

## Radionuclides from Chernobyl hot particles in the environment of North-Eastern Poland – A leaching experiment

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**Abstract.** The north-eastern Poland is the area where fallout of Chernobyl "fuel-like hot-particles" occurred. Experiment on the leaching out of radionuclides from forest litter was performed. Five samples were subsequently leached out by: a weak hydrochloric acid (fulvic acid fraction), ammonia water (humic acid fraction) and 2 M HCl (soluble fraction). Residue was analysed as well, after full mineralisation. Results on total activities and its distribution between fractions obtained for:  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{239+240}\text{Pu}$ ,  $^{238}\text{Pu}$  and  $^{241}\text{Am}$  are presented. Relatively high activities of plutonium were observed in humic acid fractions. This finding support suggestions by other authors on possible complexing of Pu by humic acid.

### 1. INTRODUCTION

A fallout of small „fuel-like hot particles” (HP) from initial Chernobyl plume was found in the farthest north-eastern Poland [1-3]. The fallout density, calculated from observed plutonium activity, gave approximately 2500 HPs per square meter [4], if the particle size was assumed to be equal to 4.4  $\mu\text{m}$  [5,6]. Those particles should be rather classified as “explosion origin” [7] particles. As treated by high temperature the radionuclides within the HP were initially most likely in an insoluble forms. Then, after many years of a decomposition (corrosion) in environmental conditions radionuclides from HPs might be leached out and might go to different chemical forms. Pu, Am or Cm could be bio-available or more general speaking leachable mostly if they are complexed by humic or fulvic acids [8-11]. To prove this feature present experiment was performed. Fulvic acid [12] is a mixture of colloids from soil solution, which are soluble at both acid and basic conditions and it could be filtrated through 0.45  $\mu\text{m}$  pore diameter filters. Humic acid [12] is also a mixture of soil solution colloids. Although it is soluble at basic conditions, it precipitates in weak acids. It also could be filtrated through 0.45  $\mu\text{m}$  pore diameter filters.

### 2. MATERIAL AND METHOD

During the Summer of 1999 in seven locations of Primeval Forest of Augustów (North-Eastern Poland, approximately 23°20' E, 53°50'N) about 20 samples of forest litter or soil were collected. Initially all the samples were measured using a low-background gamma spectrometer (results were not published yet). Besides the dominating activity of  $^{137}\text{Cs}$ , some traces of  $^{241}\text{Am}$  and  $^{154}\text{Eu}$  were observed there as well. The observation of the latest nuclide confirms the presence of HPs in samples, since it is well known indicator for Chernobyl fuel-like HPs [13,3].

An experiment on the leaching of the nuclides from the samples, among them:  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$ , and  $^{238,239+240}\text{Pu}$  was performed. Five samples originating from two locations were taken for it. Samples were subsequent layers of forest litter about 2 cm thick, collected in old spruce forest (sample 1, two layers) or in young pine wood (sample 2, three layers). Nuclides of interest were also  $^{154}\text{Eu}$  (and other rare earths isotopes, for example  $^{147}\text{Sm}$ ) and uranium as well as thorium isotopes, for comparison.

However, the measurements for the latest nuclides were not finished before the start of the Conference. This will be completed later.

Main steps of the experiment consist a sequential treatment as follow:

1. leaching out by diluted HCl (pH=3.5) and next filtration with 0.7  $\mu\text{m}$  pore diameter membrane filter (fulvic acid fraction),
2. leaching out by diluted  $\text{NH}_4$  (pH=9) and next filtration with 0.7  $\mu\text{m}$  pore diameter membrane filter (humic acid fraction),
3. leaching out by 2 M HCl solution (soluble fraction),
4. final full decomposition (ashing, HF,  $\text{HNO}_3$ , HCl,  $\text{H}_3\text{BO}_3$ ) of remaining sample matrix (refractory fraction).

