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An investigation of the biogeochemistry of the uranium radionuclide in the munitions testing contaminated soil of Kirkcudbright, New Galloway, SW Scotland

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Abstract The understanding of the bio-geochemical behavior of the uranium radionuclides in the environmental matrices is crucial for the health safety point of view. The research was carried out in munitions testing sites New Golloway (SW) of Scotland at the Dunderann firing range which is contaminated with depleted uranium and site is particularly important because it provides a controlled environment for the investigation of post depositional association of Depleted Uranium (DU) in contaminated soils. This study used the modified BCR sequential extraction method to investigates the association of DU in at the different sampling location and in a control soil and were followed by elemental analysis using inductively coupled-optical Emission spectroscopy (ICP-OES).The Certified Reference Material (CRM) were used for the validation of the concentration. The concentrations of (Bureau of Reference) BCR-extracted Uranium (U) were in the range of 4–40 (±13.2) mg kg^{-1} for the DU-contaminated sites whilst U was barely detectable in the soil from the control site (Rebury Gun) RGW. With the exception of RGH and RGW, the values for BCR-extracted U compared well with those obtained using Aqaua-regia. The obtained result showed that the maximum Uranium deposition is at RGE and it is 20 mg kg^{-1} before hitting the target, the 6 mg kg^{-1} at RGH and minimum is at RGG and RGW control site.

Keywords Dunderann · Depleted Uranium · BCR · ICP-OES · Association · CRM

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Introduction

The metal speciation and partitioning of depleted uranium (DU) is rather a difficult task due to the association of various factors which influences its presence in the soil sediment. So a very careful and detailed study is needed. The presence of depleted uranium in the sediment has the tremendous impacts on the ecological system and causes health hazards. For the laboratory analysis purpose one of the best available improved Bureau of Reference (BCR), France approved "sequential extraction method"(four-steps) has been used and the laboratory analysis is carried out in a very controlled environment [1]. The explosion dynamics and behavior of the munitions like dispersion rate and the retention time of the particulate in the ambient environment and its settling dynamics is a significant factor which is considered in this research work as well [2, 3].

Depleted uranium uses in munitions sources like medical use, power generation and its health hazards is being introduced in this research and its production as contaminants from the other possible sources is also considered in for the investigation in the study site [4].

The historical and geological aspects of particular sites could be possible factors for the presence of the level of contamination of the depleted uranium so it is of worth consideration [5]. From the 1960 to about 1995, depleted uranium (DU) weapons have been tested at several locations in the UK. This has resulted in the contamination of

soil around the firing sites. Although DU is released to the environment in the form of metal oxides, biogeochemical weathering affects the post depositional weathering and associations and mobility of DU. The studied test sites however are particularly important because they provide a controlled environment for the investigation of post depositional association of DU and its biogeochemical behavior in contaminated soils.

The assessment task depends upon many factors like the microclimate and the surrounding characteristics apart from the chemical speciation. In this research mainly speciation has been conducted and the possible behavior of Uranium is being assessed.

Experimental

Study site and sampling location

The natural occurrence of uranium oxide could be contradicts with the anthropogenic contamination in association with Depleted Uranium, the other trace metal is also investigated and the possible impact of this metal on the fate of transportation of uranium compounds and the contamination behavior is studied [2]. The careful selection of sites and planning (Figs. 1, 2) is an important issue for the investigation purpose, because the traces of uranium could possibly retains in soils in very complex ionic or molecular forms.

Kircudbright, Dunderann has a very considerable surroundings for the study of possible input of depleted uranium and its biogeochemical influences due to physiographic factors like seashore, mountainous ranges having tremendous geological changes in the past, scarcely cultivated area,

