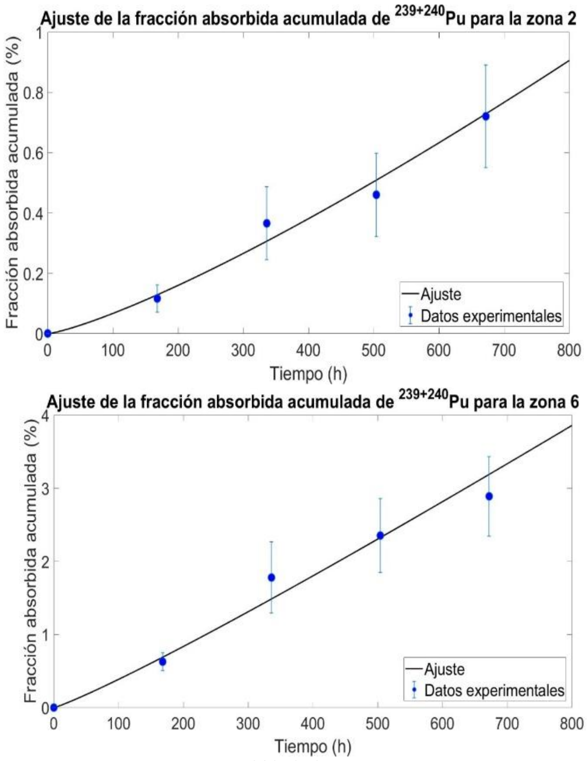


Figure 4.27 Temporal evolution of the $^{239+240}$*Pu absorbed fraction by the physiological solutions in interaction with the aliquots collected in zones 2 and 6. The fittings to Rosin-Rammler functions are also shown.*

The observation of Figure 4.27 clearly conduits to the conclusion of the appropriateness of the fittings performed. The fitting corresponding to the soil aliquot of zone is characterized for a regression coefficient r^2 = 0.9853, while in the case of the soil aliquot from zone 6, the regression coefficient was r^2 = 0.9817.

Finally, it is interesting to mention, comparing the results obtained with the two aliquots, that the percentage of Pu solubilized is higher for the soil aliquot of zone 6. This phenomenon was also observed in the conventional leaching processes performed with rainwater and 0.16M HCl as leaching agents and was explained attending to the history of the soils treated. Summarising, several reasons conducted to the conclusion that the Pu associated to the soil aliquots from zone 6 as more available that the Pu associated to the soil aliquots from zone 2.

Fortunately, the in vitro experiments performed simulating the solubilisation of Pu after Palomares contamination inhalation, reaffirm previous conclusions about the quite inert behaviour of the Pu dispersed in the accident. The percentages solubilized by the respiratory system are quite low, minimizing the doses received by this via. Estimations of the inhalation doses performed in zone 2 by Aragón et al., 2003 give values 1 to 2 orders of magnitude lower that the screening value of 1 mSv/year.

Chapter 5

Transformation processes affecting radioactive particles: Palomares versus Thule behaviour

As a direct consequence of the Cold War between the United States of America and the former Soviet Union, just after the Second World War, two different aircraft accidents involving nuclear weapons provoked the dispersion of fissile material in some defined areas belonging to two completely different vulnerable ecosystems. Both accidents were described in Chapter 2 of this PhD thesis and occurred 50 years ago.

In both accidents the disseminated nuclear fuel has been proved that was formed by a mixture of enriched uranium and weapon-grade plutonium, in both cases some remaining contamination exist in areas affected by the accident, and in both cases, the contamination was dispersed in form de micrometer particles. (Lind et al., 2007).

These facts opened new challenges in performing comparative evaluations of radioactive particle transformation abiotic experiments in the two ecosystems, because on one side both cases are characterized by similar source materials and similar formation mechanisms, but on the other side the released particles have been residing for 50 years in very different environmental compartments. The affected Palomares terrestrial area can be evaluated as a semi-desertic area although during the last 20 years a notable increase in the intensive agriculture has occurred, while the terrestrial zone affected by the Thule accident is clearly an artic ecosystem with more simplified food chains (Figure 5.1).

On the other hand, the persistence of the particles during 5 decades in the uppermost part of the unaltered soils is an indication of its in general inert behavior under the existing conditions. The evaluation of this inert behavior or possible increments in their solubility over time is the main objective of this chapter, putting special focus in the comparison between the commented two cases, because ideally the radioactive particle ecosystem behavior should be analyzed and evaluated case by case for a proper environmental impact assessment in areas affected by contamination in particulate form. Although the origin and initial composition is identical. (Salbu, 2000)

Figure 5.1.- Image of representative terrestrial areas of Thule (left) and Palomares (right) evidencing that are two different environmental ecosystems.

To assess a comparative study about the environmental impact of radioactive particles released from weapon-grade material in different ecosystems where are deposited, detailed information is required on particle characteristics such as size, composition, morphological structure and oxidation states of matrix elements such as U and Pu influencing particle weathering rates and subsequent mobilization of radionuclides from particles present in soil-water systems. (Salbu, 2000)

In the open literature, it is possible to find several works giving information about characteristics of Palomares and Thule particles. (Jiménez-Ramos et al., 2008; Jiménez-Ramos et al., 2010; Lind et al., 2005; Lind, 2006; Lind et al., 2007)

This characterization, as we comment previously, was performed after individual particle isolation applying different non-destructive analysis with advanced techniques: gamma-ray spectrometry, scanning electron microscopy in combination with Energy Dispersive X-ray analysis (SEM-EDX), micro-proton induced X-ray emission (micro-PIXE), micro-X-ray fluorescence (micro-XRF) and several synchrotron radiation techniques by Salbu et al. Such as SR micro-X-ray fluorescence (micro-SRXRF) to obtain information on the elemental composition of the particles and SR-based micro-X-ray absorption near edge structure microscopy (micro-XANES) to obtain information on oxidation states of U and Pu. In addition, the U and Pu isotopic composition of the particles were determined by dissolving individual particles and applying different mass or radiation spectrometric techniques: Inductively Coupled Plasma Mass-Spectrometry (ICP-MS), Accelerator Mass Spectrometry (AMS), and alpha-particle spectrometry.

All the individual particle characterization works conclude as it was indicated in Lind et al, 2007: Palomares and Thule particles are remarkable similar with respect to elemental distribution, morphology and oxidation states reflecting that they originate from similar source and release scenarios. In other words, the particle characteristics are more dependent on factors determined by the source and the release scenario than on the environmental conditions.

The analysis performed on Palomares and Thule particles indicated that the U and the Pu were homogenously distributed in them. In both cases the particles are characterized by low $^{239}Pu/^{235}U$ (0.62-0.78) and $^{240}Pu/^{239}Pu$ (< 0.07) atom ratios, while analyzing by scanning electron-microscopy the isolated particles from both sites appear as agglomerated crystalline grains with a relatively high degree of porosity, indicating that its specific surface area of the particles may be large, and giving some appearance of fragility.

On the other hand, the micro-XANES analyses indicated that the U and Pu matrices are in both cases U and Pu oxide mixtures, with the U oxidation state predominantly +IV (UO_2) with a minor and variable contribution of higher oxidation states (U_3O_8), while Pu seems to be present as Pu(III)/Pu(IV), Pu(IV)/Pu(V) or a mixture of all three oxidation states. Neither metallic U or Pu nor uranyl or Pu(VI) could be observed (Lind et al., 2007; Lind et al., 2005). The dominant oxidation states determined are compatible with a refractory behaviour tendency of these particles.

In both cases, Palomares and Thule, the ecosystem transfer of particle associated radionuclides can be expected that will be delayed until particle weathering and remobilization of associated radionuclides occur. In the first assessments performed just after release, extremely high distribution kd values and quite low soil to plant transfer factors, TF, and whole-body concentration ratios, CR, were evidenced, being also expected that due to weathering the apparent kd will change over time, because although initially soil and sediments will act initially as sinks for radioactive particles in our analyzed ecosystems, these soils and sediments may also act as a potential diffuse source in the future. (Salbu et al., 2018)

In Lind. 2006, was concluded that if they are properly established/justified and validated, leaching experiments can provide important data on particle characteristics. Also, the links to solubility, particle weathering rates and remobilization potential for particle associated radionuclides nowadays, 5 decades after the accident. The comparison study previously mentioned about the ecosystem behavior of the radioactive contamination in Palomares and Thule could then be carried out by performing leaching experiments.

The results obtained in the application of the protocols from chapter 3 to isolated particles and bulk samples from Palomares have be shown and discussed in the previous chapter. Now, the results obtained applying the same protocols to isolated particles and bulk samples from Thule will be shown, discussed and compared with the results of Palomares.

As it was discussed in Chapter 2, in one of the terrestrial hot-spots located in the surroundings of the Thule Air Base, several superficial soil samples were collected. From them, a couple of micrometers radioactive have been isolated by applying the binary division method combined with gamma-ray spectrometry and autoradiography. (Jiménez-Ramos et al., 2008)

The abiotic protocols described in detail in Chapter 3 were applied to the two isolated particles as well as to three different soil aliquots from the area where the particles were isolated. All the leachates and fractions obtained as well as the soil material remaining after the application of the protocol were submitted to different analysis: the ^{236}U, ^{239}Pu and ^{240}Pu levels were determined by Accelerator Mass-Spectrometry (AMS) and their elemental composition were determined by Inductively-Coupled Mass Spectrometry (ICP-MS) following the methodology also described in Chapter 3, while multivariate analysis was applied to the set of data corresponding to the soil leachates to obtain affinities and differences in the leaching behavior of different stable elements and radionuclides.

Finally, in order to confirm the main peculiarities of the radioactive particles disseminated in the Thule accident, one of the isolated particles was characterized by applying two different techniques: Scanning Electron-Microscopy with X-Ray microanalysis (SEM-EDX) and Micro-Particle Induced X-Ray Emission (μ-PIXE).

The application of both techniques in the characterization of micrometer U/Pu particles are fully described in Jimenez-Ramos et al. As an initial step the micrometer particle was identified by applying SEM in the BEI (Back-scattered) mode taking advantage of the presence of elements with very high Z (U and Pu), while, after identification, a detailed information about the size and the morphology was obtained by using the SEI mode (secondary electrons). Afterwards, elemental composition and distribution in the particles was obtained by μ-PIXE: U an Pu-mapping was then performed. (Jiménez-Ramos et al., 2006; Jimenez-Ramos et al., 2010)

Thule isolated particles: leaching experiments

One of the isolated Thule particles (code TT) was submitted as a first step to the leaching protocol using as a reagent rainwater from Palomares area. The obtaining results are compiled in Table 5.1, while the Rossin-Ramller fittings performed with the cumulative percentages found in all the fractions are represented in Figure 5.2.

Sample	^{239}Pu Bq	Time /h	Fraction	Cumulative % ^{239}Pu	^{240}Pu/^{239}Pu
TT Rain water	36,4	1	Total	0,0068±0,0004	0,046±0,004
			<0.45	0,0059±0,0002	0,039±0,010
			LMM	0,0075±0,0002	0,056±0,003
			kDa	0,0027±0,0001	
		24	Total	0,0123±0,0005	0,052±0,006
			<0.45	0,0125±0,0006	
			LMM	0,0145±0,0003	0,052±0,005
			kDa	0,0072±0,0003	0,056±0,008
		168	Total	0.0260 ±0,007	0,051±0,011
			<0.45		
			LMM	0,0265±0,0005	0,050±0,019
			kDa	0,0145±0,0004	0,046±0,007

Table 5.1.- Cumulative percentages (%) of ^{239}Pu leached from an isolated radioactive particle from Thule (TT) using rainwater as a leaching agent, and ^{240}Pu/^{239}Pu atom ratios found in each fraction.

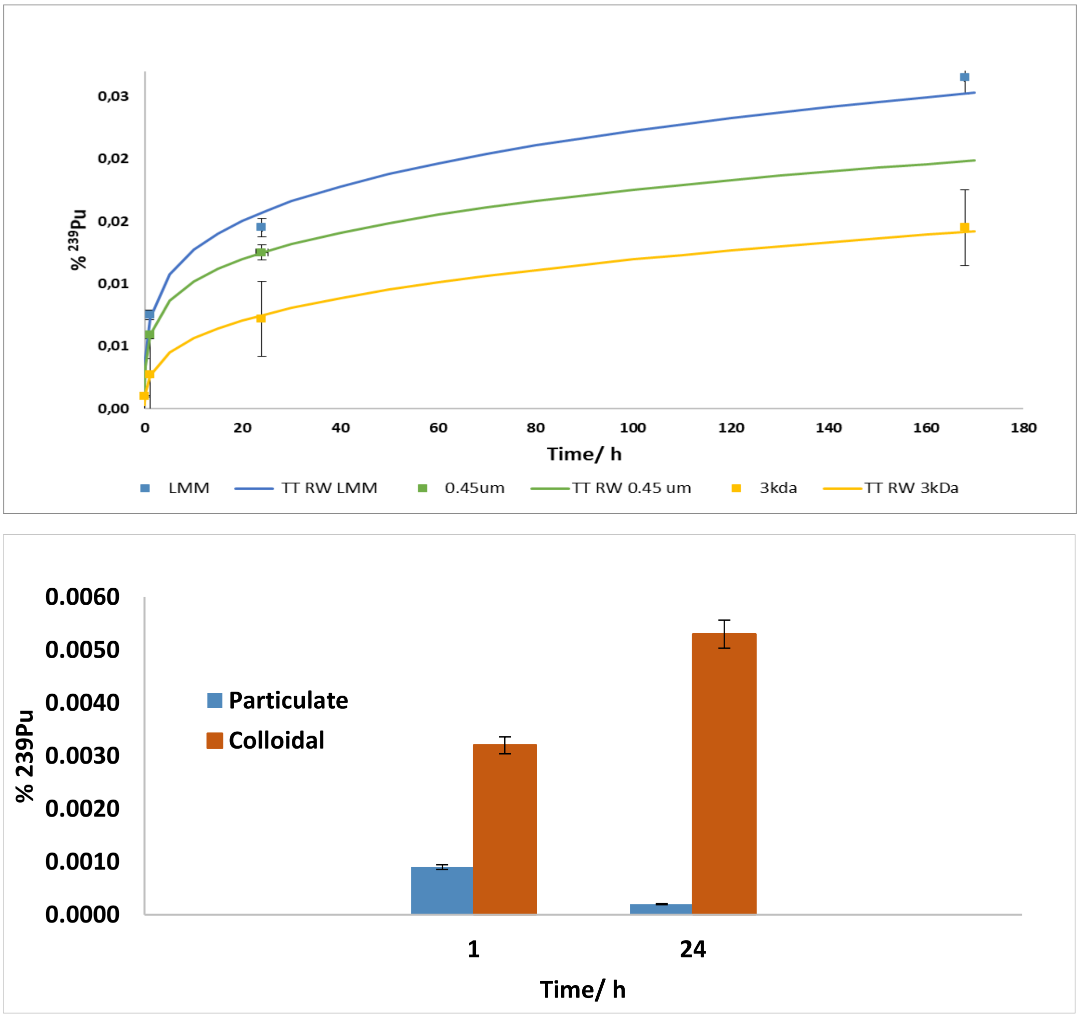


Figure 5.2.- Cumulative percentages of ^{239}Pu in leachates fractions obtained with the TT Thule particle using rainwater as leaching agent.

The obtained results clearly indicate the refractory behaviour of the particle to the action of rainwater. Only traces of Pu are found in the leachate's fractions, representing the leaching Pu less than 10^{-1} % of the Pu present in the particle. In addition, the results show that the great majority of the Pu lixiviated is present in dissolved form (the results in the total and the <0.45 μm fractions are coincident), and that a considerable fraction of the Pu lixiviated is present in the form of colloids (nanoparticles?) as it can be deduced by observing the difference of Pu lixiviated between the < 0.45 μm and the < 3 kDa fractions.

On the other hand, no isotopic Pu fractionation was observed in the leachates as it can be deduced from the ^{240}Pu/^{239}Pu atom ratios that were quite uniform in all the fractions. The average value found of 0.05 is, as expected, characteristics of weapon-grade plutonium, and concordant with the values previously published associated to the accident Eriksson et al., 2008. Due to extremely low levels present in the leachates it was not possible to determine with enough confidence the ^{236}U levels.

The same TT particle was immediately after the leaching with rainwater, submitted to the same leaching protocol, but now using 0.16 M HCl as a leaching agent. The obtained results are compiled in Table 5.2, while the cumulative percentage of ^{239}Pu found in the total and in the <0.45 mm fraction is shown in the Figure 5.3.

Sample	^{239}Pu Bq	Time /h	Fraction	Cumulative % ^{239}Pu	^{240}Pu/^{239}Pu	^{236}U/^{239}Pu
TT 0,16M HCl	36,4	1	Total	0,0032±0,0001	0,050±0,006	0,19±0,02
			<0.45	0,0022±0,0001		0,22±0,04
			LMM	0,0033±0,0001	0,061±0,004	0,19±0,01
			kDa	0,0046±0,0001	0,056±0,005	0,14±0,01
		24	Total	0,0100±0,0003	0,061±0,004	0,042±0,003
			<0.45	0,0086±0,0004	0,052±0,007	0,061±0,014
			LMM	0,0096±0,0003	0,058±0,003	0,045±0,003
			kDa	0,0097±0,0003	0,056±0,005	0,059±0,005
		168	Total	0,0141±0,0005	0,048±0,005	0,045±0,005
			<0.45	0,0160±0,0009	0,063±0,004	0,043±0,004
			LMM	0,0131±0,0004	0,056±0,003	0,041±0,004
			kDa	0,0125±0,0004	0,047±0,007	0,070±0,010

Table 5.2.- Cumulative percentages (%) of ^{239}Pu leached from an isolated radioactive particle from Thule (TT) using 0.16 M HCl as a leaching agent, and ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu atom ratios found in each fraction.

The results indicate the inert behavior of the TT particle even under the action of an acidic medium as 0.16 M HCl. The percentage of plutonium leached is minimum and even comparable with the amount of plutonium previously leached with rainwater.

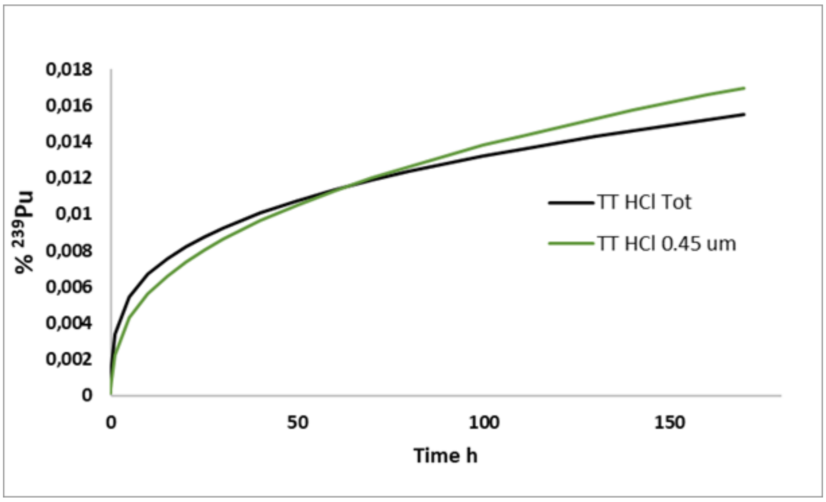


Figure 5.3.- Cumulative percentages of ^{239}Pu in the Total and < 0.45 µm leachates fractions obtained with the TT Thule particle using 0.16 M HCl as leaching agent.

The very small percentage of plutonium leached is found in dissolved form, as it can be deduced from the coincidence in the percentage of plutonium leached in the Total and in the <3 kDa fractions. The amount of particulate Pu is negligible (as it can be deduced from the coincidence between the total and the <0.45 µm fractions) and the same can be indicated for the colloidal Pu that is also negligible in the leachates (indicated by the coincidence between the Pu leached in the <0.45 µm and <0.3 kDa fractions).

