Speciation of caesium-137 and plutonium-isotopes in Chernobyl soils

Spesiering av cesium-137 og plutonium-isotoper i jord fra Tsjernobyl

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Foreword

25 years after the Chernobyl accident, the fear of nuclear accidents in the general population seemed to be diminishing. The general view aired in media was that nuclear power might be a CO_2-emission free way, a “green” way of obtaining energy and this time period was referred to by some as the nuclear renaissance. In March 2011, the Fukushima Daiishi Nuclear Power Plant at the east coast of Japan suffered a breakdown of the cooling system and had a subsequent release of radionuclides to the environment. The Fukushima accident became the second level 7 accident in the history of nuclear power, due to the release of radioactive Iodine gas. Resistance towards nuclear power might rise once more, but hopefully this would lead to decommissioning of old reactors and increased focus on building newer and safer nuclear reactors. Radioecology is as relevant now as it's ever been.

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«People often overestimate the importance of intellectual ability. Practice and perseverance contribute more to accomplishment than being smart does.»

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Abstract

The Chernobyl Nuclear Power Plant (ChNPP) accident (1986) in present day Ukraine, was the first INES level 7 nuclear accident in the history of nuclear power. About 6-8 tonnes of spend uranium fuel were released and the fallout contained a series of short- and long lived radionuclides. The main deposition was in an area 30 km around the ChNPP, and the southern parts of Belarus. The area was permanently evacuated and called the exclusion zone. Some of the most long lived radionuclides released were caesium (^{137}Cs) and plutonium-isotopes. The release consisted of volatile compounds and refractory particles (hot particles) consisting of uranium (U) with fission products. Deposition of fuel fragments occurred close to the site, while small sized particles were transported far distance to Scandinavia. The behavior of radionuclides depends on their physico-chemical form. Radionuclides with diverse physico-chemical forms (speciation), might have a different distribution and transfer, in the ecosystem.

The main hypotheses were that forest fires might change the speciation of ^{137}Cs, plutonium-isotopes and hot particles (i.e. aggregates of radionuclides). The exclusion zone has experienced between 40 – 120 forest fires each year and this is expected to increase in the future due to increased biomass.

Soil samples from within and outside of forest fire areas were collected. Sequential extraction was used to evaluate the speciation of ^{137}Cs and Pu-isotopes. Speciation of ^{137}Cs was determined for all soil cores and layers, while the speciation of Pu-isotopes was determined on selected soils and layers. Cs-137 was evaluated by gamma spectrometry of the extractions. Pu-isotopes had to be separated from other alpha emitters and residual chemicals before measurements using alpha spectrometry. Particles were isolated from soil samples and investigated by Environmental Scanning Electron Microscopy (ESEM) and synchrotron radiation based µ-X-ray Absorption Near Edge Spectroscopy (µ-XANES).

The water content, the concentration of organic material (OM) and the amount of clay as well as the pH varied between soils. When all soil samples were evaluated, the water content were defined to be between 1.9 – 10.2%, while the concentration of OM were between 0.3 - 3.6%, the amount of clay were from 0.9 – 2.3% and the acidity was between pH 4.3 – 7.2. The largest variance was seen between soils from forest areas (both affected and unaffected by forest fires) and soils from grassland and sandy areas.

Soils which were unaffected by forest fires were compared to soils affected by forest fires, and with one exception, the forest fire soils had more OM, clay and contained more water than forest soils. The pH was similar for all soils, both affected and unaffected by forest fires.

The highest activity of ^{137}Cs was at 0-4 cm depth below the humus layer. The range of ^{137}Cs was 3-120 Bq/g in unburned forest soils and from 7 – 22 Bq/g in soils affected by forest soils.

More ^{137}Cs was found in the residual fraction of the forest fire affected soils than what would be expected by comparing them to similar soils from outside forest fire areas. The increased amount of ^{137}Cs in the residual fraction indicated more irreversibly bound, or fixated ^{137}Cs. Either by direct influence from the fire or heat, or indirectly, by changed soil characteristics. The investigation of these soils indicated that forest fire changes the speciation of ^{137}Cs.

The activity concentration of total Pu outside of forest fire areas ranged from 3.5 - 200 Bq/kg and 6.8 - 96 Bq/kg for respectively ^{239,240}Pu and ^{238}Pu. The total activity concentration of Pu within forest fire areas was 20-27 Bq/kg and 13.7 - 17.8 Bq/kg for respectively ^{239,240}Pu and ^{238}Pu. Sequential extractions showed a tendency of less Pu-isotopes in the strong acid fraction and slightly more Pu in the slightly reduced fraction (e.g. organic bound fraction) in forest fire affected soils than in similar soils which were unaffected by forest fires. However, contingency tests of individual soils indicated that the difference in speciation between soils outside and within forest fire areas were not significantly different ($p=0.08$ - $p=0.71$) when they were compared.

Two hot particles were found in soils unaffected by forest fires. One particle consisted of U and analysis showed that U had an oxidation state of U^{4+}, which indicated that the matrix consisted of UO_2. UO_2 was used as reactor fuel in the Chernobyl Nuclear Power Plant and the analyzed particles did not appear to be oxidized during the release from the reactor explosion or fire. There were indications of heterogeneities in all soils, including the soils from within forest fire areas, but no particles were isolated. The pH in the forest fire affected soil was between 4.8 – 5.1 and this might have caused an increased weathering rate of hot particles. The absence of hot particles in the forest fire affected soil might be due to the forest fire incidents, but it this might also be due to an increased weathering rate due to a high acidity in the soil.

Sammendrag

Ulykken ved Tsjernobyl kjernekraftverk (1986) i nåværende Ukraina, var den første INES nivå 7 ulykken i historien. Omtrent 6-8 tonn brukt reaktorbrensel ble sluppet ut og dette førte til nedfall av en rekke kort- og langlivede radionuklider. Majoriteten av nedfall kom i et område 30 km rundt Tsjernobyl kjernekraftverk og i søndre Hviterussland. Området ble evakuert og kaldt eksklusjonssonen. Noen av de mest langlivede radionuklidene var cesium (^{137}Cs) og plutonium-isotoper. Nedfallet besto av flyktige forbindelser og hete partikler (radioaktive partikler) som besto av uran (U) med fisjonsprodukter. Avsetninger av kjernefragmenter skjedde primært rundt kjernekraftverket mens mindre partikler ble fraktet så langt som til Skandinavia. Fordelingen av radionuklider i økosystemet er avhengig av deres fysiske og kjemiske former, deres spesiering. Radionuklider med forskjellige fysiske og kjemiske former (spesiering) kan ha varierende distribusjon og overføring i økosystemet.

Hovedhypotesen som evalueres i denne oppgaven var om skogbrann kan endre spesieringen av ^{137}Cs, pu-isotoper og radioaktive partikler (dvs. aggregat av radionuklider). Eksklusjonssonen har hatt mellom 40 -120 skogbranner hvert år og det forventes at dette kommer til å øke i fremtiden på grunn av økt biomasse.

Jordprøver ble tatt i områder med og uten skogbrann hendelser. Sekvensiell ekstraksjon ble brukt for å evaluere spesieringen av ^{137}Cs og pu-isotoper. Spesieringen av ^{137}Cs ble bestemt for alle jordkjerner og lag, mens spesieringen av pu-isotoper ble gjort på utvalgte jordkjerner og lag. Cs-137 ble evaluert ved målinger utført med gammaspektrometri. Pu-isotoper måtte separeres fra andre alfa-emittere og residualkjemikalier fra ekstraksjonene før målingene utført med alfaspektrometri. Partikler ble isolert fra jordprøver og undersøkt med Environmental Scanning Electron Microscopy (ESEM) og synchrotron basert µ-X-ray Absorption Near Edge Spectroscopy (µ-XANES)

Vanninnholdet, konsentrasjonen av organisk materiale (OM) og mengden av leire i tillegg til pH varierte mellom jordkjernene. I alle jordprøvene ble vanninnholdet definert mellom 1.9 – 10.2%, OM var mellom 0.3 – 3.6%, leireinnholdet var mellom 0.9 – 2.3% og pH var mellom 4.3 – 7.2. Den største forskjellen ble sett mellom jord fra skogområder med og uten skogbrannhendelser og jord fra enger og sanddyner. Jord fra skogsområder uten skogbrannhendelser ble sammenlignet med jord fra skogbrannområder og skogbrannjorden hadde generelt sett mer OM, leire og vann enn skog uten brannhendelser.

Den høyeste aktiviteten av ^{137}Cs var 0 – 4 cm under humuslaget. Aktiviteten av ^{137}Cs hadde et intervall mellom 3 - 120 Bq/g i områder uten skogbrannhendelser og 7 - 22 Bq/g i områder med skogbrannhendelser.

Det ble funnet mer ^{137}Cs i residual fraksjonen i jord fra skogbrannområder enn det som ble forventet når de ble sammenlignet med lignende jord fra områder uten skogbrannhendelser. Den økte mengden av ^{137}Cs i residual fraksjonen indikerte mer irreversibelt bundet, eller fiksert ^{137}Cs. Enten kan dette komme av direkte påvirkning fra forbrenningen eller heten, eller indirekte ved endrete jordkarakteristikker. Undersøkelsen av disse jordprøvene indikerer at skogbrann endrer spesieringen av ^{137}Cs.

Aktivitetskonsentrasjonen av Pu i jord fra områder uten skogbrann var i intervallet 3.5 - 200 Bq/kg og 6.8 - 95 Bq/kg for henholdsvis ^{239,240}Pu og ^{238}Pu. Aktivitetskonsentrasjonen av pu i jord fra skogbrannområder var i intervallene 20-27 Bq/kg og 13.7 – 17.8 Bq/kg av henholdsvis ^{239,240}Pu og ^{238}Pu. Resultatene for sekvensiell ekstraksjon viste en tendens til mindre pu-isotoper i sterk syre fraksjonen og noe mer pu i den noe reduserte fraksjonen (dvs. fraksjonen som var bundet til OM) i jord fra skogbrannområder sammenlignet med jord uten skogbrannhendelser. Imidlertid viste statistiske tester at spesieringen var ikke signifikant forskjellig ($p=0.08$ – $p=0.71$) mellom skogbrannområder og områder uten skogbrannhendelser.

Det ble funnet to radioaktive partikler fra skogområder uten skogbrannhendelser. En av partiklene besto av U. Analyser viste at U hadde oksidasjonstilstand U^{4+}, som indikerte at matrisen besto av UO_2. UO_2 ble brukt som reaktorbrensel i Tsjernobyl kraftverket og den analyserte partikkelen så ikke ut som om de hadde blitt oksidert i forbindelse med utslippet fra reaktoren (eksplosjon/brann). Det var indikasjoner på heterogeniteter i alle jordkjerner, inklusive de fra skogbrannområder, men ingen partikler ble isolert. pH i jord fra skogbrannområdene var mellom 4.8 – 5.1 og dette har antageligvis ført til forhøyet forvitringshastighet. Fraværet av radioaktive partikler i skogbrannjord kan være grunnet skogbrannhendelsene, men det er også sannsynlig at forvitringshastigheten for partikler har vært høy på grunn av lav pH i jorden.

1. Introduction and theoretical background

In April 26th, 1986, the Unit 4 of the Chernobyl Nuclear Power Plant (ChNPP) underwent two explosions, which destroyed the reactor core and reactor hall and caused a fire. The fire was extinguished after 10 days, ending the largest known accidental release of radionuclides in the history of nuclear power so far (e.g. IAEA, 1991b).

The initial event was a high pressure, high temperature incident, but during the subsequent fires a low pressure, medium temperature scenario prevailed. At the first day of atmospheric release, the fallout was transported toward the West by the wind and reached as far as Scandinavia. This created the Western trace with fallout of non-oxidized or reduced particles. The day after the initial explosion, the wind changed direction and transported fallout to the North and South, creating the Northern and Southern trace that had fallout of oxidized particles (Salbu et al, 2001, Lind, 2006).

The majority of the fallout was deposited in the near-field area (<30 km) around the ChNPP. Residents who lived within the near-field area were relocated in the period April 27th to September 1986. The area is mainly deserted and is riddled with abandoned homesteads (Fig. 1). It is located in the present day Ukraine and Belarus and was named the exclusion zone. Belarus received the main burden of radionuclides, which was estimated to be about 70% of the total fallout (IAEA, 1991b).

Figure 1: Abandoned houses within the exclusion zone.

1.1 Physico-chemical characteristics of 137Caesium, Plutonium-isotopes and particles.

Speciation techniques define the physical and chemical characteristics of radionuclides. Physico-chemical characteristics can be defined as; size, charge, valence, oxidation state, morphology, density and degree of complexation (Salbu, 2009). The system is dynamic and the speciation of radionuclides will change with time due to influence of soil characteristics, microorganisms, climate and so on (IAEA, 1996).

Cs-137 is a fission product from both U and Pu-reactors. It has a half-life ($t_{1/2}$) of 30.1 years (Choppin et al., 2002 a). Cs is an alkali metal, and is a chemical analogue to potassium. The major identifying ^{137}Cs-signal is beta decay to ^{137m}Barium (^{137m}Ba) that in turn release gamma radiation at 661 keV. The 661 keV is used to identify ^{137}Cs (Choppin et al., 2002a). In the Chernobyl accident, ^{137}Cs was released as volatile compounds (IAEA, 1991a) and in refractory particles (Lind, 2006).

Pu is an anthropogenic element and is created by neutron capture reactions of U (Cotton, 2006). The Chernobyl accident is one of several sources of Pu to the environment (Choppin et al., 2002d). Pu-isotopes have various half-lives; ^{238}Pu has a $t_{½}$ of 87.7 years, ^{239}Pu has a $t_{½}$ of 21400 years and ^{240}Pu has a $t_{½}$ of 6570 years. These isotopes decay by alpha radiation and spontaneous fission (Choppin et al., 2002 c). The oxidation state of Pu is important for the potential mobility (Skipperud et al, 2000). Pu with a low oxidation state (+III, +IV) are particle reactive and sorb to surfaces. In comparison, Pu with a higher oxidation state than IV is more mobile and might be more bioavailable. But even Pu with higher oxidation states has low bioavailability. The greatest risk comes from inhaling particles containing Pu. According to Lind, 2006:

> “Radioactive particles are defined as localized aggregates of radioactive atoms that give rise to an inhomogeneous distribution of radionuclides significantly different from that of the matrix background, while particles larger than mm are usually referred to as fragments (IAEA CRP, 2001). Radioactive particles in the aquatic environment are defined as entities having diameters larger than 0.465 µm (IAEA CRP, 2001), while aerosol particles in air range between 1 nm and 100 µm.”

Dissolution of particles, weathering, is a process that remobilizes radionuclides from the hot particle to the environment (Salbu, 2000, Salbu et al., 1998). Several factors influence the weathering rates, such as the oxidation state of uranium refractory particles, alloys between uranium and zirconium (Lind, 2006), acidity of the soil (Kashparov et al., 2000) and the size of the particle (Kashparov et al., 2004).

1.2 Mobility, bioavailability and soil characteristics

The physico-chemical forms of the radionuclides and soil characteristics are the most influential factors for mobility and bioavailability of radionuclides (Karavaeva et al., 2008). Only low molecular mass (LMM) species such as ions and hydrolysis products are considered mobile (Salbu, 2009, Salbu et al., 1998) and have the potential to cross biological membranes (Salbu et al, 2004). High molecular mass (HMM) species such as complexes, colloids and particles are considered to be biologically inert (Salbu et al, 2004). Small soil particles and colloids with radionuclides can be moved down the soil profile by water or bioturbation (Lee and Lee, 2000). Even though HMM species most likely have some mobility, they need to be transformed to a biological active state in order to cross cellular membranes. Transformation processes can mobilize radionuclides from immobile species for instance by dissolution and desorption processes. Mobile and bioavailable species can be immobilized by for instance growth mechanisms such as complexation or irreversible sorption to soil particles (Salbu, 2000).

Fallout which deposits on soil might sorb to clay, organic molecules, hydroxides, sulfites and on ion exchange sites on various soil particles (Lee and Lee, 2000). Wild fires influence the soil characteristics and processes and might in itself potentially influence speciation by heating or oxidation of the soil. Particles with an oxidized surface weather faster than particles with neutral or reduced surfaces (Kashparov et al, 2000). Wildfires occur frequently in the exclusion zone, at a frequency ranging from 40 to 120 each year. Increased biomass growth will increase the frequency and severity of wildfires in the years to come (Yoschenko et al., 2006).

The soil pH influences sorption and solubilization of trace metals, including radionuclides. Particles are more susceptible to weathering if they reside in an acidic environment (Kashparov et al, 2000). H^+ also influences the amounts of cations in the soil. Cations in the soil can be replaced by other cations by ionic competition, ionic exchange processes and the Cation Exchange Capacity (CEC) of soils is important for radionuclide speciation.

Fires tend to increase the soil pH. Potassium (K^+), calcium (Ca^{2+}), sodium (Na^+) and magnesium (Mg^{2+}) are released from burned debris, and these increase the soil pH by replacing H^+ and Al^{3+} ions in the soil (Arocena and Opio, 2003). Forest fires cause increased amounts of ions in the soil, which subsequently should cause less Cs to be bound to soil due to increased ionic competition. This should be observed by more Cs deeper in the soil and less irreversibly bound to the soil.

Schimmak and Bunzl (1991) found that ^{137}Cs did not leach from organic rich soil horizons as easily in limed areas as in control areas. Stevenson (1982) explained this by assuming an increased binding of metal ions to OM with increased pH.

Lee and Lee (2000) found that Pu formed complexes or chelates with organic acids, especially humic acids. They discussed that Pu (IV), that is usually particle reactive and the form of Pu expected in fallout, might be stabilized by organic acids and thus be kept soluble. Cs-137 was also investigated by Lee and Lee (2000), but the association between ^{137}Cs and organic acids were weaker. The potential association might have been masked by fixation to clay.

Fires change the OM characteristics in soil. The most obvious change would be reduction of the amount of carbon in the top layer because of combustion of carbon (C). Some of the loss might be replenished by incompletely incinerated plant material. The amounts of organic acids also changes, and the organic acid with the largest decrease of mass was found to be humic acid (Fernandez et al, 1997). Pu has a high boiling point (>3000ºC) and if organometallic complexes consisting of humic acids and Pu were burned, the amount of humic acid would decrease due to the combustion, while Pu remained. Without humic acids, the mobility of Pu should decrease. However, if the fires oxidized Pu, it might potentially still be mobile as Pu in higher oxidation states are considered to be more mobile than Pu in lower oxidation states. Still – even mobile Pu would need a medium to migrate through and in soil, this should be water.

Ovsiannikova et al (2010), found variations in the distribution of Pu down two mineral soil profiles; one with the highest activity in the upper 0-5 cm of the soil profile and one with a more homogenous distribution. The soil with the activity concentration in the top had a higher probability of particles and was far drier than the other soil, that was situated close by a river, frequently flooded and as the site was farther away from the ChNPP than the first soil, the probability of the presence of hot particles were less.

Cs form small hydrated ions that make the ion come closer to clay surfaces, thus creating strong, practically irreversible bonds between ion and surface. (Lee and Lee, 2000). Pu-isotopes might also form bonds to clays, but not to the degree or amount as expected for ^{137}Cs. Fixation is observed as an increased activity of ^{137}Cs and Pu-isotopes in the residual fraction when the grain size decreases.

Lee and Lee (1997), found that samples with 20-30% OM did not show an increased activity when the grain size decreased and they discussed the possibility of the presence of organometallic complexes with ^{137}Cs and Pu-isotopes that might be too large to become fixated to clays (Lee and Lee, 1997).

A water repellant layer is often observed in soils after fires. This layer might occur due to migration of vaporized organic compounds that moves down the soil profile until it reaches cooler temperatures, where the organic compounds are deposited and creates a hydrophobic layer. This layer might cause increased runoff and erosion and decreased infiltration of radionuclides (DeBano, 2000). However, Dyrness (1976), found that the wettability of soils, no matter how burned, were practically the same as unburned soils 6 years after the fire incident. If 6 or more years had elapsed since a forest fire event, the infiltration of radionuclides might have been affected, but there might be no sign of changed soil characteristics.

