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Phytotechnology – is there a possibility to use it for land reclamation of areas contaminated by Technologically Enhanced Naturally Occurring Radioactive Materials?

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Abstract. Presently, excavation and shipping to a distant waste disposal site is the most commonly used method for handling waste contaminated with radionuclides. Due to international recommendation waste containing enhanced concentration of natural radioactivity should be treated in the same way. In case of TENORMs, which usually occur in huge quantity, this method would be very expensive and can be disruptive to the environment in which the contamination was found as well as direct effects of this pollutant occurrence.

Biological treatment methods, such as phytoextraction or at last phytostabilisation could provide an attractive alternative to the excavation of waste. It is entirely possible that methods successful for heavy metals may be successful for the radioactive elements. Seven-years observation of the a settling pond contaminated with radium isotopes showed that even natural plant transgression into contaminated area can be an effective tool to stabilize pollutants. On the other hand, the assessment of the effectiveness of phytoextraction based on natural plants gave not so promising results.

1. INTRODUCTION

Usually the total amount of TENORM-type *(Technologically Enhanced Naturally Occurring Radioactive Material)* waste collected in one dump reaches hundreds of thousands of cubic meters or tonnes. As a result of the lack of appropriate regulation it has been a common practice to put such kinds of waste into heaps or dumps, without any means of protection. So, exposure to meteorological processes such as a rainfall or a wind can cause an uncontrolled migration contaminated waste into every each compartment of environment. Also, TENORM placed directly into the environment can set some additional chemical or physical processes in motion, leading to the selective transfer and accumulation of particular radionuclides and disequilibrium in decay series of natural radionuclides. These can result in severe disturbance to the surrounding environment.

Content of radioactive elements in TENORM-type waste, expressed in mass unit, is by far less than the noticed concentration of heavy metals in some industrial waste, for which the phytotechnologies were successfully used. Also, the activity concentration of natural radionuclides in TENORM is usually not high enough to classify them as a radioactive waste, so, from formal point of view there is no strong need to carry out technical land reclamation i.e. excavation and shipping to a distant waste disposal site. Such circumstances create conducive situation to apply phytoremediation as phytoextraction or at least phytostabilisation for efficient end effective land reclamation of territories contaminated by TENORM.

2. SITE OF INVESTIGATION

The Upper Silesian Coal Basin (USCB) is located in the southern part of Poland and there had been working up to 65 underground coal mines. Total outflow of waste waters from these mines reached 900 000 m^3/day. Due to their very high salinity (sometimes higher than 200 g/l) they caused severe damages to the natural environment. Additionally, these waters often contained elevated concentrations

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of radium isotopes ^{226}Ra, ^{228}Ra as well as barium and other metals [1]. In hard coal exploitation process a settling ponds were applied to allow mechanical suspensions, carried out by underground brines, to settle before discharging into inland waters. For this purpose also some natural lakes or fishing ponds had been adapted.

For the exemplary observation the former natural fishing pond that had been adapted as a settling pond was chosen. The pond is situated at Upper Silesia, Poland, at the territory of commune Bojszowy. The area of the pond is 16 hectares. The pond had been exploited for over 20 years. During this period more than 240 000 m^3 of suspended material was deposited in it. In 2002 the discharge of water to the pond was stopped. The pond was abandoned and dried. The thickness of the sediment layer usually does not exceed 1 meter. The average activity concentration of the both radium isotopes (^{226}Ra $+^{228}$ Ra) in these sediments is slightly above 1000 Bq kg^{-1}. The maximum observed radium activity concentration in the sediment reaches 15 000 Bq kg^{-1}. The total activity of ^{226}Ra and ^{228}Ra had been collected in the pond was evaluated in 2000 as 66 GBq and 100 GBq respectively [2].