All the leaching were performed by immersing the powdered and air dried samples within a plastic 1 L bottle containing 700 ml of a given solution. The bottle was shaken for about 10 minutes. For fulvic and humic acids fractions the pH was then adjusted to proper value (3.5 or 9, respectively). The solution was left overnight, always several time shaken during this period. The solution was roughly filtered using a glass fibre filter (Whatman EPM 1000). The filter itself, after drying, was then combined with sample for next steps. Then, in cases of two first fractions (fulvic and humic acids) of all five samples the solutions were purified by a second filtration, using vacuum pump and membrane filters of 0.7  $\mu\text{m}$  pore diameters to remove any possible tiny particles. We used 0.7  $\mu\text{m}$  filters instead of 0.45  $\mu\text{m}$  ones, which should be used accordingly to exact definitions [12]. It was done only due to some practical problems with equipment – we have such filters with practically unlimited area what helped a lot with effective filtration. Each liquid fraction was then evaporated (some nitric acid was added during this to do an initial mineralization). Dry material was then measured on low-background gamma spectrometer with HPGe detector (Silena Ltd).

For first three liquid fractions the procedure consist of the treatment with hot  $\text{HClO}_4$ ,  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ . The refractory fraction samples were ashed in 450°C. For a sub-sample of about 10 g of ash of each one original sample a typical mineralisation procedure [14] was applied next. Tracers ( $^{236}\text{Pu}$ ,  $^{232}\text{U}$ ,  $^{243}\text{Am}$ ,  $^{148}\text{Gd}$ ) were added in all cases prior to the wet mineralisation. Added activities were below 10 mBq per sample for each tracer, except for Gd isotope for which it was 21.7 mBq/sample. Radiological purity of each tracer was tested. A combined radiochemical procedure was available for the subsequent determination of all examined nuclides. The separation order was: Cs before any radiochemistry, Th and Pu, Sr, U, rare earths and Am - Cm. Plutonium and thorium were separated after the adjustment of the Pu oxidation step [14] using DOWEX-1 anion exchange pressurised columns [4] when the samples were dissolved in 8 M  $\text{HNO}_3$ . Strontium was separated just from 8 M  $\text{HNO}_3$  effluent using Sr-resin produced by Eichrom Ltd., and the polyethylene columns long for 9 cm and having 7 mm of inner diameter. The recovery was only assumed on the basis of the tests using blanks spiked with  $^{90}\text{Sr}$  (the average recovery was then assumed equal to  $80 \pm 10\%$ ). Uranium was separated in effluent of Sr-resin column after coprecipitation of hydroxides at pH =9. The precipitate was centrifuged, dissolved in concentrate HCl, converted to 9 M HCl and passed through the free-flow DOWEX-1 anion exchange column, 12 cm high with 7 mm inner diameter. Uranium was then stripped off using 8 M  $\text{HNO}_3$  and then water [15]. From the effluent the rare-earths and Am - Cm isotopes were separated using a typical procedure [16] only very slightly modified, as it was described in a previous article [17]. All alpha spectrometric sources were prepared using NdF<sub>3</sub> method [18,14], and measured on Silena AlphaQuattro spectrometer with Canberra PIPS detectors. The  $^{90}\text{Sr}$  was measured using liquid scintillation spectrometer Wallac Gurdian 1414-003 with Hi-Safe 3 cocktail and plastic, diffuse type vessels. The total activity of samples was calculated by summing up the activities of given nuclide in all four fractions.