1.3 Hypotheses and goals

Little is known about how forest fires might influence the speciation of fallout ^{137}Cs and Pu-isotopes. Forest fires might either change the soil characteristics or act as an oxidizing event by itself. Based on this, three hypotheses were formulated:

> Hypothesis 1: The speciation of caesium-isotopes in soils affected and unaffected by forest fires are different.
> Hypothesis 2: Speciation of plutonium-isotopes in areas with and without forest fires is different.
> Hypothesis 3: Forest fires change the speciation of particles, leaving them more oxidized and more susceptible to weathering.

This requires that the samples are obtained in a way that makes it possible to test the hypothesis. Sufficient amounts of samples from areas within forest fire areas and outside such areas were required to perform sound statistical analysis on the data. Possible confounding factors in the soil must be evaluated. Radioactive particles, if present, would be expected mainly in the top 0-2 cm soil layer and particle search should primarily be done in this layer.

Speciation of radionuclides in soils can be investigated using sequential extractions. This is a method where extraction chemicals of increasing dissolution or displacement power are added to an aliquot. The relative amount extracted in each fraction identifies the amount of mobile, bioavaliable and irreversibly sorbed radionuclides.

The objectives of this work were to investigate the speciation of ^{137}Cs and Pu-isotopes within and outside forest fire areas to evaluate if fires increased the mobility of radionuclides.
In order to test the above hypothesis, the goals were:

- To determine of soil characteristics in areas with and without forest fires.
- To do sequential extraction to evaluate if radionuclides in forest fire soils were more or less bound to the soil phase than similar soils without fire incidents.
- To isolate, identify and characterize hot particles, from sites within and outside forest fire areas.

2. Method and materials

Several methods, techniques and instruments were used to characterize soil and determine the speciation of ^{137}Cs and Pu-isotopes. They are briefly described in this chapter.

2.1 Fieldwork

Fieldwork was conducted by a joint team from Universitetet for Miljø- og Biovitenskap (UMB), Norwegian Radiation Protection Authority (NRPA), Belarus State University and staff from the Polessie State Radiological Ecological Reserve (PSRER). The fieldwork was done in May 2009 and May 2010 in the PSRER, Gomel county, Belarus. The location of the sites where the cores of soil were obtained is shown in figure 2. The yellow line represents the border between Belarus and Ukraine. The Pripyat River runs diagonally from upper left corner. ChNPP is located at the bottom right in the image, and is marked in the image by several boxes. The PSRER have brown and darker green areas, and the inhabited area has defined fields.

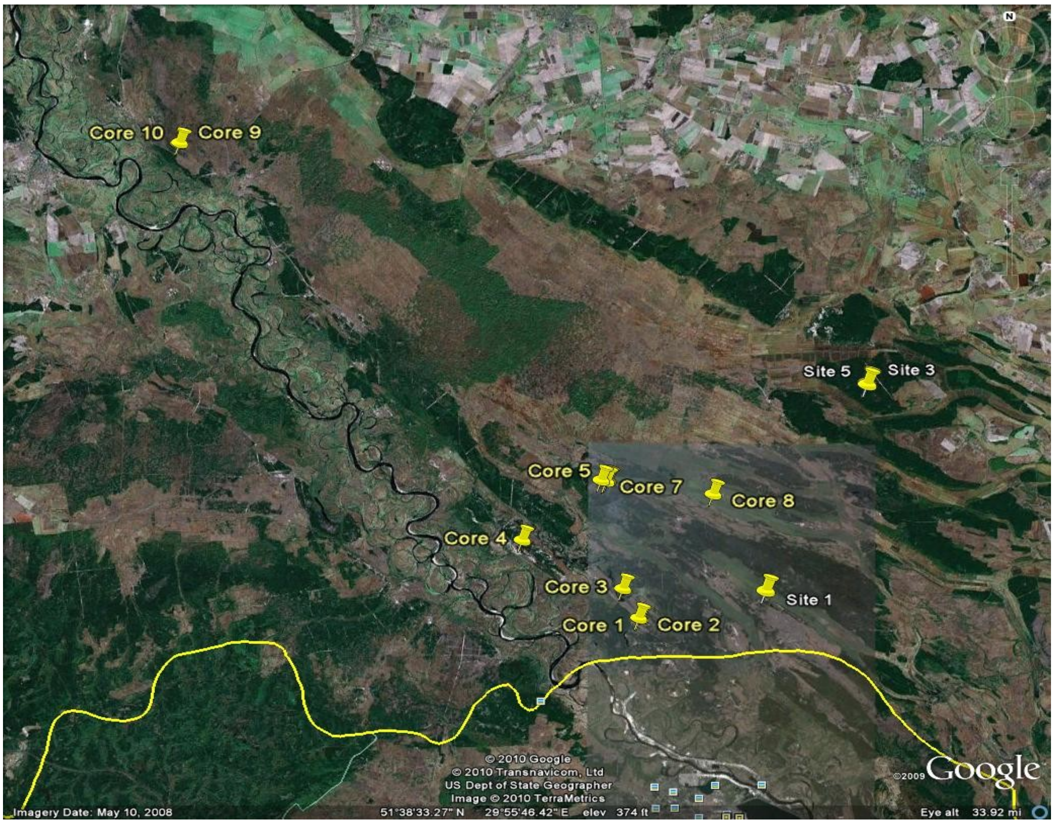

Figure 2: Map of the PSRER with sites where soil samples 1 – 10 were obtained in 2009 and sites 1, 3 and 5 that were sites of the fieldwork in 2010.

2.1.1 The forest, topography and climate of the exclusion zone

Before evacuation, the zone was used for farming – from large collective farms to small private farms. The main dedication was ploughed land, fodder production, dairy and cattle (UNSCEAR, 1988). The area of PSRER where the samples were taken was dominated by flat topography with small hills leading down to brooks, rivers and boggy areas. There were open grasslands with minor regrowth of trees and forest. Pine and birch seemed to be the main families of trees. The soil was predominantly sandy mineral soil. For the municipality Bragin, close by the border to the PSRER, the average air temperature in January is -6 ºC, average temperature in July is 18 ºC and annual precipitation is 533 mm. The growth season is 194 days (Bragin, 2010).

2.1.2 May 2009 fieldwork

The samples obtained were soils 1 – 10. Soils 9-10 were from areas where there had been forest fires after 1986, and the rest were from areas which had not had any fires after 1986. The sites were determined in advance. Besides this, no specific sampling strategy was applied. Site descriptions and specifications were given in the appendix (A.1).

The cores were taken with a cylindrical corer, shown in figure 3. The cores were divided into 7 layers based on depth below humus layer; 0-2 cm, 2-4 cm, 4-6 cm, 6-8 cm, 8-10 cm, 10-15 cm and 15-20 cm.

Figure 3: Corer with front panel pushed back and revealing a soil sample. This specific sample was from site 3, 2010. The burned top soil is visible.

2.1.3 May 2010 fieldwork

Additional samples were taken in 2010. The sites were once more selected in advance. The sites were screened for hotspots and all sites had homogenous gamma rates, both at the ground and at 1 meter height. Samples were taken of the corners at a 10 x 10 meter square using a cylindrical corer. The depth of the cores was 10 cm from below the humus layer. The humus and soil were deposited in separate bags. Site descriptions and specifications are in the appendix (A.2).

2.2 Soil characterization

Since soil characteristics influence the speciation of radionuclides, the characteristics can be confounding factors. The characteristics must be determined to avoid false assumptions about the influence of forest fires on the speciation.

pH

pH was measured as a part of the sequential extraction procedure and consisted of adding MilliQ-water (reverse osmosis and purified through a MilliQ-filter) to the soil and sediment samples in the weight ratio 1:10. The sample was then shaken and pH was measured using a pH meter (IntroLab WTW series pH 720 pH meter).

Dry mass and LoI estimation

Aliquots of ≥2 g soil were weighed (Sartorius A 200 S, analytic weight) in furnace dried porcelain crucibles. The aliquots were dried at 105ºC for 24 hours in a Termaks oven and weighed. These weights were the basis for the dry mass estimation.
Lids were placed over the crucibles. The furnace was heated slowly to 375ºC and then kept at this temperature for one hour. The heating continued until the temperature reached 550ºC. The temperature was kept stable for 16-20 hours. Samples were cooled, weighed without lids and Loss on Ignition (LoI) was calculated to evaluate the amount of organic content of the soil.

Determination of clay content

Organic matter (OM) had to be removed by oxidation and the clay had to be dispersed before the analysis. This preanalytic treatment was done by obtaining a total of ≥ 10 g of air dried soil from several layers within each core and placing it in 200 mL beakers. 20 mL H_2O and 10 mL 35% H_2O_2 were added to the samples. The samples were stirred, covered with glass lids to prevent loss of water and placed in a fume hood. When the reaction decreased, more H_2O_2 was added until all OM was oxidized. Deionized water was added until the total volumes of the samples were 200 mL. Samples were heated (Präxitherm LHG heater) until a total of 90 mL remained. 20 mL ≈1M HCl was added. The samples were stirred for one minute and then transferred to 1000 mL beakers. The beakers were filled with distilled water until a total volume of 800 mL were attained. After the samples settled, the solutions were removed and water was added until the volume of the total samples were 800 mL. The solutions were removed after clearing. To disperse the clay in the samples, 50 mL 0.05 M $Na_4P_2O_7 \cdot 10\ H_2O$ were added and the samples were stirred for one minute using a mechanical stirrer.

After dispersion, the samples were transferred to glass cylinders that were then filled with distilled water until the volumes of the samples were 400 mL. The samples were then ready for the grain size analysis, that were performed by Leif Vidar Jakobsen, IPM, UMB, after the procedure given in "Manual for kornfordelingsanalyse etter pipettemetoden" written by Krogstad et al. (1991).

2.3 Radiochemical methods

Radiochemistry is the branch of chemistry that is concerned with radionuclides. This includes chemical reactions amongst anthropogenic and natural radioactive materials with each other or other substances. Radiochemical methods are based on analytical chemistry and the main differences are the concentration of reactants.

2.3.1 Repeated splitting to find hot particles

The original samples were split in two after the fieldwork in 2009 and before the analytical work started. One series of samples were send to the NRPA and the other series of samples were kept at UMB. All layers from every core were measured on the NaI detector to establish the total activity of ^{137}Cs. The most active layers were selected for particle search, therefore aliquots from the 0-2 cm depth layer of all soils (with the exception of soils 2 and 4, where the 2-4 cm depth soil of soil 2 was evaluated and the 15-10 cm depth layer of soil 4 was examined) were all dried in room temperature and measured again on NaI detector (Wizard 3" 1480 Automatic Gamma Counter Perkin Elmer life sciences). The most active aliquots were selected, split into new aliquots and measured on the NaI detector. The procedure was repeated until small volumes of radioactive soil were attained. The final aliquots were evaluated on a Ge-detector to investigate the final activity of ^{137}Cs. After a positive indication by a ^{137}Cs signal >LD, the samples were then investigated by digital autoradiography to evaluate the sample for hotspots and isolation of potential hot particles.

2.3.2 Digital autoradiography

The small volumes of the samples were spread in patterns on pieces of cardboard covered with adhesive plastic with the glue side up. Each sample had its own designated area on the cardboard. Both the creation of a pattern on the adhesive plastic and indication of designated areas aided the localization of the hotspots and identifying which soil it originated from. A layer of plastic was put on top of the samples and the adhesive plastic and the cardboard pieces were placed next to an autoradiography screen (Amersham Biosciences – storage phosphor screen, Molecular Dynamics) and then put in a cassette (Amersham Biosciences exposure cassette, Molecular Dynamics).

The duration of the exposure was 3-5 days. The screen was scanned (Typhoon 8600, Molecular Dynamics) and an image was obtained.

2.3.3 Isolation and characterization of hot particles

Hotspots were identified on the autoradiography image, where they appeared as black spots (figure 15). The placements of the hotspots on the adhesive plastic were estimated using coordinates from the autoradiography image and the patterns of the sample compared with the obtained image. Coordinates was obtained using the program ImageJ. The locations of the hotspots were checked with a portable gamma detector (Automess 6150 AD6). An area of 2 x 2 cm around the hotspots were cut out of the plastic and investigated on a Ge-detector. If the activity was <LD for ^{137}Cs, the sample was rejected as it would be impossible to know if the hot particle was successfully transferred to a stub prior to investigation by electron microscope. If the sample was rejected on this basis, a larger area around the 2 x 2 cm primary cutout was cut out of the plastic and investigated by Ge-detector. This was to reduce the chance of missing a hot particle because of inexact coordinates. If the ^{137}Cs signal was >LD, the piece of plastic was divided into smaller pieces and investigated by Ge-detector. This procedure was repeated until the ^{137}Cs signal came from a small piece of plastic.

The potential hot particle was transferred from the small piece of plastic to an aluminum stub covered with carbon tape. The stub was used as a sample holder in the electron microscope. The transference was done by pressing the piece of plastic against the carbon tape. The stub was checked on the Ge-detector to check if the potential hot particle was successfully transferred. The sample was now ready for investigation by electron microscopy.

The sample was first investigated by environmental scanning microscopy (ESEM) using a scanning electron microscope (Zeiss EVO- 50- EP. Produced by Carl Zeiss SMT Ltd), shown in figure 6.
At first, the sample was evaluated in scanning electron imaging (SEI) mode, followed by backscattered electron imaging (BEI) mode. In BEI mode, the heavy nuclides in a potential hot particle were observed as bright areas in the sample. The potential hot particle was then investigated using X-ray micro analysis (XRMA) with the instrument INCA 450 Xstream/Mics Produced by Oxford Instruments Analytical to evaluate which nuclides were present.

µ-XANES analysis was performed at Beamline L at HASYLAB, Germany and was organized by Dr. Ole Christian Lind. The spectrum was analyzed with the help of Prof. Koen Janssens and PhD fellow Wout de Nolf from the University of Antwerpen.

2.3.4 Sequential extraction

For sequential extraction, 2 grams of soil were added to centrifuge tubes (Oak Ridge centrifuge tubes 50 mL, polyallomer with cap of polypropylen) together with 20 mL MilliQ-water. The pH of this soil solution was measured prior to extraction. The sample was placed on a roller mixer (Roller Mixer SRT2 Stuard Scientific) for 1 hour. The sample was centrifuged at 10 000 g (Beckman Avanti TM 30 Centrifuge) for 25-30 minutes. After centrifugation, the solution was filtrated through a 110 mm round filter (S & S blue band) and collected in 20 mL polyethylene vials (Packard, Canberra corp). This step was identified as the water soluble fraction. The setup is shown in figure 4.

The easily exchangeable fraction was identified using 20 mL 1M NH_4Ac adjusted to soil pH by concentrated HCl. The sample was placed on the roller mixer for 2 hours. It was then centrifuged at 10 000 g for 25-30 minutes before it was filtrated.

The attempt to identify the reversible carbonate fraction was done by adding 20 mL 1M NH_4Ac adjusted to pH below soil pH, adjusted by concentrated HCl until the pH was 0.5 below the soil pH. The sample was placed on a roller mixer for 2 hours. The sample was centrifuged at 10 000 g for 25-30 minutes. The sample was then washed with 10 mL MilliQ-water followed by centrifugation for 15 minutes and filtrated.

The irreversible oxide (Fe/Mn) bound fraction was attempted identified by adding 20 mL 0.04M $NH_2OH \cdot HCl$ in 25% (v/v) HAc, adjusted to pH 3 with concentrated HCl or concentrated HNO_3. The sample was heated for 6 hours in a water bath (GRL 1092 shaking water bath) at 80°C. It was then centrifuged for 25-30 minutes. The sample was washed with 10 mL MilliQ-water followed by centrifugation for 15 minutes and then filtrated.

The irreversible organic bound fraction or evidence for the presence of refractory particles was identified by adding 15 mL H_2O_2 (30%) adjusted to pH 2 with concentrated HCl or concentrated HNO_3. It was heated carefully on a sand bath until the reaction was completed. The sample was then warmed in a water bath at 80ºC for 5.5 hours. Then 5 mL 3.2 M NH_4Ac in 20% (v/v) HNO_3 was added to the sample and solvent. It was placed on a roller mixer for 0.5 hours followed by centrifugation at 10 000 g for 25-30 minutes. The sample was washed with 10 mL MilliQ-water before being centrifuged for 15 minutes and filtrated.

Figure 4: The setup used in sequential extraction; a funnel holder, funnels, filters and sample vials.

The final extraction step was identified by adding 20 mL 7M HNO_3 to the sample. It was heated in a water bath at 80ºC for 6 hours before being centrifuged at 10 000 g for 25-30 minutes. The sample was washed with 10 mL MilliQ-water before being centrifuged for 15 minutes and filtered. This was the irreversible strong acid fraction.

Residue and filter were dried and transferred to a vial and measured for the residual fraction.

All sample solutions were measured on the gamma spectrometer Wizard 3" 1480 Automatic Gamma Counter Perkin Elmer life sciences. The data that were used for evaluation was the corrected counts per minute (ccpm). Each step was represented as a percentage of the total activity. Ccpm from the extraction and the wash water were added and the uncertainties were calculated by using this equation;

$$\sigma_A + \sigma_B + \ldots + \sigma_X = \sqrt{(\sigma_A^2 + \sigma_B^2 + \ldots + \sigma_X^2)}$$

(eq 1)

Count uncertainty and precision were added using this formula:

$$\sigma_A + \sigma_B = \frac{\sqrt{([X_A + X_B])}}{t}$$

(eq. 2)

Where X_A was the total counts of the sample, X_B was the standard deviation of the control measurements given in counts and t was the count time in minutes. This is the absolute uncertainty.

2.3.5 Sample digestion prior to Pu-determination

2 grams of soil were dried in air temperature and divided in aliquots of 0.5 grams in separate Teflon tubes in a rack specially designed for UltraCLAVE. As a yield monitor, 0.250 mL ^{242}Pu tracer with an activity of 0.1567 Bq/mL was added to all aliquots. The samples were digested in 0.5 mL concentrated HNO_3. The load was prepared with 320 mL H_2O, 3 mL P.A quality H_2SO_4 and 20 mL technical quality H_2O_2. The load was put in the reactor and the sample rack was inserted in the UltraCLAVE (UltraCLAVE III, MLS-MILESTONE). A program for slow dissolution of soil was selected, where the maximum temperature was 250ºC and the maximum pressure was between 120-130 bar. After the program was completed, 15 mL concentrated HNO_3 were added to the aliquots and the samples were transferred to new vials. The samples were then brought to dryness on a sand bath before proceeding with alpha spectrometry method.

2.3.6 Radiochemical separation of Plutonium

A relatively high activity of ^{137}Cs indicated a higher probability of significant amounts of Pu-isotopes in the soil; therefore samples with a high ^{137}Cs activity were selected for further investigation. The same extractions used for ^{137}Cs- analysis were used for Pu-analysis. These samples were the 0-2 cm layer of soils 4 and 6. In addition, the 2-4 cm layer of soil 1 was selected based on the high activity and the large amount of potentially bioavailable ^{137}Cs. Both forest fire soils, from sites 9 and 10, were selected and the investigations of these soils were done on the 0-2 cm layer.

The investigations done by Ovsiannikova et al (2010), Qiao and Hou (2010), Lujanienė et al (2002) and Komosa (2002) found the majority of Pu in the strongly bound fractions. It was therefore assumed that Pu-isotopes would most likely be extracted in the organic bound and strong acid fractions. Thus, only the strong acid to organic bound fractions and exchangeable fraction were initially extracted. The oxide bound and exchangeable fractions served as controls. Any activity in these fractions indicated that there might be some activity in the other fractions as well.

One of the samples, soil from site 6, had a relatively high amount in these fractions and thus the carbonate bound and water soluble fractions of this specific sample were analyzed. Miscalculation of the total activity in soil 4 caused the fractions of this soil to be wrongly rejected as it was assumed that the activity were too low for evaluation by alpha spectroscopy.

An evaluation of the activity of Pu in a solution requires that the Pu is separated from interferences and transformed to a state where it can be measured. Sequential extraction served both as a method of determination of speciation and as a way to separate Pu from soil.