Fig. 1 The study site

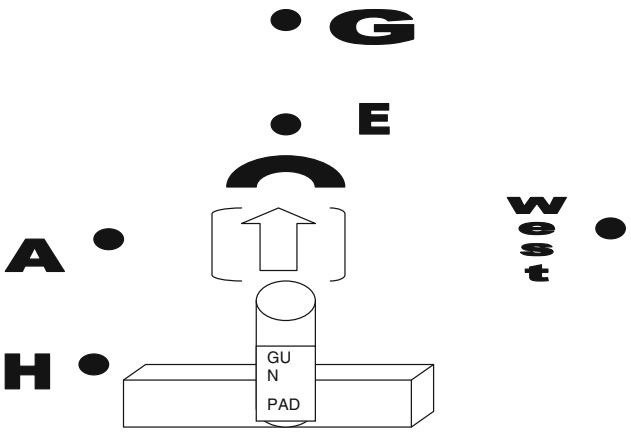

Fig. 2 The schematic sampling location

Fig. 3 The munition testing sites "Target Turns In rubbles"

industrial towns having power plant emissions and effluents directly discharging into the water bodies and in ambient environment, temperate climate with moderate rainfall helping in the particle settling on the grounds. The sampling point were designated around the firing pad at varied distances in all the direction and the controlled RGW was in the upwind of the Raebery Gun Pad (Fig. 3).

Methodology

The soil sample were collected from the study sites and processed in laboratory as per the BCR protocol and finally metal concentration was measured by using ICP-OES. All the four step (reducible, ox disable, exchangeable and residual) generated elemental concentration data is summarized in result section The residual forms in aqua-regia digestion is the modified BCR method which is an additional step in this work [1]. Along with Uranium the other seven metal of alkaline groups Al, Ca,Cu, Fe, Mg, Pb and Zn were also analysed and the concentration detection limit

of the ICP-OES for Cu and Fe 100–200 ppt (parts per trillion), for Mg, Ca, Al, and Zn 100 ppt for Pb 50–100 ppt and for Uranium (U) less than 10 ppt.

The sample were taken in triplicate for avoiding the measurement error from the designated sampling location (Fig. 2 and Table 1). Among these five sampling location RGW was taken as control sites. The certified reference materials (CRM) was used for the validation and cross checking of the generated data (Fig. 4). The extraction were conducted using the regents in subsequent stages (0.11 M acetic acid, 0. 1 M hydroxylamine hydrochloride, 100 volume hydrogen peroxide/1 M ammonium acetate and aqua regia (3:1 11:8 M HCl/16 M/HNO_3) and were followed by elemental analysis using inductively coupled-optical Emission spectroscopy (ICP-OES) [1, 6]. After centrifugation at 6000 rpm for 10 min, the solution was ready for analysis. The obtained concentration was finally compared to the reference soil concentration for all these elements (Fig. 4).

Formula used in the calculation of cumulative or total concentration

Total concentration = Mass × Volume × Dilution factor.

Average concentration = (RGW1 + RGW2 + RGW3)/3.

Similarly all steps and finally = 1st step + 2nd step + 3rd step + 4th step.

Results

The obtained results step wise after the performance of BCR is summarized in the (Tables 2, 3, 4, 5) along with standard error in measurement.

Discussion

The total concentration of extracted U were in the range 4–40 (SD ± 13.2) mg kg^{-1} at the DU-contaminated sites whilst U was barely detectable in the soil from the control site, RGW. With the exception of RGH and RGW, the values for BCR-extracted U compared well with those obtained using Aqua-regia digestion (Figs. 4, 5) As figure shows (Fig. 5) the measured concentration of uranium was