Since the sediments became more or less dried the settling pond was under observation. Up to 2007 no efforts to start any intended land reclamation were done. Only the process of transgression of plants into the area of the pond was initiated in natural way. The vegetation transgression commenced in spring 2003, starting from the dried places where the salt water from the subsurface layer was either washed out or diluted by precipitation. During three seasons of observation the overgrown area has visibly increased. The first observed plant species, occurring as an irregular clusters of vegetation were *Atriplex hastatum*, *Puccinellia distans*, *Spergularia salina* (three species typical for salinated soil), and *Chenopodium glaucum* and *Polygonum aviculare* [3]. In 2007 almost all surface of the former bottom of the pond was overgrown by plants.

The huge amount of sediments containing enhanced radium activity concentration collected at the bottom of the pond is an effective source of external radiation. Besides the exposure to external radiation the main pathway of radiation risk on the territory of this pond and its neighborhood are the resuspension of contaminated dust, radionuclides migration and possible biota contamination. The resuspension is especially important due to the fact that the radionuclide activity concentrations are inversely proportional to the dust particle diameter.

In this work possibilities of the use of the following phytotechnologies were evaluated:

- phytostabilisation
- phytoextraction
- phytodilution.

3. MATERIALS AND METHODS

In order to assess the radiation risk and the homogeneity of the contamination's distribution the ambient dose equivalent (H*(10)) was measured 1 meter above the top of the sediment layer. Measurement were carried out using the portable gamma spectrometer "InSpector 1000" with $3'' \times 3''$ scintillating (NaI(TI)) probe calibrated according to ISO 17025 requirements. Observed variation of H*(10) confirmed that the distribution of contamination did not change significantly in comparison to data collected in 2001, before draining the pond. The measured values were in range 0.4–1.1 for the significant proportion of the pond but some "hot spots" were observed where the ambient dose equivalent reached 3.5 μSv/h. Based on these results the sampling points of plants and sediment were chosen.

In the vegetation season 2007 the inventory of the vegetation transgressing to the pond territory was carried out. 45 plant species were observed and identified. The individual plant samples were collected and photos in the natural habitats were taken. Among them the 13 species were dominant: *Calamagrostis epigejos, Phragmites australis, Cirsium vulgare, Matricaria perforate, Cirsium arvense, Tancetum vulgare, Lepidium ruderale, Polygonum aviculare* L., *Tussilago farfara, Artiplex prostrata, Chenopodium glaucum, Senecio vulgaris, Funaria hygrometrica*. Samples of them have been collected. In order to asses the transfer factor (TF) the sediments were sampled respectively.

The variation of radium activity concentration in the sediment creates a good possibility to make an evaluation of the relationship between the TF and radium activity concentration in ground, where plants are growing. So, for two species: *Calamagrostis epigejos* and *Cirsium vulgare* the pairs plant and sediment have been sampled at the points suspected to contain different contamination concentration (based on H*(10) measurement). In both cases 8 pairs of samples were taken. Also, in case of these species of plant there was a possibility to distinguish small areas overgrown uniformly by them. These opportunities were used to take samples in order to assess the efficiency of the process of natural phytoextraction. For each plant the 1 square meter test areas were chosen. All upper parts of plants overgrowing them were collected respectively. The total fresh mass of the each plant sample was measured. Also, the sediment was sampled from these areas using the envelope method.

The radium isotopes' initial activity concentration in sediment samples were measured by high resolution gamma spectrometer equipped with 30% relative efficiency broad energy range germanium detector (BGE) from CANBERRA. Measured samples were crushed into grains with diameter smaller than 2 mm and dried at 105°C up to stable mass. After that, samples were put into 1 litre Marinelli beakers. Spectra were collected for several hours, depending on a sample activity. For the spectra analysis the GENIE 2 K software was applied. The radium isotopes were determined by their progeny after equilibrium had been reached. For ^{226}Ra the following gamma energies were taken into account: 186 keV directly for ^{226}Ra, 295 keV and 351 keV for ^{214}Pb and 609 keV for ^{214}Bi. ^{228}Ra was measured by ^{228}Ac at 338 keV and 911 keV. The minimum detectable activity for all radium isotopes was less than 1 Bq kg^{-1} at a confidence level of 0.05. For spectrometer calibration as reference materials IAEA Gamma Spectrometry Reference Materials were used: RGU-1, for uranium series and RGTh-1 for thorium series.