After digestion and sequential extraction, both the total samples and samples from the sequential extractions followed the same procedure. The samples were first heated until dryness. A few drops of concentrated HNO_3 were added to reduce the interference from residual chemicals. Pu-242 (250µL with an activity of 0.1567 Bq/mL) was added as a yield monitor to the solutions. The solutions were dried and then solved in 40 mL 8M HNO_3. Approximately 50 mg Fe-sulfate was added to reduce Pu to a +3 oxidation state and the samples were heated until all Fe-sulfate was dissolved. The samples were cooled and 1 mL 15% $NaNO_2$ was added to oxidize Pu to a +4 oxidation state. The samples were carefully heated for 15 minutes and then cooled to room temperature and was ready for Pu separation on Dowex columns.

Separation of alpha-emitters

Columns (Disposable polystyrene columns PIER 29920, 0.5 – 2.0 mL, Pierce biotechnology) were prepared with Dowex resin in MilliQ-water and regenerated with 20 mL 2M $NaNO_3$ followed by 50 mL 8M HNO_3. 110 mm round filters (S & S brand, blue band-filter) were placed in the funnels and the samples were filtrated into the columns. Pu reacted with NO_3 to form $Pu(NO_3)_6^{2-}$, that was retained in the Dowex resin (Ramirez et al., 1996, Skipperud, 2007). Thorium (Th), U and Americium (Am) were eluted from the resin by addition of 50 mL 8M HNO_3 followed by 50 mL 9M HCl. Pu was eluted off the column as $PuCl_3$ by 40 mL freshly made solution consisting of 1 mL 50% HI solved in 100 mL 9M HCl (Skipperud, 2007).

Deposition

The samples were heated and a few drops concentrated HNO_3 were added to remove iodine (I) and chloride (Cl). As electrolyte, 8 mL 15% $NaHSO_4$ was added and then the samples were heated until dryness. A few drops concentrated HNO_3 were added and the samples were dried again to get a clean “white cake”. 6 mL MilliQ-water were added to the samples and the samples were then ready for deposition. The deposition cells were mounted with planchet and electrodes and checked for leakage. The cells were then filled with 15 mL electrolyte solution consisting of 15% $NaSO_4$ and 0.26M ammonium oxalate. The samples were transferred to the electrodeposition cells where they were deposited for 2.5 hours using Mascot Type 719, with 10V and 0.4A (figure 5). 1 mL 4M KOH was added one minute before the current was stopped.

The cells were emptied of electrolyte solution and flushed with MilliQ-water. The planchets were rinsed with MilliQ-water and acetone and then fixated by heating. After fixation, the planchets were cooled and placed in marked plastic bags for storage until measurement. Measurements were done by placing the planchet with alpha-emitters in the sample holder in the alpha spectrometer (Alpha Spectrometer model 7401, Canberra Industries), vacuum was instilled and the measurement was made. The program used for spectrum acquisition was Genie 2000, Alpha acquisition & analysis from Canberra Industries.

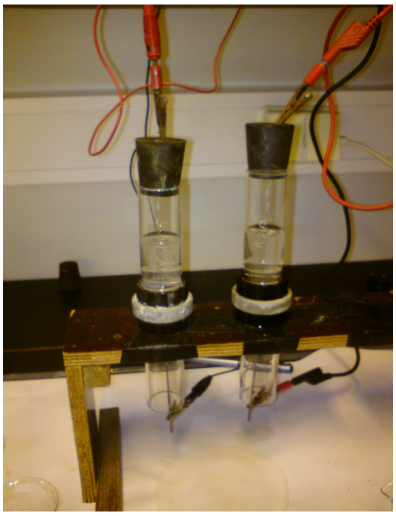

Figure 5: Setup of deposition cells used in deposition of Pu-isotopes.

2.4 Quality assurance

Radioactive decay is a random process which is governed by probability. If the number of decay events is above 100, the distribution will assume a Poisson distribution. Thus, the count has an intrinsic uncertainty that must be evaluated.

2.4.1 Statistical errors

Absolute uncertainty is used for determination of LD. LD for ^{137}Cs was determined by calculating the uncertainty of background, $\sigma_{A,\ background}$ and multiplying it by 3 to include all background radiation. This summed up to 5.68 counts per minute (cpm) for ^{137}Cs. All ^{137}Cs samples were counted for 10 minutes on the NaI detector. To avoid overlapping confidence intervals and thereby the possibility of sample and background being from the same population, the samples needed a minimum of about 12.2 ccpm, or 0.20 Bq ^{137}Cs per sample. For alpha spectroscopy, the LD was <0.001 Bq unit^{-1}. Background radiation was previously measured and was automatically subtracted by the software.

The uncertainty of the count was calculated the same way as the LD and every count that had overlapping uncertainty with $3 \cdot \sigma_{A,\ background}$ was excluded. The probability of correct identification is 99.7%. However, low activities might have wrongly been rejected.

2.4.2 Precision and accuracy

Evaluation of the accuracy of the sequential extraction method is problematic since the selectivity of the extractants is less than perfect. The completeness of extraction is known to vary.

One way of estimating accuracy would be to evaluate the added counts from all extractions of an aliquot to the activity of the total samples. Pu-chemistry was monitored by adding a known amount of a defined tracer, which was used as a yield monitor and was the basis for calculation of the activity of Pu-isotopes.

The method lacks standard reference material (Sahuquillo et al., 2002, Kennedy et al., 1997) and therefore it is practically impossible to assess the accuracy of the extraction. Precision can be determined using several parallels. However, a limited number of particles can also give large differences amongst individual aliquots. A precision of 10% are considered adequate (Salbu, 2000).

2.4.3 Errors

pH measurements were initially done incorrectly. The ratio between soil and water was too large. A 1:2.5 ratio between sediment and water should have been used instead of a 1:10 ratio. The slurry stood for 5-20 minutes, enough for the reading to be relatively stable, but the ideal would be to leave it overnight (Krogstad, 2009).

The pH of the 2010 sites was not checked by traditional methods, and the best estimate of soil pH came from an evaluation of the vegetation at the sites. Site 1 had birch, pine and grasses, which prefer moderately to very acidic soil. Site 3 had all these and alders, which prefer slightly acidic soils. Site 5 had a mosaic of vegetation, which included all species mentioned plus apricots and blueberries. Indicated pH was from slight to very acidic (Brady and Weil, 2002).

For evaluation of water content and LoI, porcelain crucibles were used. Porcelain crucibles contain some water and therefore the crucibles were heated at 550 ºC for 24 hours before usage. This should have evaporated all additional water in the porcelain.

Crystalline water that did not vaporize by drying the sample at 105ºC will vaporize during the LoI procedure and samples with clay content above 5% must be adjusted for this (Krogstad, 2009). As none of the samples had above 2.3% clay, adjustments were not done. Heating at 550ºC should not oxidize carbonates (Krogstad, pers. comm.) and this is not a problem in evaluating OM.

It was assumed that the clay was evenly distributed in the soil and that a bulk sample from each soil would be representative. As the grain size distribution work was done outside of the isotope laboratory, the most active layers were excluded, i.e. the selected samples were from the deeper layers. The grain size distribution is presented in figure 8.

The initial dry weight and LoI analysis of the 2009 soils was done on unrepresentative samples. The original aliquot weight was too low, and the procedure was done again in 2010. However, some of the samples showed a lower amount of water than observed in 2009. The lids on the sample vials had not been appropriately closed. The unintentionally dried samples were rejected and the old data were used instead. The samples concerned were the 10-15 cm layer of soil 2, 4-6 cm layer of soil 3, 0-2 and 15-20 cm layers of soil 4, 0-2 cm layer of soils 5, 7 and 8, 6-8 cm layer of soils 7 and 8. No adjustments were done for the amount of OM.

3. Instruments

Several instruments were used to determine the activity of samples and to characterize particles.

3.1 UltraCLAVE

Acid digestion by UltraCLAVE has similar dissolution strength as extraction by traditional open system digestion by aqua regia. A study done by Nemati et al. (2010), compared open system acid digestion to microwave digestion and concluded that the yield of heavy metals from compost improved by use of microwave digestion rather than using an open strong acid digestive method.

The UltraCLAVE is a high pressure microwave oven used to digest samples. Microwaves are electromagnetic radiation with a frequency of $3 \cdot 10^2$ - $3 \cdot 10^5$ MHz. The microwaves can be absorbed by dipole molecules, typically water and ions, which move in accordance to the shift in the electromagnetic waves. This creates increased kinetic energy (Bye, 2009). By heating the sample and reagents, the activity of the reagents increase, which in turn give a more total digestion.

The samples were contained in Teflon tubes, which were placed in a rack (MILESTONE, 2010). Teflon does not absorb microwaves and the waves enter the tubes and heat the samples directly. This gives one of the method's great advantages: fast heating (Bye, 2009).

The load was prepared of water and acids to keep the water polar and peroxide to decrease NO_x development. The load also ensures even temperature in all Teflon tubes and it is the temperature reference. The reactor encloses the Teflon tubes and rack, and the system is put under pressure before applying the microwaves. After the program was completed, the reactor and samples were cooled and atmospheric pressure was instilled. The reactor was lowered and the samples were retrieved (MILESTONE, 2010).

3.2 Gamma and alpha detectors used

Detectors are used to measure the amount of radiation at specific energy ranges.

3.2.1 NaI scintillation detectors

Scintillation detectors emits light (scintillate) when it is hit by radiation. Several types of scintillation detectors are used and the most frequently used are the inorganic alkali halide detectors.

The basic scintillation mechanism is the absorption of energy by electrons. The electrons are then excited from the valence band, via the forbidden band, to the conducting band.

The electrons will de-excite back to the valence band and in the process release the previously absorbed energy as light photons (Knoll, 2010a).

The light must be transformed to an electrical pulse that can be registered by the equipment. This can be attained by photomultiplier tubes (PMT). The PMT convert light photons into electrons. The photon is absorbed and the energy is transferred to an electron that migrates to the surface of the photocathode and then escapes the surface. The electron then strikes the inside of an anode. This produces secondary electrons, whose magnitude is proportional to the energy of the initiating electron. The secondary electrons are registered as an electric pulse, and the shape of the pulse is mathematically analyzed (Knoll, 2010b).

Even though the NaI is a sensitive detector, it has broad peaks in the spectra and thus low resolution. Semiconducting detectors have narrower peaks and thus higher resolution than scintillation detectors.

Semiconductors are crystals, and as for the scintillation crystal detectors, electrons are divided into valence and conductive bands with a forbidden band between. A common semiconductor is the germanium gamma-detector (Ge-detector). Absorbed energy creates electron-hole pairs, which creates a current, which is transformed and detected (Knoll, 2010c).

3.2.2. Alpha detectors

The alpha particle detector was a passivated, implanted, planar, silicon (PIPS) detector (Canberra, 2007). Silicon detectors are semiconductors (Choppin et al., 2002b), which is crystals that creates electron-hole pairs when the alpha particle deposit energy in the crystal. By getting excited to the conductive band, the electron creates a vacancy in the valence band. This is a hole and the combination of electron and hole are the electron-hole pair. If an electrical current are applied to the crystal, the electron in the conductive band will move with the current and the positive hole will move against the current. This changes the conductivity of the crystal (Knoll, 2010d). The electron-hole pairs create a detectable current, which is in proportion to the energy deposited in the crystal.

Doping changes the conductive properties of the detector. This is usually done by adding impurities in the semiconductor crystal. However, an alternate to this doping is to subject the surface to ions created by an accelerator. This creates n- and p- layers within the crystal. N-layers have lightly bound electrons, which can rise to the conductive band and thus increase electron density.

P-layers increase hole density. Implanted detectors are generally more stable and can have thinner entrance windows (Knoll, 2010d).

Some of the alpha particles will transfer their energy to recoil nuclei with a varying rate. This loss cannot be adjusted for. Other factors are variation in the deposited energy in the dead layer and incomplete charge collection. This causes peak broadening and the band width is usually no better than 10 keV (Knoll 2010d).

3.3 Digital autoradiography

Digital autoradiography is an imaging technique, where radiation reacts with a reusable screen, which is made of a photosensitive material. This creates an image of the distribution of radiation in the sample (Lind, 2006). The screen has crystals of $BaFBr:Eu^{2+}$, which stores the energy from the radiation. Scanning the screen with a laser with a wave length of 600 nm releases the stored energy, which can be read by the scanner and converted into a digital image (Reinprecht et al., 2002).

3.4 Electron microscopy

Modern microscopy techniques are techniques that give information on the surface of a specimen. Mapping of physical structures may aid evaluation of how easily it weathers. Identification and mapping of elements can also be done with modern electron microscopes.

The electron microscope can be roughly divided into an electron gun, several magnetic lenses, a sample holder and detectors that operate under vacuum or a few torr. Environmental Scanning Electron Microscopes (ESEM) don't need an absolute vacuum and the sample needs a minimum of preparation (Lind, pers.comm.).

The electron gun consists of a tungsten filament that ejects electrons when subjected to an electrical current. The electrons are condensed and contained by a magnetic lens. Due to the electromagnetic property of electrons, they spiral to a focus point before spreading.
The electron beam then goes through an aperture that narrows the beam. A magnetic lens focuses the beam at the surface of the specimen (Postek et al., 1980). When the electrons hit the surface, several processes occur; the surface is ionized and release secondary electrons, backscattered electrons, characteristic X-rays and other signals (Lind, pers.comm.).

Backscattered electrons can be used to map elements of varying nucleic weight by creating an image, called backscattered electron imaging (BEI). Bright areas indicate areas with nuclei of higher atomic number (e.g. Salbu et al., 1998).

The chemical composition of the sample can be identified using X-ray micro-analysis (XRMA). The sample is irradiated by x-rays (photons) and when the photons are absorbed, electrons from the inner shells are ejected, creating a void. The void is filled with an electron from a higher energy level. The excess energy is emitted as X-rays. Different elements have various energy levels, which gives unique X-ray spectra. XRMA can be used for mapping of areas or investigation of lines or points in the sample (Lind, 2006).

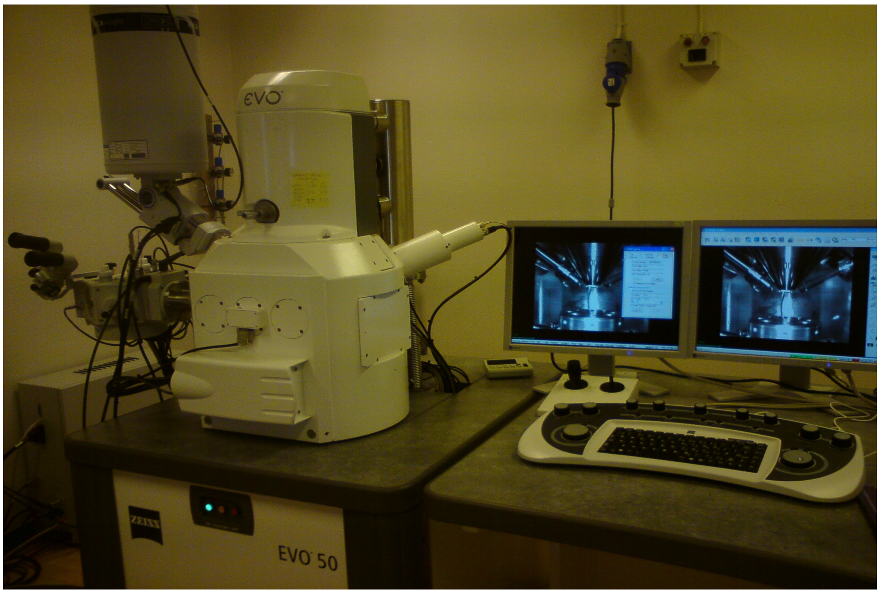

Figure 6: Electron microscope with XRMA equipment which was used to investigate topography and elemental composition of potential hot particles.

3.5 µ-X-ray Absorption Near Edge Spectroscopy (µ-XANES)

According to Lind et al., (2007):

> “XANES are used to provide information on the oxidation state of actinides (Salbu et al., 2003; Powell et al., 2006). By tuning the energy of an X-ray beam (with a monochromator) over the ionization energy of a shell, an abrupt increase in the absorption occurs, termed the absorption edge. The features of absorption edges and peaks (white lines) are influenced by the chemical speciation of the absorbing element, i.e. the energy and shape of the spectra are correlated with valence and site symmetry (Conradson et al., 1998). Decreased shielding of core electrons with increasing valence results in increased binding energy of core electrons and can be observed as a chemical shift in the XANES spectra. The most important factors determining the XANES spectra of U and Pu oxides are the valence state and the presence or absence of actinyl species. To differentiate between oxidation states appropriate well-defined oxidation state standards should be applied.”

4. Results and discussion

These are the results of the work of determining soil characteristics, followed by performing sequential extraction to evaluate the speciation of ^{137}Cs and Pu-isotopes, then isolation and characterization of hot particles led to an evaluation if forest fires changes the speciation of ^{137}Cs and Pu-isotopes .

4.1 Quality assurance

In order to estimate the precision of the sequential extraction procedure for ^{137}Cs, a total of three aliquots from three series (2-4 cm layer of soil 1, 7 and 10) were compared. These soils were selected because of a relative high activity of ^{137}Cs and since these layers were not used in the particle search, there were more matter available for investigation. The results were analyzed using ANOVA statistics. Results indicated a similar population ($F = 0.07$ $p=1.00$). The 95% CI overlapped in every case and can be viewed in the appendix (A.3). The H_0 hypothesis was kept – there were no statistical differences within each series. A graphical summary of the parallels are seen in figure 7. Even though ANOVA indicated that the mean of the populations as a whole were similar, it is seen in figure 7 that the error bars of several of the parallels (for instance, but not limited to) all residual parallels) do not overlap and was thus not similar. The precision of the extractions were quite bad.

Blanks

In the sequential extraction procedure, two series of blanks were extracted parallel to the samples at various times; one at the first extractions, one when half the samples had been extracted and two series of blanks were extracted parallel to the control series, which were the last samples extracted. For ^{137}Cs, no indication of contamination was found in any blank sample.

Reagent blanks followed both the total Pu samples and the extraction samples. The total Pu blank followed the total samples from the weighing of the dried soil sample in Teflon tubes, where the soil was replaced with 0.5 mL MilliQ-water. The blank received 0.250 mL ^{242}Pu with an activity of 0.157 Bq/mL and was subjected to dissolution by UltraCLAVE and the same extraction procedure as the total samples.

The blanks that followed the determination of Pu-isotopes in sequential extractions was a blank series that was extracted parallel to the control series for ^{137}Cs. The reagent blank extractions were treated as the sample extractions.

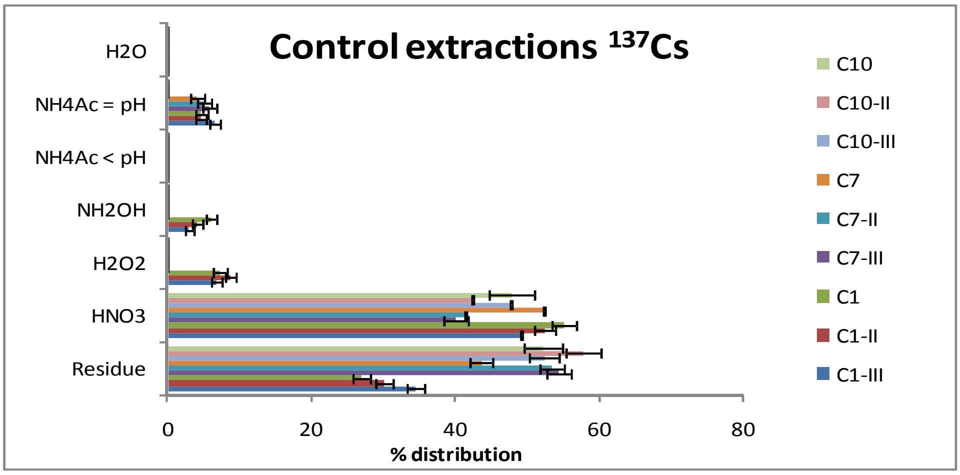

Figure 7: Extractions used for precision estimation. Only count error is indicated. C1 comes from the 2-4 cm layer of the soil from sample site 1, C7 from the 2-4 cm layer of the soil from site 7 and C10 from the 2-4 cm layer of the soil from site 10. Roman numerals separate the series and the samples with no roman numerals were the extractions produced for the sequential extraction.