While the values obtained for the ^{240}Pu/^{239}Pu atom ratios reinforce the no existence of isotopic fractionation, with uniform weapon-grade values, it is important to mention the peculiar results obtained for the ^{236}U/^{239}Pu atom ratios. As it is clearly observed in Figure 5.4, this atom ratio has clearly higher values in the fractions corresponding to the leachate obtained after 1 hour of treatment, while in the leachates obtained at 24h (1 day) and 168h (1 week) are comparable. This fact indicates the initial presence in the radioactive particle of an available amount of ^{236}U (in comparison with Pu) that is immediately leached after the addition of the 0.16 M HCl. After this initial enhanced leaching the behaviour of U and Pu is similar under the action of the acidic medium. On the other hand, both

U and Pu are present in the leachates in dissolved form according to the conclusions obtained previously for Pu and the quite uniform $^{236}U/^{239}Pu$ obtained for the four different fractions in each obtained leachate.

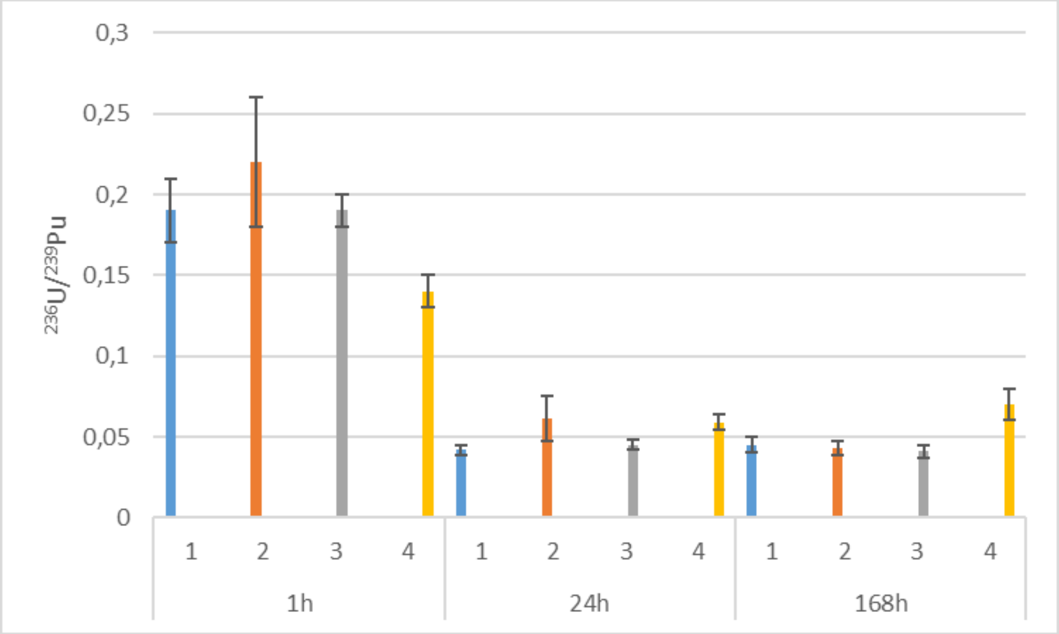


Figure 5.4.- $^{236}U/^{239}Pu$ atom ratios determined in the different fractions of the three leachates (1h, 24 h, 168 h) obtained with the particle TT of Thule using 0.16 M HCl as leaching agent. (Blue: Total fraction, Brown: < 0.45 µm fraction, Grey: LMM fraction, Yellow: < 3 kDa fraction).

Finally, the application of the leaching abiotic protocol to another isolated terrestrial Thule particle (PT 29) using again 0.16 M HCl as a leaching agent conducted to obtaining the set of results compiled in Table 5.3 and shown in Figure 5.5. These results are quite different to the previously observed with the particle TT, because in this case, around 30% of the Pu originally associated to the particle is leached.

This leaching process is temporally characterized, as can be observed in the Figures 5.5 and 5.6, by the incorporation of the great majority of the Pu to the HCl 0.16M during the first hour of treatment. The amounts of Pu released from the particle after the quick and initial leaching during the first hour of the experiment is quite moderate and clearly lower.

Sample	^{239}Pu Bq	Time /h	Fraction	% ^{239}Pu	^{240}Pu/^{239}Pu	^{236}U/^{239}Pu
PT29 0,16M HCl	30,8	1	Total	26,8±0,7	0,054±0,002	0,014±0,001
			<0.45	28,4±0,6	0,053±0,002	0,016±0,001
			LMM	29,3±0,7	0,056±0,002	0,013±0,001
			kDa	25,5±0,6	0,057±0,002	0,013±0,001
		24	Total	29,9±0,8	0,052±0,003	0,022±0,002
			<0.45	31,2±0,7	0,051±0,002	0,010±0,001
			LMM	32,9±0,8	0,053±0,002	0,012±0,001
			kDa	28,7±0,6	0,055±0,002	0,021±0,001
		168	Total	30,8±0,9	0,057±0,004	0,030±0,003
			<0.45	33,6±0,8	0,055±0,002	0,016±0,001
			LMM	34,7±0,8	0,053±0,002	0,016±0,001
			kDa	29,9±0,7	0,058±0,002	0,002±0,001

Table 5.3.- Cumulative percentages (%) of ^{239}Pu leached from an isolated radioactive particle from Thule (PT29) using 0.16 M HCl as a leaching agent, and ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu atom ratios found in each fraction.

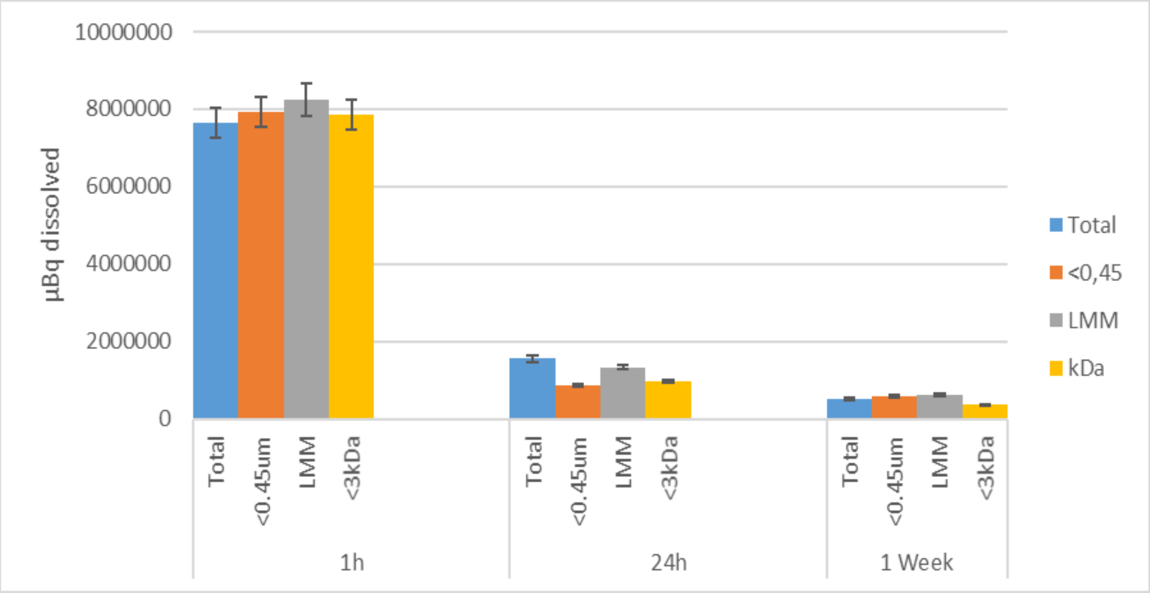


Figure 5.5. Amount of ^{239}Pu found in each fraction of the three leachates analyzed from the PT29 Thule particle.

On the other hand, the higher Pu levels found in all the leachates analyzed has allowed to determine in all the fractions with good accuracy the ^{240}Pu/^{239}Pu atom ratio (Figure 5.7). The set of ratios are quite uniform, as expected, and are characterized by an average value of 0.054 which can be taken as a clear fingerprint of the Pu dispersed in the Thule accident. The ^{236}U/^{239}Pu atom ratios are also quite uniform and low in relation to the determined ones in the leaching of the particle TT, indicating that: a) the U/Pu ratios between nuclear weapons and even inside each nuclear weapon could be different, and b) the magnitude of the amount of U and Pu leached during the first hour mask the possible initial presence of a modest amount of U in more available form that the Pu, as it was observed in the leaching experiment with the particle TT.

The sudden, and no uniform in time, Pu leaching observed in this particle is a phenomenon that could be explained assuming the fragility and physical unstable behavior of the particle. Along the leaching processes, very small fragments were initially incorporated in particulate form, to experiment after that, and under the action of the acidic agent, its dissolution.

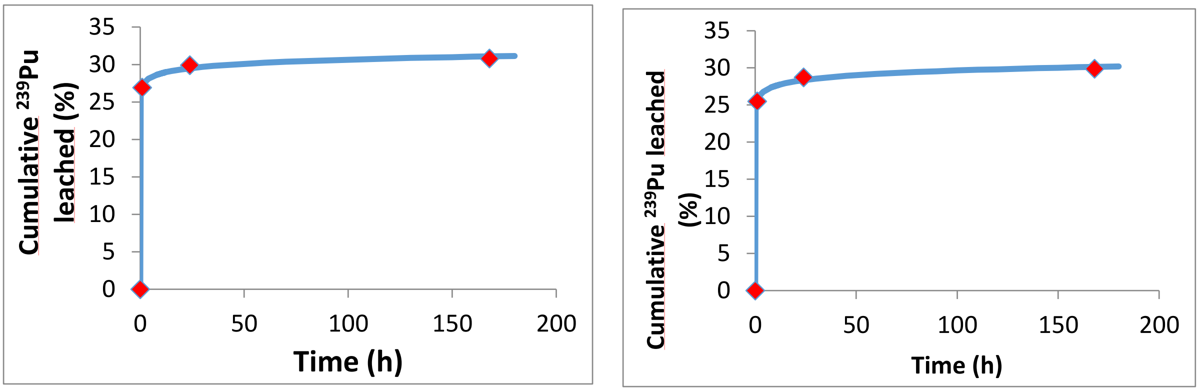


Figure 5.6.- Cumulative percentages of ^{239}Pu in the Total (left) and < 3 kDa (right) leachates fractions obtained with the TT Thule particle using HCl 0.16 M as leaching agent.

The fractionation analyses confirm that all the Pu in the leachates is in dissolved form because the Pu found in the total fraction is in coincidence with the Pu found in the < 0.45 μm and in the < 3 kDa fractions. This coincidence is observed in the three different leachates obtained taking into account their uncertainties.

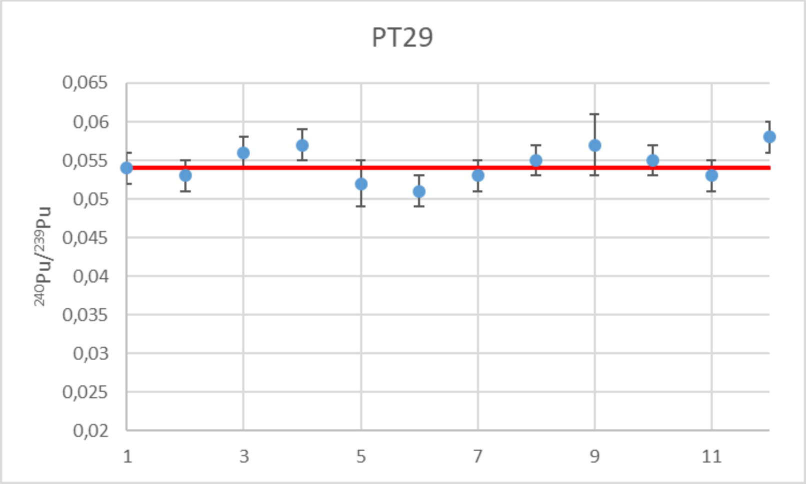


Figure 5.7.- ^{240}Pu/^{239}Pu atom ratios determined in all the fractions of the three leachates obtained from particle PT 29 using 0.16 M HCl as leaching agent.

The fragility and tendency of fractionation is not a new characteristic of the Thule particles. The morphology of some of these particles shown in Lind et al. 2007, and Jimenez-Ramos et al. 2010, are in agreement with these characteristics. While more recently this fragility was commented and evidenced during the construction of a database of radioactive particles of different origin constructed on the frame of the EU-project where, also the leaching protocol was agreed (COMET, 2017). And as it was commented previously in chapter 4, this fragility is a characteristic observed also associated to the terrestrial Palomares particles.

Reinforcing the previous comments Figure 5.8 shows optical images of some typical Thule particles, while in Figure 5.9, we show graphically the fragmentation suffered by one Thule particle simply by mechanical pressing as evidence of its fragility. In addition, in the following section a characterization study performed with the Thule TT particle before the application of the leaching protocols will be detailed.

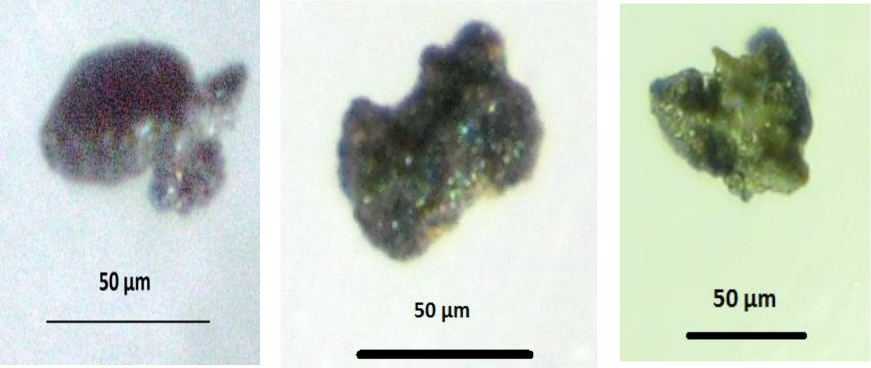


Figure 5.8.- Images obtained with an optic microscope of several radioactive particles isolated from soils collected in Thule contaminated areas. (COMET, 2017)

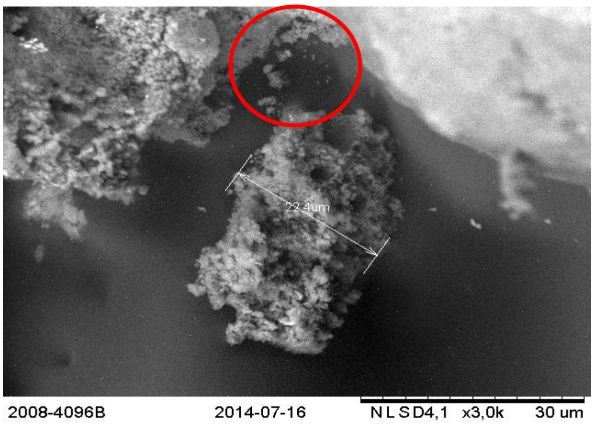


Figure 5.9.- Fractionation suffered by a Thule particle after being mechanically pressed. A "shower" of 1-5 μm particles are generated with all the implications associated to their mobility and dissolution in the leaching experiments (COMET, 2017).

Characterization of a terrestrial Thule particle using Advanced Techniques

The terrestrial Thule particle TT was characterized by applying the SEM and μ-PIXE techniques before being submitted sequentially to leaching protocols with rainwater and 0.16M HCl. With this end, the particle was mounted on double-faced carbon tape adhered to a metallic planchet.

The BEI image of the isolated particle is shown in Figure 5.10. The bright signal obtained along the particle is an indicative of the presence of elements of high atomic number Z in its composition, as was confirmed through the performance of X-ray microanalysis in some random points of its surface which indicates the presence of U and Pu as expected, because its isolation process was based in the identification of a clear signal of ^{241}Am by gamma-ray spectrometry as a daughter of ^{241}Pu.

The clear BEI image obtained allowed to determine with accuracy its dimension. The particle has an ellipsoid form with the higher axis taking the values of 31 and 52 μm, respectively. A volume of about 5000 μm^3 and a weight of about 20 ng could be estimated, taking into account the quite high-density values that characterise these radioactive particles (densities of about 4 g/cm^3). (Salbu et al., 2018)

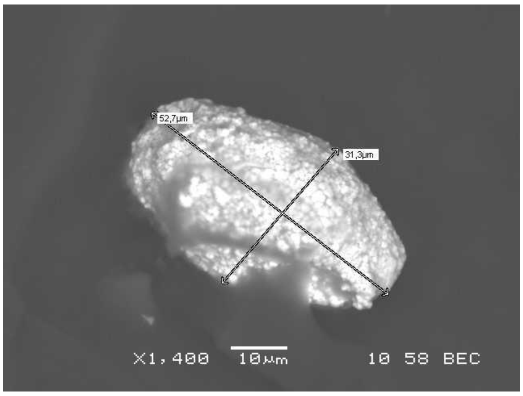


Figure 5.10.- BEI image of the TT radioactive particle from Thule.

A very detailed information about the morphology of the sample was obtained also by applying the SEM technique, but now through the collection of the generated secondary electrons (SEM-SE), Figure 5.11. As it was indicated in the introduction, from the image it is possible to deduce that the particle is formed by agglomerated crystalline grains with a relatively high degree of porosity. This structure reflects that the specific surface area of the particles may be large and gives some appearance of fragility.

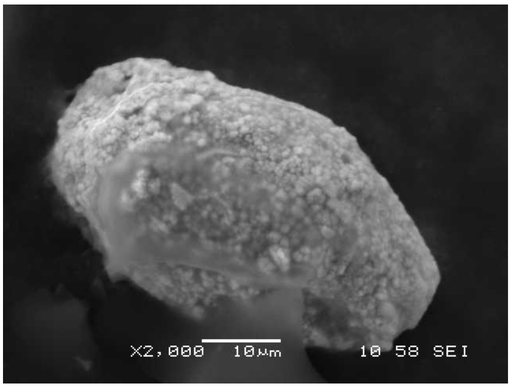


Figure 5.11.- SEI image of the TT radioactive particle from Thule.

The granular structure of the particle is more clearly observed with SEI images taken from different zones of the Thule TT particle with a higher level of resolution (Figure 5.12). The thought that some of these grains can be released under chemical, environmental or mechanical actions is unavoidable looking to the mentioned Figure.

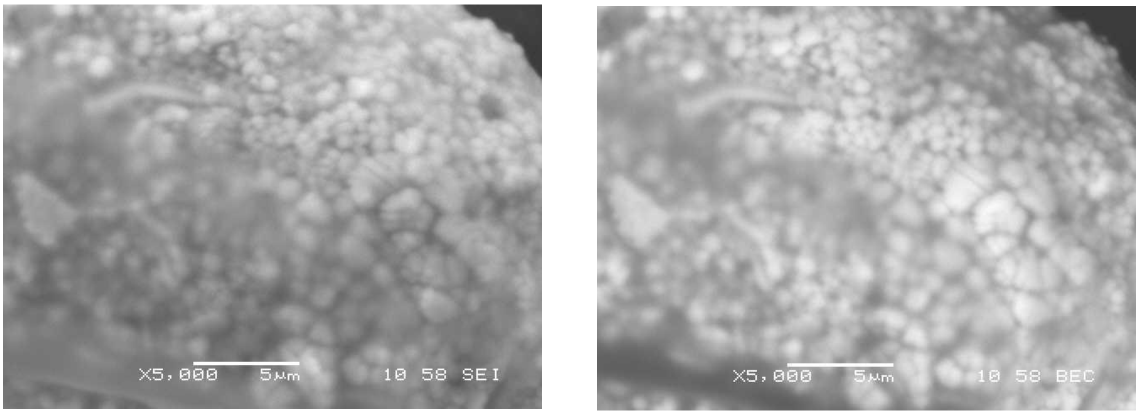


Figure 5.12.- Images with high resolution showing the granular structure of the particle, obtained by SEM, by collecting the generated secondary el (SE mode, left) and the back-scattered electrons (BE mode, right).