Radium activity concentrations in plants were measured, according to the same measurement and calibration procedure as in case of samples of sediment but using a well-type HPGe detector (model GCW5021, 50% relative efficiency, CANBERRA) completed with active anticoincidence cover. The samples of plants were washed, dried and then burned at a temperature of 400 °C. The wet, dry mass and mass of obtained ash were measured for each sample. Finally, samples about 1 gram of ash each, were put into 2,5 ml measurement glass vials and measured as above.

4. RESULTS

The average measured activity concentration of radium ^{226}Ra and ^{228}Ra in sediments was 1886 Bq kg^{-1} and 1784 Bq kg^{-1} respectively. The observed range of concentrations was 598–7175 Bq kg^{-1} for ^{226}Ra and 350–6776 Bq kg^{-1} for ^{228}Ra with the medians equal 950 Bq kg^{-1} and 847 Bq kg^{-1} respectively.

The transfer factor was calculated for both radium isotopes according to the following formula:

$$TF = \frac{A_P}{A_S}$$

where A_p and A_s specific mass activities of radium isotopes in ash from plant sample and dry sediment, both expressed in Bq kg^{-1}. Such way of calculating the TF let one exactingly evaluate the transfer of matter form ground to plant avoiding the mistakes related to relative content of water in fresh plants or organic content in dry mass. Obtained in this way TF values are normalized and then can be compared with other values measured for different species of plants.

For both cases of investigated plant species the relationship between the radium isotopes concentrations in sediment and the sediment/plant TF was non-linear (Fig. 1.)

The possibility of phytoextraction was evaluated for two plant species *Cirsium vulgare and Calamagrostis epigejos*. The balance of radium ^{226}Ra in plant and sediment at the tested 1 square-meters areas is presented in Table 1. Radium ^{226}Ra activity concentration extracted during one vegetation season was calculated as a ratio of its total activity in harvested plants and activity enclosed in one cubic

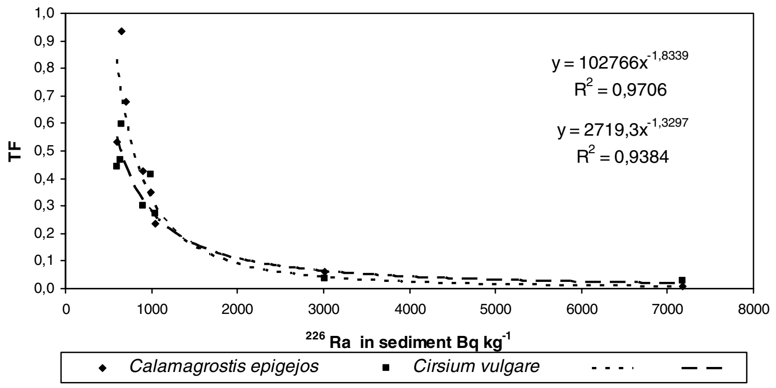

Figure 1. Radium ^{226}Ra sediment/plant TF as a function of ^{226}Ra activity concentration in sediment.

Table 1. The evaluation of the natural phytoextraction efficiency.

	ash content	plant fresh mass	^{226}Ra activity concentration		density of dry sediment	activity concentration extracted during one vegetation season
			ash	*sediment*		
	%	kg	Bq kg^{-1}		kg m^{-3}	%
Cirsium vulgare	6,35	2,25	291	637	800	0,0082
Calamagrostis epigejos	5,88	1,9	477	702	800	0,0095

meter of sediment at the top which the plants had been growing. The uniform distribution of radium in sediments was assumed.