Both the total reagent blank and the extraction reagent blanks showed contamination of ^{238}Pu. Of the total of 7 blanks, 5 had an activity of 0.004 Bq unit^{-1}. The average was calculated to be 0.0046 Bq unit^{-1},which was subtracted from the ^{238}Pu activities. This is probably contamination of ^{238}Pu that came from impurities in the ^{242}Pu tracer solution.

4.2 Soil characterization

Pictures and notes from the 2009 fieldwork showed that the sites 1-3 were grasslands, site 4 was covered with dunes and sites 5-10 were from pine forest. Sites 9 and 10 were forest fire sites, and the images indicate that high intensity fires had occurred at the sites (figure 8 A and B). The soil characteristic intervals for the entire soils are summarized in table 1 and more detailed specifications are given in the appendix (A.4 and A.5).

All samples (soils from sites 1-10)

The soil characteristic intervals of the samples from forest fire areas were within the intervals observed in all soils. The same is observed when forest fire soils were compared to the forest sites without fire incidents. No obvious deviance in the soil characteristics was seen in areas with and without forest fire. Even though the trends in the soil characteristics could be seen in the raw data, statistical tests were done to see if there were significant differences among the categories of all soils, forest soils and forest fire soils. To evaluate variance, the Kruskal-Wallis test was used since the soil characteristics were non-parametric. The H_0 hypothesis of the Kruskal-Wallis is:”The population means are equal.”

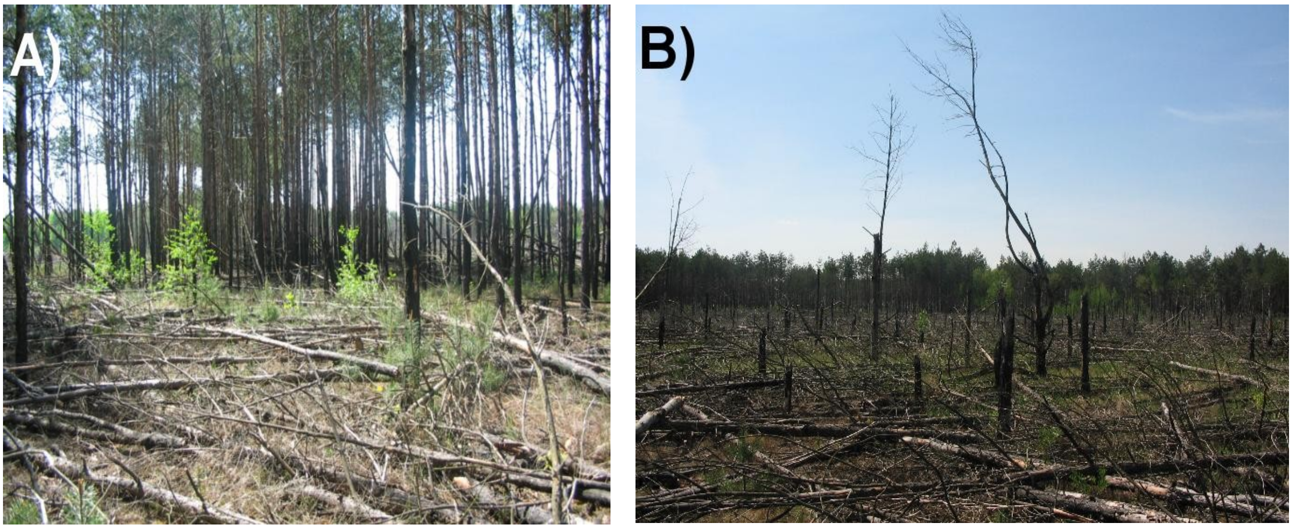

Figure 8 – Images from forest fire sites 9 and 10. The images were not properly named, thus it is unknown which of the images is from site 9 and which is from site 10. A) Burned and felled trees, with some regrowth. Burned and felled trees are indications of high intensity forest fires. B) The fire at this site was apparently larger than the fire in image A) as a larger area of forest were burned and while there were some remaining trees in the image A), only charred stubs remains of the trees in image B).

The p-value are used to test the H_0 hypothesis, and the selected cut off value (α value) was defined as $p<0.05$. P-values> α indicated that the H_0 hypothesis was correct. The test also gave a z-value, which indicated if the mean of the sample was above or below the average mean and to which degree. Here, a significant z-value was defined as being > ±1.

As it was expected that the upper layers of the soil would be most affected by forest fires, the following investigations were done on the average values of the soil characteristics in the 0-2, 2-4 and 4-6 cm layers. As soil from site 2 lacked the 0-2 cm layer, the 6-8 cm layer was used to get an average over three layers for the soil from site 2. The clay content in all soils was not evaluated by Kruskal-Wallis as only one value was determined for clay in each soil and thus no mean could be calculated.When the entire cores of all sites were evaluated, the result of the Kruskal-Wallis test showed that pH, OM and water content varied among the cores ($p<0.05$).

Table 1: Summary of average soil characteristic intervals for the entire core of soil in varying categories of sites.

Soil Characteristic	Average intervals for all cores (1-10)	Average intervals for forest cores (5-8)	Average intervals for forest fire cores (9 and 10)
pH	7.2 – 4.3	5.1 – 4.3	5.1 – 4.8
OM %	3.6 – 0.3	3.6 – 1.0	2.7 – 2.6
Water %	10.2 – 1.9	7.0 – 3.4	6.3 – 4.9
Clay %	2.3 – 0.9	1.7 – 0.9	1.8 – 1.6

The pH values were rounded because of the uncertainty in the pH measurement. Soil from site 10 was the only soil from the forest fire areas with significant negative deviance from the mean pH, which indicated that it was more acidic than the average. From outside forest fire areas, the soil from sites 1 – 3 had significant positive deviance from the mean and thus these sites were more alkaline than the average. The forest soil samples from sites 6 and 7 were significantly more acidic than the mean. The other soil samples did not deviate significantly from the mean. In general, the forest soils were more acidic than the grassland soils.

The grassland soils at sites 1 and 2 had significantly more OM than the mean, as did the forest soil at site 7. The grassland soil at site 3, the sandy soil at site 4 and forest soil from site 8 had significantly less OM than the mean.

Considering the water content, the forest fire affected soils did not show significant difference from the mean. Grassland soil from sites 1-3 and soil from site 7 had significantly more humid than the mean of all samples. Soil samples from sites 4, 6 and 8 were significantly drier than the mean.

The highest amount of clay was observed in soils from sites 1-3. The forest fire affected soils had slightly more clay than the other unaffected forest soils. The soil with the least clay was forest soil from site 8. A summary of the grain size distribution in all cores are given in figure 9.

Forest samples (soils from sites 5-10)

It is assumed that vegetation and soil characteristics correlate. It might therefore not be appropriate to compare soil from forest fire affected sites with unburned soil from areas without pine forest. The samples from grassland and sandy sites show significant deviance from the mean in acidity, amount of OM, clay and water. As the soil characteristics of the fire affected soil and unburned forest samples were generally closer to the mean than the grassland and sandy soils, the assumption seemed to hold.

Therefore, the statistical investigation of the soil properties was done again on samples from sites 5-8 as representatives from the outside of forest fire areas and samples from the sites 9 and 10 within the forest fire areas. To ensure that the forest fire samples were taken from soil which had definitively been burned, layers of soil from the forest fire sites were evaluated under light microscope to find charcoal.

Several large particles of charcoal (~0.5mm) that were black, shiny and with visible cellular structures was found in the soil and this was a positive identification that the soil was burned at the exact place of sampling (Ohlson and Tryterud, 2000).

The soil characteristics could change as a result of the forest fires. The pH is expected to increase after a fire. Arocena and Opio (2003) found a significant rise in the pH in fire affected soils compared to control soils. The A-horizon, that is a mineral rich horizon under the litter, had a rise of pH of about 1 pH unit. The horizon below the A-horizon, the B-horizon, is enriched with OM, iron and aluminum. The depth of horizons vary and the only soil characteristic which could aid in determining which horizon the investigated UMB soil samples came from, was the amount of OM. There were no significant change in the amount of OM at any depth in any soil and was assumed that the entire soil cores were from the A-horizon. As the fire affected soils were moderately to strongly acidic after the fire and assuming the pH of the A-horizon would rise with 1 pH unit, the soil of soil 9 had to be very acidic before the fire and soil 10 had to be severely acidic before the fires.

The investigation of the pH of the forest samples (sites 5-10) was done on rounded numbers as for investigation of all soils. The investigation of pH confirmed the H_0 hypothesis of equal means (p= 0.11). However, while the forest samples 5-6 and 8-10 had a mean of pH 5; the soil from site 7 had a mean pH of 4. The Kruskal-Wallis test showed a large negative deviance in soil from site 7 which indicated that the means of pH were not equal even though the Kruskal-Wallis test concluded it was equal.

The amount of OM was expected to be less in samples where there had been fires as fires oxidize carbon from the soils as well as from trees. The forest samples with and without fire incidents were investigated by Kruskal-Wallis and the result was given in table 2. The test showed variations in OM and water content among the soils ($p<0.05$). Soils from sites 7 and 8 were the only soils with a significant deviance from the mean. Soil from site 7 had more OM than average and soil from site 8 had less. The amount of OM in the 0-6 cm layers of the forest fire affected soils did not have significant deviance from the mean. This is contradictory of the expectation of lessened amount of OM.

Table 2: Soil characteristics of the forest (5-8) and forest fire (9 and 10) soils.

Kruskal-Wallis test of soil characteristics of sites 5-10			
Core	**pH vs core**	**OM vs core**	**Water vs core**
5	0.9	-0.6	0.2
6	-0.3	0.3	-2.7
7	-2.3	3.0	3.0
8	0.4	-3.0	-2.4
9	0.4	-0.5	0.3
10	0.8	0.9	1.8
P-value	0.107	<0.5	<0.5

Pictures from the forest fire areas (figure 8 A and B) showed heavily charred and felled trees. This indicated high intensity fires that should severely burn the soil. The images, together with the charcoal found in the samples, showed that the soils from sites 9 and 10 were clearly from fire areas and was affected by the forest fires. The amount of OM must have been replenished at some point after the active phase of the forest fire.

The humidity of the soil from fire areas was within the interval observed in forest soils. Soils from sites 6 and 8 were drier than the mean, while soils from sites 7 and 10 were more humid than the mean. These tendencies were also seen when all soils were evaluated.

Burning soils might affect the grain size distribution and the structure of clays. Arocena and Opio (2003) found that soil aggregates and sand might crack after thermal shock, and can change the X-ray diffraction (XRD) spectrum of clays. However, the maximum amount of clay in forest fire soils only differed with 0.1% from the maximum amount of clay from forest soils. Because of intrinsic uncertainties of the grain size distribution analysis, this deviance was deemed to be insignificant as the unknown uncertainty might contribute more to the deviance than 0.1%.

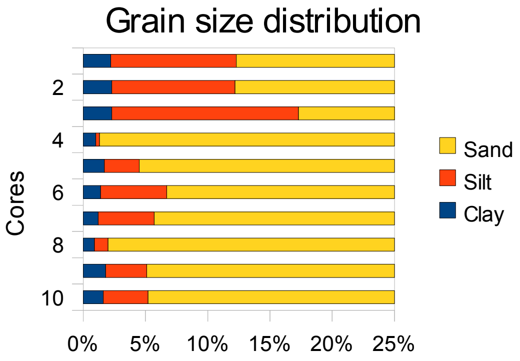

Figure 9: Overview of the grain size distribution of grassland soils (sites 1-3), sandy soil (site 4), forest soils (sites 5-8) and forest fire soils (sites 9 and 10). Sites are indicated as cores in the figure.

4.3 Caesium-137

Caesium-137 is regarded as a persistent pollutant because of the relatively long physical half-life (30.1 years) and the tendency of being retained in soil. It is a β, γ emitter that can be measured directly from soil samples or from extractions.

4.3.1 Heterogeneous activity of ^{137}Cs in soil samples

Bunzl's repeated splitting (eq 3) was used to investigate the variations between the ^{137}Cs activity measured by NRPA and UMB and the results can be found in the appendix (A.6). This estimation used only two aliquots, which is not reliable for estimation of hot particles.

The variations between NRPA and UMB numbers (figure 10) might originate from the non-homogenized original soil samples, a various amount of particles and the activity and differences in count times and detectors. The only conclusion is that all cores of soil had heterogeneities at various depths. To determine the nature of the heterogeneities, further work must be done.

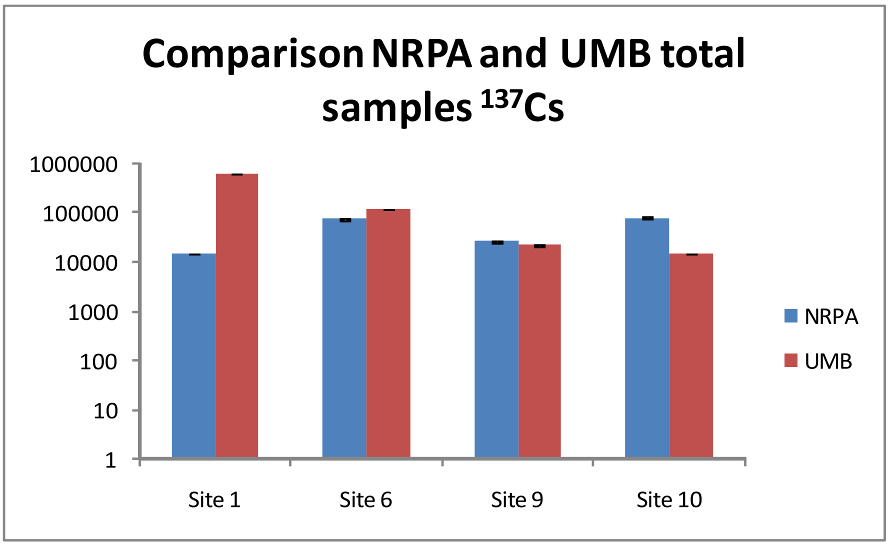

Figure 10: Comparison of the NRPA and UMB numbers for total ^{137}Cs Bq/kg dry weight in selected soils and layers. The sample from site 1 was taken from the 2-4 cm layer, while all the other samples were from the 0-2 cm layer.

4.3.2 Total activity concentration of ^{137}Cs in soil samples

The total activity in all samples ranged from below LD (0.20 Bq unit^{-1}) to 120 Bq/g dry weight. The highest activity were found in the 0-2 and 2-4 cm depth layers, except the sandy soil of site 4, that had the highest activity (92 Bq/g dry weight) at the 15-20 cm layer.

The range of activity in the 0-2 and 2-4 cm layers of all soils (sites 1-10) were 2 – 120 Bq/g dry weight, while soils outside forest fire areas (sites 5-8) had activities of 3 – 120 Bq/g dry weight. The forest fire soils (sites 9 and 10) ranged from 7 – 22 Bq/g dry weight. Detailed information is given in the appendix (A.7).

The activities in the forest fire affected soils were within the range of activities in soils outside forest fire areas. However, only soil from site 3 had lower activities than the forest fire soils with 4 Bq/g dry weight at the 0-2 cm layer and 2 Bq/g dry weight at the 2-4 cm layer. A figure of the total activity in soils from within and outside forest fire areas was given in figure 11. The total activities determined for the soils were within the activities reported by Korobova (1998), Agapkina et al (1994) and Odintsov et al (2004).

What can be observed in both forest fire (sites 9 and 10) soils and soils unaffected by fire (sites 1-8), is that the main activities were in the top 0-2 cm of the soils and that the activity decreased rapidly with increasing depth. In the forest fire soils, the activity of soil from site 9 in the 0-2 cm depth was higher than in the 0-2 cm layer of soil from site 10 and the activity decreased faster in soil from site 9 than soil from site 10. The decrease of activity in soil from site 9 had an exponential shape. The decrease in activity in soil 10 looked more linear than soil 9. This might be due to differences in the soil characteristics which were not evaluated, such as variations in the CEC. As the images from the forest fire areas showed that one of the sites were more severely burned than the other and thus the CEC should vary between the sties, the notion that variations in CEC might change the distribution of ^{137}Cs with depth is strengthened.

The decrease of ^{137}Cs down the soil profiles from outside forest fire areas (sites 1-8) also had an exponential shape, as observed in soil 9. Most of the activity is in the 0-2 cm layer, followed by the 2-4 cm layer. Two soils deviated from this. These were soil from site 1, which had the most of the activity in the 2-4 cm layer, followed by the 0-2 cm layer and soil from site 4, which had the highest activity in the 15-20 cm layer and the second most activity in the 0-2 cm layer.

The deviance in the 15-20 cm layer of soil from site 4 was first believed to be mistaken identity. However, the sandy soil found in this core was unique as it was apparently unaltered river sediment while the other cores were soils. The trends in the soil characteristics indicated that the identity of the 15-20 cm layer was correct as no deviance from the trends of OM, water or acidity was observed.

The large value of Bq/g dried matter in the 15-20 cm layer sample might be caused by particles. Particle search was performed, but no particles were found.

This lack of hot particles combined with a relatively large amount of potentially bioavailable Cs extracted in the sequential extraction procedure leads to the possibility that the Cs-signal might originate from LMM species Cs adsorbed to grains and possibly clay. Other possible explanations were that this high activity in the 15-20 cm layer of the soil was because of bioturbation or that the wind moved the sand above the 1986 surface.

A Kruskal-Wallis test was used to evaluate if the activity concentration of ^{137}Cs differed among sites 1-10, and it used the activities from the entire cores. The results were that the means of the soils from all sites were similar to each other (p= 0.84). Even though the activity in the soils from forest fire sites 9 and 10 were low, their means did not differ significantly from the means of soils unaffected by forest fires.

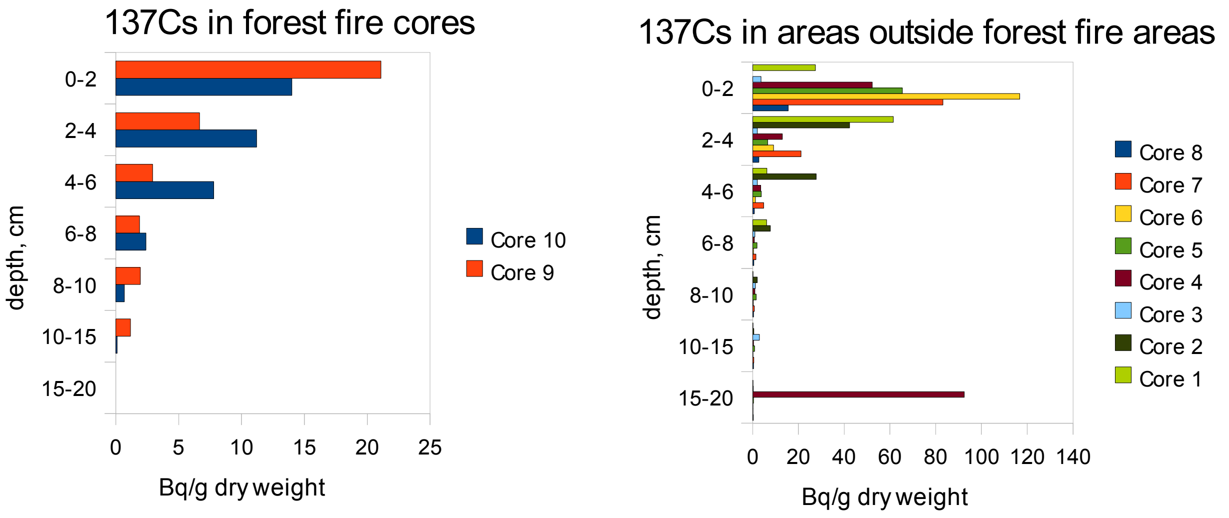

Figure 11: Cs-137 Bq/g dry weight down the soil profiles within and outside forest fire areas

4.3.3 Sequential extractions results for ^{137}Cs

Sequential extraction is a method that can be used to investigate the strength of the bonds among radionuclides and soil or sediments by performing extractions with chemicals of increasing chemical strength (e.g. Kennedy et al., 1997). The fractions were, with extractants in brackets; water soluble (H_2O), exchangeable (NH_4Ac adjusted to soil pH), carbonate bound (NH_4Ac adjusted to be below soil pH), (Fe/Mn-) oxide bound ($NH_2OH \cdot HCl$), organic bound (H_2O_2, pH 2), strong acid soluble (HNO_3) and irreversibly bound to residue (Kennedy et al., 1997).