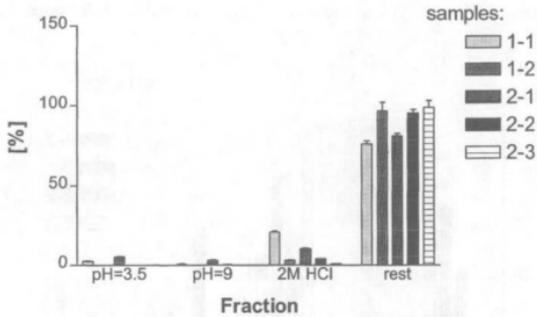
### 3. RESULTS AND CONCLUSIONS

At present stage the results for  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{238, 239+240}\text{Pu}$ , and initial for  $^{241}\text{Am}$  are available. The results on total activity of all those radionuclides (and for  $^{134}\text{Cs}$ ) are presented in Table 1. Observed activities do not differ much from the typical values found on this area before [3,4,16,19]. This confirms the previous

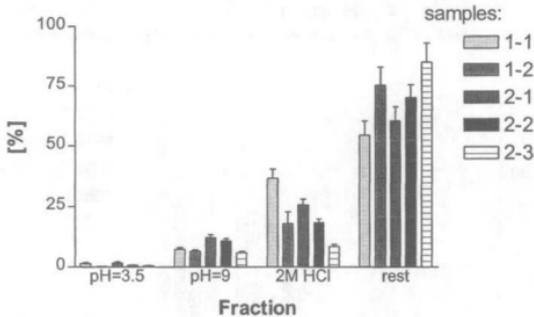
suggestions on quasi-homogenous deposition of small hot particles [3] fallout on this area. Results on leaching experiment for  $^{137}\text{Cs}$ ,  $^{239+240}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$  are presented in Figs. 1-5, respectively.

**Table 1** : Results on the total activity determined for samples at site 1 (two layers) and site 2 (tree layers), activities are corrected for decay for sampling date (1.08.1999). Uncertainties are 1 $\sigma$ , counting only.

Activity [Bq/kg]	1-1 (0-2 cm)	1-2 (2-4 cm)	2-1 (0-2cm)	2-2 (2-4 cm)	2-3 (4-6 cm)
$^{137}\text{Cs}$	172 $\pm$ 4	123 $\pm$ 6	229 $\pm$ 6	316 $\pm$ 6	197 $\pm$ 9
$^{134}\text{Cs}$	0.8 $\pm$ 0.4	1.0 $\pm$ 0.2	0.7 $\pm$ 0.3	2.1 $\pm$ 0.2	1.4 $\pm$ 0.2
$^{239+240}\text{Pu}$	0.30 $\pm$ 0.02	0.83 $\pm$ 0.06	0.31 $\pm$ 0.02	1.22 $\pm$ 0.06	1.03 $\pm$ 0.06
$^{238}\text{Pu}$	0.11 $\pm$ 0.01	0.21 $\pm$ 0.01	0.12 $\pm$ 0.1	0.42 $\pm$ 0.02	0.31 $\pm$ 0.02
$^{90}\text{Sr}$	24.7 $\pm$ 0.5	9.9 $\pm$ 0.4	10.5 $\pm$ 0.4	32.3 $\pm$ 0.4	15.2 $\pm$ 0.4
$^{241}\text{Am}$	0.87 $\pm$ 0.20	0.46 $\pm$ 0.04	1.04 $\pm$ 0.09	1.09 $\pm$ 0.07	0.76 $\pm$ 0.29



**Figure 1** : Percentage of the total activity of  $^{137}\text{Cs}$  observed in given sample and for given chemical fraction



**Figure 2** : Percentage of the total activity of  $^{239+240}\text{Pu}$  observed in given sample and for given chemical fraction.

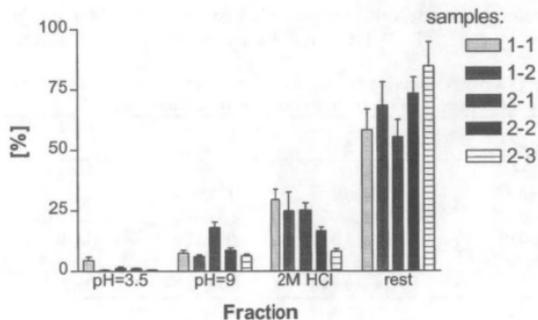


Figure3 : Percentage of the total activity of  $^{238}\text{Pu}$  observed in given sample and for given chemical fraction.