Some additional information about the composition of the sample was obtained by applying the µ-PIXE technique using for that the 3 MV Tandem accelerator at the Centro Nacional de Aceleradores, CNA. By using a microprobe and impinging a well-focused 3 MeV proton beam to the particle it was possible to analyse the uniformity of the U/Pu atom ratio in the particle. This atom ratio showed clear fluctuations in relation to an average value, not following these fluctuations any sectorial pattern, although it was possible to observe also that the U and Pu are distributed over all the particle. This last fact was confirmed by performing U and Pu-mapping analysis in the sample (Figure 5.13).

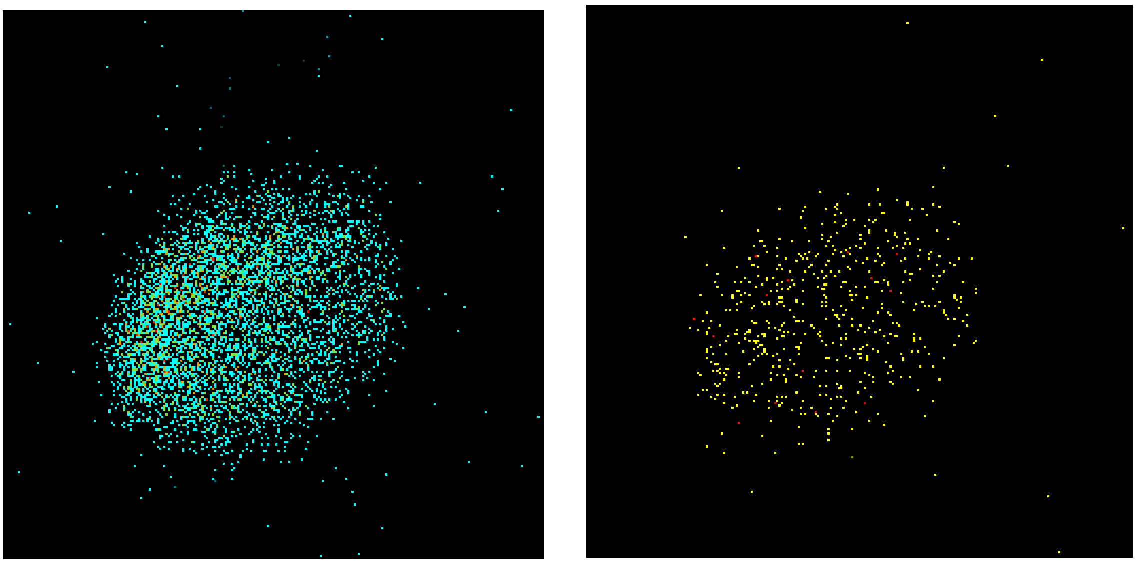


Figure 5.13.- U an Pu mapping of the TT particle performed by applying the micro-PIXE technique: The identification of the characteristics La peaks of U and Pu are used for the map construction.

Thule soils: leaching experiments

The abiotic studies carried out associated to the Thule accident were completed with the application of the leaching protocol to a total of three soil aliquots, using 0.16 M HCl as a leaching agent, in order to mimic the possible solubilisation of Pu after an unnoticed ingestion of contaminated Thule soil. The results obtained through the application of the soil leaching protocol are compiled in Table 5.4, while the evolution of the cumulative Pu leached from two of these soils are shown in Figure 5.14.

After exposition of the Thule soils to the acid medium during a week various percentage of Pu were leached, ranging in the interval between 7 and 30%. It was found on the other hand a clear inverse correlation between the total Pu activity initial present in the soil aliquot and the proportion of Pu leached, with lower percentages of leaching in the more contaminated aliquots.

Soils	^{239}Pu mBq in aliquot	Time h	% cumulative leached ^{239}Pu mBq	^{240}Pu/^{239}Pu	^{236}U/^{239}Pu
Soil 1	37,79±0,88	1	3,85±0,13	0,055±0,005	2,96±0,20
		24	7,92±0,25	0,051±9,993	2,51±0,16
		168	15,25±0,48	0,051±0,004	1,17±0,08
Soil 2	60,75±1,40	1	2,45±0,05	0,051±0,003	0,42±0,02
		24	4,65±0,10	0,051±0,003	0,41±0,02
		168	6,98±0,16	0,049±0,003	0,51±0,03
Soil 3	11,54±0,29	1	14,28±0,41	0,051±0,003	0,17±0,01
		24	18,47±0,44		
		168	30,72±0,69	0,052±0,002	0,29±0,01

Table 5.4.- Cumulative percentages (%) of ^{239}Pu leached from soil aliquots from Thule (TT) using 0.16 M HCl as a leaching agent, and ^{240}Pu/^{239}Pu and ^{236}U/^{239}Pu atom ratios found in each fraction.

Due to the characteristics of the soils treated that contains high organic content, the acidity of the leaching agent remains during the application of the leaching protocol in opposition to the observed with the Palomares soils, where the buffering effects were dominant. But even under these permanent acid conditions the percentage of Pu leached is lower than the obtained treating contaminated soils by another nuclear events or releases such as Chernobyl, depleted uranium and Mayak contaminated soils.(Salbu et al., 2018)

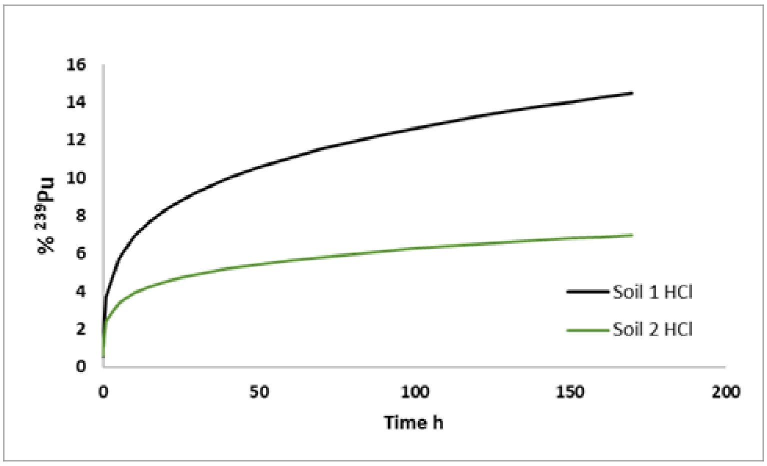


Figure 5.14.- Cumulative percentages of ^{239}Pu in two soil Thule aliquots obtained using 0.16 M HCl as leaching agent.

The ^{240}Pu/^{239}Pu atom ratios were as expected quite uniform in all the soil leachates analysed, with independence of the aliquot treated and coincident with the determined ones in the leachates of the isolated particles (average value of 0.05, fingerprint of weapon grade plutonium). While the ^{236}U/^{239}Pu atom ratios on the opposite were quite different between the aliquots analysed, although all the leachates from the same aliquot present similar values. However, for all the soils, the ^{236}U/^{239}Pu atom ratios are clearly higher than the obtained ones in the 0.16 M HCl leachates obtained treating the isolated particles, fact that can indicate the presence in the soils of ^{236}U in a more available form, and the no uniform U/Pu atom ratio in the fissile material disseminated in the accident.

Finally, in aliquots of the 9 soil leachates obtained (3 leachates per aliquot) we have determined their elemental composition by applying the ICP-MS technique. The amount of As, Cu, Cr, Fe, Th and U was determined in these leachates, being this set of data (together with the ^{239}Pu activities determined by AMS) submitted to a Principal Components Analysis (PCA). The Graph corresponding to the PCA results in the case of the Thule soils is shown in Figure 5.15.

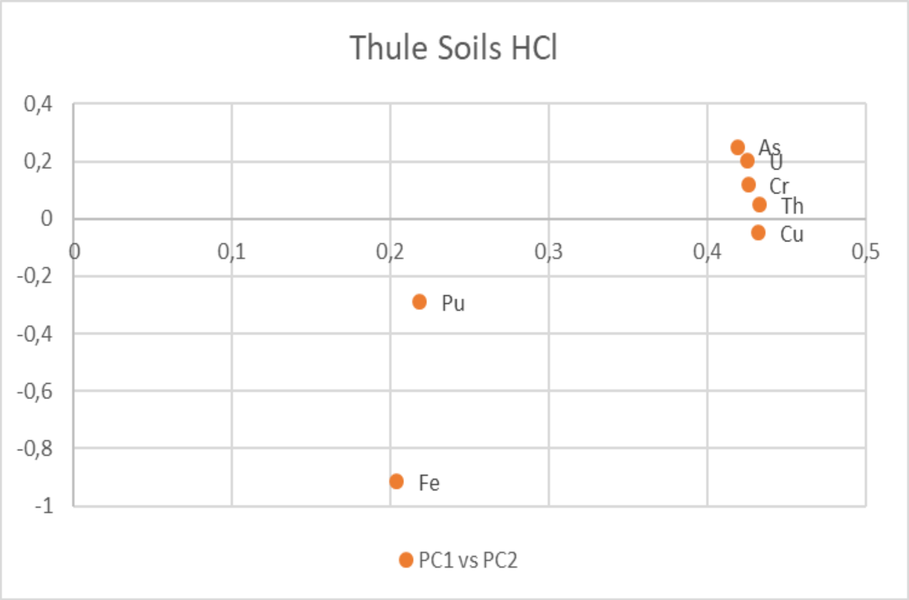


Figure 5.15.- PCA results (loading plot of variables) associated to the 0.16 M HCl leachates obtained from 3 soil Thule aliquots (7 elements).

The PCA shows that 88.2% of the data set total variance is accounted by the two first components (F1: 75.7%, and F2: 12.5.2%), and with independence that the majority of elements can be classified in a big group positively correlated with component 1, the most important observation is the different pattern and behavior observed for the Pu, isolated from the rest of the elements. This fact is an indicative of the presence of Pu in the soil aliquots in a peculiar form, i.e., in particulate form with a different behavior that the majority of the leached elements from the treated soils.

An additional and independent PCA analysis was performed by taking a higher number of elements together with the Pu determined by AMS**.** A total of 14 elements plus the Pu were considered. The new PCA shows that 97.2% of the data set total variance is accounted by the three first components while the corresponding three-dimensional graph taking into account the three mains component is the one shown in Figure 5.16.

Again, the most important observation is the different pattern and behavior observed for the plutonium, isolated from the rest of the elements that reinforce the comments and conclusions indicated in the previous PCA analysis. It is remarkable the high value of the PC3 parameter for Pu in comparison with the values of the same parameter for the other elements that can be associated to its peculiar origin and association to the soils.

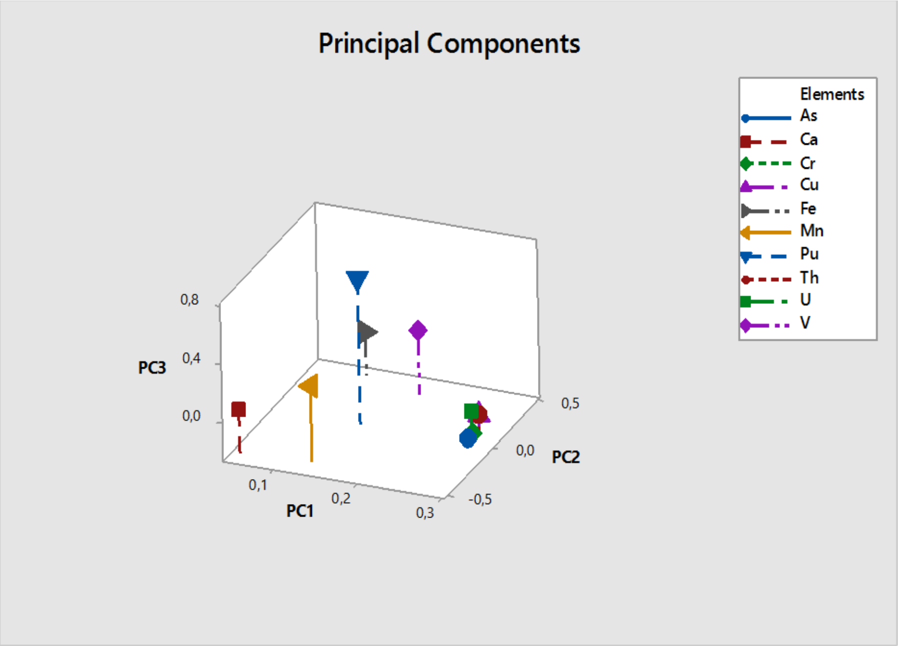


Figure 5.16.- PCA three-dimensional analyses associated to the 0.16 M HCl leachates obtained from 3 soil Thule aliquots (15 elements, represented in the figure only 10).

Thule versus Palomares environmental behaviour: Comparison of the leaching results

As it has been highlighted in a previous section of this chapter, the characterization of radioactive particles collected from contaminated terrestrial areas in Palomares (Spain) and Thule (Greenland), isolated some decades after its dispersion conducted to a clear conclusion: the particles from the two accidents are quite similar presenting the same morphology, the same elemental composition, the same actinide atom ratios and quite similar U and Pu oxidation states. And this similarity exists in spite of the very different ecosystems where these particles were deposited: a semi-desertic environment in the case of Palomares and Artic environment in the case of Thule. Lind et al. 2007 shows isolated particles from both sites which are also characterized for its granular composition, its high porosity and in general for its fragile aspect and tendency for fractionation/disintegration.

The behaviour of radioactive particles in the environment can be on one side source and released-scenario dependent, and on the other side ecosystem dependent (Salbu et al., 2018). It seems from the previous studies performed that the ecosystem influence is minor in this case in relation with the dominant influence of the origin of the contamination.

With the previous information in mind, it could be theoretically expected the same behaviour in the leaching experiments applied to isolated particles and soils from the two sites: Palomares and Thule. The results shown in this work confirm this similarity.

The behaviour of the isolated particles from Thule and Palomares submitted to the leaching protocol is summarized in a qualitative form in Table 5.5. In all the cases, the particles from both sites show an inert behaviour where rainwater was used as leaching agent, but when 0.16 M HCl was used, the results need from a more detailed comment: although the refractory and inert behaviour of the particles is observed in some cases with very low percentage of Pu leached, in others cases the combination of the acid action and the fragility of the particles provoked their fragmentation and even their disintegration. (Lind et al., 2018)

From a radioecological point of view it is the progressive fragmentation of the particles due to environmental factors the main pathway for the mobility and migration of actinides, in both analysed ecosystems. This conclusion was suggested by some researchers previously and confirmed with our experiments. (Aragón, 2003; Espinosa, 2003; Espinosa et al., 2005)

	Palomares Isolated Particles	
	Rainwater	**0.16 M HCl**
PP-2	Extremely Low	Very Low
421	Extremely Low	High, Disintegration
	Thule Isolated Particles	
	Rainwater	**0.16 M HCl**
TT	Extremely Low	Very low
PT29		High, Disintegration

Table 5.5.- Qualitative evaluation of the percentage of Pu leached from the isolated Palomares and Thule Particles, after applying the agrees leaching protocol.

The results obtained by treating soil aliquots from the two ecosystems, confirm the conclusions obtained with the isolated particles, although in this case with some peculiarities. The percentage of Pu leached from all the treated soils with rainwater is very low, while in the case of soils treated with 0.16 M HCl the following classification, from minor to major percentage of Pu released, can be stablished:

Palomares zone 2 < Palomares zone 6 < Thule soils

This classification is in agreement with the results obtained in previous leaching studies treating contaminated soils collected from a variety of sites affected by nuclear events or releases, (Salbu et al., 2018, Figure 5.17), and can be explained with basis in the following facts:

a) It is not surprising the minor percentage of Pu leached from the Palomares soils in relation to Thule, attending to their behaviour when the acid leaching agent is added and mixed with the soils. The Palomares soils, due to its calcareous composition, suffer quick buffering effects, being the acidity moderated and even neutralized in few minutes. This buffering effect diminishes the leaching capacity of the agent used while in the case of the Thule soils, the acidity of the leaching solutions remains during all the process.

b) The percentage of ^{239}Pu leached from the soils collected in zone 6 were higher than the obtained with the soils aliquots treated in soil 2, even having some of the aliquots comparable Pu contamination. These results can be linked to the associated history of these soils. While the soils from the so-called zone 2 correspond to unaltered soils affected directly from the explosion of one of the nuclear weapons, the soils collected from the so-called zone 6, correspond to material accumulated in the basement of a hilly area and transported to the accumulation point by run-off effects. It is the previous weathering history of the material collected from zone 6, the possible reason of the difference observed in the percentage of Pu leached, being the particulate contamination more fractionated and relatively more available in zone 6 that in the samples from zone 2.

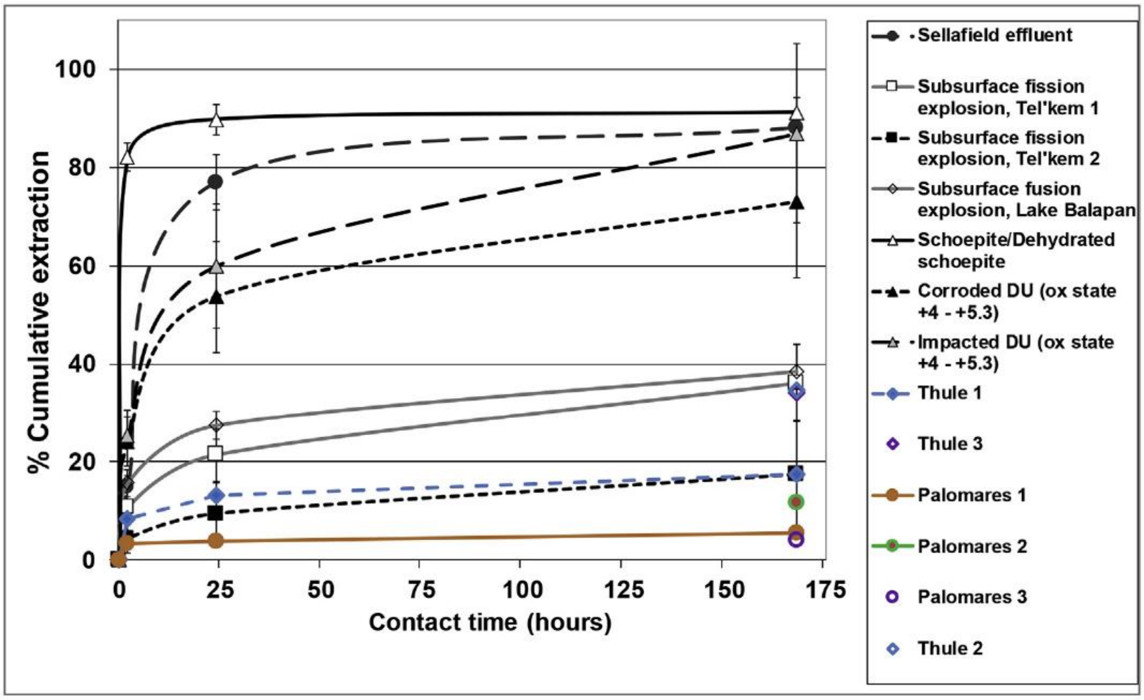


Figure 5.17.- Cumulative extraction (%) of ^{241}*Am from Irish Sea and Semipalatinsk soil samples, U from DU contaminated samples from Kosovo and Kuwait and* ^{239}*Pu Palomares soils and Thule sediments using 0.16 M as extraction agent at room temperature. Figure taken from Salbu et al.,2018 modified from Lind et al., with additional data from COMET.* (COMET, 2017; Lind, 2006; Salbu et al., 2018)

As a final comment, and from a radiological perspective, it is important to highlight that the similarity found until now between the two ecosystems from a radioecological (and radiological) point of view disappear if we have in consideration the inhalation route. While in the case of Thule the high moisture of the soils avoids, or limits drastically, the possible resuspension of contaminated soils and their potential breathing, this effect is known historically, Iranzo et al., that can be a route of dose increments for the public in the Palomares area. Nevertheless, and as it was demonstrated in Chapter 4, this inhalation route provokes quite modest dose increments, clearly below the recommended limits. (Iranzo et al., 1987) (Galvan et al., in press)

Chapter 6

Assessment of U and Th weathering rates in a terrestrial NORM ecosystem

In this chapter, the abiotic and biotic leaching processes constructed and defined along the EU-funded project (RAdioactive particle Transformation procEsses, RATE) and the IAEA-Coordinated Research Program (CRP) on Environmental behavior of radioactive particles, will be applied in the analysis of transformation processes affecting several NORM particles and in the analysis of a dozen of soil aliquots. All collected from a High Background Radiation Area located in Southeast of Norway, the Fen Site, as a paradigmatic example of the radionuclide behavior in areas with presence of NORM particles.