The water soluble, exchangeable and carbonate bound fractions are fractions which identify reversible bound species and these are considered to be bioavailable fractions.

The water soluble to organic bound fractions are considered to be potentially bioavailable fractions, which is either readily mobilized or could be mobilized under the right conditions, such as decomposition of OM (Fawaris and Johanson, 1995) or heating. The strong acid fraction needs strong oxidizing acids to be extractable and this fraction would be of less concern as the conditions which might break the bonds between ^{137}Cs and soil are unlikely to occur in nature.

Ideally, an analysis concerned with estimating the potential bioavailability of radionuclides should be done on soil solution, but it is difficult to get a representative sample with a high enough activity, and the compromise is to use chemical extractants on solid soil to estimate mobility and bioavailability (Kennedy et al., 1997)

Several different schemes have been developed, most of them based on Tessier et al. (1979). Some schemes demand pre-treatment of the sample such as drying and homogenization. However, manipulation of the sample may expose more binding sites than what are available in nature. The time of exposure should be long enough for a steady state to be instilled. Re-absorption may occur if the ratio between sample and solvent is too low. A common solid: solution ratio used is 1:10 (Kennedy et al., 1997).

Seven soils were moderately to very acidic (sites 4-10). Estimation of exchangeable ^{137}Cs was done with NH_4Ac adjusted to soil pH and estimation of carbonates was performed by using NH_4Ac adjusted to below soil pH as an extractant. However, the difference in electrolyte pH (~0.5 pH units) between the exchangeable and carbonate bound fractions might have been too similar to extract more radionuclides in the carbonate fraction than in the exchangeable fraction.
The acidity of the soils indicate that carbonates were not present and the small difference in pH between the fractions would be of no concern as there would not be any carbonates to extract ^{137}Cs from.

Figures 12, 13 and 14 show the speciation of ^{137}Cs at 0-2 cm, 2-4 cm and 4-6 cm depth. Soil from site 2 did not have a 0-2 cm layer, and the graph for this soil was therefore given for the 2-8 cm depth layers. Soil 4 had a significant amount (22.4%) extracted in the 15-20 cm layer and this is included in the graph.

The grassland and sandy soils had 12 - 67% potentially bioavailable ^{137}Cs. The forest soils had negligible potentially bioavailable ^{137}Cs compared with the grassland and sandy soils (0-16%). The forest fire affected soils had no ^{137}Cs in other fractions than the strong acid and residual fractions.

Forest soil samples, within and outside forest fire areas

In order to evaluate if forest fires change the speciation of ^{137}Cs, the forest fire soils (9 and 10), shown in figure 12, should be evaluated against the forest soils (sites 5-8) shown in figure 13. The forest soil samples (sites 5-10) conformed to the expectation that the ^{137}Cs would mainly be extracted by strong acid or remain in the residual fraction. Even the soil with the highest amount of potentially bioavailable ^{137}Cs (site 8) had the majority of the activity in the residual and strong acid fraction.

The distribution of ^{137}Cs in the forest soils (sites 5-10) was primarily evenly distributed over the residual and strong acid fraction with minor variations within and between the soils.

Soil from site 5 had somewhat more ^{137}Cs in the strong acid fraction than the residual fraction and this trend became more apparent with increasing depth. Soil 5 had some potentially bioavailable ^{137}Cs (<7%) and had strong acid extractable ^{137}Cs in the 8-10 cm layer as well.

The 0-2 and 2-4 cm layers of soil from site 6 had somewhat more ^{137}Cs in the residual fraction than the strong acid fraction. The 4-6 cm layer had more ^{137}Cs in the strong acid fraction than the residual. In addition to the ^{137}Cs indicated in figure 13, this soil had 100% of the extracted ^{137}Cs in the strong acid fraction of the 6-8 cm, 8-10 cm and 10-15 cm layer.

Similar to soil from site 6, soil from site 7 had slightly more ^{137}Cs in the residual fractions of the 0-2 cm and 4-6 cm layer than in the strong acid fraction. The 2-4 cm layer had slightly more in the strong acid fraction than the residual fraction.

The ^{137}Cs in soil from site 8 was equally distributed between the strong acid and residual fractions of the 2-4 and 4-6 cm layers. This soil had 6 – 16% potentially bioavailable ^{137}Cs and most of this were in the exchangeable and oxide-bound fractions.

The general trend for the forest soils was either an even distribution of ^{137}Cs between the residual and strong acid fraction, or somewhat more in the strong acid fraction than the residual fraction. This trend increased with depth.

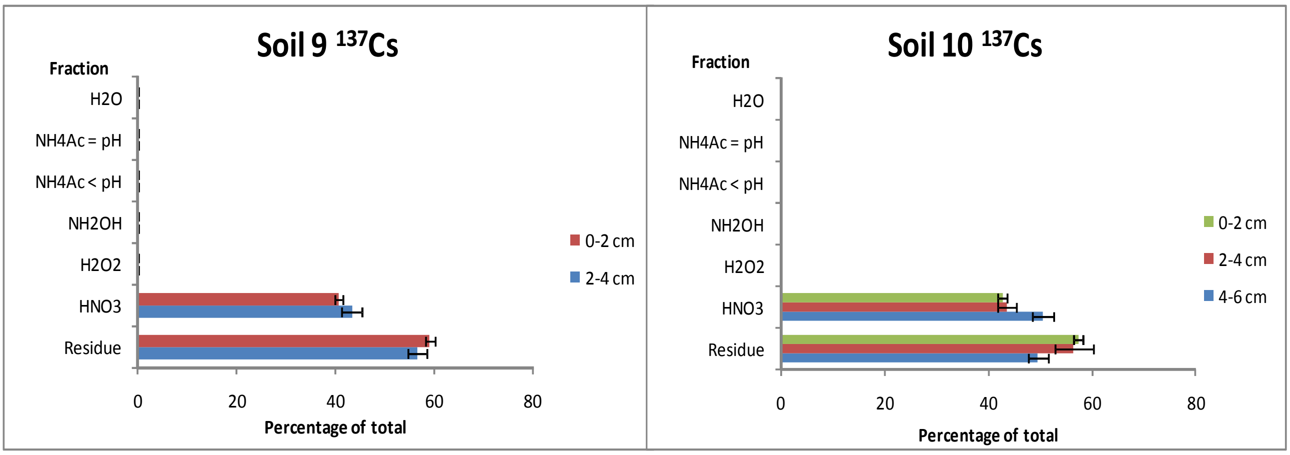

Figure 12: Speciation of ^{137}Cs in forest fire affected soils.

The forest fire soils (9 and 10) did not have any potentially bioavailable ^{137}Cs. Soil from site 9 had extractable ^{137}Cs only in the 0-2 and 2-4 cm layers. Here, about 60% of the ^{137}Cs was found in the residual fraction and the rest in the strong acid fraction. The trend in soil from site 9 was a larger amount of fixated ^{137}Cs in the residual fraction than what was found in the forest soils (sites 5-8). Soil from site 10 had just below 60% of the ^{137}Cs in the residual fraction in the 0-2 and 2-4 cm layers. The 4-6 cm layer had ~50% in the residual and strong acid fractions. This soil had an apparent increasing amount of ^{137}Cs the strong acid fraction with increasing depth. As soil from site 6, this soil had ^{137}Cs extracted in the strong acid fraction in layers between 6 and 15 cm depth was well. Cs-137 in the forest fire area appears to be more fixated to soil than ^{137}Cs in forest areas without fires.

The distribution down the soil profile and sequential extractions of the forest soils from sites 5-10 looked like the Gomel soils Salbu et al. (1994) and Krouglov et al (1998) investigated. Salbu et al (1994) analyzed soils from two different locations using the same sequential extraction scheme as the one used for this thesis. Even with different soil characteristics, the results for the two samples were quite similar. Most of the activity (~50%) was in the strong acid fraction, followed by the residue fraction (~30%) and organic bound (~15%). They assumed that the larger than expected extraction in the organic bound fraction was due to hot particles. The other fractions had negligible amounts of activity. This is similar to what has been observed in other areas within the Chernobyl 30 km zone. A profile from Vilyun, Ukraine, had 60-65% of the ^{137}Cs in the residue fraction and the rest mainly in the strong acid fraction.

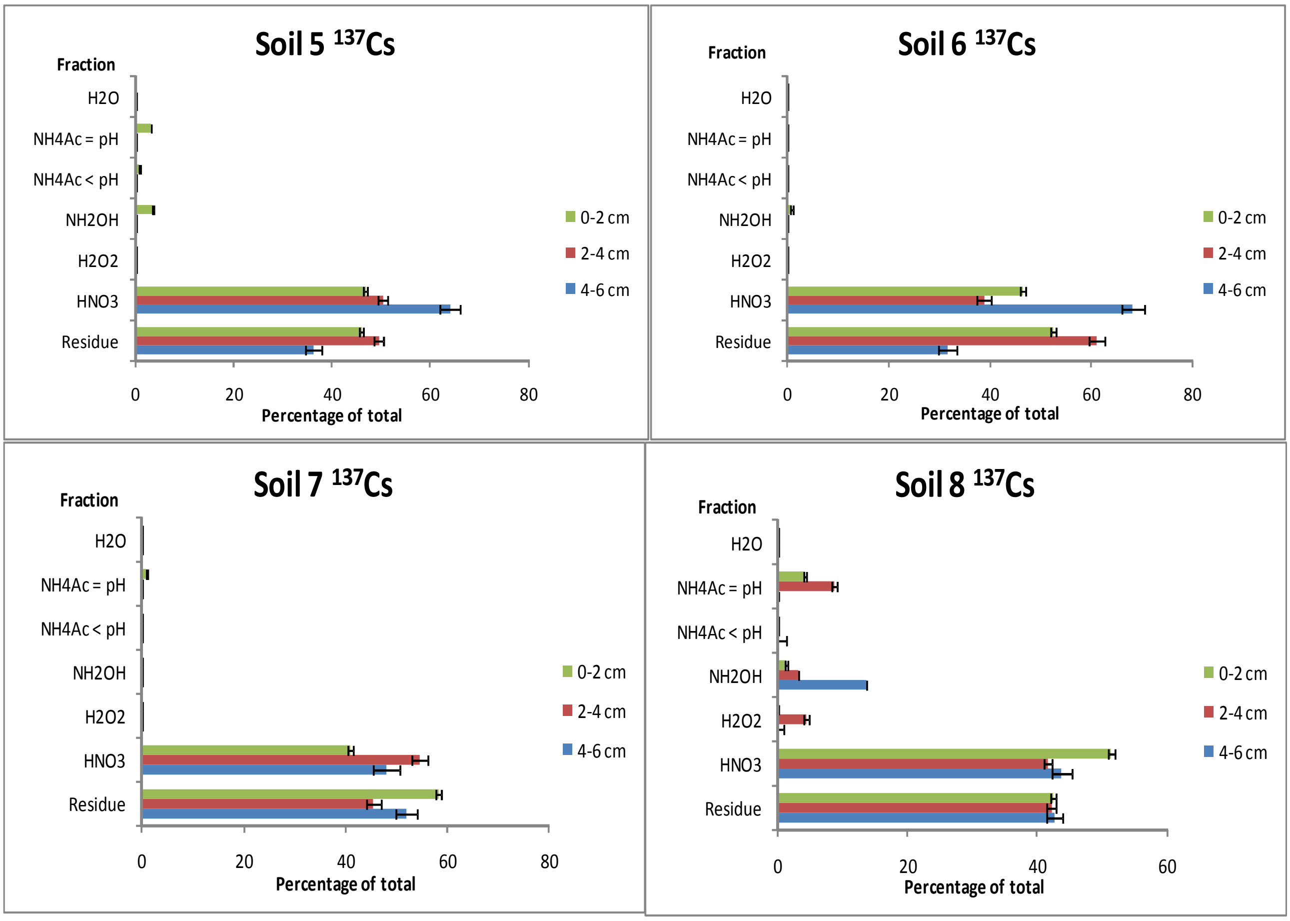

Figure 13: Speciation of ^{137}Cs in pine forest soils.

Krouglov et al. (1998), used a different extraction scheme and they extracted 59% in the strong acid fraction. 10% of the ^{137}Cs was extracted in a diluted acid and 0.2-2% of the ^{137}Cs was extracted in the water soluble and exchangeable fractions.

Grassland and sandy soils

Even though the grassland and sandy soils (1-4) were not used in evaluation of forest fire soils, the large amounts of potentially bioavailable ^{137}Cs should be discussed as well. The speciation of these soils is given in figure 14.

Oughton et al. (1992) investigated soils from Belarus, Norway and in the near-field area of the ChNPP. They found 30-40% of the ^{137}Cs in the strong acid fraction, 20-25% in the organic bound and residual fractions and the remainder in the exchangeable and carbonate bound fractions.

Oughton et al. (1992) assumed that the observed distribution could be due to hot particles, or a larger than expected amount of ^{137}Cs associated with non-specific ion-exchange sites within the soil or differences in the distribution of stable Cs and ^{137}Cs.

In comparison, soil from site 1 had 50% of the extracted ^{137}Cs in the strong acid fraction, 25% in the residual fraction and <10% in each of the organic, oxide-bound and exchangeable fractions and was thus quite similar to the soils extracted by Oughton et al. (1992).

In soil from site 2, 30% of the extracted ^{137}Cs was found in the strong acid fraction, 20% in the exchangeable fraction and <10 - <20% in each of the fractions; carbonate, oxide-bound, organic bound and residual. The soil from site 2 had less irreversibly bound and more reversibly bound ^{137}Cs than was found by Oughton et al. (1992).

Soil from site 3 had 50% in the strong acid fraction, 20% in the residual fraction and <10% in every fraction from exchangeable to organic bound fraction. This soil had less ^{137}Cs in the organic bound fraction, more in the strong acid fraction and approximately the same as Oughton et al. (1992) in the other fractions. The ^{137}Cs in soil from site 3 were more irreversibly bound than found by Oughton et al. (1992).

Based on the assumptions of Ougthon et al (1992) and Salbu et al (1994), it is assumed that the relatively large amount of ^{137}Cs extracted in the organic bound fractions of the soils at sites 1, 2 and 3 might be due to hot particles.

The soil from site 4 deviated from the other soils by having most of the activity in the 15-20 cm layer and that this layer had a large amount of potentially bioavailable ^{137}Cs. The 0-2 cm layer of soil 4 had all the ^{137}Cs in the strong acid fraction. The 2-4 and 4-6 cm layers had most of ^{137}Cs in the strong acid fraction and the remainder mainly in the residual fraction. The 15-20 cm layer had <60% in the strong acid fraction, ~20% in the residual fraction and the rest was found in the exchangeable to organic bound fractions.

The mobility of ^{137}Cs was highest in the 15-20 cm layer. However, investigation of the 15-20 cm depth layer of the sandy soil yielded only a diffuse image and there were not seen indications of hot particles.

In general, the grassland and sandy soils had most of the activity in the strong acid fraction, followed by the residual fraction and also activity in most or all fractions from the exchangeable to organic bound fractions. Cs-137 seems to be less fixated in the grassland and sandy soils than was observed in the forest soils.

Mobilization and fixation of ^{137}Cs are believed to depend amongst others on the amount of clay, OM, water, soil pH and the presence of hot particles. Investigation of clay, OM, water content and soil pH in grassland and sandy soils (sites 1-4) compared with the forest soils (sites 5-10), indicates that the groups had comparative amount of OM. The forest soils had less clay, less potentially bioavailable ^{137}Cs and more fixated ^{137}Cs than the grassland soils. The water content might influence and increase the potentially bioavailability of ^{137}Cs in the grassland soils (sites 1-3). The grassland soils were also the most alkaline soils of all. The sandy soil (site 4) had less clay, OM, water content and was more acidic than the grassland soils. Other soil characteristics such as CEC, the amount of K and stable Cs might influence the speciation, but these factors were not evaluated. The results and discussion of the search for hot particles are given in chapter 4.5.

The large amount of potentially bioavailable ^{137}Cs in the grassland soils, despite a relatively high clay content, was contradictory to what was expected. Lee and Lee (1997), stated that OM might hinder sorption of Cs to clay. The high mobility in the soils of sites 1 and 2 might be due to a high content of OM which protected ionic and mobile ^{137}Cs from fixation to clay. The grassland soils of sites 1 and 2 was compared with soil of site 3 in order to evaluate if the OM could be the reason for the potentially bioavailable ^{137}Cs. Soil from site 3 had similar soil characteristics as the mobile soils, and was similar to the soils from the sites 1 and 2 considering clay, water and acidity. However, the soil in site 3 was slightly acidic, while the soils from sites 1 and 2 were slightly alkaline. The forest soils and the sandy soil was moderately to very acidic and the soils from sites 1, 2 and 3 were therefore more similar to each other than the other soils. The characteristic that had the highest degree of discrepancy between soil from site 3 and sites 1 and 2 was the OM. Soil from site 3 had half the average OM than soils from sites 1 and 2.

Stevenson (1982), stated that metal ions have increased binding to OM in soils with increased pH. This might retain ^{137}Cs in the upper, organic rich layers in alkaline soils. However, it also suggests that ^{137}Cs would bind strongly to OM and be mainly extracted in the organic bound fraction and not necessarily be extracted in the reversible fractions. Increased binding to OM in alkaline soils might not be the reason for the large amount of extractable ^{137}Cs in the exchangeable to oxide bound fraction of the grassland soils. There were relatively high amounts of ^{137}Cs in layers with significantly less OM than the upper OM rich layers. If ^{137}Cs was primarily bound to OM, it should be limited to the 0-2 cm layer of soil at site 1 and the 2-4 cm layer of soil at site 2, as these had far more OM than deeper layers.

And in soil from site 2, the organic bound fraction are less than the exchangeable fraction, which is opposite of what was expected if ^{137}Cs formed complexes with OM.

However, a high decomposition rate might release more exchangeable ^{137}Cs as LMM species from OM. In addition, microorganisms might constitute a significant amount of the OM in these samples, and they might solubilize ^{137}Cs.

Microorganisms were not evaluated in this thesis and the effect of them is largely not regarded in traditional models (Tamponnet et al, 2008). Even though the cause of the unexpected large amount of ^{137}Cs in the potentially bioavailable fractions in soil of sites 1 and especially in the soil from site 2 are unknown, the high amount of OM and alkalinity might be a part of the explanation.