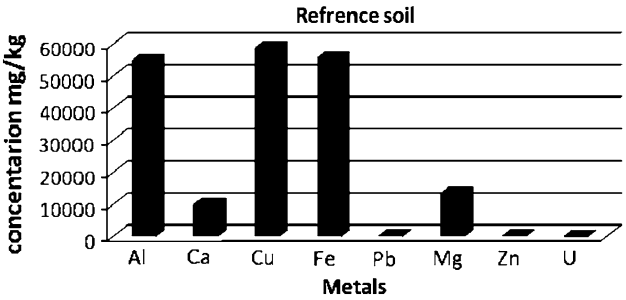

Fig. 4 Reference soil metals concentration

same at the two sampling point RGW, and RGG (Target point). RGE, projectile pathway or the firing base received high contaminants and concentration was maximum 20 mg kg^{-1}. It could be because of just after the explosion the smokes cloud laden with particulate or aerosol's of uranium oxides is get settled over on the way and ligands formation with the iron oxide is evident, or its ions present in the soil is became obvious and playing significant role in the accumulation of the DU in the soil surface the presence of Iron was significant over there and was 15000 (SD ± 17671) mg kg^{-1} (Fig. 6). The concentration of DU was higher than the certified reference material (CRM) reference soil which was 13 mg kg^{-1} (Fig. 4).The transport of the depleted uranium was in the form of oxide which was deeply associated with the others metal ions particularly Fe^{++} (Figs. 4, 5) [7]. The prescribed or studied site does not have the history of the presence of uranium before the 1980 more than 3 mg kg^{-1} but after the munitions testing and shell explosion which started contributing the uranium in soil [2, 5]. As the result is shown in (Fig. 5), its concentration was over the prescribed limit. However in the soil it is satisfactory to be the concentration 3–11 mg kg^{-1} but the obtained concentration was almost twice the limit which means the area has got the high contamination by the presence of armour dust and the explosive over a period of time. The researches shows that the uranium is enriched in the soil, mainly in the residual form and there was a very trace or negligible amount which was present in the exchangeable forms (Table 3) or in others forms which means it is more likely to be traced out from the aqua-regia digestion [5].The natural presence of uranium being supported by the geological history of the

Table 1 Sampling location

Sampling site	Label	Grid reference	Description
Raebury Gun A	RGA	54°46′27.3″N, 004°00′51.9″W	15 m south of firing pad
Raebery Gun E	RGE	54°46′27.3″N, 004°00′51.9″W	18 m south of firing pad
Raebery Gun G	RGG	54°46′27.3″N, 004°00′51.9″W	35 m south of firing pad
Raebery Gun H	RGH	54°46′27.3″N, 004°00′51.9″W	3 m east of firing pad
Raebery Gun West	RGW	54°46′27.9″N, 004°00′54.1″W	Control site upwind (west)

Table 2 Step 1 (the reducible form metal concentration)

Sampling site	Metal concentration measured in (mg kg^{-1})							
	Al (SD ± 21.65[a])	Ca (SD ± 19260.6)	Cu (SD ± 39.22)	Fe (SD ± 6244.9)	Mg (SD ± 462.5)	Pb (SD ± 70.04)	Zn (SD ± 2064.13)	U (SD ± 13.58)
RGW	7.47E+01	3.03E+01	9.17E+01	1.400E+01	74.58E+01	9.49E+01	32E−04	4.5E−01
RGH	2.51E+01	4709E+01	8.00E+01	2.932E+01	91.70E+01	24.00E+01	480E+01	3.05E+01
RGE	6.67E+01	696E+01	11.00E+01	1.067E+01	192E+01	9.00E+01	35.00E+01	3.80E−01
RGG	7.43E+01	549E+01	11.00E+01	6.91E+01	136E+01	11.00E+01	32.45E+01	1.00E−04
RGA	7.57E+01	521E+01	1.50E+01	3.47E+01	104E+01	6.00E+01	11.00E+01	16E+01

SD Standard deviation

Table 3 Step 2 exchangeable form (Hydroxylamine)

Sampling site	Metal concentration measured in (mg kg^{-1})							
	Al (SD ± 335.21)	Ca (SD ± 9753)	Cu (SD ± 32.8)	Fe (SD ± 3276.7)	Mg (SD ± 2700.4)	Pb (SD ± 26.25)	Zn (SD ± 53.66)	U (SD ± 0.19)
RGW	1.81E+01	1.026 E+01	7.86E+01	20.28E+01	351E+01	2.75E+01	23E−04	1.9E−04
RGH	31E+01	3.565E+01	6.89E+01	742E+01	936E+01	7.16E+01	4.78E−06	1.3E−02
RGE	78E+01	1.760E+01	7.93E+01	8.06E+01	299E+01	2.15E+01	19E−04	2.5E−04
RGG	86E+01	1.544E+01	6.57E+01	3.09E+01	331E+01	2.24E+01	10E−04	2.7E−03
RGA	90E+01	1.549E+01	8.3E−01	6.35E+01	356E+01	4.00E−03	12E+01	3.91E−01