The study site contains both, undisturbed naturally occurring radioactive materials (NORM) and legacy NORM from past mining activities, representing convenient environmental laboratories to study and compare transformation NORM processes trough the performance of abiotic leaching experiments.

Several soil aliquots have been collected in two different places at the Fen site for the application of the leaching protocols, see Chapter 2. Soil aliquots were collected at the former mining Sove site and in the undisturbed site of Bollodalen. The site Bolladalen (N 59°16.424'E 009°18.945') is part of the large wooded zone in the central area of the Fen Complex, being the rødbergite the main rock type in the bedrock at this site. This rock type is highly enriched in ^{232}Th with concentrations reaching 0.5% in weight.

Both places were selected because their soils are characterized for very different levels of thorium. While in the former mining site of Sove the soils collected contains about 20 mg/kg of Thorium, in the case of Bollodalen the concentrations are two orders of magnitude higher, in the range 1000-1500 mBq/kg. In addition to the mentioned soil aliquots, in the Fen site were collected some rock aliquots, characterized for extremely high concentrations of Th (some mg per Kg) in order to be submitted also to the leaching protocols. The rock aliquots were milled just before analysis.

Finally, several particles isolated from soils of the site, and containing very high levels of Th (minimum in the order of 1% in weight, because were identified by SEM-EDX) have been selected for transformation studies.

All the soil and rock aliquots collected have been submitted to the abiotic leaching protocol using rainwater as a leaching agent. Sequentially, the soil aliquots of Sove were summited to an additional leaching but with 0.16 M HCl solutions while the Bollodalen aliquots were submitted to a biotic leaching experiment using cow rumen as extracting agent. All the radioactive particles were submitted to two consecutive leaching experiments: first with rainwater and afterwards with 0.16 M HCl solution.

The U and Th concentrations in the different leachates generated by applying the leaching protocols to soils and particles have been determined by applying the ICP-MS technique. The versatility of this technique, and its relatively low time demanding in comparison with radiometric techniques such as alpha-particle spectrometry, make it as the most appropriate one for these type of studies where low U and Th levels need to be determined in a high number of samples. In addition, the application of the ICP-MS technique allows the determination of the concentration of a good number of stable elements in the same leachates which can be useful in the discussion of the results obtained.

The low concentrations expected in some leachates for U and Th demands of the use of a quite sensitive ICP-MS system. For that reason, in this work we have used a Triple Quadrupole ICP-MS (Agilent 8800), as was detailed in Chapter 3.

Principal component analysis (PCA) was conducted using Minitab 16 (Minitab Inc.). PCA was performed to evaluate variations and patterns in the data related to the elemental concentrations obtained from the different leachates (including U and Th). The data set contains in some cases elemental concentrations below LOD. To evaluate such data, a commonly applied method is used: to substitute samples data corresponding with concentrations below LOD with the LOD value. However, if a chemical element appears with concentrations below LOD in too many of the samples, it was excluded from the analysis.

The data were log (x+1) transformed to reduce the effects of extreme values, and in addition, centered and standardized (i.e., bringing their means to zero and their variances to one.

Application of leaching protocols to bulk soil and rock materials

The leaching studies in the Fen site started with the application of the abiotic protocol to three aliquots of the rock milled material, using in this case simply rainwater as a leaching/extracting agent. With this set of experiments, the intention was to confirm the inert behavior of the bedrock material in the area, and how the availability of U and Th by rainwater weathering from them is negligible.

The application of the abiotic leaching protocol to three different aliquots of the rock milled material gives the results that are compiled in Table 6.1. In this table (which format will be reproduced in all the leaching experiments included in this chapter) are indicated a) the amount of U and Th originally present in the aliquot treated (columns 2 and 3), b) the cumulative percentage of U and Th leached after each leachate obtained (columns 5 and 6), and c) the U/Th mass ratio in each leachate in the column 7. In the column 4, is indicated for each leaching experiment the time of interaction between the bulk material and the extracting solution.

Soils	U ng	Th Ng	Time h	U (%)	Th (%)	U/Th mass ratio
Rock Milled 1	33000	7000000	1	0,0214±0,0003	0,0027±0,0001	0,039±0,001
			24	0,0430±0,0003	0,0033±0,0001	0,192±0,001
			168	0,0537±0,0004	0,0048±0,0001	0,034±0,001
Rock Milled 2	27500	5500000	1	0,057±0,0014	0,0014±0,0001	0,204±0,002
			24	0,092±0,0014	0,0250±0,0021	0,150±0,005
			168	0,099±0,0006	0,0340±0,0005	0,040±0,001
Rock Milled 3	28500	5000000	1	0,015±0,0004	0,0045±0,0001	0,019±0,001
			24	0,029±0,0026	0,0062±0,0004	0,045±0,001
			168	0,035±0,0009	0,0091±0,0001	0,013±0,001

Table 6.1.- Cumulative percentages dissolved by applying the abiotic leaching protocol (with rainwater as a leaching agent) to the three aliquots of Fen rock milled material.

As it can be observed, the amount of U and Th incorporated to the leachates is extremely low, only detectable due to the high sensitivity of the measurement technique used. In all the cases the cumulative amount leached does not reach the 0,1% of U and the 0.04% in the case of Th.

In spite of the small proportions of U and Th dissolved, their cumulative percentages over time can be parametrized. The accumulative desorption values obtained for the rock milled samples for U and for Th have been fitted in each case to a Rosin-Rammler function.

Only as an example, the fittings obtained for one of the aliquots analyzed for U and Th are compiled in Figure 6.1. With the experimental data, the fitting to the mentioned function can be easily done by linearizing and solving by minimum squares the values of the parameters.

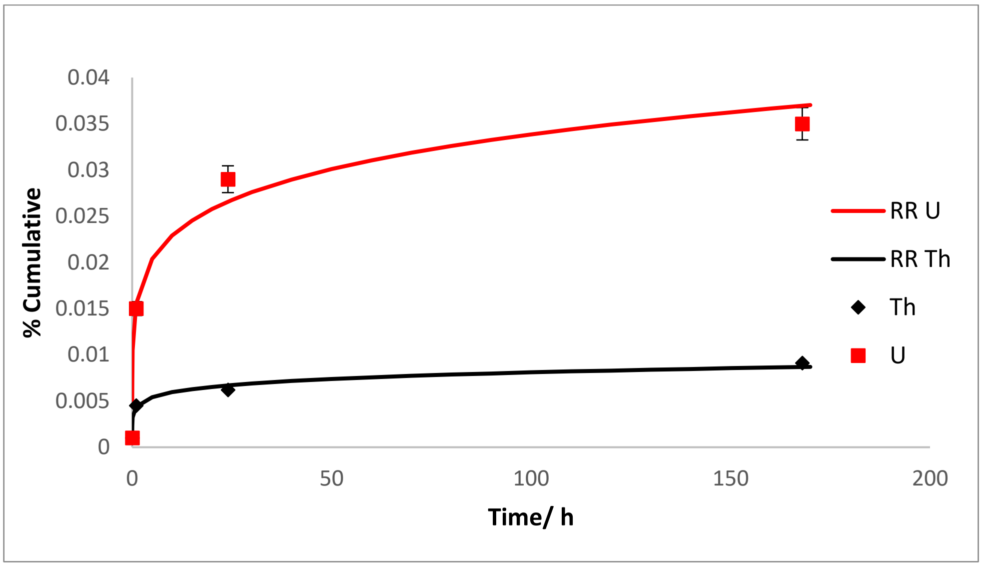


Figure 6.1- Cumulative percentages of U and Th in the leachates obtained treating one of the rock milled aliquots from Fen using rainwater as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.

Moreover, the obtained results, in spite of the very low levels found in the leachates for U and Th, show two evidences: a) the proportion of Th extracted from the rock material in absolutely all the leachate samples analyzed is lower than the percentage of U extracted. b) The relative proportion of U and Th extracted and incorporated to the leachates is variable, without presenting clear patterns (quite variable U/Th mass ratios in the different leachates from the same aliquot). All the facts indicate that the presence of Th and U in the treated rocks should not follow the same pattern and distribution. This fact has been confirmed by applying several microanalytical techniques to particles collected in the area (Cagno et al.,2020). The particles in this case are aggregates of compounds distributed inhomogenously and corresponds to small fragments of bedrock liberated.

The abiotic leaching protocol also using rainwater as extracting agent was afterwards applied to five soil aliquots collected from the Bollodalen area in the central part of the Fen site. The obtained results are compiled in Table 6.2.

Soils	U ng	Th ng	Time H	U %	Th %	U/Th mass ratio
Bollodalen 1	17500	1200000	1	0,43±0,02	0,083±0,001	0,077±0,001
			24	0,95±0,01	0,220±0,001	0,055±0,001
			168	N.D.	0,248±0,002	----
Bollodalen 2	18750	1055000	1	1,47±0,04	0,153±0,002	0,171±0,001
			24	2,71±0,04	0,267±0,004	0,193±0,001
			168	2,73±0,01	0,296±0,002	0,011±0,001
Bollodalen 3	18000	1300000	1	0,89±0,01	0,061±0,001	0,202±0,001
			24	1,75±0,01	0,141±0,001	0,148±0,001
			168	1,77±0,01	0,162±0,002	0,015±0,001
Bollodalen 4	19200	1400000	1	----	-----	----
			24	0,13±0,001	0,053±0,001	0,033±0,001
			168	0,15±0,01	0,077±0,001	0,0139±0,0001
Bollodalen 5	19500	1375000	1	0,51±0,01	0,151±0,003	0,048±0,001
			24	1,18±0,01	0,472±0,003	0,030±0,001
			168	1,22±0,01	0,483±0,001	0,040±0,001

Table 6.2.- Results obtained by applying the abiotic leaching protocol (with rainwater as a leaching agent) to the five soil aliquots collected in the Bollodalen area, see Figure 6.2).

The five aliquots analyzed are characterized for presenting very high concentrations of Th and U. Levels of Th, ranging between 1000 and 1400 mg/kg and levels of U ranging between 17 and 20 mg/kg, have been determined in the bulk soil aliquots. These results are not surprising attending to the radiation levels measured in the area of collection and the extremely high levels of Th in the type of bedrock dominant in the site, as was commented previously.

The cumulative percentages of U and Th extracted from each aliquot can be fitted to Rosin-Rammler functions in the same way and with the same fundaments that was done in the case of the rock milled samples. In Figure 6.2 the fittings obtained for Th and U in a couple of aliquots are shown.

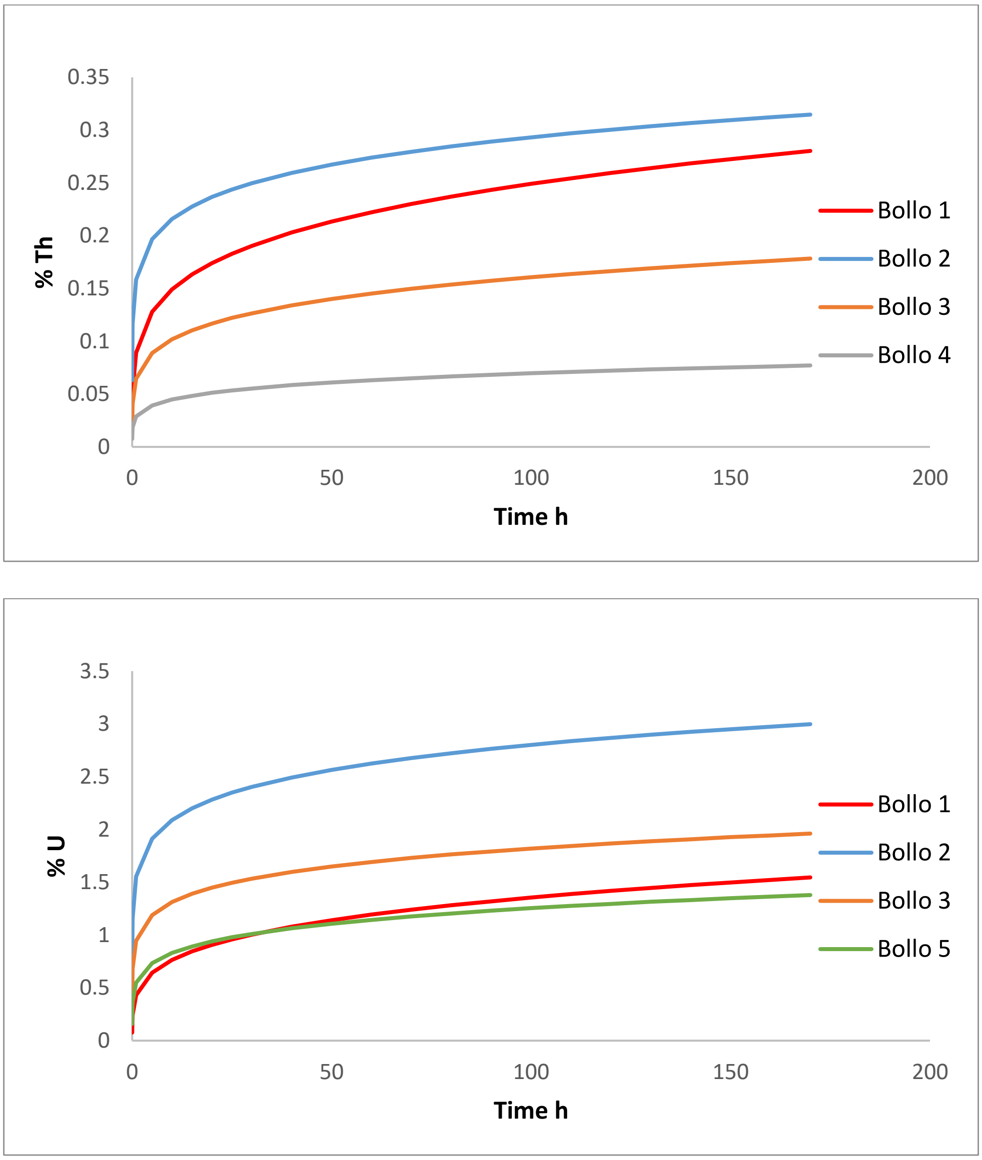


Figure 6.2- Cumulative percentages of Th (up) and U (down) in the leachates obtained treating Bollodalen soil aliquots using rainwater as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.

The percentages of U and Th extracted in the different rainwater leachates are for the five aliquots treated very low, but they do not reach the extremely low percentages found by the treating the milled rocks. The percentage of U extracted do not overpass the 2.5% while the percentage of the Th do not overpass the 0.5%.

The availability of U and Th is quite limited as it was evidenced independently in previous studies. Sequential extractions performed by Popic et al. in soils aliquots collected in an undisturbed area called Rullekoll, located nearby to the Bododallen area and with similar radiation levels and underlying type bedrocks (see chapter 2), indicate that the majority of U and Th is associated to the most refractory forms. The amount of U and Th extracted in the first two extraction fractions (H_20 and NH_4Ac at soil pH) was extremely low (see Figure 6.3) in agreement with the results obtained in this work.

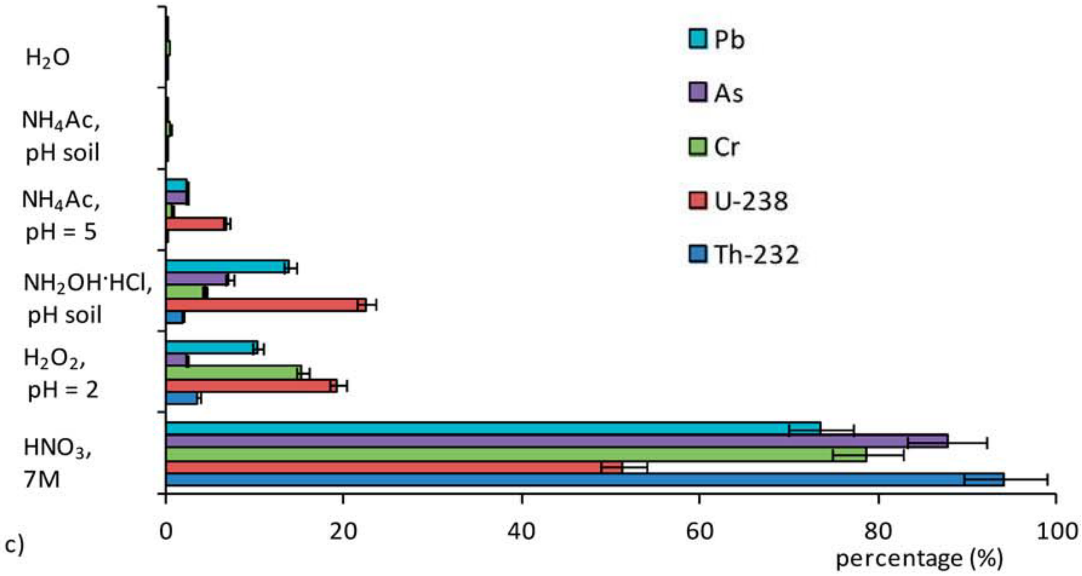


Figure 6.3: - Sequential extraction of soil from undisturbed ^{232}Th rich area Rullekoll (taken from Popic et al., 2014).

The results obtained through the application of the leaching protocol to the 5 Bollodalen aliquots, in addition, confirm some tendencies observed in the leaching of milled rock material. Being in both cases very low the percentages of U and Th extracted, it is clear than the percentage of Th incorporated to the leachates is lower than the percentage of U. This fact is observed in all the aliquots treated and confirm on the frame of extremely low transfers, the relatively more availability of U than Th. On the other hand, and as in the case of the milled rock, it can be observed that the U/Th mass ratios in the extracted leachates are quite variable and do not follow an observable pattern.

The high levels of Th and U found in the soils and the similarities in the pattern of Th and U with the observed ones in the leachates of the milled rock induced to think that a considerable fraction of the U and Th in the Bollodalen soils analyzed could be present in the form of small particles fragmented from underlying rocks. This theory was suggested by Popic at al., 2014 with basis in sequential extraction studies, and the results obtained in this work go in the direction of confirming this theory.

In the 15 leachates corresponding to the five soil aliquots analyzed from Bollodalen, the levels of Al, As, Si, Ti, Cr; Mn, Fe, Cu, Zn, Cd; La, Ce, Nd and Pb were determined by ICP-MS, in addition and simultaneously to the U and Th determinations. This set of data, including U and Th have been submitted to a Principal Components Analysis (PCA).

A PCA is a method for reducing a large number of variables, finding new variables (principal components), which make the data easier to understand. The PCA is used to study the relationship between variables and identify how groups of variables change with respect to each other.