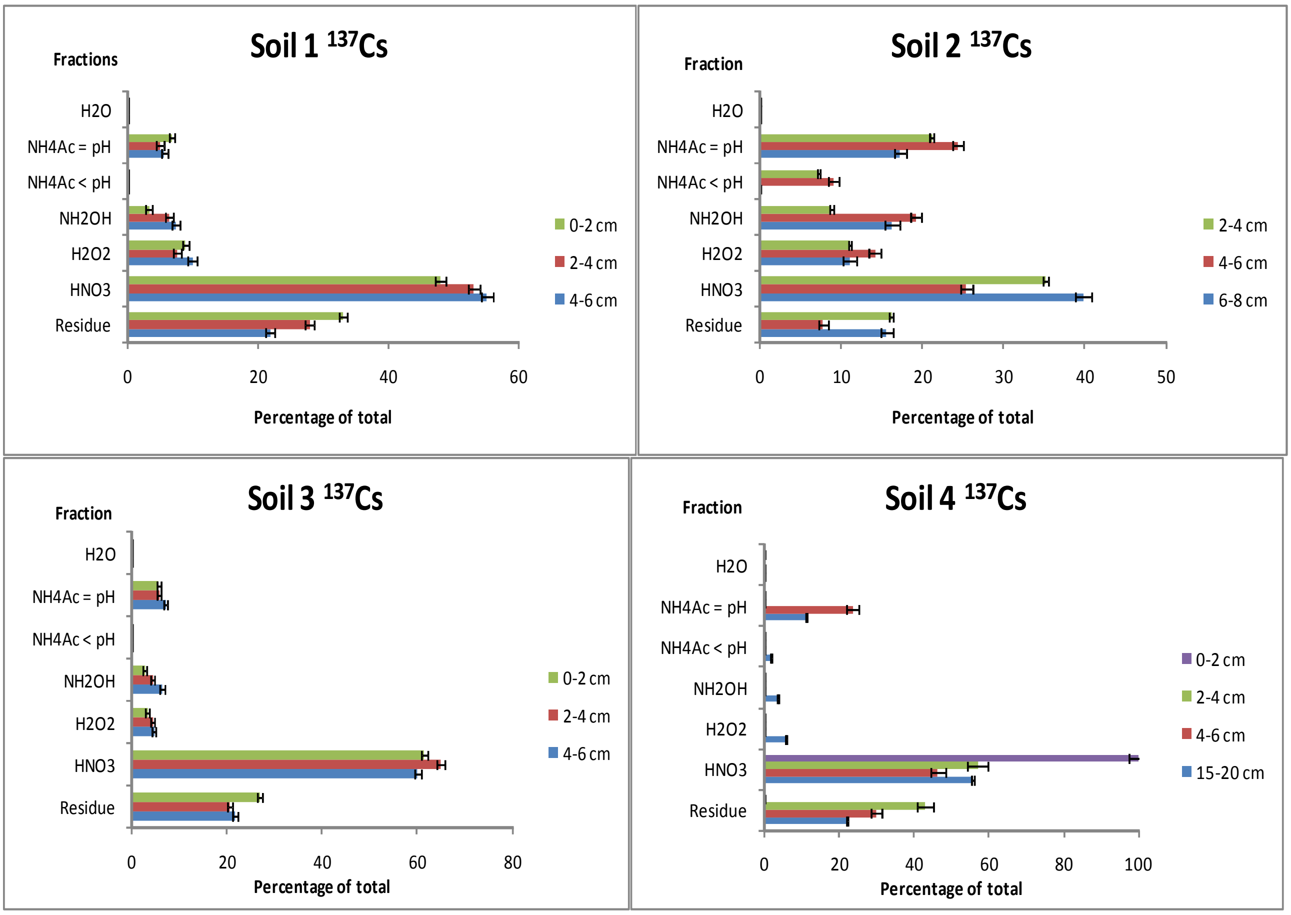

Figure 14: Speciation of ^{137}Cs in grassland (1-3) and sandy (4) soils

4.3.4 Statistical investigation of speciation of ^{137}Cs in soils.

To statistically investigate if forest fires changed the speciation of ^{137}Cs, contingency tests were used to evaluate if there were a different probability distribution of the activity concentrations in the different fractions in the forest fire soils compared with soils that were not affected by fires. The soil characteristics should be as similar as possible to reduce the possibility of confounding factors. Therefore the forest fire soils were compared with forest soils unaffected by fire. If the distribution of the forest fire soils always differed from the forest soils, this would strengthen the hypothesis. If the distribution probability of forest fire soils were similar to soils unaffected by forest fires in every case, then the hypothesis are weakened.

The H_0 hypothesis of the contingency test is: «columns and rows are independent, or all rows have the same probability of distribution». The test uses the total observed values and the categorical values, the activity in specific fractions in ccpm, and estimates a ccpm value which would be expected if H_0 was true.

In addition, there was calculated a test observator, Q, which estimates the deviance between expected and observed values. H_0 was rejected if Q was large. Finally, the p-value was used for an evaluation of α. The selected α-value was $p = 0.05$. If $p > \alpha$, the hypothesis was kept (Løvås, 2004).

As ^{137}Cs was primarily found in the 0-2 and 2-4 cm layers and since these layers should be more influenced by fires than layers deeper down the soil profile, the contingency test were done using the average of the top layers at 0-2 cm and 2-4 cm depth. When all soils were evaluated, the result was that H_0, “all rows had the same probability of distribution”, had to be rejected ($p < 0.05$).

When all soils were compared, it was observed that the soils from sites 1-4 had less activity than expected in the residual fraction, while soils 5-10 had more activity than expected in this fraction. Thus, the forest soils had significantly more irreversibly bound ^{137}Cs than the grassland and sandy soils. Soils from the sites 1, 3 and 5 had significantly more activity than expected in the strong acid fraction, while the other soils had significantly less or no significantly deviance in activity between observed and predicted activity. Soils from sites 1 and 2 had significantly more than expected activity in the potentially bioavailable fractions, while soils from sites 5-10 had significantly less activity than expected. Soils from sites 3 and 4 had insignificant deviance from the expected value.

In this part of the evaluation, the most prominent deviance in the forest fire soils (sites 9 and 10) was the indication that the amount of ^{137}Cs in the residual fraction of soil 10 was significantly higher than expected. The results of the contingency test for all soils are summarized in table 4.

The evaluation of difference in the speciation of soils from within and outside forest fire areas was based on evaluation of individual soils against one of the forest fire soils (table 5). Since soil from site 9 had few layers with activity, the soil from site 10 was selected as the primary representative for the forest fire soils.

The probability distribution of forest soils (sites 5-8) were compared to the soil from site 10. The result when the soils from sites 6 and 7 was compared to the soil from site 10 were that the H_0 hypothesis had to be accepted with p-values of respectively 0.27 and 0.28, that indicated that the speciation of soils 6, 7 and 10 had the same probability distribution, i.e., they had similar speciation. When the soils from sites 5 and 8 were compared with the soil from site 10, the H_0 were rejected ($p<0.05$) and thus these soils had a different speciation of ^{137}Cs than the soil from site 10.

The probability distribution of the forest soils were also compared to the soil from site 9 to evaluate if the trends persisted. The H_0 hypothesis for similar probability distribution were accepted for the soils from sites 6 and 7, with ($p= 0.31$, $p= 0.77$). The H_0 hypothesis were rejected for the soils from sites 5 and 8 ($p<0.05$), and these soils had a different probability distribution than both soils from the fire sites 9 and 10.

When the probability distribution of the soils from sites 5 and 8 were evaluated against soil from site 10, it was observed that the largest deviance was seen in the residual fraction of the soil from site 10, which had more activity than expected. Soil from site 10 also had less activity than expected in the strong acid and potentially bioavailable fractions. Soils from the sites 5 and 8 had less activity than expected in the residual fraction and more in the strong acid and potentially bioavailable fraction. Thus, the soil from the fire sites had more irreversibly sorbed ^{137}Cs than the forest soils that were not affected by fires.

The soil characteristics of soils with similar and dissimilar speciation to the soil of sites 9 and 10 were evaluated to see if there were any trends in the soil characteristics which might explain the difference in speciation.

One problem of selecting the two top layers of the soils is that it is not possible to compare the soil characteristics of the selected layers with each other using the Kruskal-Wallis test as this test calculates a mean from a population of five or more values. Therefore, to compare the soil characteristics, the Kruskal-Wallis test was done on the soil characteristics of the total soil cores.

Table 3 gives an overview of the Kruskal-Wallis test of the soil parameters. The soils with dissimilar speciation as both soils 9 and 10 had either insignificant or less of the soil characteristics than the fire soils.

Soils from sites 5 and 8, which were the forest soils with dissimilar speciation to the soils from fire sites 9 and 10, had insignificant deviance of soil characteristics compared to both fire soils or had less OM and water than the fire soils. Soils from forest sites 6 and 7, which had similar speciation as the fire soils, had different variances compared to the forest fire soils. Soil 6 had insignificant differences of OM and pH, while it had less water than both fire soils. Soil 7 had more OM and water than the fire soils and was more acidic than the fire soils.

Table 3: Comparison of soil characteristics from forest soils from sites 5 - 8 vs. forest fire affected soils from sites 9 and 10 Similar or dissimilar speciation between the compared soils is indicated. 0 indicate insignificant deviance between the forest and forest fire soils. – indicate where the forest soil had significantly less of the indicated soil characteristic than the forest fire soil, + indicate where the forest soil had significantly more of the indicated soil characteristic than the forest fire soil.

9	**Dissimilar**		**Similar**	
	Soil 5	**Soil 8**	**Soil 6**	**Soil 7**
OM	0	-	0	+
pH	0	0	0	-
Water	0	-	-	+
Clay	0	-	-	-
10	**Dissimilar**		**Similar**	
	Soil 5	**Soil 8**	**Soil 6**	**Soil 7**
OM	-	-	0	+
pH	0	0	0	-
Water	-	-	-	+
Clay	0	-	0	-

The clay distribution could not be investigated using Kruskal-Wallis, as there were only one value for each soil and the Kruskal-Wallis needs above 3 and preferably above 5 points of data from the populations in order to calculate a mean. To evaluate a possible deviance between the clay content of the soils, a simple calculation of the percentage deviance were done and any deviance above 15% are defined to reject the assumption of equal amounts of clay.

Soils from forest sites 5 and 6 had insignificant deviance in the amount of clay compared to soil from forest fire site 10, while forest soils from site 7 and 8 had significantly less clay than soil from site 10. When the soils were compared to forest soil from site 9, soil from site 5 had insignificant deviance, while the other soils had significantly less clay than soil from site 9.

Clay is known to irreversibly bind ^{137}Cs, and soil 10 had more clay than the forest soils. This was also seen when the forest soils were compared to fire affected soil from site 9. The clay could irreversibly sorb ^{137}Cs in the forest fire soils.

However, it is noticeable that soil from site 5, that had insignificant variance of clay from both fire soils, had dissimilar speciation as the fire soils. Compared with this soil, the soil from site 10 still had significant more ^{137}Cs in the residual fraction than expected. The soil from site 5 had significantly less OM and water than the soil from site 10.

Compared to the forest fire soil 9, there was no significant difference in the soil characteristics between the soil from sites 5 and 9, yet the speciation was dissimilar here as well. This deviance might come from variations in the CEC, or possibly due to heating. Otherwise, there was no indications of why the forest fire affected soils had ^{137}Cs in the strong acid and residual fraction and no ^{137}Cs in other fractions, while a site with similar soil characteristics do not have this amount of irreversibly sorbed ^{137}Cs and have far more potentially bioavailable ^{137}Cs.

Thus, it can be assumed that the less fixated ^{137}Cs in the unburned forest soils than in the forest fire affected soils cannot solely be explained by the clay content. Less OM and water might also influence the speciation, as the dissimilar forest soils had either an insignificant deviance of OM and water from the forest fire soils or had less of these characteristics. Fires in general reduce the amount of OM and perhaps the reduction followed by replenishing of the OM caused changes in the speciation. The forest fires might have changed the wettability of the soil and thus it might have caused increased erosion and possibly washed out the more potentially bioavailable ^{137}Cs.

If this is so, it should be expected an enrichment of ^{137}Cs downhill from fire sites. Thermal shock might have caused cracks in sand, aggregates and other soil structures, creating more binding sites for ^{137}Cs in the soil and during the extractions the cracks might give some protection towards the extraction chemicals.

Table 4: Contingency tests based on the average of the 0-2 and 2-4 cm layer in all soils. The number on top of the column for each soil was the average ccpm for the fraction calculated from the soil. The middle numbers were the expected value based on the χ^2 test. The bottom numbers are the test observator. At the bottom of the table, the test observator is given for all soils, the degrees of freedom (DF). Water soluble fraction was removed and the numbers are rounded.

	Average ccpm in the 0-2 and 2-4 cm layers for each core by fraction					
ID	**Residual**	**HNO3**	**H2O2**	**NH2OH**	**NH4 <pH**	**NH4 = pH**
1	118	188	32	19	0	15
	154	167	11	12	6	23
	8	3	40	4	6	3
2	212	468	152	128	99	289
	557	605	40	43	21	82
	214	31	313	171	285	524
3	103	271	16	16	0	25
	178	194	13	14	7	26
	32	31	<1	<1	7	<1
4	29	81	6	4	2	13
	56	605	40	4	2	82
	12	7	<1	<1	<1	3
5	601	614	0	38	8	35
	536	582	4	41	20	79
	8	2	<1	<1	8	24
6	509	436	0	7	0	0
	394	427	28	30	15	58
	34	<1	28	18	15	58
7	719	530	0	0	0	11
	521	566	38	40	20	77
	76	2	38	40	20	56
8	510	529	11	19	6	56
	467	508	34	36	18	69
	4	<1	152	8	8	2
9	62	43	0	0	0	0
	43	47	3	30	2	6
	8	<1	3	30	2	6
10	157	121	0	0	0	0
	115	125	8	9	4	17
	154	<1	8	9	4	17

X^2= 2274.92; DF= 45; P-value= 0.000

There were observed more ^{137}Cs in the residual fraction of forest fire soils than what would be expected by comparing them to similar soils. The increased amount of ^{137}Cs in the residual fraction indicates more irreversibly bound, or fixated, ^{137}Cs in soils affected by forest fires.

This might be either due to direct influence from the fire or heat or indirectly by fires affecting the soil, thus changing the soil characteristics. At least, the investigation of these soils indicate that forest fire changes the speciation of ^{137}Cs in the soil.

Table 5: Contingency tests of the top soils 0-6 cm of individual soils from forest sites unaffected by forest fires (sites 5 -8) compared with a soil from a forest fire site (site 10). Observed activity is at the top of the column rows, the expected activity in the middle of the column rows and the observator value at the bottom column rows.

χ^2 test between cores 5 and 10

ID	Residual	HNO3	H2O2	NH2OH	NH4 <pH	NH4 = pH	H2O
5	601	614	-	38	8	35	-
	624	605	-	31	7	29	-
	<1	<1	-	1	<1	1	-
10	157	121	-	0	0	0	-
	134	130	-	7	1	6	-
	4	<1	-	7	1	6	-

X2 = 22.95; DF = 4; P-value= 0.000

χ^2 test between cores 6 and 10

ID	Residual	HNO3	H2O2	NH2OH	NH4 <pH	NH4 = pH	H2O
6	509	436	-	7	-	-	-
	515	431	-	5	-	-	-
	<1	<1	-	<1	-	-	-
10	157	121	-	0	-	-	-
	151	126	-	2	-	-	-
	<1	<1	-	2	-	-	-

X2 = 2.65; DF = 2; P-value= 0.266

χ^2 test between cores 7 and 10

ID	Residual	HNO3	H2O2	NH2OH	NH4 <pH	NH4 = pH	H2O
7	719	530	-	-	-	11	-
	718	533	-	-	-	9	-
	<1	<1	-	-	-	<1	-
10	157	121	-	-	-	0	-
	158	118	-	-	-	2	-
	<1	<1	-	-	-	2	-

X2 = 2.56; DF = 2; P-value= 0.279

χ^2 test between cores 8 and 10

ID	Residual	HNO3	H2O2	NH2OH	NH4 <pH	NH4 = pH	H2O
8	510	529	11	19	6	56	-
	535	522	9	15	5	45	-
	1	<1	<1	<1	<1	3	-
10	157	121	0	0	0	0	-
	132	128	2	4	1	11	-
	5	<1	2	4	1	11	-

X2 = 29.23; DF = 5; P-value= 0.00

4.4 Plutonium

Due to the extensive work needed to isolate and analyze Pu, only selected soils and layers were analyzed. The selection was based on the ^{137}Cs activity and if the soils had been subjected to forest fires or not.

4.4.1 Total soil samples

Grassland soil from site 1 had 39 Bq/kg dry weight ^{238}Pu and 75 Bq/kg dry weight ^{239,240}Pu. Sandy soil from site 4 had 6.8 ^{238}Pu and 3.5 Bq/kg dry weight ^{239,240}Pu. Unburned forest soil from soil 6 had the highest activity of all with 96 Bq/kg dry weight ^{238}Pu and 200 Bq/kg dry weight ^{239,240}Pu. The soil from forest fire affected site 9 had 17.9 ^{238}Pu and 27.0 Bq/kg dry weight ^{239,240}Pu, while the soil at fire affected site 10 had 13.7 ^{238}Pu and 20.5 Bq/kg dry weight ^{239,240}Pu. The total activities are summarized in figure 15 and details are given in the appendix (A.8).

The total samples from the soils at the sites 1, 4, 9 and 10 were within the activities reported by Qiao and Hou (2010) and Ovsiannikova et al (2010). The soil from site 6 had an activity higher than those observed by both Ovsiannikova et al (2010) and Qiao and Hou (2010) and might therefore be a hotspot with radioactive particles.

In order to evaluate if the Pu-isotopes found in the soil of site 6 were of Chernobyl origin, the ratio between ^{238}Pu and ^{239,240}Pu were examined. According to Varga (2007), the typical ^{238}Pu/^{239,240}Pu ratio of Chernobyl origin Pu was in the interval 0.49 – 0.56. The ratio of ^{238}Pu/^{239,240}Pu observed in the soil of site 6 was 0.47. Weapons-grade Pu has a ^{238}Pu/^{239,240}Pu ratio of 0.015 – 0.42. Since the ratio was closer to the Chernobyl origin interval, the sample appeared to be of Chernobyl origin. An explanation for the high activity in soil sample 6 would be that the activity originated from hot particles.

One reason to evaluate the total samples was to investigate if the activities were high enough for analysis done by Inductively Coupled Plasma – Mass Spectrometer (ICP-MS), which had a LD of 0.1 Bq. As Pu have a tendency of irreversibly sorption to particles in soil, a total sample could be used as a point of reference, from which the activity of the extractions could be removed and thus gain an estimation of the residual.

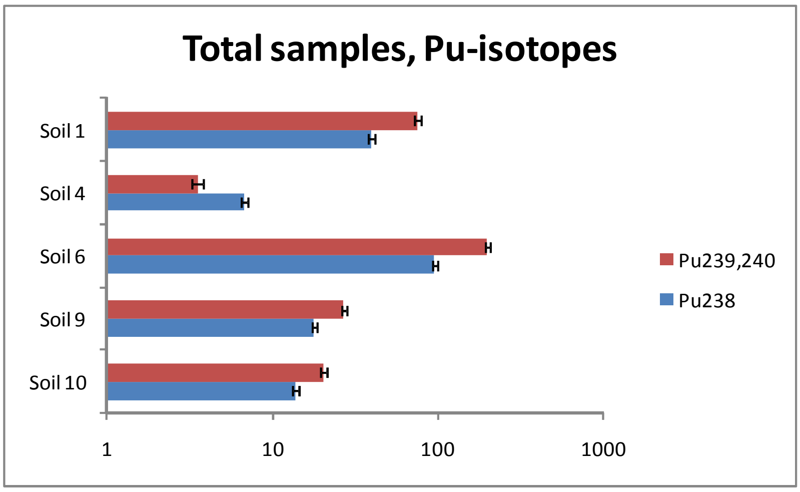

Figure 15: Total samples of a grassland soil (site 1), sandy soil (site 4), forest soil (site 6) and forest fire affected soils (sites 9 and 10)

4.4.2 Sequential extraction results for Pu

Figure 16 shows the speciation of Pu-isotopes in the selected soils. For all soil samples and isotopes, the organic bound fraction dominated the speciation, followed by the strong acid fraction and a low to negligible activity in the oxide bound and exchangeable fractions. The residual fractions were excluded as Pu associated with this fraction needs extreme measures to be dissolved and are assumed to be strongly bound to the mineral lattice. The residual fraction will hardly be mobilized in the environment, and therefore of minor problem when doing risk assessment.

In the investigation of the speciation of ^{137}Cs, it was determined that the soil characteristic of the grassland soil at site 1 deviated from the forest soils by a more alkaline pH, and a higher content of OM, water and clay than the average. The soil characteristics of the unburned forest soil from site 6 were compared to the soils affected by forest fires from sites 9 and 10. The soil from site 6 was drier and had less clay than the soil in site 9 and it was drier than soil from site 10. Otherwise, the differences in soil characteristics were insignificant.

The speciation of soil sample 6 was therefore compared to soil from sites 9 and 10. The speciation of Pu-isotopes in the soil of site 6 appeared similar to the speciation of Pu in the soil of site 9. Soil sample 6 had 16% ^{239,240}Pu in the strong acid fraction, while soil sample 9 had 13% ^{239,240}Pu in this fraction. Soil sample 6 had 73% ^{239,240}Pu in the organic bound fraction, while soil sample 9 had 80% in the same fraction. If the fraction that was extracted in the soil of site 6 but not in soil from site 9 was removed (the bound to carbonates fraction), soil at site 6 had 75% ^{239,240}Pu in the organic bound fraction.