Table 4 Step 3 per-oxide (in oxi-disable form the metal concentration)

Sampling site	Metal concentration in (mg kg^{-1})							
	Al (SD ± 16347)	Ca (SD ± 3848.6)	Cu (SD ± 130.8)	Fe (SD ± 9174)	Mg (SD ± 3606)	Pb (SD ± 147.4)	Zn (SD ± 296.56)	U (SD ± 83.40)
RGW	8.73E+01	82E+01	16E+01	4.36E+01	6.28 E+01	4E+01	48E+01	3E+01
RGH	4.18E+01	977E+01	46E+01	6.14E+01	1,291.61E+01	39E+01	81E+01	2E+01
RGE	5.88E+01	139E+01	20E+01	2,06E+01	637E+01	5E+01	51E-04	20E+01
RGG	8.14E+01	126E+01	23E+01	2.57E+01	614E+01	6E+01	53E+01	1.00E+01
RGA	2.320E+01	124E+01	13E+01	2.120E+01	858E+01	14E+01	33E+01	5.00E−01

Table 5 Step-4 residual stage aqua-regia digestion

Sampling site	Metal concentration measured in (mg kg^{-1})							
	Al (SD ± 47447)	Ca (SD ± 2.49E+04)	Cu (SD ± 115681)	Fe (SD ± 51990)	Mg (SD ± 27176)	Pb (SD ± 458)	Zn (SD ± 1142)	U (SD ± 351)
RGW	12.662E+01	96E+01	9.00E+01	9.686 E+01	3.660 E+01	65.00 E+01	13.00 E+01	0.00E+00
RGH	1.1620E+01	7.45E+01	35E+01	4.276 E+01	109E+01	104E+01	265E+01	6.00E−01
RGE	16.842E+01	2.44E+01	19.00E+01	12.419E+01	5.885E+01	115E+01	12E+01	6.00E−01
RGG	14.995E+01	2.26E+01	16.00E+01	11.357E+01	4.874E+01	93.44E+01	14E+01	2.6E−01
RGA	23.617E+01	56.108E+01	25.887E+01	158E+01	7.00E+01	7.46E+00	3.80E−01	7.871E−01

area as it faces a lot of geological evolution of the rock and soil so the traces would be intact historical and earlier ages (Fig. 7).

Regarding the major sources the nearby Sellafield nuclear power plant which effluents is highly laden with radioactive substances is dumped in the nearby Irish sea is the another additional factors apart from the munitions testing and even after practicing safe disposal system the scenario is same as it is not functioning well and one can easily see the effluents carrying pipe is being leaked in the

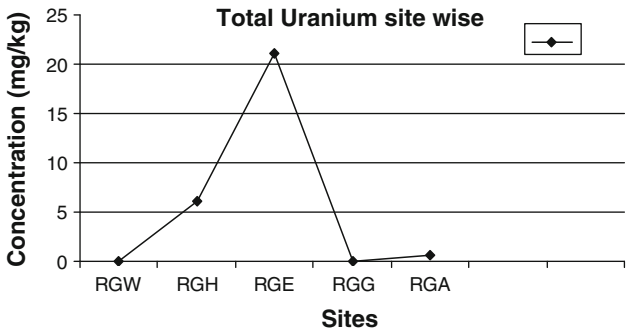

Fig. 5 Uranium concentration variation profile at the planned sampling site

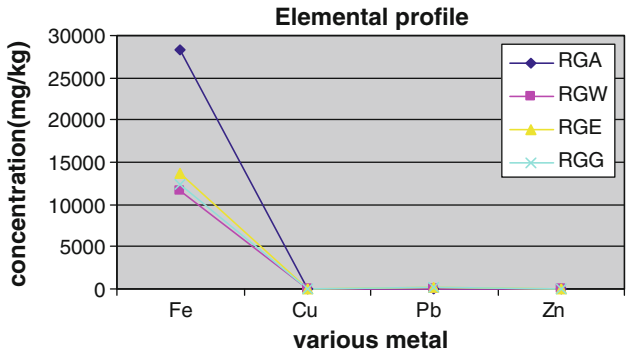

Fig. 6 Alkaline metals concentration profile along with planned sampling location