The Graph corresponding to the PCA results obtained with the Bollodalen leachates is shown in Figure 6.4 (variable loadings),

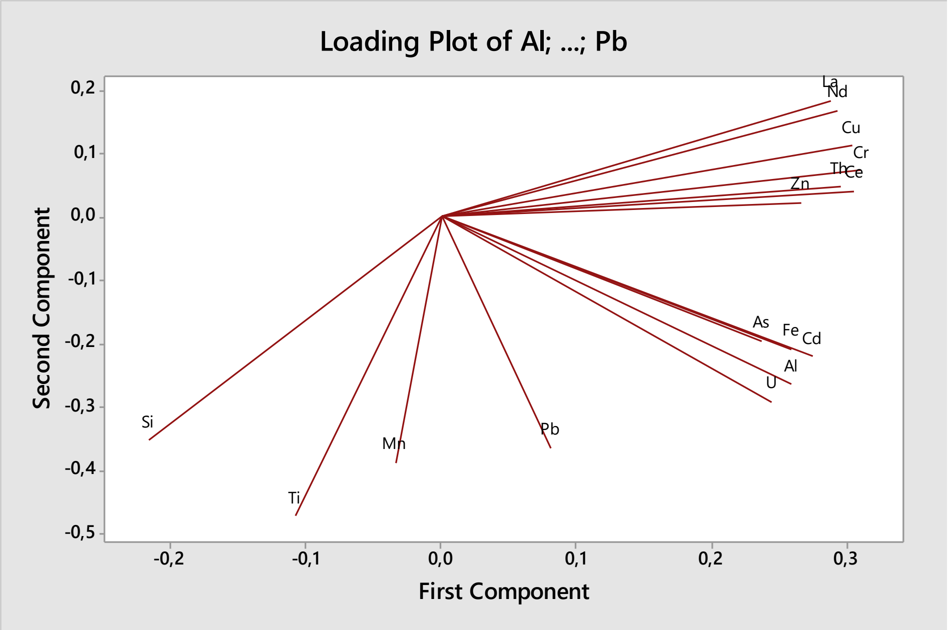


Figure 6.4.- PCA results (loading plot of variables) associated to the rainwater leachates obtained from 5 soil aliquots of Bollodalen. (16 elements)

The PCA shows that 84.7% of the data set total variance is accounted by the two first components (F1: 61,2%, and F2: 23.5%), and with independence that most elements are positively correlated with component 1, it is possible to observe how the majority of them can be associated to two different groups differentiated in the correlations found with component 2.

The Th and U are present in different groups confirming the theory indicated previously that the mobilization pattern from the soil to the leaching solutions of both elements are different. The major proportion of U leached in comparison with Th, and the variability of the U/Th mass ratios in the different leachates is clearly reflected in the PCA graph.

The leaching behavior of Th is similar to the observed one for the rare earth elements analyzed, particularly with Ce (Fen area is rich in rare earth elements) suggesting some type of association, and is similar to the behavior observed for Cr, fact that should not be considered surprising because the association between these two elements was observed also by Popic at al., 2014, analyzing the extractants obtained applying a sequential extraction procedure to soil aliquots of Fen. U, Fe, Al, As and Cu forms a second group, showing also similar behavior and indicating the possible presence of U in the treated soils associated with iron hydroxides. It is remarkable the association found in the leachates between U and As also observed by Popic et al, 2104 in the work previously commented.

The set of experiments with the Bollodalen soil aliquots was completed by carrying additional biotic leaching experiments. The remaining soil aliquots from the performance of the initial leaching abiotic experiments were sequentially submitted to the action of cow rumen during 24 h and a temperature of 39ºC following the protocol described in detail in chapter 3 and in the supplementary material. The proportion of Th and U extracted by the cow rumen leachate was determined by ICP-MS following the methodology previously applied for the U and Th determinations in the aqueous leachates.

The results obtained for the five Bollodalen soil aliquots are compiled in Table 6.3. In the columns 2 and 3 are reflected the levels of U and Th originally present in the soil aliquots treated before the application of the different leaching experiments, while in columns 4 and 5 are indicated the percentages of U and Th extracted with the cow rumen in its interaction with the soil aliquots. The interaction time was fixed in all the experiments.

Soils	U ng	Th ng	% U	% Th
Bollodalen 1	1700	1200000	ND	0,36±0,02
Bollodalen 2	18750	1055000	ND	0,219±0,003
Bollodalen 3	18000	1300000	ND	0,181±0,001
Bollodalen 4	19500	1375000	ND	0,19±0,01
Bollodalen 5	23000	1600000	0,12±0,06	0,13±0,01

Table 6.3.- Results obtained by applying the biotic leaching protocol (with cow rumen as a leaching agent, only 24 h) to the five soil aliquots collected in the Bollodalen area.

The Th and U levels found in the cow rumen leachates confirm the quite inert behavior of these elements in the soils analyzed under the action of mild solutions. The percentages of Th extracted by the cow rumen are comparable with the previously obtained using rainwater as extractant (see Table 6.4) and the percentages of U are lower, being even under the limit of detection of the technique.

Soils	Th % rainwater	Th % cow rumen	Soils	Th % rainwater	Th % cow rumen
Bollodalen 1	0.25	0.36	**Bollodalen 4**	0.08	0.19
Bollodalen 2	0.30	0.22	**Bollodalen 5**	0.48	0.13
Bollodalen 3	0.16	0.18			

Table 6.4.- Comparison of the percentage of Th extracted from five soil aliquots of the undisturbed Bollodalen area, using rainwater and cow rumen as leaching extractants.

The negligible amounts of Th and U extracted with the cow rumen solutions have clear implications about the possible incorporation of these two elements in the food chain by the inadvertent ingestion of soils from the undisturbed areas by ruminants living in the area. This ingestion can be produced in association with or adhered to the vegetation ingested by these animals. The biotic leaching data indicate that, if some amount of soil enriched in Th and U from Bollodalen is ingested by ruminants, the transfer of this element in the digestive system to the rumen fluids will be extremely limited, being excreted the soil ingested with practically all the Th and U remaining.

We can then conclude from the studies performed until now that in the undisturbed Th rich areas from the Fen site, the transfer of this element and uranium from the soils to surrounding environmental compartments is extremely limited. The area will be characterized then by potential very high kd values and extremely low transfer factors in their interaction of the soils with surrounding compartments (waters, plants). Information that should be taken clearly in consideration in any radioecological modelling study in the zone and in the assessment of radiological risk impacts. This theory has been experimentally demonstrated by Popic et al. (2020) which determine concentration ratios in the Fen area, finding values one order of magnitude lower than the default values introduced in the ERIKA radioecology model. Some mobilization occurs from to soil to the roots of the plants, but these roots act as barriers for the transfer of radionuclides and compounds to the aerial part of the plants. (Popic et al., 2020)

The information gained in the previous study performed in the Bollodalen undisturbed area, cannot be extrapolated by default to the anthropogenically modified site areas located in the Fen site. Cannot be extrapolated to the former mining Sove site where:

a) the radiation levels and the type of the dominant underlying bedrock are different than in Bollodalen, and

b) remediation actions were taken covering the affected site with a layer of sand.

To show analogies and differences between unmodified and anthropogenically modified NORM areas in the Fen site under the application of leaching protocols, a total of 5 soil aliquots from the former mining Sove site have been collected and submitted sequentially to abiotic leaching using rainwater and 0.16 M HCl as extracting agents.

The results obtained through the application of the abiotic leaching protocol to the 5 aliquots in interaction with rainwater are compiled in Table 6.5, while the temporal evolution of the cumulative percentage of U and Th extracted in some of the aliquots are shown in Figure 6.5, together with their fitting to a Rossin-Rammler function.

Soils	U ng	Th ng	Time h	U	Th	U/Th
Sove 2	3250	12750	1	6,29±0,32	3,96±0,16	0,23±0,01
			24	9,49±0,74	9,47±1,14	0,33±0,04
			168	10,81±1,08	10,92±0,76	0,23±0,01
Sove 3	3975	20250	1	0,61±0,01	0,31±0,01	0,39±0,01
			24	1,32±0,02	0,76±0,01	0,31±0,01
			168	1,40±0,08	0,96±0,02	0,099±0,001
Sove 4	4025	20450	1	1,11±0,01	0,52±0,01	0,42±0,01
			24	2,27±0,06	1,12±0,02	0,36±0,01
			168	2,44±0,17	1,80±0,02	0,049±0,001
Sove 5	3130	9774	1	0,40±0,02	0,69±0,03	0,56±0,02
			24	2,85±0,08	1,89±0,02	0,16±0,01
			168	3,28±0,01	2,27±0,03	0,28±0,01
Sove 6	9450	25500	1	0,15±0,01	0,24±0,02	0,61±0,03
			24	1,03±0,05	0,78±0,04	0,23±0,01
			168	1,18±0,01	0,90±0,01	0,30±0,01

Table 6.5.- Results obtained by applying the abiotic leaching protocol (with rainwater as a leaching agent) to the five soil aliquots collected in the former mining Sove area.

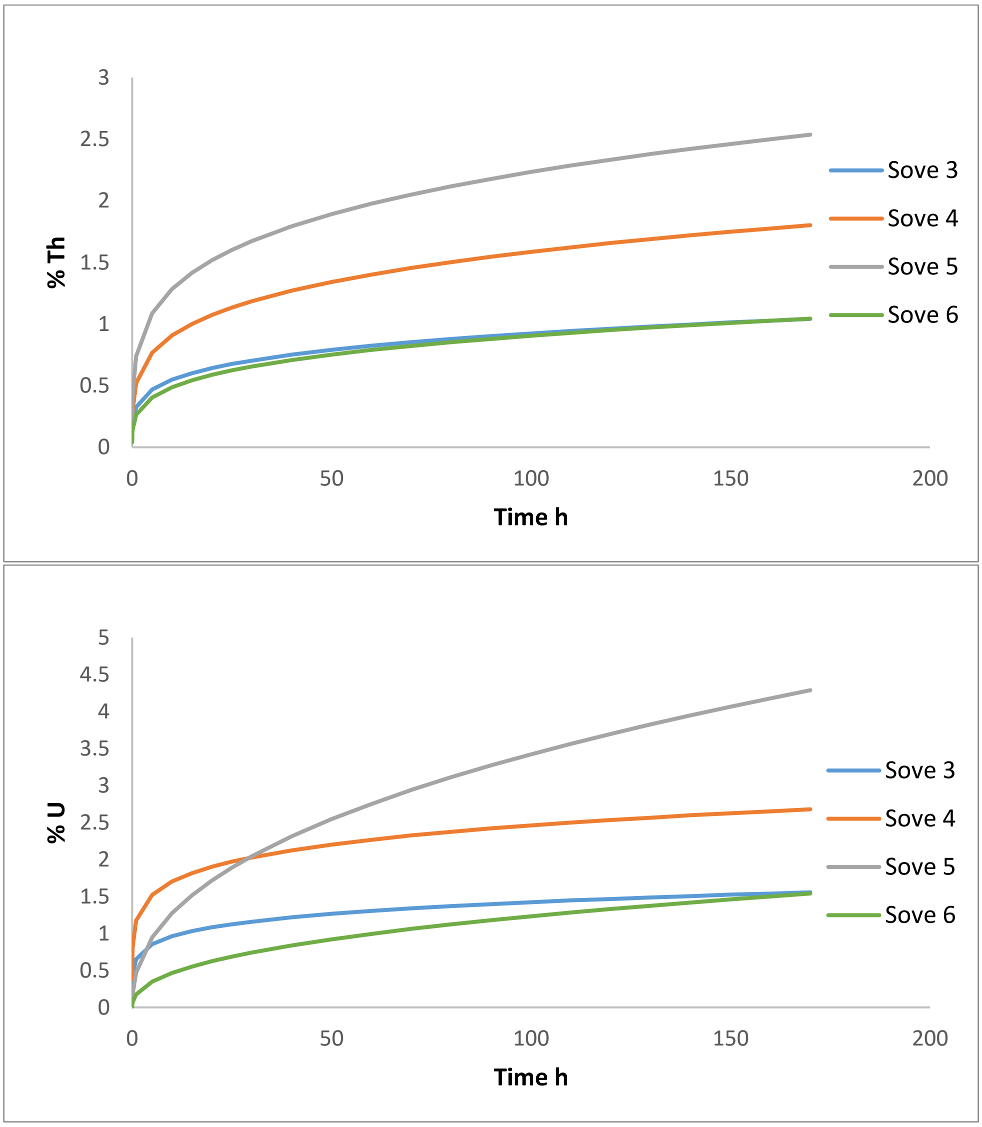


Figure 6.5- Cumulative percentages of U and Th in the leachates obtained treating Sove soil aliquots with rainwater as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.

The first point that need to be commented looking to the obtained results is the clearly lower levels found for U and Th in the soil aliquots analyzed. Maximum values of 25 mg/kg of Thorium and 9 mg/kg of uranium have been determined. According to the radiation levels found in the area of collection, these results could be considered as expected being possibly affected in addition by the remediation actions taken in the area and commented previously.

It is interesting also to mention, that being the percentages of U and Th extracted with rainwater from the Sove soils low, relatively are higher compared with the obtained ones in the undisturbed rich Th area of Bollodalen. The percentages of

U and Th extracted are on the other hand not uniform in all the aliquots treated fact than can be related with the anthropogenic activities carried out in the area in the past.

In all the soil aliquots it is possible to observe also that the percentage of Th extracted is lower than the percentage of U, indicating a slightly higher availability of this last element (fact observed also in the leaching experiments performed with rock milled and Bollodalen soils with independence of the leaching agent used), but in addition the U/Th mass ratio found in the leachates, with very few exceptions, is quite uniform, showing in opposition to Bollodalen, a quite similar pattern of both elements in their interaction with the extracting agent.

This similar pattern should be reflected in the PCA analysis performed with the stable elements determined simultaneously to the U and Th in the 15 rainwater leachates obtained. In all these leachates the levels of Al, Si, Ti, Cr, Th, U, Mn, Fe, Cu, Zn, Cd, La, Nd, Pb, and Ce were determined.

The Graph corresponding to the PCA results obtained is shown in Figure 6.6 (variable loadings). PCA shows that 84.3% of the data set total variance is accounted by the two first components (F1: 69,6%, and F2: 14.7%), with a clear predominance of the first one. A big number of elements show practically its association with the first component, indicating that most of them follow similar pattern in the interaction between the soil aliquots and the leaching agent.

In the mentioned group, are found the U, Th, Fe and the rare earths (Ce, La, Nd) ratifying the previously commented similar pattern of U and Th in the leaching process, as it was deduced from the uniformity of the U/Th mass ratios found in the leachates.

It is interesting also to mention that in opposition to the study performed in Bollodalen, in the former mining Sove site the Cr is not associated with the Th, and Cu and Cd is not associated with the U. All the facts go in the direction of showing the clear differences in the two zones from the Fen site analyzed and confirming how the results obtained in one site cannot be extrapolated to the other. Case by case studies should be performed when, as in this case, both areas show clearly different levels of Th and U, and they have different history (unmodified vs. anthropogenically modified NORM areas).

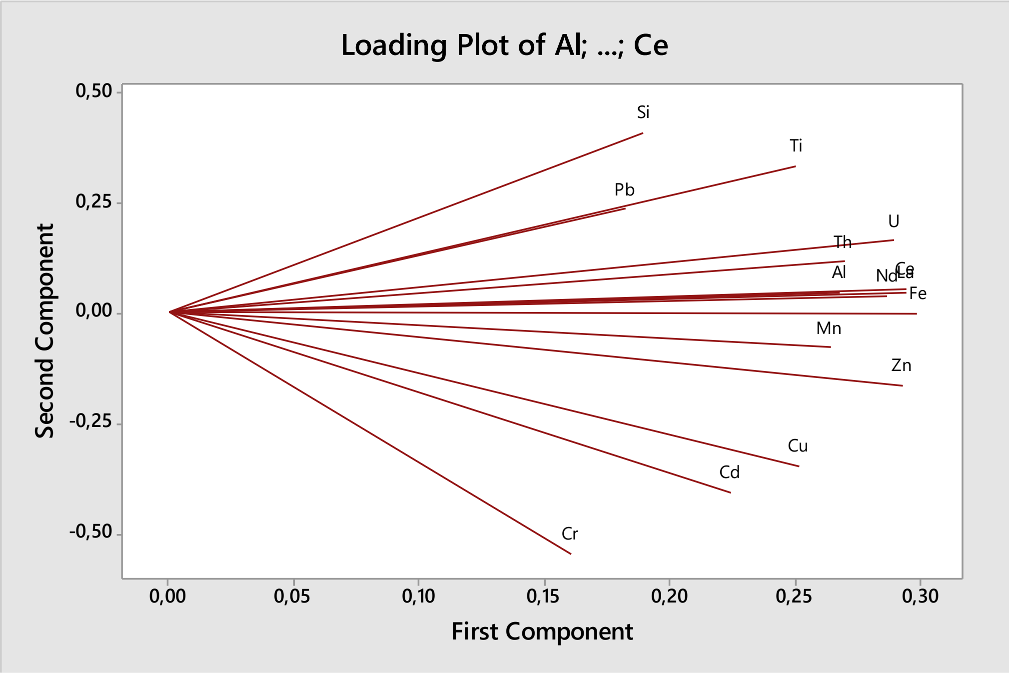


Figure 6.6.- PCA results (loading plot of variables) associated to the rainwater leachates obtained from 5 soil aliquots of the former Mining Sove site (15 elements).

The soil aliquots of Sove, after the leaching with rainwater were submitted sequentially to the same leaching protocol, but now applying 0.16 M HCl as an extracting agent. With this extract we try to mimic the action of human gastric juices after their potential inadvertent ingestion and gives quite interesting information about the potential mobility of U and Th in these soils under the action of acid solutions. If the remediated zones of Sove are used with agricultural purposes, the use of acidic fertilizers can mobilize a fraction of the U and Th associated to the treated soils.

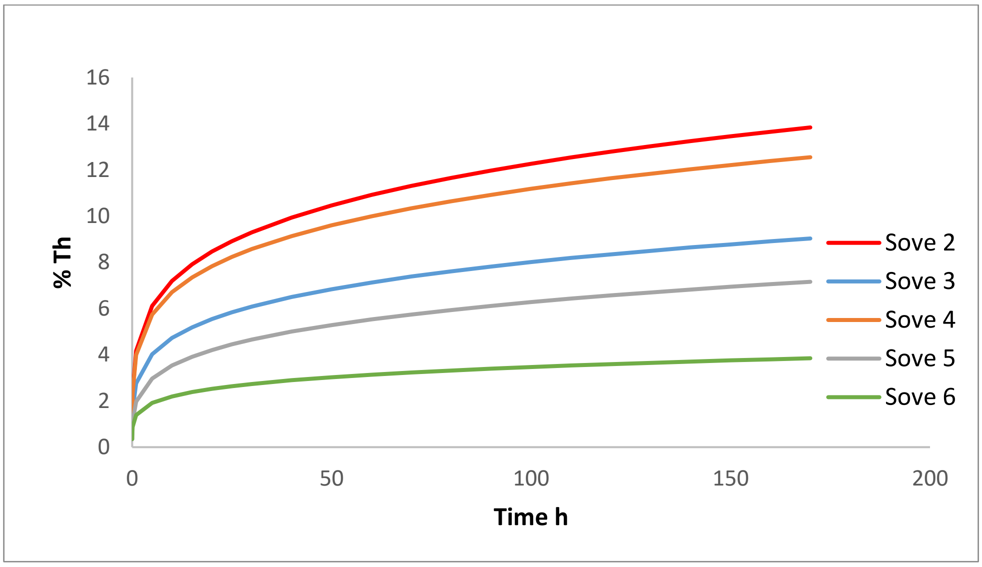
The results obtained through the application of the abiotic leaching protocol to the 5 aliquots in interaction with 0.16 M H are compiled in Table 6.6, while the temporal evolution of the cumulative percentage of U and Th extracted in some of the aliquots are shown in Figure 6.7, together with their fitting to a Rossin-Rammler function.

Soils	U	Th	Time h	U	Th	U/Th
Sove 2	3250	12750	1	12,02±0,17	4,18±0,03	0,73±0,01
			24	24,57±0,27	8,79±0,07	0,69±0,01
			168	38,23±1,15	13,84±0,33	0,69±0,02
Sove 3	3975	20250	1	10,67±0,53	2,84±0,12	0,74±0,03
			24	19,72±1,93	5,41±0,44	0,69±0,06
			168	29,89±1,23	9,38±0,28	0,50±0,01
Sove 4	4025	20450	1	13,09±0,07	3,99±0,08	0,45±0,01
			24	28,11±0,90	8,17±0,47	0,52±0,01
			168	40,02±0,44	12,51±0,24	0,37±0,01
Sove 5	3130	9774	1	5,11±0,26	1,96±0,12	0,83±0,06
			24	11,12±0,38	4,50±0,16	0,76±0,05
			168	15,97±0,38	7,04±0,16	0,61±0,04
Sove 6	9450	25500	1	2,54±0,03	1,41±0,03	0,67±0,12
			24	4,58±0,03	2,53±0,03	0,68±0,02
			168	6,43±0,05	3,92±0,05	0,49±0,01

Table 6.5.- Results obtained by applying the abiotic leaching protocol (with rainwater as a leaching agent) to the five soil aliquots collected in the former mining Sove area.