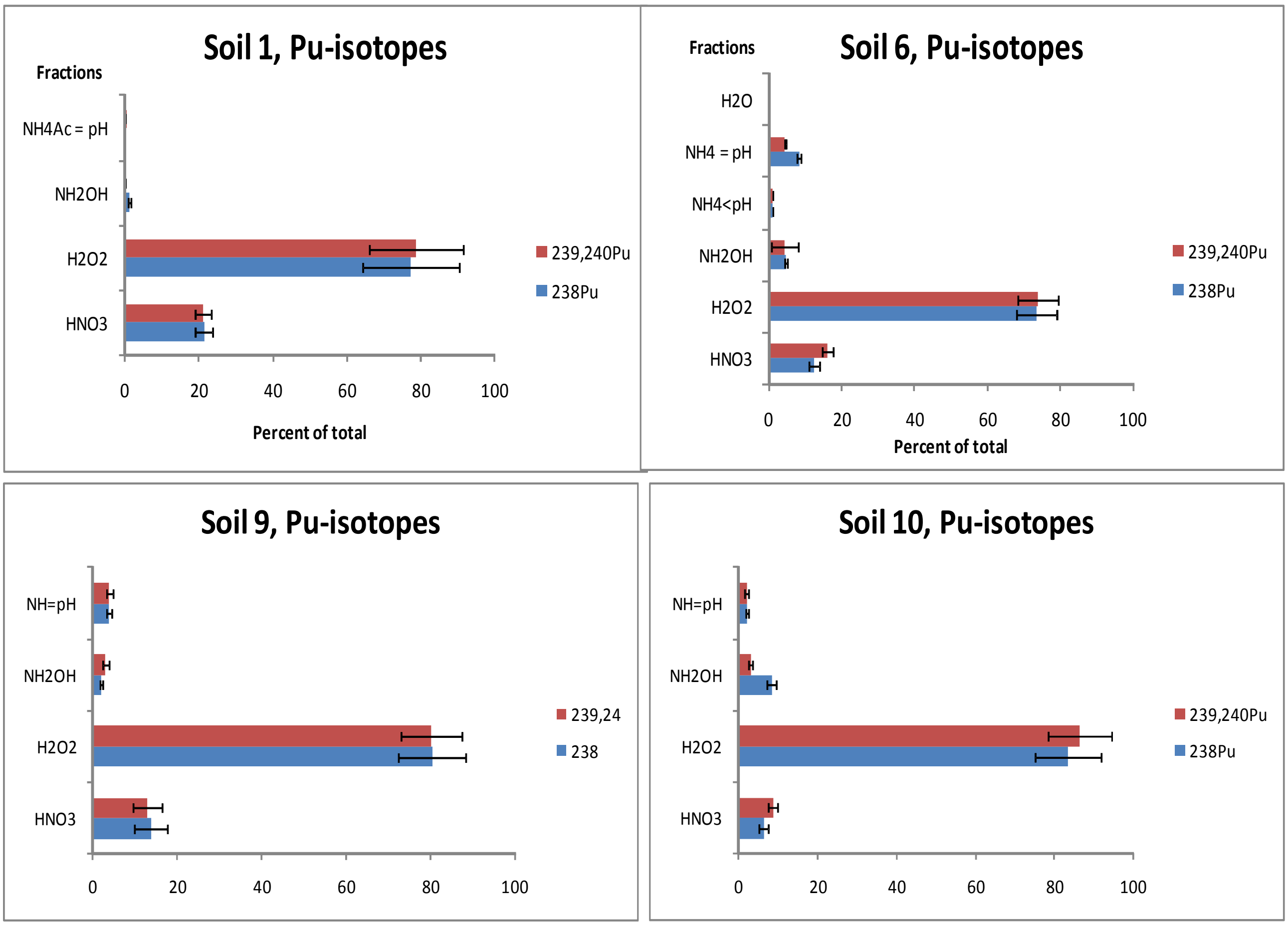

Figure 16: Sequential extractions of grassland soil (site 1), forest soil (site 6) and forest fire soils (sites 9 and 10).

Soil from site 10 had less Pu in the strong acid fraction than soil from site 6; 9% in soil from site 10 versus 16% in soil from site 6. The organic fraction of soil sample 10 had 86% of the Pu, while soil from site 6 had 75% of the Pu in this fraction.

There seemed to be a tendency of less Pu in the strong acid fraction and slightly more Pu in the organic bound fraction in forest fire soils than in similar soils with no fire incidents.

Ovsiannikova et al., (2010), used sequential extraction of a similar scheme as used for this thesis and the soils which they examined were soddy-podzolic soils and peat. Ovsiannikova et al (2010), also found most of the Pu in the organic bound fraction, but only <50% was in this fraction, while the Pu-isotopes in the organic bound fraction in the UMB samples were ~80%. Ovsiannikova et al., (2010) extracted between 10-20% in each of the carbonate bound, oxide bound and strong acid fractions, with the remainder in the exchangeable, water soluble and residual fractions.

However, Ovsiannikova et al., (2010), also extracted Pu from peaty soil samples, and the speciation of Pu in this soil was far more similar to the UMB results, with 50-76% of the Pu in the organic bound fraction, 15-32% in the strong acid fraction and the remainder distributed over the other fractions. The organic content of the peat analyzed by Ovsiannikova et al,. (2010) was around 80% OM, while their soddy-podzolic soil had between 0.2 – 5.0% OM and thus the UMB samples were far more similar to the soddy-podzolic soils than the peat with respect to the content of OM. Ovsiannikova et al., (2010) assumed that the variations observed between the peat and soddy-podzolic samples were due to deposition of hot particles rather than differences in soil characteristics.

Due to miscalculation, the soil of site 4 was wrongly believed to have a very low Pu activity and was therefore not evaluated.

4.4.3 Statistical investigation of difference in speciation

Even though there seems to be a slight deviance of speciation in soils with and without forest fire incidents, the difference might not be statistically significant. As for ^{137}Cs, contingency tests were done for Pu. The counts for ^{239,240}Pu were used and to avoid the problem of an expected value below 1, which causes an error in the contingency test function in Minitab, the counts were given as mBq/unit. Contingency tests were done for all soils and as the unburned soil from site 6 had the most similar soil characteristics to the forest fire soils, it was compared to fire affected soils from sites 9 and 10.

When all samples were compared, differences were indicated in the speciation of Pu in the soil samples ($p<0.05$). The soils from sites 1 and 6 had more activity in the strong acid fraction than expected and less in the organic bound fraction than the mean, which indicate more irreversibly bound Pu in the forest soils than in the forest fire soils. The results are summarized in table 6.

The soil from site 6 was from a forest area and thus it should be expected that this soil had more similar soil characteristics and speciation as soil from site 10 and any changes in speciation might be due to the effect of fire, either on the Pu directly or indirectly via temporarily changed soil characteristics. The investigation indicated that the difference in speciation between soils of the sites 6 and 10 were not significantly different ($p=0.08$). When soil from site 6 was compared to soil from site 9, the speciation in the soils were almost identical ($p= 0.71$).

However, in the forest fire soils, there were observed less than expected Pu in the strong acid fraction and more Pu in the organic bound fraction than expected.

Even though the results were not statistically significant, it is noticeable that the trend of less Pu in the strong acid fraction than expected in forest fire affected soil appears when all soils were compared and persist when the forest soil were compared to both forest fire soils. As only one of the compared samples was from an area with similar soil characteristics as the forest fire soils, and was unaffected by forest fires, it might be reasons to believe that more samples might cause a clearer answer if forest fires indeed change the speciation of Pu-isotopes. As soil from site 10 also seemed to be more influenced by forest fires than soil from site 9, perhaps local variations in fire intensity and deposition of debris such as ashes and uncombusted plant residue might influence the speciation of Pu-isotopes.

The speciation of ^{137}Cs in soil from site 6 was similar to the speciation of soils from sites 9 and 10. Investigation of soils from sites 5 or 8, which had significantly different speciation of ^{137}Cs than the forest fire soils, might have given another result for Pu as well. Due to lack of time, the speciation of soils from sites 5 and 8 could not be evaluated for this thesis.

Table 6: Results of contingency test of all soils and individual soils vs. a forest fire soil, activity given in mBq/unit.

Contingency test all soils

	HNO3	**H2O2**	**NH2OH**	**NH=pH**
1	153	573	0	1
	129	565	16	17
	5	<1	16	15
6	114	526	30	32
	124	546	15	17
	<1	<1	14	14
9	13	81	3	4
	18	78	2	2
	1	<1	<1	<1
10	9	89	3	2
	18	80	2	2
	5	1	<1	<1

X2 = 73.9; P-value <0.05

Contingency test soil 6 vs soil 10

	HNO3	**H2O2**	**NH2OH**	**NH=pH**
6	114	526	30	32
	107	536	29	30
	<1	<1	<1	<1
10	9	89	3	2
	15	79	4	4
	3	1	<1	1

X2 = 7; P-value =0.081

Contingency test soil 6 vs soil 9

	HNO3	**H2O2**	**NH2OH**	**NH=pH**
6	114	526	30	32
	111	530	29	31
	<1	<1	<1	<1
9	13	81	3	4
	16	76	4	5
	1	<1	<1	<1

X2 = 1.39; P-value =0.707

4.4.4 Ratios of total ^{137}Cs vs. total Pu

When the ratio of total ^{137}Cs to total Pu was evaluated, the ratio was defined to be 0.0014 ± 0.0003 in the forest (site 6) and forest fire soils (sites 9 and 10). The grassland soil (site 1) had a ratio of 0.0028, while the sandy soil (site 4) had a ratio of $6.8 \cdot 10^{-5}$. The ratio appears to vary between forest soils and grassland, sandy soils, but not between forest soils and forest fire soils. This indicates that the ^{137}Cs and Pu-isotopes in the different forest soils that were and was not affected by forest fires came from the same plume of fallout. This strengthened the hypothesis that the variations in speciation originated from direct influence by forest fires or indirectly from changed soil characteristics.

4.5 Particles

^{137}Cs is a fission byproduct, and can therefore be used as an indicator for hot particles.

4.5.1 Particle search in samples obtained in 2009

An aliquot with a high level of ^{137}Cs activity per unit has a higher probability of containing particles than an aliquot with lower levels of activity per unit. Hot particles can also be detected by the speciation of Cs or Pu-isotopes and can be indicated by a higher than expected yield in the organic bound fraction as the chemicals used in this step dissolve particles. As the activity of ^{137}Cs was generally highest at the 0-2 cm depth of the soils and as it was assumed that any remaining particles would not migrate down the soil column to a significant degree, the top 0-2 cm layers were selected for particle search, with two exceptions. Soil from site 1 had the highest ^{137}Cs activity in the 2-4 cm layer and this layer was chosen from site 1. Soil from site 4 had the highest ^{137}Cs activity in the 15-20 cm layer and this layer was selected for particle search as one of the theories for the abnormal high activity in the 15-20 cm layer in this soil were that the activity came from particles.

In order to characterize hot particles, they have to be identified and isolated. By definition, a hot particle has an activity considerably higher than the surrounding matrix (Bunzl, 1998). This characteristic can be used to isolate individual particles in bulk samples. Repeated splitting is a method where the original sample is split into aliquots, which are then measured. Differences between aliquots can be defined by the formula

$$\Delta \text{ A aliquot} = \frac{\text{A aliquot, max} - \text{A aliquot, min}}{\text{A aliquot, max}} \quad \text{(eq. 3)}$$

If ΔA aliquot exceeds a certain percentage (30% or 50%), the sample have a certain probability of containing a hot particle. Many hot particles in one sample need several aliquots to be detected. However, a percentage difference less than 30% does not prove that hot particles are not present. The probability of finding 2-10 hot particles with 2 aliquots was 46 to 78% (Bunzl, 1997).

Digital autoradiography of the 2-4 cm layer of soil from site 1 showed a hot spot that was typical for a hot particle (Figure 18 A). It was located by coordinates from the autoradiography image and a portable gamma spectrometer (Automess) and cut out of the plastic. The activity of the particle was measured to 18 Bq ^{137}Cs and 1.5 Bq ^{241}Am on the Ge-detector. ESEM showed a particle approximately 10-12 µm across (figure 19). The topography showed what appeared to be a microblock structure, which is common in Chernobyl hot particles (Lind, pers.comm). It was bright in BEI mode, which indicated heavy atom nuclei. XRMA confirmed U.

It was send to HASYLAB, Germany for further analysis of the oxidation states by μ-XANES at Beamline L. Result of μ-XANES showed U^{+4}, which indicated a matrix of UO_2 (figure 17). The white line of the hot particle spectrum lies at the same place as the white line for the UO_2 standard, while the white line for the U_3O_8 standard lies at a somewhat higher energy. The UO_2 standard showed a small and flat but defined elevation behind the white line and so did the spectra for the hot particle. An additional μ-XANES spectrum are given in the appendix (A.9)

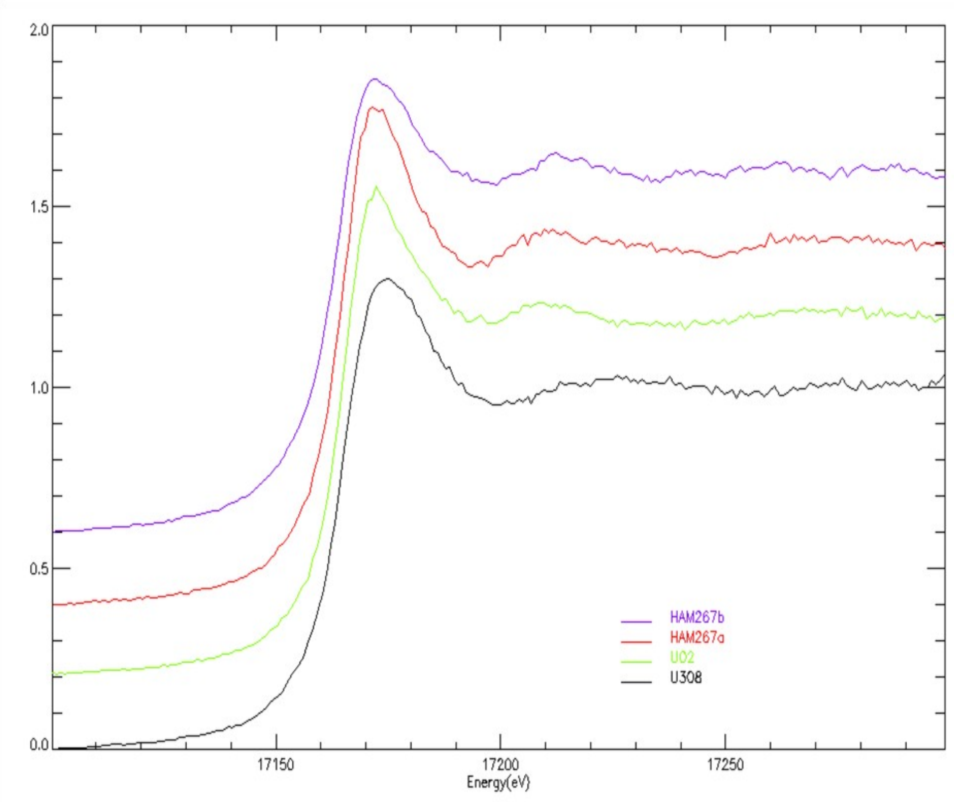

Figure 17: U LIII XANES profiles of U standards and particle from soil 1

UO_2 was the chemical composition of nuclear fuel used in the ChNPP. The oxidation state of U did not change from the time of the accident to the present day. This has also been observed in other hot particles. μ-X-ray diffraction (μ-XRD) was performed on the particle, but it was too small to attain a reliable diffraction pattern.

UO_2 particles were usually found in the western trace. The site where soil 1 was obtained was approximately 14 kilometers from the ChNPP to the north-northeast and the hot particle might have been ejected in the first explosion. The particle could also have been released in the subsequent fire without becoming oxidized.

Digital autoradiography of soil from site 2 showed a signal that appeared to be a particle. ESEM with BEI mode showed a particle with heavy nuclei and XRMA confirmed a complex matrix consisting of U, K and other elements. It looked far more weathered than the soil 1 particle as it did not have a microblock structure and with uneven edges. The particle strengthened the hypothesis of weathered particles as the source of the unexpected speciation of ^{137}Cs.

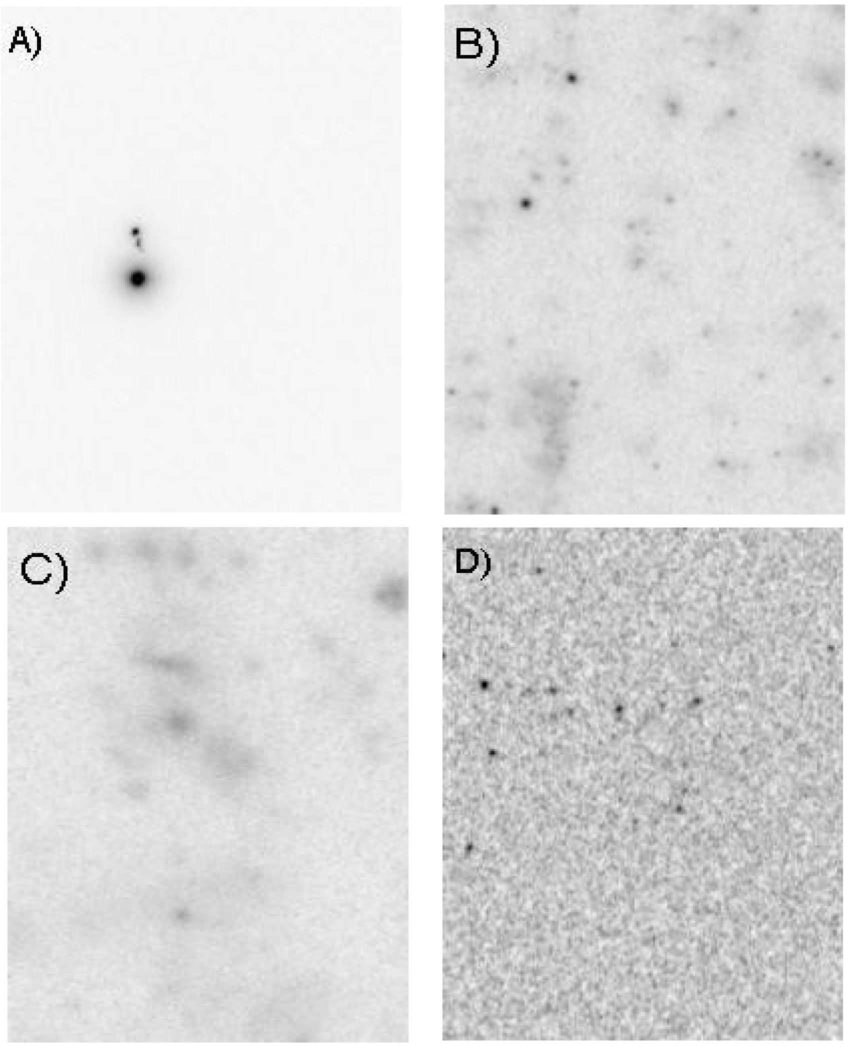

Figure 18 Digital autoradiography images. A) Hotspots from the 2-4 cm layer of site 1 B) Hotspots from the 0-2 cm layer of site 6 C) Diffuse spots from the 0-2 cm layer of site 9 D) Hotspots from the 0-2 cm layer of site 10

Two samples from the 15-20 cm layer of the soil in site 4 were investigated by digital autoradiography followed by ESEM with BEI and XRMA, but no signs of heavy nuclides were found.

Soil from sites 5 and 8 was investigated by digital autoradiography, but the samples were <LD and no further investigations were performed.

Digital autoradiography of the 0-2 cm layer of soil in site 6 showed minor hotspots, and two samples were cut out of the adhesive plastic. However, the samples had activity <LD and no further investigation were performed. Sequential extraction of soil from site 6 showed negligible amounts of ^{137}Cs in the organic bound fraction, with the majority extracted in the strong acid and residue fractions. The amounts of Pu-isotopes were far higher in the total samples of the 0-2 cm layer in soil from site 6 than in the total samples of the other soils. Pu was in the strong acid fraction and organic bound fraction. This might indicate the presence of hot particles, as discussed by Odintsov et al (2004). However, the presence of particles are usually indicated by significant amounts of ^{137}Cs in the organic bound fraction and this was absent in soil from site 6. The acidic soil at site 6 could have dissolved hot particles prior to sampling.