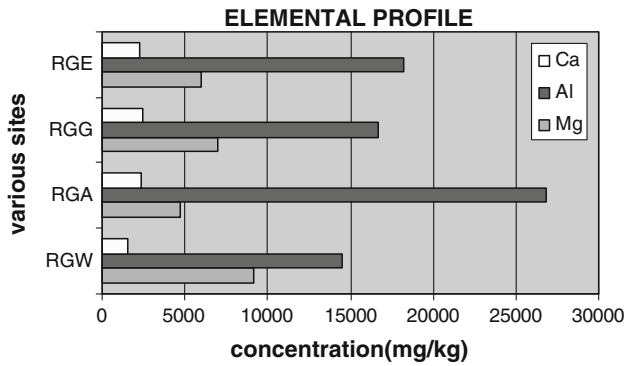

Fig. 7 Alkaline metals concentration profile site wise

Irish sea and contributing the radionuclides to the nearby shore (Fig. 8). The transportation by the tremendous present of the other alkaline metals ions exchangeable and oxidisable form (Tables 4, 5) at the site RGW, particularly Fe^{++} was in tremendous amount (Fig. 6) which support the mobility of the Uranium ions through the formation of ligands, and that part was quite near to the sea shore and opposite in the wind flow direction (Fig. 2). In the vicinity of the gun platform RGA and RGH (Figs. 1, 2) the concentration remained intact i.e. it was same as before.

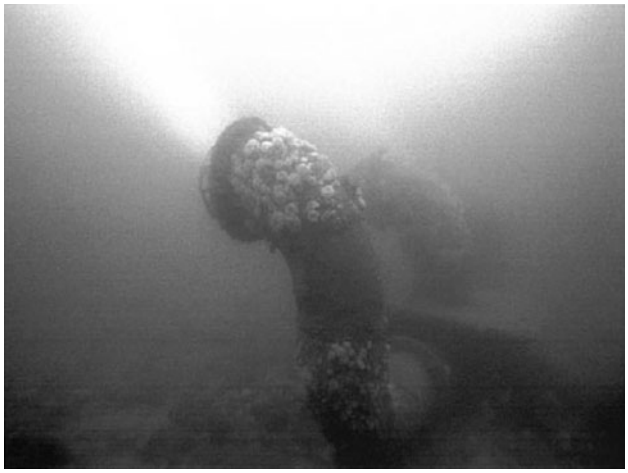

Fig. 8 Leaked effluents carrying pipe

Therefore, in case of DU which presence was in such a quantity which could affect the surrounding advertently and causes health hazard if the proper mitigation and the remediation measure will not be implemented appropriately.

Previous works showed that the soils close to the Raebery gun pad at the Dunderann firing range, south west Scotland, were contaminated with DU. The result showed that DU was predominantly associated with natural organic matter (NOM) in the contaminated soils (Table 3), whilst in the control sites natural uranium was in the form of resistant minerals (Table 4).

Natural Uranium characteristics, concentration and mobility was also guided by the presence of the other heavy metal, particularly Iron, which was helping in migration of Uranium by complex formation. The climatic factor could be also a responsible factor for the un-uniform distribution of the uranium at the different sampling point in the area. The biogeochemical phenomenon was clearly indicative of the DU and other heavy metal in the soil sediment and the organic death and decay, bacterial degradation of the sediment was although very low in comparison of heavily cultivated a but it was occurring and affecting the distribution and the accumulation of the DU. The other potential sources cannot be ignored for the contamination such as the effluents discharge in the Irish sea. Further the coastal area could contamination through this sea spray and the other power plant emission in the form of aerosols particle reaching to the sites.

Conclusion

The association of DU at the contaminated sites appeared to be independent of soil p^H (5.3–6.4 ± 0.1) or NOM contents. The observed strong association of DU with

NOM in contrast with presence of natural uranium in much less available form is important as this may lead to short term differences in mobility. In conclusion it is obvious that the contamination potential of heavy metal due to the weapon testing is enormous and has affected the sites severely after the 1980 [5].The concentration of other alkali metals was also raised and testing exercise has a significant contribution.

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