The levels of U and Th extracted with 0.16 M HCl are clearly higher than the obtained ones using rainwater as leaching agent. The ratio between the percentages of Th extracted with 0.16 M HCl and rainwater ranges between 3 and 10 depending of the soil aliquot considered. After 1 week of interaction soil-acidic solution the percentage of Th extracted ranges between 3 and 14% while the percentage of U extracted ranges between 6 and 40%. Again, is possible to observe the no homogeneity of the percentages of Th and U between aliquots, fact that was previously associated to the peculiarity of the studied area.

As a common feature observed in all the leaching experiments included in this work, it can be observed that for all the aliquots the percentage extracted of Th is lower than the percentages extracted of U. The U is clearly under acidic conditions more available than the Th. Also, it is interesting to mention that in similarity with the rainwater leaching experiments, the U/Th mass ratios in the different leachates obtained with 0.16 M HCl are quite uniform indicating that both elements follow the same pattern in the interaction soil-extractant, with independence of the percentages extracted. However, this uniform U/Th mass ratio is higher in the acidic leachates than in the rainwater leachates, indicating the relative increment in the availability of U in relation with Th under acidic conditions.



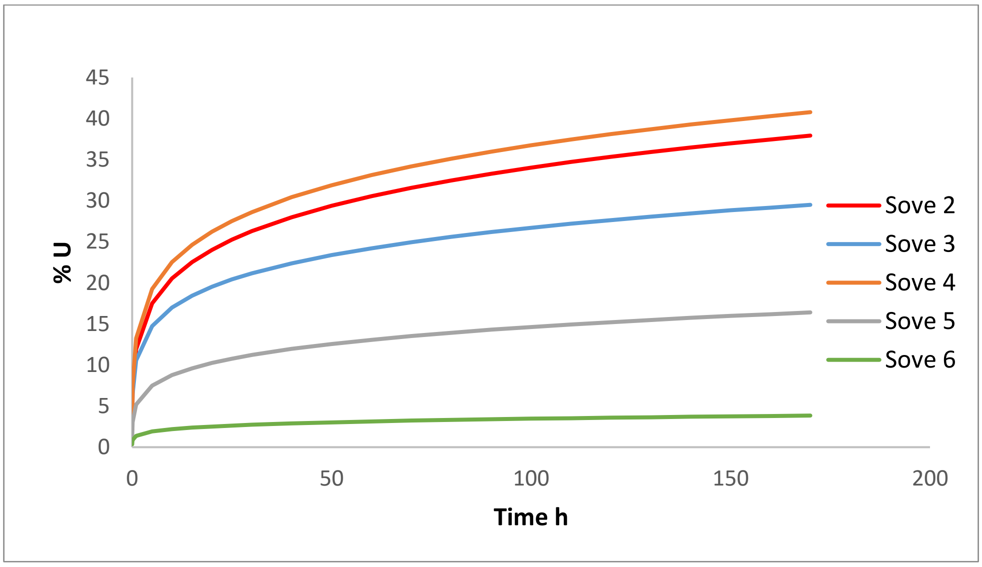


Figure 6.7 - Cumulative percentages of U and Th in the leachates obtained treating Sove soil aliquots with 0.16M HCl as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.

As in the previous leaching experiments, simultaneously to the U and Th determinations performed in the acid leachates, the levels of Al, Si, Ti, Cr, Mn, Fe, Cu, Zn, Cd, La, Nd, Pb and Ce have been determined. The set of data compiled for the 15 acid leachates involved in the experiment, have been submitted to a Principal Components Analysis (PCA). The Graph corresponding to the PCA results obtained with the Sove 0.16 M HCl leachates is shown in Fig. 6.8 (variable loadings),

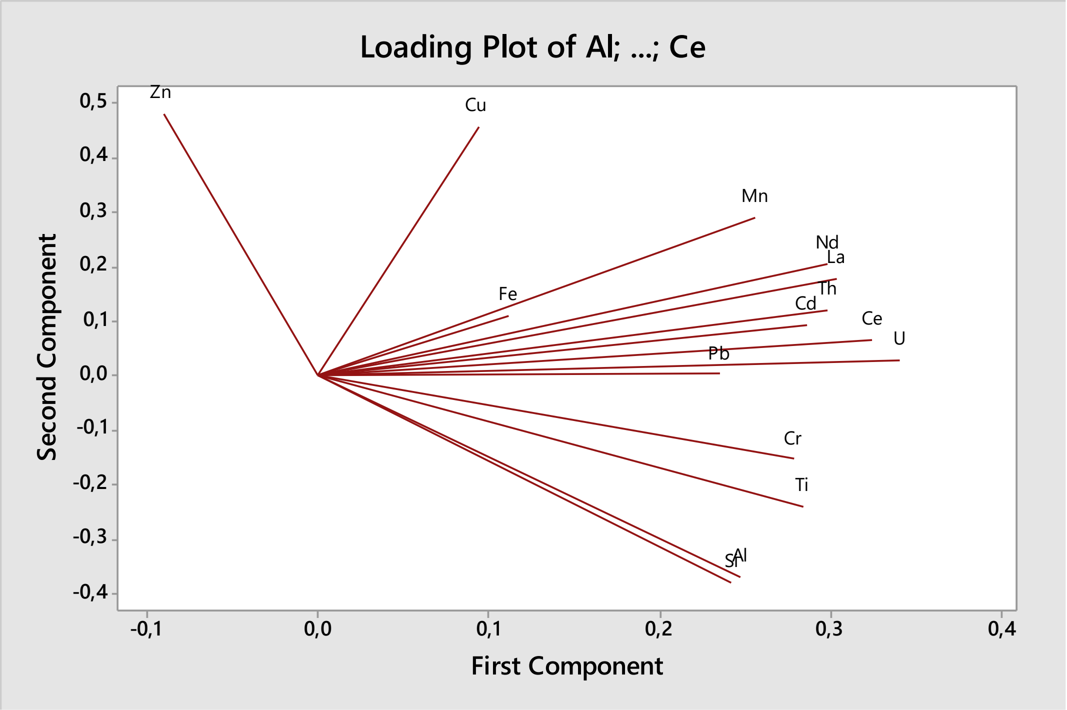


Figure 6.8.- PCA results (loading plot of variables) associated to the 0.16 M HCl leachates obtained from 5 soil aliquots of the former Mining Sove site (15 elements).

The PCA shows that 80.3% of the data set total variance is accounted by the two first components (F1: 56,5%, and F2: 23,6%) and that big number of elements show practically its association with the first component, indicating that both of them follow similar pattern in the interaction between the soil aliquots and the leaching agent.

In the mentioned group are found the U, Th, and the rare earths (Ce, La, Nd) ratifying the previously commented similar pattern of U and Th in the leaching process as it was deduced from the uniformity of the U/Th mass ratios found in the leachates.

A qualitative summary of the main conclusions obtained from the leaching experiments performed with soil aliquots and milled rock is compiled in the Table 6.6. It is evident that there’s clear differences in the percentages of actinides leached depending of the zone, the type of sample and the extracting agent used. Case by case studies are needed to obtain a confident information about the transfer behavior of the actinides of interest.

Sample type	*Rainwater*	*Rumen*	*0.16 M HCl*
Rock milled	*Extremely low*	------------	-------------
Bollodalen soils	*Very low*	*Very low*	-------------
Sove soils	*Low*	-------------	*Moderate*

Table 6.6.- % Th and U leached from the Fen bulk materials (soils and milled rocks).

Application of leaching protocols to isolated particles

With all the experience and knowledge gained with the leaching experiments performed in the bulk soil aliquots, the leaching protocols have been applied to a total of 4 radioactive particles from the Fen area. These particles were identified in the screening of soil aliquots by SEM-EDX and they correspond to heterogeneities of several decens of micrometer size, embedded in the soils and characterized for presenting high levels of Th (Cagno et al., 2020).

After their isolation three of these particles (codes 362, 364 and 365) were submitted to the particle leaching protocol using rainwater as leaching agent, including the fractionation of all the leachates.

Determinations were performed in the total, < 0,45 μm, LMM and < 3 kDa fractions of each leachate, following the practical steps detailed in chapter 3. Remembering the protocol's concepts, total fraction corresponds to an aliquot representing the bulk leachate obtained, the <0.45 μm fraction is obtained by submitting an aliquot of the leachate to filtration through filters of the mentioned size, the LMM fraction (low molecular mass) corresponds to the supernate of the leachate aliquot submitted to ultra-centrifugation and finally, the < 3 kDa fraction corresponds to the filtrate material obtained by ultra-filtrating a final leachate aliquot. In addition to the results obtained in the mentioned fractions, information about the concentrations of the elements of interests associated to the so-called particulate fraction (> 0.45 μm fraction) and to the so-called colloidal fraction can be deduced recovering the expressions:

(Particulate fraction) = (total fraction) – (<0.45 μm fraction), and

(Colloidal fraction) = (<0.45 μm fraction) – (< 3 kDa fraction)

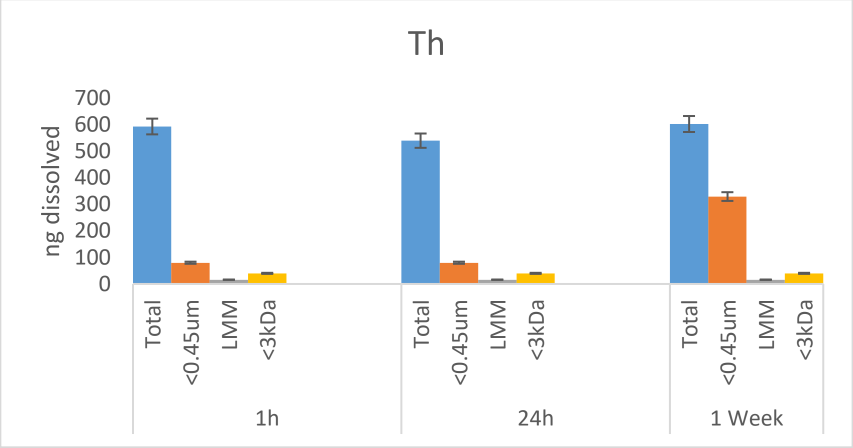
The behavior of the three particles analyzed when were leached with rainwater was no homogeneous.

Two of them (codes 364 and 365) were characterized because the levels of Th and U in all the fractions were below the limit of detection. Considering the sensitivity of the experimental technique used for the characterization, these results are a clear indicative of the inert behavior of the particles under the action of mild solutions. This behavior on the other hand cannot be considered surprising, taking into account the results obtained previously in the leaching experiments performed with milled rock and with soil aliquots from the undisturbed Th rich area of Bollodalen using also rainwater as leaching agent. The particles analyzed should correspond to material fragmented from the bedrock dominating in the area and incorporated to the soils to were transported by physical weathering procedures.

Total different results were obtained when the particle with code 362 was submitted to the same leaching protocol with rainwater. The results obtained are shown in a graphic form in the Figure 6.9. The results are given indicating the massic amount of Th and U found associated to each fraction, and not in percentages leached, because as was indicated previously, the particles after the leaching experiments were not sacrificed to determine its remaining Th and U content.

As it can be observed in the mentioned Figure considerable amounts of Th and U were found in the leachates, but with a clear peculiarity: the great majority of both elements was found in the total fraction, with minimum amounts in the other three fractions. In other words, the great majority of the Th and U leached is found in the particulate fraction (> 0.45 μm fraction).

The data obtained indicates that the particle along the leaching process experiments mechanical disruption, releasing small fractions which are incorporated to the leachates analyzed. This mechanical disruption occurs along all the time of the interaction particle-extractant because similar amounts of Th and U in particulate form were found in the three leachates obtained (1 hour, 1 day, 1 week).



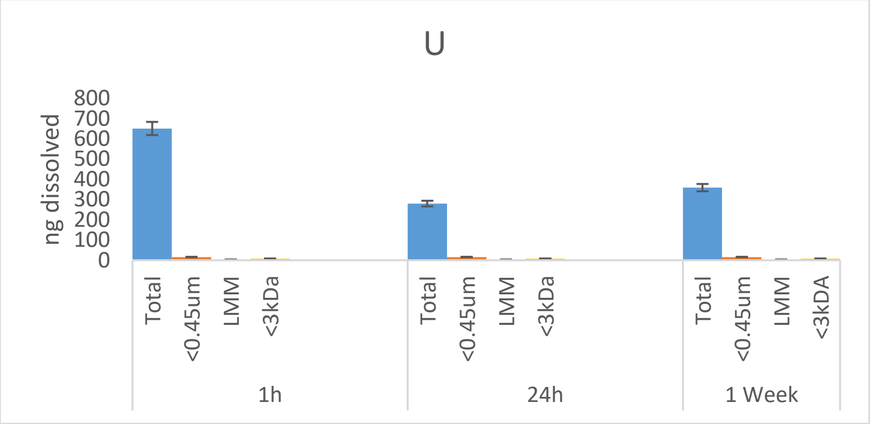


Figure 6.9.- Amounts of U (down) and Th (up) found in the different fractions of the leachates obtained for the isolated particle 362 from Fen using rainwater as a leaching agent.

Another feature that can deduced from the results is that the U/Th mass ratio in the different leachates are different. If we consider the particulate association of these elements in the leachates, this fact implies the no similar distribution of Th and U inside the particles, with varying ratios in the small fractions mechanically disrupted along the interaction time between the particle and the extractant.

The microscopic studies performed by Cagno et al., (2020) confirms this theory.

The mentioned variability in the U/Th mass ratios in the leachates can also be deduced from Figure 6.10, where the temporal evolution of the cumulative amounts leached for both elements are represented. The data, as usual have been fitted to Rosin-Rammler distributions.

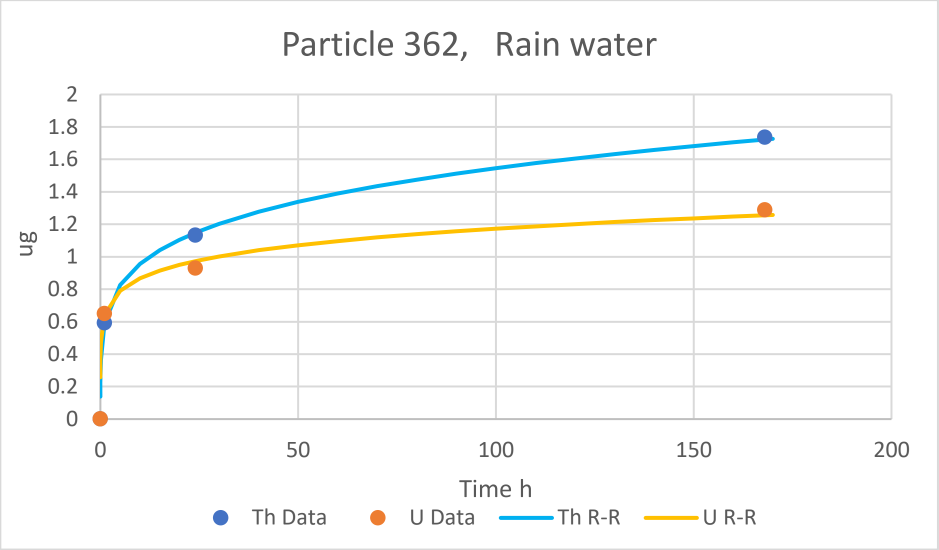


Figure 6.10- Cumulative amounts of U and Th in the leachates obtained treating the isolated particle 362 with rainwater as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.

The particles 362 and 365 after the initial leaching with rainwater were submitted sequentially afterwards to the same leaching protocol by using 0.16 M HCl as a leaching agent. In addition, a new particle, code PFG4, was submitted to the same leaching agent.

The results obtained with the particle 362 by applying 0.16 M HCl, are shown in the Figure 6.11, using exactly the format applied for presenting the results obtained with the same particle when rainwater was applied.

The lixiviation pattern observed for this particle with rainwater is reproduced totally when was treated with the acid medium. Considerable amounts of U and Th were found in all the leachates extracted with 0.16 M HCl, being in addition the great majority of the U and Th extracted associated to the particulate fraction. The amount of both elements found in dissolved form is minimum. The mechanical disruption and the consequent releases of small fragments from the particle continued and even was enhanced with the action of the acidic medium, because the amounts of U and Th leached with 0.16 M HCl were clearly higher that with rainwater.

The U/Th mass ratios in the 0.16 M HCl leachates take also slightly different values, reinforcing the idea suggested previously that the U and Th are distributed differentially inside the particle. The fragments released along the experiments by the particles are characterized by different U/Th mass ratios.

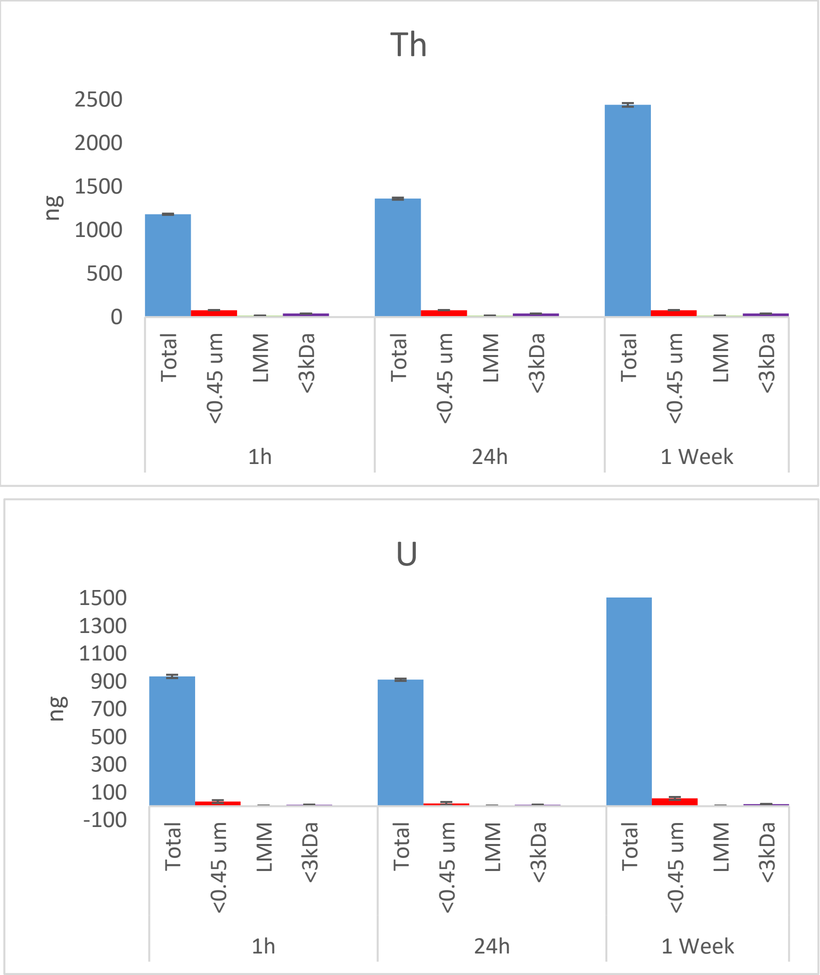


Figure 6.11.- Amounts of U (down) and Th (up) found in the different fractions of the leachates obtained for the isolated particle 362 from Fen using 0.16 M HCl as a leaching agent.

As in the rainwater case, the mentioned variability in the U/Th mass ratios in the 0.16 M HCl leachates is also reflected in Figure 6.12, where the temporal evolution of the cumulative amounts leached for both elements are represented. The data have been also fitted to Rosin-Rammler distributions.