Digital autoradiography of the soil in site 7 showed one apparent hotspot. Further inspection by light microscope showed that the signal came from an aggregation of soil. The aggregation was measured on the Ge-detector before it was divided into several smaller fragments. Individual fragments were measured, but all had insignificant activity. When all the fragments were measured together, the original activity was found. Repeated use of digital autoradiography did not yield any clear signs of particles.

The 0-2 cm depth layer of the forest fire soils (9 and 10) was evaluated, but all signals were <LD. As the soils at these locations were determined to be moderately to very acidic after forest fire incidents, any particles which might have been present would most likely have been dissolved partially or totally before the fire incidents.

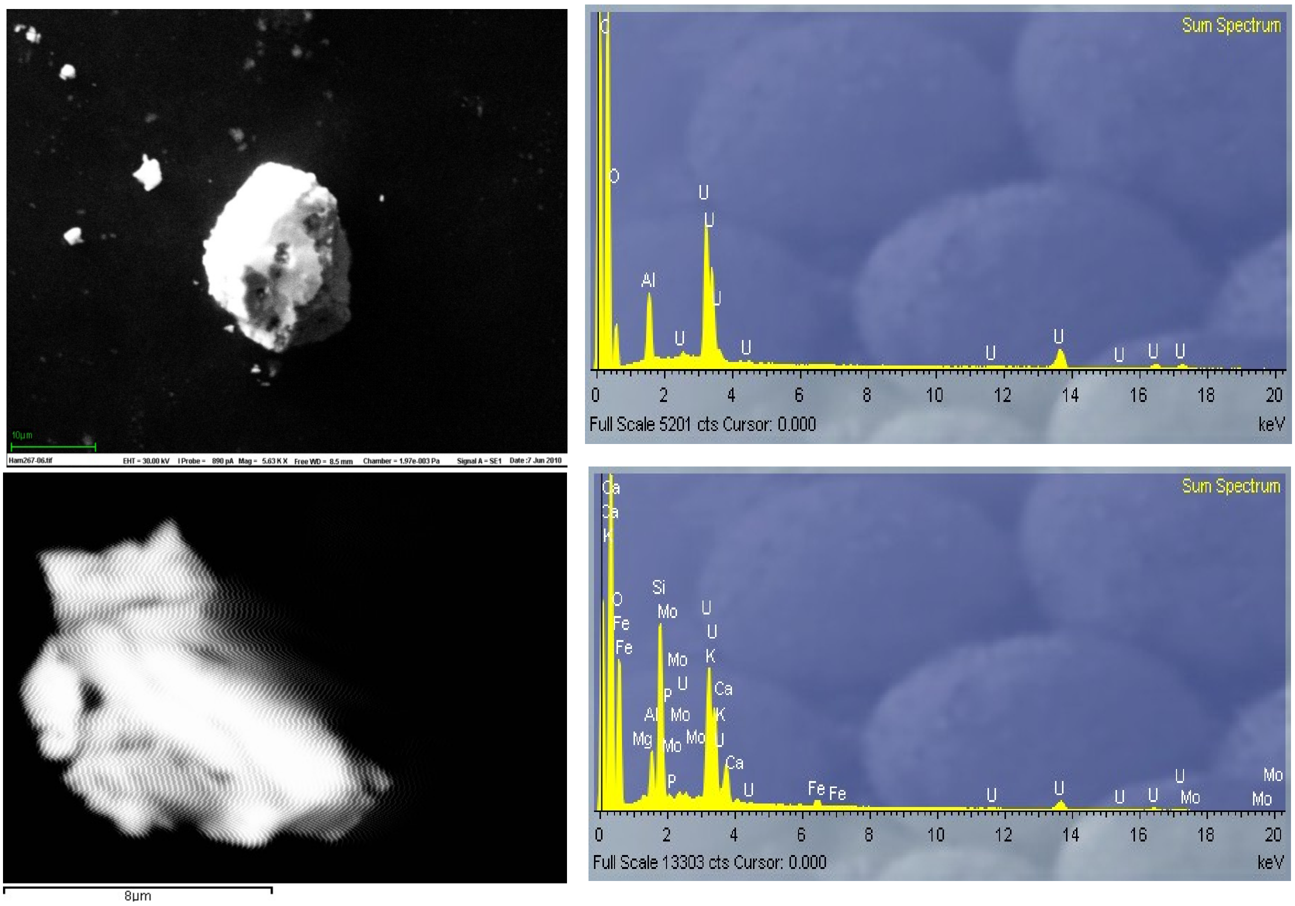

Figure 19: Upper left: hot particle from soil 1. Upper right: XRMA spectrum of the soil 1 hot particle. Lower left: hot particle from soil 2, lower right: XRMA spectrum of the soil 2 hot particle. The aluminum signal in XRMA spectrum for both hot particles came from the stub.

ESEM with BEI-mode and XRMA were also used to look for other kinds of particles, such as Zirconium (Zr) -Niobium (Nb) alloys which could originate from reactor construction material. Although several Zr composite particles were found, they did not include Nb in the matrix and their rounded and weathered shape indicated that these particles might have natural origins. No further investigation was performed.

4.5.2 Particle search in samples obtained in 2010

On each site, four samples were obtained. The samples from three forest fire sites were screened using the Ge-detector and the sample with the highest activity of ^{137}Cs from each site were selected for further investigation. A sample from the upper layer of the soil was taken, dried and divided into aliquots until a small volume was attained. Two aliquots from site 3, 2010, were examined by digital autoradiography and one of them showed a hotspot (figure 20).

However, when investigated by Ge-detector, it gave a ^{137}Cs signal barely above LD. ESEM with BEI-mode and XRMA, did not reveal any sign of heavy nuclides. There were plant material and soil aggregations in the sample, and if the signal truly originated from a particle, it might be hidden within the soil aggregation. Site 1 and 5 had signals <LD and were not further investigated.

Main hypothesis 3 could not be investigated as no particles were found in forest fire soils. pH measurements of soil slurry and understory growth indicated slight to very acidic soil, which is known to cause a higher weathering rates of particles. Further search in neutral to slightly alkaline soils within fire areas may still yield particles. As most pine forest has acidic soils, a possible investigation should be targeted on grasslands or in areas with had soft-leaved trees prior to fire incidents.

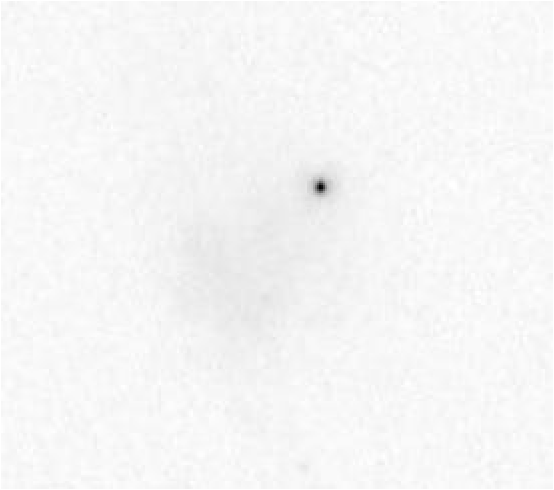

Figure 20: Hotspot obtained from site 3, 2010.

5. Conclusion

Soil characteristics and speciation of ^{137}Cs, Pu-isotopes and particles were evaluated for ten soil and sediment samples from within and outside forest fire areas obtained in the Polessie State Radio-Ecological Preserve, Gomel county, Belarus in 2009.

The content of the soil characteristics pH, organic matter (OM) and water were determined for all soils and layers. The characteristics varied most between forest soils (affected and unaffected by fires) and soils from grassland and sandy sites. When the soil characteristics of the forest fire affected soils was compared with the unaffected forest soils, the fire affected soils had generally more OM, clay and water than the unburned forest soils. The acidity was similar for all soils. The high amount of OM in the fire affected soils was contradictory to what was expected and this might be due to replenishing of OM from incomplete combustion of plant material.

The highest activity of ^{137}Cs was at 0-4 cm depth below the humus layer. The range of ^{137}Cs activity concentrations in these layers was 3- 120 Bq/g in unburned forest soils and from 7 – 22 Bq/g in forest fire affected soils.

An investigation of the speciation of ^{137}Cs in the different soil samples was performed. There seemed to be more irreversibly fixated ^{137}Cs in the forest fire affected soils than in the unburned forest soils. Statistical investigation strengthened this notion as the forest fire affected soils had significantly more ^{137}Cs in the residual fraction than expected. This increased irreversibly bound ^{137}Cs could be either due to a direct influence from the fire or heat or indirectly by changed soil characteristics. The investigation of these soils indicate that there is a statistically significant change in the speciation of ^{137}Cs in soils which were affected by forest fires.

The soils from grassland and sandy sites had an unexpected high amount of potentially bioavailable ^{137}Cs despite the relatively high amount of clay. This might be due to soil characteristics such as the relatively high content of OM and pH or presence of hot particles.

The amount of total Pu in unaffected forest soil ranged from 3.5 - 200 Bq/kg and 6.8 - 96 Bq/kg for ^{239,240}Pu and ^{238}Pu, respectively. Total amount of Pu in burned soil was 20-27 Bq/kg for ^{239,240}Pu and the activity of ^{238}Pu was 13.7 - 17.8 Bq/kg.

Sequential extraction showed that there might be a tendency of less Pu in the strong acid fraction and slightly more Pu in the organic bound fraction in forest fire affected soils compared with soils with no fire incidents. When all samples were compared using contingency tests, a low p-value ($p<0.05$) indicated differences in the speciation among the soil samples. However, tests of individual soils indicated that the difference in speciation between the soils at sites affected and unaffected by forest fires were not significantly different ($p=0.08$- $p=0.71$). Forest fires did not cause a statistically significant change in the speciation of Pu-isotopes compared to similar soils with no forest fire incidents.

There were found particles in two samples in soil unaffected by forest fires. One of them had a topography typical for Chernobyl origin particles and investigation of oxidation states showed U^{4+}, which indicated a UO_2 matrix, which were the original fuel in the ChNPP. The other particle had a weathered appearance and a matrix consisting of several elements, including U. Although there were indications of heterogeneities in all soils, no particles within forest fire areas was radioactive enough to be >LD and thus could not be positively identified. However, there were defined confounding factors in the soils and the absence of hot particles in burned soils may be due to forest fires, but could also be related to soil conditions which had partially or totally dissolved the hot particles prior to the fires.

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7. Appendix

A.1 Site descriptions of the samples obtained in 2009

Site description 2009				
Id	**Location**	**Gamma μSv/h**	**Description**	**Vegetation**
Core 1	N 51° 30' 22.1214" E 30° 1' 17.616"	3.1	Grassland	Soft leaved trees, grass
Core 2	N 51° 30' 23.3712" E 30° 1' 14.5734"	4.2	Grassland near house	Soft leaved trees, grass
Core 3	N 51° 31' 29.298" E 30° 0' 25.11"	2.7	Grassland near water	Soft leaved trees, reeds
Core 4	N 51° 33' 19.0908" E 29° 55' 12.0534"	1.0	Dunes	Shrubs
Core 5	N 51° 35' 30.357" E 29° 59' 33.9468"	5.7	Forest	Pines, lichen, moss
Core 6	N 51° 35' 32.19" E 29° 59' 39.6306"	5.6	Forest	Pines, lichen, moss
Core 7	N 51° 35' 32.9814" E 29° 59' 18.6828"	9.2	Highest dose area	No information
Core 8	N 51° 35' 0.708" E 30° 5' 7.9362"	7.4	No information	No information
Core 9	N 51° 48' 11.0592" E 29° 37' 21.4098"	0.82	Burned forest	Pine, birch
Core 10	N 51° 48' 9.7308" E 29° 37' 18.5622"	0.85	Burned forest	Pine, birch

A.2 Site descriptions of the samples obtained in 2010

Site description 2010 fieldwork					
ID	Location	Gamma 0 m μGy/h	Gamma 1 m μGy/h	Description	Vegetation
Site 1	N 51°31'20" E 030°7'49"	8.28	7.41	Low intensity forest fire	Pine, birch, grass
Site 3	N 51°39'09.4" E 030°13'17,8"	1.98	1.40	High intensity forest fire	Pine, birch, alder, grass
Site 5	N 51°39'03,8" E 030°13'17,7"	2.51	1.75	Low/medium intensity Forest fire	Pine, birch, alder, apricot grass and blueberries

A.3 Precision evaluation

ANOVA: C1; C1II; C1III; C7; C7II; C7III; C10; C10II; C10III
F-value: 0.07, P-value: 1.000, R2(adj): 0.00%

```
                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level   N   Mean  StDev  -----+---------+---------+---------+----
C1      6  819,2  523,1         (----------*-----------)
C1II    6  869,3  478,7          (-----------*----------)
C1III   6  911,0  527,7            (----------*-----------)
C7      4  904,0  438,3         (-------------*-------------)
C7II    4  922,0  523,8         (-------------*-------------)
C7III   4  957,5  567,8          (-------------*-------------)
C10     3  742,3  268,5  (---------------*---------------)
C10II   3  840,0  359,5     (---------------*---------------)
C10III  3  922,0  378,5       (---------------*----------------)
                         -----+---------+---------+---------+----
                            350       700      1050      1400

Pooled StDev = 481,8
```

A.4 Summary of soil characteristics soils 1-10

			Soil properties			
Core	Average pH	Range pH	Average %OM	Range %OM	Average % water	Range % water
1	7.1	7.7-6.4	3.0	5.8-2.3	9.3	10.9-7.2
2	7.2	7.6-6.8	3.6	7.5-1.7	10.2	14.1-6.7
3	6.3	6.9-5.8	1.3	2.0-0.6	8.4	10.5-5.9
4	5.1	5.9-4.2	0.3	1.3-0.1	1.9	3.7-0.4
5	5.0	5.8-4.3	2.0	5.4-0.5	4.8	9.8-3.3
6	4.7	5.4-4.2	2.3	6.4-1.3	3.0	3.8-2.5
7	4.3	4.5-4.1	3.6	5.7-2.5	7.0	7.6-5.7
8	5.0	5.3-4.2	1.0	4.6-0.0	3.4	9.6-1.2
9	5.1	5.4-4.6	2.7	9.9-1.3	4.9	10.0-3.1
10	4.8	5.9-4.4	2.6	6.1-1.4	6.3	9.3-4.2

A.5 Grain size distribution in all cores

Grain size distribution in %			
Core	Clay	Silt	Sand
1	2.2	10.1	87.7
2	2.3	9.9	87.8
3	2.3	15.0	82.7
4	1.0	0.3	98.6
5	1.7	2.8	95.5
6	1.4	5.3	93.3
7	1.2	4.5	94.3
8	0.9	1.1	97.9
9	1.8	3.3	94.9
10	1.6	3.6	94.8

A.6 Comparison NRPA/UMB numbers using eq. 3

Core	Depth cm	Bunzl ratio	Core	Depth cm	Bunzl ratio
1	0 – 2	0.21	6	0 – 2	0.37
	2 – 4	0.76		2 – 4	0.10
	4 – 6	0.76		4 – 6	0.68
	6 – 8	0.33		6 – 8	0.79
	8 – 10	0.94		8 – 10	0.82
	10 – 15	0.92		10 – 15	0.79
	15 – 20	-		15 – 20	0.74
2	0 – 2	-	7	0 – 2	0.41
	2 – 4	0.72		2 – 4	0.55
	4 – 6	0.35		4 – 6	0.66
	6 – 8	0.65		6 – 8	0.61
	8 – 10	0.86		8 – 10	0.42
	10 – 15	0.76		10 – 15	0.49
	15 – 20	0.78		15 – 20	-
3	0 – 2	0.86	8	0 – 2	0.87
	2 – 4	0.91		2 – 4	0.85
	4 – 6	0.87		4 – 6	0.79
	6 – 8	0.82		6 – 8	0.71
	8 – 10	0.37		8 – 10	0.35
	10 – 15	0.92		10 – 15	0.11
	15 – 20	0.40		15 – 20	0.61
4	0 – 2	0.95	9	0 – 2	0.20
	2 – 4	0.86		2 – 4	0.40
	4 – 6	0.49		4 – 6	0.68
	6 – 8	0.29		6 – 8	0.69
	8 – 10	0.16		8 – 10	0.73
	10 – 15	0.89		10 – 15	0.53
	15 – 20	0.09		15 – 20	-
5	0 – 2	0.54	10	0 – 2	0.82
	2 – 4	0.57		2 – 4	0.61
	4 – 6	0.09		4 – 6	0.31
	6 – 8	0.48		6 – 8	0.12
	8 – 10	0.10		8 – 10	0.66
	10 – 15	0.41		10 – 15	0.94
	15 – 20	0.17		15 – 20	-

A.7 Soil activity of ^{137}Cs in all soils and layers.

Soil activity in dry weight							
Core	Depth cm	Cs-137 Bq/g	% Uncertainty	Core	Depth cm	Cs-137 Bq/g	% Uncertainty
1	0 – 2	27.36	0.47	6	0 – 2	120.28	0.22
	2 – 4	63.59	0.29		2 – 4	9.13	0.70
	4 – 6	6.23	0.88		4 – 6	1.17	1.73
	6 – 8	6.75	1.22		6 – 8	0.40	2.59
	8 – 10	0.16	3.65		8 – 10	0.28	2.98
	10 – 15	0.08	4.38		10 – 15	0.18	3.57
	15 – 20	<LD	4.65		15 – 20	0.13	3.82
2	0 – 2	-	-	7	0 – 2	83.12	0.26
	2 – 4	42.21	0.47		2 – 4	21.38	0.46
	4 – 6	28.04	0.56		4 – 6	4.9	1.05
	6 – 8	7.78	0.91		6 – 8	1.39	1.73
	8 – 10	2.06	1.80		8 – 10	0.71	2.29
	10 – 15	0.43	2.90		10 – 15	0.43	2.75
	15 – 20	0.18	3.58		15 – 20	0.14	3.76
3	0 – 2	3.56	1.21	8	0 – 2	15.52	0.60
	2 – 4	2.05	1.41		2 – 4	2.8	1.22
	4 – 6	1.95	1.46		4 – 6	0.74	2.15
	6 – 8	0.91	1.87		6 – 8	0.45	2.62
	8 – 10	1.14	1.74		8 – 10	0.39	2.74
	10 – 15	2.9	1.12		10 – 15	0.34	2.75
	15 – 20	0.26	3.04		15 – 20	0.30	3.00
4	0 – 2	52.3	0.25	9	0 – 2	21.85	0.57
	2 – 4	13.14	0.51		2 – 4	6.7	0.86
	4 – 6	3.53	1.02		4 – 6	2.94	1.24
	6 – 8	0.70	2.08		6 – 8	1.88	1.47
	8 – 10	1.01	1.76		8 – 10	1.95	1.47
	10 – 15	0.34	2.87		10 – 15	1.20	1.79
	15 – 20	92.46	0.22		15 – 20	<LD	5.22
5	0 – 2	65.45	0.30	10	0 – 2	14.33	0.66
	2 – 4	6.55	0.77		2 – 4	11.49	0.61
	4 – 6	3.73	1.05		4 – 6	7.76	0.77
	6 – 8	1.9	1.41		6 – 8	2.43	1.23
	8 – 10	1.58	1.53		8 – 10	0.69	2.20
	10 – 15	0.76	2.16		10 – 15	0.11	3.90
	15 – 20	0.38	2.81		15 – 20	-	-

A.8 Total Pu samples, adjusted for pollution of ^{238}Pu

ID	Bq/unit 238Pu	Bq/kg dry weight 238Pu	% uncertainty	Bq/unit 239,240Pu	Bq/kg dry weight 239,240Pu	%uncertainty
C1	0.09	39.91	4.92	0.16	20.47	4.36
B4	0.02	6.79	5.24	0.01	26.96	8.02
B6	0.15	95.62	3.04	0.30	200.11	2.39
B9	0.05	17.86	3.79	0.06	3.55	3.57
B10	0.04	13.67	4.39	0.05	75.55	4.11

A.9 U LIII XANES profiles of U standards and particle from soil 1