5. DISCUSSION

Despite of in this case contamination is caused by both radium isotopes; ^{226}Ra from uranium series and ^{228}Ra from thorium series, from point of view a long-term effects of contamination crucial role is played only by ^{226}Ra. ^{228}Ra, in this case is an "orphan" radionuclide. In these sediment there are not parent radionuclides supporting it. So, taking into consideration the half-life of radium ^{228}Ra one can expect that radioactive decay can be utilized and after few decades the problem of this contamination will solve itself. In case of radium ^{226}Ra the half-life is long enough to cause severe radiation risk for next generation.

In investigated case the specific activity of radium is in general lower that the limit for radioactive waste (10 kBq/kg), so that there are not needs to apply countermeasures defined for them. Moreover, taking into account the total amount of sediments of concern there are not technical capabilities to undergo them process complying all requirements determined for radioactive waste with reasonable cost. Besides all, excavation of sediment and shipping it to a distant waste disposal site can be disruptive to the environment in which the contamination is found as well as direct effects of this pollutant occurrence.

On the other hand the total activity and related dose rate is high enough to excide the dose limits (1 mSv/year) and in untoward circumstances can cause the detrimental effect on environment. These justify enough necessity of application appropriate countermeasures in order to limit the propagation of contamination as migration with rainfall water or resuspension together with fine particle of dust (phytostabilisation). Also process of extraction of radionuclides by plants can be used to reduce significantly volume of contaminated material need to be shipped-out (phytoextraction) or to create a biomass layer at the surface of contaminated sediment and start the process of soil creation (phytodilution).

Six-year-lasting observation of contaminated area let one notice that the process of natural transgression is so effective and, even without any support, good enough to stop the physical propagation of contamination. The plants overgrowing the pond create a tight cover able to stop water and air land erosion. Finally, even the proper habitats for fauna were established. It supposes that in case of controlled propagation selected species of plant it would be actually effective and cheap method for first approach to immediate land reclamation of contaminated with TENORM areas.

In the light of obtained results the possibility of phytoextraction seems not promising as well as phytostabilisation. The percentage of extracted by plants radium is small. It would take hundreds years to remove the contamination. But one should take into consideration that total amount of extracted radium was calculated in relation to the total amount of radium. Some authors reported that in such waste radium isotopes are immobile. The reported values are at the level by far less than 1% [4, 5]. So, if one take into consideration the phytoextraction of only the mobile part of radium it seems much better. Especially, such process can be efficient as a tool for the creation of a level of biomass, with decreased concentration of radium at the top level of contaminated areas. Such process was observed in other mining spoil banks, where after about 50 years at the top of mining waste heap the 20 to 30-centimetres-thick level of soil was created, where concentration of natural radionuclides was only one forth of initial activity concentration in waste rock [6].

The long-term restorations of ecosystems and contaminated sites have been attributed to natural attenuation processes. The efficiency of this mode of remediation will vary based on the biological and chemical nature of the contaminated site. For example, the impact of an effluent from uranium mine tailing to groundwater could naturally be mitigated if the soil is rich in carbonate or other reducing agents. Another example of a natural attenuation process is seen in aquatic systems, which serve as a medium for the assemblage of algae, bacteria, and phytoplankton [7]. Therefore, in case of other TENORM waste, that are different in chemical composition and where the mobile part of radionuclides is higher, for example sludge from oil industry [7] the application of phytoextraction seems more interesting. On the other hand the observed fact of non-linearity of the relationship of radium TF and radium concentration in ground create some doubts. It should be investigated for other species of plant and explained, probably based on the metabolic processes going on in plants.

6. CONCLUSION

The observation of the abandoned settling pond provide the evidence that even the transgression of wild plants into contaminated sites can be an efficient way to stabilize the contamination and avoid the dispersion of pollutants as dust resuspension. Preliminary measurement of TF and the balance of radionuclides extracted by plants gave very poor hopes about applicability of phytoextraction for land reclamation. But one should remember that the investigation was done on natural process and wild plants. In case of planned phytoremediation the use of fertilizers and plant species with better TF would influence the process efficiency. From economical point of view such approach could by far more effective than each other method of technical land reclamation.

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