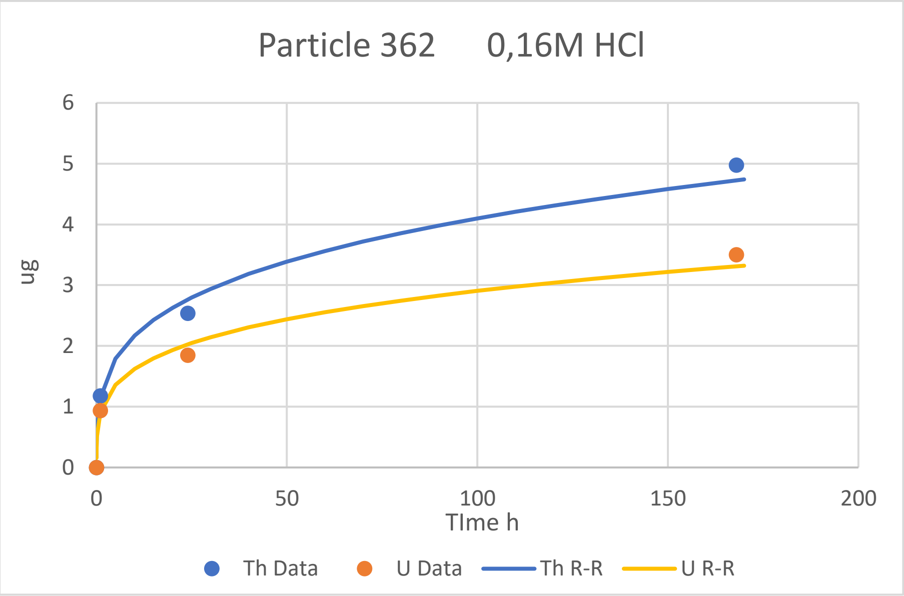


Figure 6.12- Cumulative amounts of U and Th in the leachates obtained treating the isolated particle 362 with 0.16 M HCl as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.

Totally different pattern for the U and Th was found in the 0.16 M HCl leachates corresponding to the particle 365. The amounts of U and Th lixiviated in this particle were 1 to 2 orders of magnitude lower than the amounts leached in the particle 362 and with a totally different distribution between fractions as it can be observed in Figure 6.13, where the results obtained in the different fractions of the three leachates are represented.

For both elements, U and Th, it is observed in the three leachates that the amounts in the particulate and non-particulate fractions are comparable, with additionally a non-negligible amount present in colloidal form. The lixiviation pattern in the particle 365 indicates that in this case mechanical disruptions effects no relevant. This is the reason why the amounts of U and Th determined in the leachates of 365 are quite low, and coherent with the obtained ones in the leachings performed with rainwater: the particle has a clear refractory behavior. The different pattern in the leaching process is reflected also in the U/Th mass ratios that take quite similar values in the three leachates analyzed, as indirectly is observed in Figure 6.14 where the temporal evolution of the cumulative amount of U and Th leached is shown.

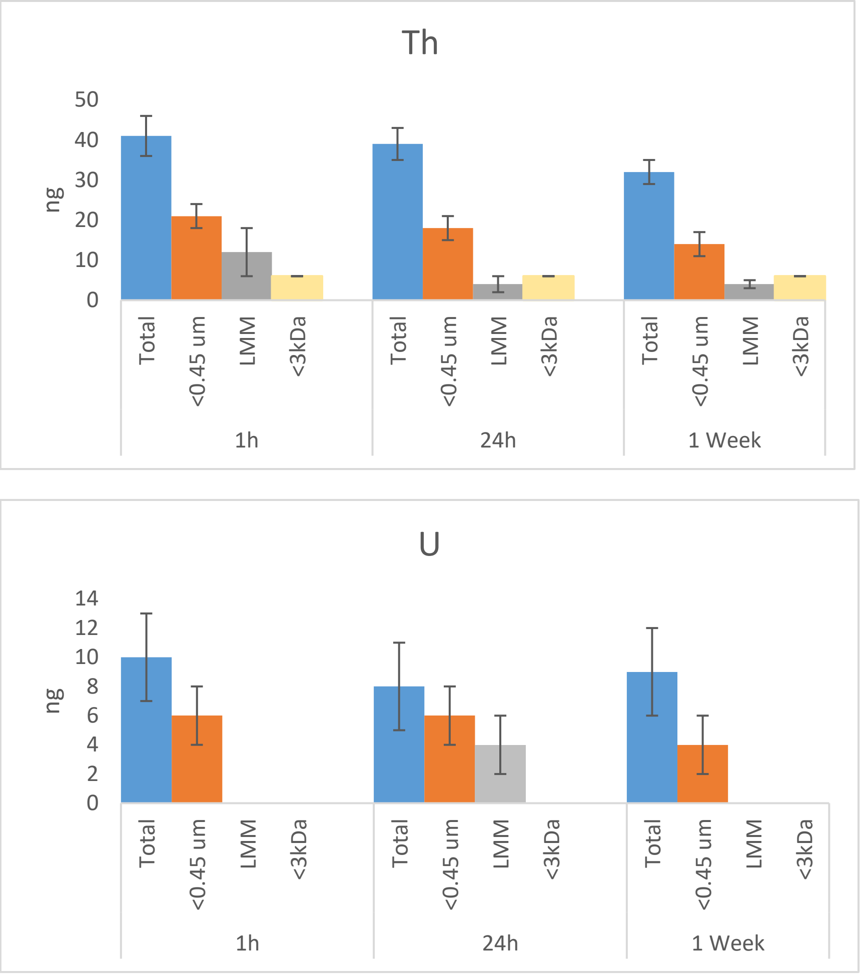


Figure 6.13.- Amounts of U (down) and Th (up) found in the different fractions of the leachates obtained for the isolated particle 365 from Fen using 0.16 M HCl as a leaching agent.

The results obtained with the last particle submitted to the leaching protocol with HCl 0.16 M, code PFG4, reproduces the pattern observed with the particle 362 under the action of the same leaching agent, see Figure 6.15. Considerable amounts of Th and U are found in the three leachates and with the similar characteristic distribution between the different fractions: the great majority of the U and Th released along the interaction between the particle and the acid solution can be found in the particulate fraction (more than 90% in the three leachates analysed). In this particular case the U/Th mass ratios in the different leachates was quite uniform as it can be deduced from Figure 6.16.

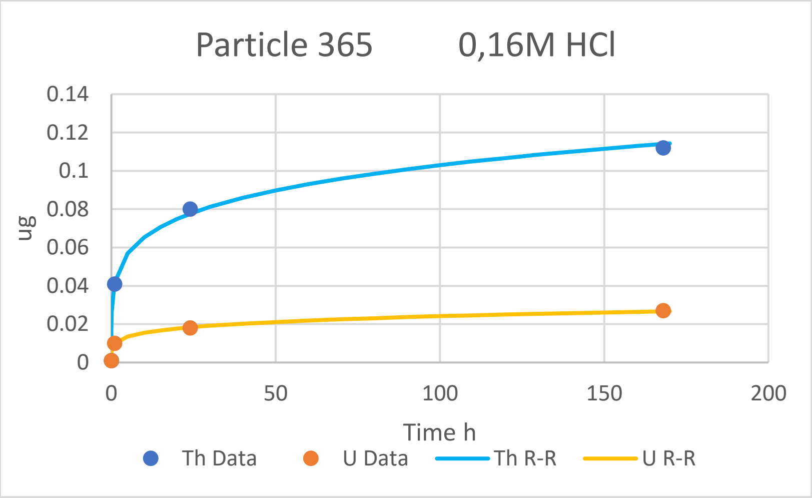
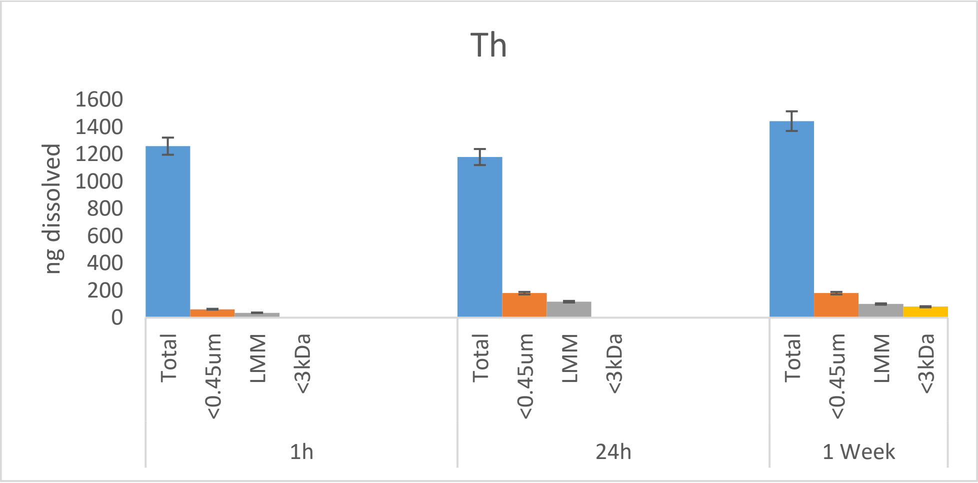


Figure 6.14- Cumulative amounts of U and Th in the leachates obtained treating the isolated particle 365 with 0.16 M HCl as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.



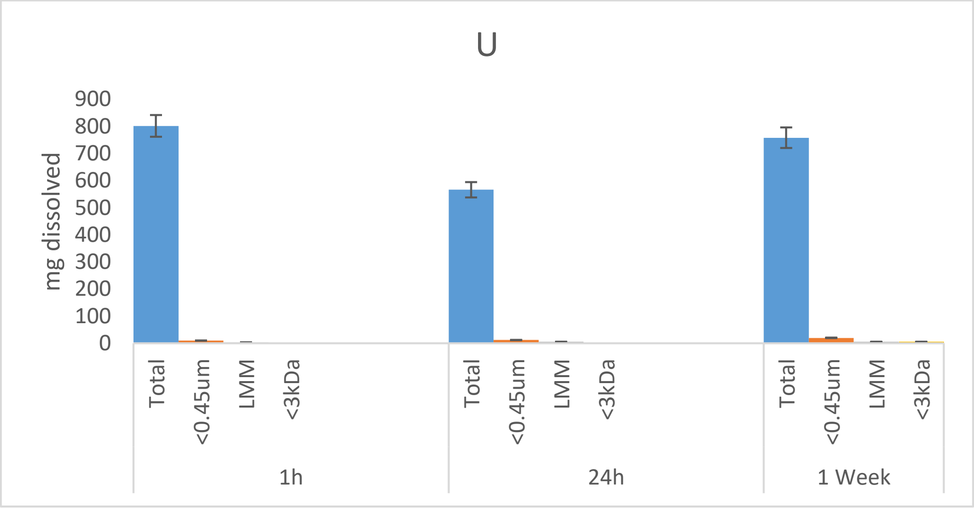


Figure 6.15.- Amounts of U (down) and Th (up) found in the different fractions of the leachates obtained for the isolated particle PFG4 from Fen using 0.16 M HCl as a leaching agent.

All the comments given in the analysis of the results for the particle 362 when was treated with 0.16 M HCl, can be translated to this last experiment. The mechanical disruption and the consequent releases of small fragments from the particle due to the action of the acidic medium is the clear explanation of the results. The only difference can be associated to the fact that the released small fragments have the same U/Th ratio as reflected in the uniformity of this ratio in the different leachates.

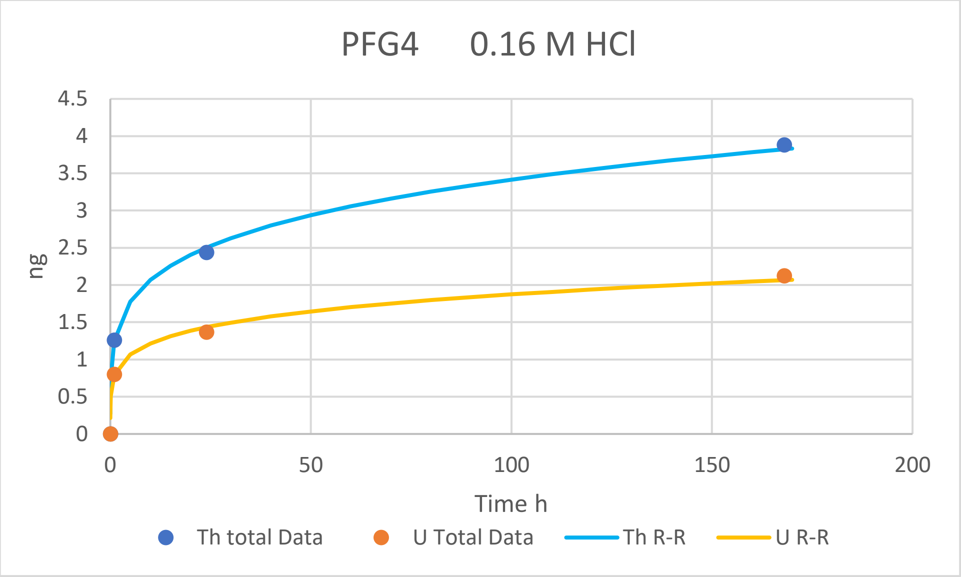


Figure 6.16- Cumulative amounts of U and Th in the leachates obtained treating the isolated particle PFG4 with 0.16 M HCl as leaching agent. In both cases the experimental data have been fitted to a Rosin-Rammler function.

A good summary of the main conclusions obtained after the different leachings submitted to the 4 isolated particles from the Fen area, is compiled in table 6.7.

Particle	*Rainwater*	*0.16 M HCl*
362	*High mechanical disruption*	*High mechanical Disruption*
364	*Negligible*	*------*
365	*Negligible*	*Quite Low*
PFG4	*------*	*High mechanical disruption*

Table 6.7.- % of U and Th leached from single isolated Fen particles.

It is clear that the particles per-se can be considered formed by refractory material with a low tendency to transfer in dissolved form appreciable amounts of Th and U. Only when the integrity of the particles is not maintained, the percentage of U and Th leached from the particles can be high. In other words, the % of Th and U leached from Fen particles ranges from very low to high, and when the % is high this Th and U can be found in the leachates in particulate form.

The last conclusion is important, in order to evaluate the implications of the possible transfer of the Th and U associated initially to the particles to other environmental compartments. The presence of Th and U in leachates in particulate form prevent the transfer for example of these elements to plants and vegetation by root uptake and limit the potential entrance of both elements in the trophic chain, ratifying studies about transfer soil to plants in the area characterized by quite low concentration ratios (Popic et al., 2020). The evolution of the Th and U particulate fraction in the leachates, and their possible dissolution over time (high surface/volume ratios) is something to be investigated in the future.

Chapter 7

Summary and Conclusions

Radioactive environmental impact assessments are usually based on average bulk concentrations of radionuclides in various media, such as water (Bq/L), soil or sediment (Bq/kg or Bq/m^2) and tissues of animals and plants (Bq/kg). Assuming homogeneous distribution of radionuclides and without to have in consideration their distribution between species, i.e., their speciation. This fact can conduits in many cases to erroneous impact assessments, for not consider properly the behaviour of the artificial radionuclides once released and incorporated to an environmental compartment. This particularly can occurs in areas affected directly by nuclear events where it is possible to find radioactive particles.

In the past, inherent differences in transport, mobility and bioavailability of particle-bound radionuclides compared to simple ions have largely been ignored in radiochemistry, radioecology, radiation dosimetry and radiation protection. This fact it is extremely important, because radioactive particles containing refractory radionuclides have been released following a series of past nuclear events, being more common that generally expected. Associated to the radioactive particles generated in different nuclear events, on the other hand, it has been demonstrated that characteristics such as elemental composition depend on the source, while other characteristics such as particle size distribution, structure, and oxidation states, with high influence in the ecosystem transfer, depend also on the release scenarios, i.e., on the way that they were released to the environment and on the characteristics and particularities of the area contaminated.

It is then evident, that to assess appropriate environmental impacts, and risks associated, in ecosystems contaminated with radioactive particles, links must be established between the source term, the deposition, and the ecosystem transfer.

Particle weathering rates and the subsequent remobilization and ecosystem transfer of particle-associated radionuclides will depend strongly on the particle characteristics (e.g., composition, structure, oxidation states). Soil and sediment will act initially as sinks for particles and will act as diffuse source of radioactivity if particle weathering occurs. Thus, information on particle weathering rates is essential for assessing long-term consequences.

Leaching experiments can provide important data on particle characteristics and the links to solubility particle weathering rates and remobilization potential for particle associated radionuclides (and metals). With this end, and within the EU-funded RATE project, and in collaboration with the IAEA Coordinated Research project on Hot Particles, a leaching protocol has been established with the aim of identifying key parameters affecting properties of particles when exposed to a variety of different water qualities, temperatures and single abiotic leaching agents. This protocol has been presented and detailed in this thesis taking into consideration that when leaching experiments on single radioactive particles are performed, the same procedure should be applied on bulk samples from which the particle was isolated. This will aid the interpretation of results obtained on particle transformation processes, and also link new data to literature data.

Due to weathering of particles, associated radionuclides are remobilized and the ecosystem transfer increases with time. Thus, the distribution of radionuclides between solid and solution is a time dependent process and the thermodynamic constant Kd should be replaced by a time function. Consequently, the leaching protocols stablished have taken in consideration the time as a variable to be taken into account.

In order to improve the knowledge needed to link particle characteristics to sources, to transfer and to biological effects on which sound environmental assessments can be made, we have performed in this thesis leaching experiments with different abiotic and biotic leaching agents to isolated radioactive particles and associated radioactive contaminated soils collected in two areas affected in the past by non-critically accidents involving nuclear weapons (e.g., Thule, Greenland; Palomares, Spain), In both nuclear events, the source was the same (nuclear weapons with similar composition), the processes of dissemination of the radioactive content was also very similar, but the scenario where the radioactive particle contamination was deposited it is clearly different: a semi-desertic terrestrial area affected by Mediterranean climate in the case of Palomares, and an artic area in the case of Thule. The similarities and differences found in the characterization of the radioactive particles and in the performed leaching experiments with isolated particles and with contaminated soils from the two areas, allow evaluating the influence of the ecosystem affected by the radioactive contamination in their radioecological behaviour.

The presence of radioactive particles in the environment is not a phenomenon associated in exclusivity to nuclear events and artificial radionuclides. In a lot of high natural background radioactive areas distributed over the world, and in association to the mining and processing of some minerals and raw materials with elevated amount of natural radionuclides, the presence of the mentioned radionuclides as particles is frequent. Particularly, in the high natural background radioactive areas with the presence of highly radioactive particles and aggregations, the performance of leaching experiments will have the same justification and will provide the same type of information that in the areas affected by nuclear events, being then possible to gain information about the ecosystem transfer of radionuclides, its magnitude and kinetics. This will allow decreasing the uncertainties in radioecological models adapted to these particular ecosystems, and a more proper evaluation of the radionuclide transfer between different compartments (soil-water, soil-plant, etc). For that reason, the leaching experimentation have been also extended and applied in a high natural background radioactive area located in Southern Norway, the Fen area.

Leaching experiments and measurements

In this thesis, radioactive particles (RP) and soil aliquots have been submitted to different leaching agents sequentially to evaluate the degree of particle transformation and soil solubilization over time. The agents used are either representative of the ones that can affect the particles and the soils in the affected ecosystem (rainwater, groundwater), compounds mimicking the acidity of the human stomach juices (0.16 M HCl) or directly cow rumen fluids, in order to evaluate the possible incorporation of radionuclides by ingestion. In addition, a synthetic solution mimicking the lung fluids has been used in an independent leaching procedure to analyze the possible assimilation of radionuclides by the human body via the inhalation route.

A total of four different leaching protocols have been applied in this PhD thesis. They are the following:

a) Radioactive particle protocol (rainwater, groundwater, 0.16 M HCl)
b) Abiotic soil protocol (rainwater, groundwater, 0.16 M HCl)
c) Biotic soil protocol (cow rumen)
d) Biotic soil protocol (lung fluid)

The leaching protocols applied to radioactive particles presents the peculiarity that the different leachates were submitted to fractionation procedures, being obtained information about the particle, colloidal and dissolved phase radionuclide distribution in each leachate. While the soil protocols are characterized for the analysis of the different leachates obtained in bulk form.