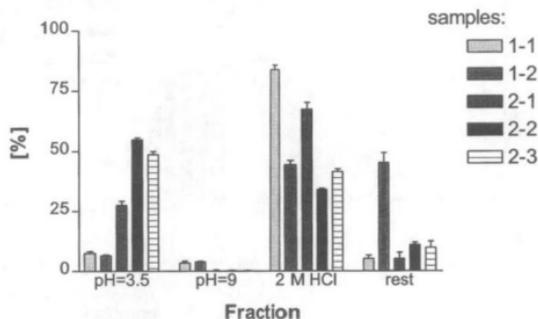


Figure 4 : Percentage of the total activity of  $^{90}\text{Sr}$  observed in given sample and for given chemical fraction.

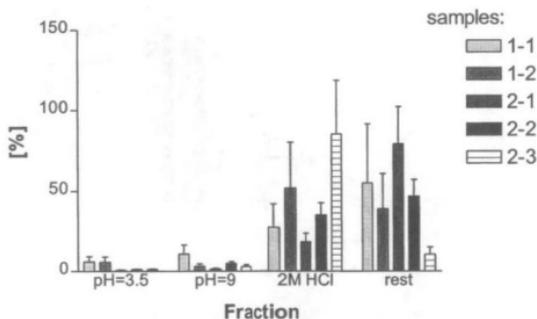


Figure 5 : Percentage of the total activity of  $^{241}\text{Am}$  observed in given sample and for given chemical fraction.

An important differences between the radionuclides behaviour might be noticed. Almost all radiocesium was not leached off the samples with any used liquids, whereas for example  $^{90}\text{Sr}$  seems to be relatively easy leachable in weak or stronger acid conditions. Cs and Pu from upper layers seems to be more a little bit more easy leachable in 2 M HCl while compare it to that from deeper layers. However, the most interesting feature is relatively high activity of plutonium isotopes in humic acid fractions, i.e. in basic conditions, at pH such high as equal to 9. Although a little to large pore diameter filters were used, which might allow some of tin particles to go through it, the lack of other nuclides (especially Sr, Cs) excludes this explanation. It rather suggests complexing by humic acid as the only reason of plutonium presence. This results strongly supports some earlier results by other authors [8-11] on the possibility of a humic acid complexation of plutonium, (but not the fulvic acid complexation) which then might be sometimes (in basic conditions) far more mobile in the environment then it was classically assumed.

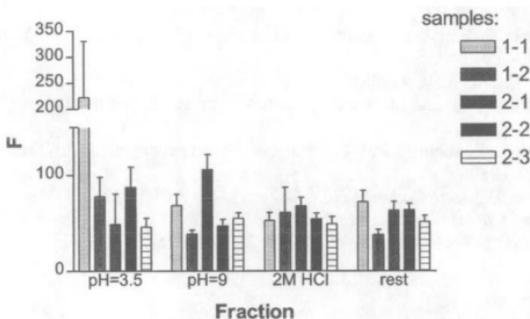


Figure 6 : Chernobyl fraction F of plutonium (calculated from the simple formula given in the previous article [4]) observed in different chemical fraction of samples.

In Fig. 6 the Chernobyl fraction of plutonium calculated on the basis of  $^{238}\text{Pu}$  to  $^{239+240}\text{Pu}$  activity ration analyses [4] is presented. As one could expect, Chernobyl plutonium is relatively a little more abundant in surface layers than in deeper ones. However, from figures 2 and 3 it seems that Pu from upper layers seems to be more easy leachable than from deeper ones. This might suggests, that Chernobyl plutonium is a little more easier leachable than the global fallout one.

### Acknowledgements

The author is grateful to Polish Science Committee for Scientific Researches for the financial support of the investigations and his participation to the Conference within a grant No 6P04G07520.

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