The fractions and the bulk leachates obtained by applying the different leaching protocols to radioactive particles and contaminated soil samples associated to the Palomares (Spain) and Thule (Greenland) has been analyzed, being the objective the determination of ^{239}Pu, ^{240}Pu and ^{236}U in them. This fact was performed by applying the Accelerator Mass Spectrometric Technique (AMS). In the case of the Fen studies, the objective was the determination of the U and Th levels, fact that was performed by applying the Inductively Coupled Mass Spectrometric Technique.

The AMS determinations have been performed using SARA. A 1 MV compact AMS system designed and manufactured by High Voltage Engineering Europa H.V. Pu-isotopes and the ^{236}U determinations have been particularly benefited from several improvements performed in the SARA facility during the last years, the most important being:

a) The off-axis Faraday cup at the exist of the HEM (FC3) used for the monitoring formed using of the normalisation isotope as a current, was upgraded with new Gated Charge Pump Digitizers (GCPD) supporting the measurement of pA.

b) Stripper gas was changed from Ar to He motivated by the very promising ionization yields obtained at the lowest terminal voltages for the heaviest radionuclides in the 3+ charge state.

c) Original gas ionization chamber provided by HVEE, was replaced by a miniaturized one designed by ETH and featuring less electronic noise and a better charge collection efficiency in the active volume of the detector.

In fact, for ^{236}U, without the upgrade of FC3, it would not be possible to monitor the ^{236}U from small samples (the ^{238}U generates signals at pA level) and without the high ionisation yield achieved for actinides in 3+ charge states in He-based stripping process, getting good counting statistics for the minor actinides would have been an issue. With He, our system has the potential to offer the most efficient measurement conditions for actinides at low energies. However, in the case of ^{236}U, the abundance sensitivity that can be actually achieved is limited by the background caused by scattered ^{235,238}U molecular fragments.

Our specific applications were characterized for the coexistence of U and Pu species in the same cathode (no isolation between U and Pu is applied). For that reason, the interference of the naturally-occurring ^{238}U on ^{239}Pu and ^{240}Pu should systematically checked during the measurement to avoid wrong results. This no chemical purification of either the U or the Pu fractions gives an added value to the work done.

The U and Th in the Fen leachates were determined used a Triple Quadrupole ICP-MS (Agilent 8800), because the low concentrations expected in some leachates for U and Th demands of the use of a quite sensitive ICP-MS system. In our case, once the leachates were obtained, the measurement of the U, Th and several stable elements concentrations was done using the Method 200.8 (Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry) redacted by Environmental Monitoring Systems Laboratory of U. S. Environmental Protection Agency (USEPA). For quantitative analyses a minimum of three replicate determinations were required. The mean value of these measurements was used for data reporting. A rinse blank is used to flush the system between samples.

Palomares studies

The applied Palomares leaching experiments have been performed on single radioactive particles, but also on bulk samples from where the particles were isolated because it will help in the interpretation of results obtained on particle transformation processes including re-adsorption processes.

In particular, we have analyzed the transformation processes of a couple of isolated hot-particles: one from zone 2 and one from zone 6. In addition, and in the surroundings (less than 10 meters) of the places from where the particles were isolated, several soil samples were collected to be submitted to the bulk sample leaching protocol. The zone 2 was the area were one weapon crushed and used immediately after the accident for the disposal of all the contaminated material picked-up during the clean-up operations, while the zone 6 is a hilly area located near the coast, at the east of the denotation points (zone 6), where the radionuclide deposition was produced due to the impact of the generated radioactive clouds travelling to the sea following the direction of the dominant winds at the time of the accident.

The analysis of the leachates obtained treating one particle from zone 2 and other from zone 6 with rainwater firstly indicates that the total amount of ^{239}Pu incorporated to the rainwater solution along the leaching experiment is very small: in the order of 10^{-2} to 10^{-1} % after a week of interaction. This evidence indicates that the transformation processes affecting to the particles disseminated in the terrestrial area under the action of dissolution agents (rainwater, irrigation water) are quite slow.

Quite different results were obtained by applying to the two previously mentioned particles the same leaching protocol but in this case using 0.16 M HCl as extracting agent. The incorporation of ^{239}Pu to the leachates in the case of the particle of zone 6 has increased, due to the 0.16M HCl action, one order of magnitude in relation with the previously observed with rainwater, but still continues being extremely low its total amount. A ^{239}Pu leaching percentage not reaching after a week of interaction even 1% evidences that the weapon material disseminated in the Palomares area remains in a quite refractory form, mostly as Pu oxide.

On the opposite, the results obtained in the application of the leaching protocol with 0.16 M HCl to the particle of zone 2 were totally different. After a week of leaching treatment practically 100% of the Pu present in the particle has been incorporated to the different leachates, reflecting the practical disintegration of the particle. These results should not be interpreted as contradictory with the conclusions obtained in the analysis of the previous particle. The data suggests that the fragility and physical unstable behavior of these particles is behind the results obtained in this case, and that along the leaching processes, very small fragments were initially incorporated in particulate form to experiment after that and under the action of the acidic agent its dissolution.

It can be concluded that the obtained data suggest that is the fragile behavior of the particles the main factor which can affect the possible incorporation of actinides to the acid leaching solution. In the particle where its integrity remained, the percentage of Pu and U incorporated to the leached fraction was minimum, while, on the opposite, high actinide incorporation was observed in the particle that experimented its fragmentation/disintegration during the application of the leaching protocol.

In order to complement the information obtained, and to evaluate also the role that can play the soil/sediment material where these particles are embedded in the possible incorporation or inhibition of the contamination to the extracting agents, leaching experiments have been carried out also on a set of soil aliquots 5 soil aliquots collected in zone 6, and 4 soils collected in zone 2,

The cumulative percentages of ^{239}Pu determined by treating over time 3 soil aliquots from zone 6 with rainwater can be evaluated in principle as quite low, ranging in the interval 0.8 – 2.5% after a week of interaction, but if these values are compared with the results published in similar experiments performed in the past, they are relatively higher. In experiments performed in the 80´s and 90´s the incorporation of Pu to water were in all cases clearly lower than 1%. In order to understand these results it is necessary to remark that these soils were collected from a sedimentary place at the basis of the hills located in the zone and where material is deposited/accumulated after their transport (mostly by runoff from the hills). A fraction of the contamination, due to the transport processes experimented by the material analyzed could be more available and can be incorporated to the leached fraction, either in dissolved or in particulate form.

The soils from zone 6 previously treated with rainwater were afterwards submitted to the biotic protocol using cow rumen as a leaching agent. The percentage of Pu leached with the cow rumen is an all the cases higher than the percentage previously leached with rainwater, but with quite moderate values that ranges from 1.5 to 3.5%. The quite refractory behavior of the Pu is dominant even under the action of these juices.

The percentage of the Pu leached with the 0.16 M HCl extractant from two additional soil aliquots from zone 6 is clearly higher than the obtained ones with rainwater and also higher than the obtained with cow rumen. However, the cumulative percentages leached after a week (from 10% to 15%) continues being a relative minor fraction of the total amount of Pu contaminating the aliquots analyzed. The refractory behavior of the Pu contamination present in the contaminated soils, can explain these low percentages, although a peculiarity of the Palomares soils can also have a high influence: their high carbonates content. The soils provoke a buffering effect neutralizing the strength of the acidic solutions used as a leaching extractants.

The leaching studies in Palomares soils have finally included analysis of different soil aliquots collected in the zone 2, for comparison purposes. In the case of the aliquots treated with rainwater the cumulative percentage of leached ^{239}Pu in the three cases was quite low and any case after one week of leaching the value of 1% is approached, while the percentage of ^{239}Pu leached from the aliquots treated with 0.16 M HCl as extractant was clearly higher than the leached with rainwater but at the same time, lower than the percentage leached from the soils of zone 6 following the same tendency that the observed previously with the soils treated with rainwater. Although in both areas (zone 6 and 2), the proportion was quite low, the percentage of ^{239}Pu leached with rainwater from the soils collected in zone 6 were higher than the obtained with the soils aliquots treated in soil 2, even having in some of the aliquots comparable Pu contamination. The previous run-off and weathering history of the material collected from zone 6, could be the reason of the difference observed with the particulate contamination more fractionated and relatively more available that in the samples from zone 2.

Finally, in the Palomares area, additional leaching experiments were performed taking into consideration that a possible important route of radiological impact is through inhalation of resuspended soil material. The arid and semi-desertic conditions dominating in Palomares favors the resuspension of contaminated soils, its possible inhalation by the farmers and people living in the surroundings, and the possible incorporation of Pu to the human body though it solubilization in the pulmonary system.

A set of experiments have been carried to study the possibility of solubilization of some of the Pu present in Palomares contaminated soil aliquots by physiological solutions, mimicking the composition and action of the fluids of the human respiratory system. The results indicate that some solubilization of Pu in the physiological solutions occurs, although the magnitude of the solubilization is extremely low. Fortunately, the in vitro experiments performed simulating the solubilisation of Pu after Palomares contamination inhalation, reaffirm previous conclusions about the quite inert behaviour of the Pu dispersed in the accident. The percentages solubilized by the respiratory system are quite low, minimizing the doses received by this via.

Palomares versus Thule studies

The similarities between the Palomares and Thule accidents opened new challenges in performing comparative evaluations of radioactive particle transformation abiotic experiments in the two ecosystems, because on one side both cases are characterized by similar source materials and similar formation mechanisms, but on the other side the released particles have been residing for 50 years in very different environmental compartments.

All the individual particle characterization works done during the last years conclude indicating that the Palomares and Thule particles are remarkable similar with respect to elemental distribution, morphology and oxidation states, reflecting that they originate from similar source and release scenarios. In other words, the particle characteristics are more dependent on factors determined by the source and the release scenario than on the environmental conditions. The analysis performed on Palomares and Thule particles indicated that U and Pu were homogenously distributed in them, appearing in both cases as agglomerated crystalline grains with a relatively high degree of porosity, indicating that that specific surface area of the particles may be large, and giving some appearance of fragility.

The ecosystem behaviour and transfer of radionuclides in both cases could be dependent not only of the particle characteristics but also of the scenarios where the particles were deposited. For that reason, similar leaching experiments were performed in both areas in isolated particles and bulk soils.

From the terrestrial area affected by the Thule accident, a couple of radioactive particles were isolated and submitted to leaching experiments. The first particle was submitted as a first step to the leaching protocol using rainwater as leachate agent, being observed its refractory behaviour. Only traces of Pu are found in the leachate's fractions, representing the leaching Pu less than 10^{-1} % of the Pu present in the particle. The same particle was immediately after submitted to the same leaching protocol, but now using 0.16 M HCl, confirming the results its inert behavior because the percentage of plutonium leached is minimum and even comparable with the amount of plutonium previously leached with rainwater.

The second isolated particle was only submitted to the leaching protocol with 0.16 M HCl, being the results totally different that the obtained ones with the first particle. A sudden and considerable Pu fraction is incorporated to one of the leachates, reflecting the fragility of the particle. Along the leaching processes, very small fragments were initially incorporated in particulate form, to experiment after that, and under the action of the acidic agent, its dissolution. This behavior was also observed in one of the Palomares particles analyzed, indicating that although the Palomares and Thule particles show a refractory behavior, its fragility can play a non-negligible role in the proportion of Pu that can be mobilized.

The abiotic studies carried out associated to the Thule accident were completed with the application of the leaching protocol to a total of three soil aliquots by using 0.16 M HCl as a leaching agent. After exposition of the Thule soils to the acid medium during a week various percentage of Pu were leached, ranging in the interval between 7 and 30%. It was found on the other hand, a clear inverse correlation between the total Pu activity initial present in the soil aliquot and the proportion of Pu leached, with lower percentages of leaching in the more contaminated aliquots. Due to the characteristics of the soils treated that contains high organic content, the acidity of the leaching agent remains during the application of the leaching protocol in opposition to the observed with the Palomares soils, where the buffering effects were dominant.

In conclusion, after passing more than 40 years since both accidents and in spite of the fact that the areas affected are very different, the radioecological behavior of the particles in both cases are similar, with a tendency to show their refractory behavior, although its fragility and tendency to fractionation should not be neglected. From a radiological point of view, it is also important to highlight that the similarity found until now between the two ecosystems from a radioecological (and radiological) point of view disappear if we have in consideration the inhalation route. In the case of Thule, the high moisture of the soils avoids, or limits drastically, the possible resuspension of contaminated soils and their potential breathing.

Studies in a NORM site

The leaching protocols have been finally applied to the analysis of transformation processes affecting several NORM particles and to the analysis of a dozen of soil aliquots. All collected from a High Background Radiation Area located in Southeast of Norway, the Fen Site, as a paradigmatic example of the radionuclide behavior in areas with presence of NORM particles. The study site contains two kinds of scenarios. Undisturbed naturally occurring radioactive materials (NORM) and legacy NORM from past mining activities. Both, representing convenient environmental laboratories to study and compare transformation NORM processes trough the performance of abiotic leaching experiments.

Soil aliquots were collected at the former mining Sove site and in the undisturbed site of Bollodalen. Remembering the details and values commented at chapter 6, these places were selected because their soils are characterized for very different levels of thorium. Sove’s soils contains about 20 mg/kg of Thorium, and in the case of Bollodalen the concentrations are in the range 1000-1500 mBq/kg. Finally, several particles isolated from soils of the site, and containing very high levels of Th (minimum in the order of 1% in weight, because were identified by SEM-EDX) have been selected for transformation studies.

The abiotic leaching protocol using rainwater as extracting agent was first applied to five soil aliquots collected from the Bollodalen area, in the central part of the Fen site. The percentages of U and Th extracted in the different rainwater leachates were for the five aliquots treated very low. The percentage of U extracted do not overpass the 2.5% while the percentage of the Th do not overpass the 0.5%. The percentage of Th incorporated to the leachates is lower than the percentage of U. This fact is observed in all the aliquots treated and confirm on the frame of extremely low transfers, the relatively more availability of U than Th.

The set of experiments with the Bollodalen soil aliquots was completed by carrying additional biotic leaching experiments. The remaining soil aliquots from the performance of the initial leaching abiotic experiments were sequentially submitted to the action of cow rumen during 24 h and a temperature of 39ºC. The Th and U levels found in the cow rumen leachates confirm the quite inert behavior of these elements in the soils analyzed under the action of mild solutions, with the percentages of Th extracted by the cow rumen being comparable with the previously obtained using rainwater as extractant and the percentages of U being lower, even under the limit of detection of the technique. The biotic leaching data indicate in conclusion that, if some amount of soil enriched in Th and U from Bollodalen is ingested by ruminants, the transfer of this element in the digestive system to the rumen fluids will be extremely limited, being excreted the soil ingested with practically all the Th and U remaining.

As a second step, in order to show analogies and differences between unmodified and anthropogenically modified NORM areas in the Fen site under the application of leaching protocols, a total of 5 soil aliquots from the former mining Sove site have been collected and submitted sequentially to abiotic leaching using rainwater and 0.16 M HCl as extracting agents. The percentages of U and Th extracted with rainwater from the Sove soils were also low, but relatively higher compared with the obtained ones in the undisturbed rich Th area of Bollodalen. The percentages of U and Th extracted are on the other hand not uniform in all the aliquots treated fact than can be related with the anthropogenic activities carried out in the area in the past. In all the soil aliquots it is possible to observe also that the percentage of Th extracted is lower than the percentage of U, indicating a slightly higher availability of this last element (fact observed also in the leaching experiments performed with Bollodalen's soils with independence of the leaching agent used), but in addition the U/Th mass ratio found in the leachates, with very few exceptions, was quite uniform. Showing in opposition to Bollodalen, a quite similar pattern of both elements in their interaction with the extracting agent.

On the other hand, the results obtained through the application of the abiotic leaching protocol to the 5 Sove aliquots in interaction with 0.16 M HCl, indicate that the levels of U and Th extracted with 0.16 M HCl are clearly higher than the obtained ones using rainwater as leaching agent. The ratio between the percentages of Th extracted with 0.16 M HCl and rainwater ranges between 3 and 10 depending on the soil aliquot considered. After 1 week of interaction soil-acidic solution, the percentage of Th extracted ranges between 3 and 14%, while the percentage of U extracted ranges between 6 and 40%. In all the aliquots the percentage extracted of Th is lower than the percentages extracted of U. The U is clearly under acidic conditions more available than the Th, while in similarity with the rainwater leaching experiments, the U/Th mass ratios in the different leachates obtained with 0.16 M HCl are quite uniform, indicating that both elements follow the same pattern in the interaction soil-extractant, with independence of the percentages extracted. However, this uniform U/Th mass ratio is higher in the acidic leachates than in the rainwater leachates.

The study was completed by applying the leaching protocols to a total of 4 radioactive particles from the Fen area. After their isolation three of these particles (codes 362, 364 and 365) were submitted to the particle leaching protocol using rainwater as leaching agent, including the fractionation of all the leachates. The behavior of the three particles analyzed when were leached with rainwater was no homogeneous.

Two of them (codes 364 and 365) were characterized because the levels of Th and U in all the fractions were below the limit of detection. Taking into account the sensitivity of the experimental technique used for the characterization, these results are a clear indicative of the inert behavior of the particles under the action of mild solutions.

Total different results were obtained when the particle with code 362 was submitted to the same leaching protocol with rainwater. Considerable amounts of Th and U were found in the leachates, but with a clear peculiarity: the great majority of both elements was found only in the total fraction, i.e., in the particulate fraction (> 0.45 μm fraction). This particle along the leaching process experiments mechanical disruption, releasing small fractions which are incorporated to the leachates analyzed. This mechanical disruption occurs along all the time of the interaction particle-extractant because similar amounts of Th and U in particulate form were found in the three leachates obtained (1 hour, 1 day, 1 week).

The particles 362 and 365 after the initial leaching with rainwater were submitted sequentially afterwards to the same leaching protocol by using 0.16 M HCl as a leaching agent. In addition, a new particle, code PFG4, was submitted to the same leaching agent.

The lixiviation pattern observed for the particle 362 with rainwater was reproduced totally when was treated with the acid medium. Considerable amounts of U and Th were found in all the leachates extracted with 0.16 M HCl, being in addition the great majority of the U and Th extracted associated to the particulate fraction. The amount of both elements found in dissolved form is minimum. The mechanical disruption and the consequent releases of small fragments from the particle continued and even was enhanced with the action of the acidic medium because the amounts of U and Th leached with 0.16 M HCl were clearly higher that with rainwater.

Totally different pattern for the U and Th was found in the 0.16 M HCl leachates corresponding to the particle 365. The amounts of U and Th lixiviated in this particle were 1 to 2 orders of magnitude lower than the amounts leached in the particle 362 and with a totally different distribution between fractions. For both elements, U and Th. It is observed in the three leachates that the amounts in the particulate and non-particulate fractions are comparable, with additionally a non-negligible amount present in colloidal form, indicating that in this case mechanical disruptions effects no relevant. This is the reason why the amounts of U and Th determined in the leachates are quite low, and coherent with the obtained ones in the leachings performed with rainwater: the particle has a clear refractory behavior.

The results obtained with the last particle submitted to the leaching protocol with HCl 0.16 M, code PFG4, reproduces the pattern observed with the particle 362 under the action of the same leaching agent, Considerable amounts of Th and U are found in the three leachates and with the similar characteristic distribution between the different fractions: the great majority of the U and Th released along the interaction between the particle and the acid solution can be found in the particulate fraction. The mechanical disruption and the consequent releases of small fragments from the particle due to the action of the acidic medium is the clear explanation of the results.

As a summary after the leaching experiments applied to the NORM particles, we can indicate that it is clear that the particles per-se can be considered formed by refractory material with a low tendency to transfer in dissolved form appreciable amounts of Th and U. Only when the integrity of the particles is not maintained, the percentage of U and Th leached from the particles can be high. In other words, the % of Th and U leached from Fen particles ranges from very low to high. When the % is high this Th and U can be found in the leachates in particulate form.

Looking finally all the results obtained in the Fen area as a whole, it is evident that the soils and particles show a quite refractory behaviour, with some peculiarities in the different areas analysed. The percentages of Th and U in the leachates are generally quite low with independence of the solutions applying, reflecting the quite inert behaviour of soils and particles and the limited transfer of radionuclides between compartments, with all the associated consequences in estimations of dose assessments.

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