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Modelling of the Behavior of Natural Radionuclides and the Environmental Risk in the Sites from the Mining Uranium Ore in Bulgaria

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Abstract. In the article are included some parts of the results of the modelling of the behavior of the natural radionuclides and the risk for the environment for the technogenic soils formed after underground and open uranium ore extraction and zonal soil types in the area of 30 sites in the forests of Bulgaria (Stara Planina massif, Rila-Rhodope massif and Transko Kraishte). The modelling performed is based on the established strong negative linear correlations between the studied radionuclides and the pH. With reducing the acidity with one pH unit – the prognosis is for increasing the content of radionuclides (^{232}Th - section "V shaft" mine, ^{238}U - "Ribaritsa" mine, ^{40}K, ^{232}Th - "Yavorovets" mine, ^{40}K, ^{232}Th, ^{226}Ra, ^{238}U - "Selishte" mine, ^{226}Ra, α-activity - "Zdravetz" mine). The environmental risk is significant due to the stimulation of the processes of weathering and release of pollutants. In conclusion, some good practice examples have been proposed as possibilities for reducing the environmental risk, following the re-cultivation of the "Kurilo" mine - "Iskra" section and the "V shaft" section. The technologies used in the re-cultivation are developed on the basis of the specific activity of ^{226}Ra in the soil. These technologies can be used in sites with a similar activity of ^{226}Ra in the soil.

Key words: model, radionuclides, mining uranium ore.

Introduction

By the 1990s Bulgaria ranks fourth in uranium mining in Europe, when uranium production was closed. Unfortunately, a huge part of the 50 uranium deposits have not been reclaimed in the most appropriate way. Complexity is determined by the specificity of the processes, and it depends on the petrographic and mineral differences, climate conditions, technogenic relief features, long exposure on the Earth's surface, the applied extraction technologies etc. In most of these sites, there is a proven radiological risk to the environment and human health due to the increased activity of natural radionuclides (^{238}U, ^{226}Ra, ^{232}Th, ^{40}K, α- and β-activity). All this points to the necessity for regional assessment of the environmental risk of the formed technogenic soils obtained after the uranium mining.

In recent years, studies of environmental hazards that come from abandoned uranium mines in specific regions of the Balkan Peninsula have been carried out for Bulgaria (Bogoev *et al.*, 2010; Tsekova & Bogoev, 2010; Petrova, 2012; Tsekova & Lozev, 2017) for Serbia (Dragovica *et al.*, 2008; Dragovica *et al.*, 2014; Tanić *et al.*, 2014; Abdulqader *et al.*, 2018), for Turkey (Turhan *et al.*, 2012; Aközcan, 2014; Cengiz, 2017; Turhana *et al.*, 2018) for Croatia

(ŠOŠTARIĆ *et al.*, 2017; PETRINEC *et al.*, 2018; IVANIĆ *et al.*, 2019) and others.

Materal and Methods

The technogenic soils, which are formed after lifting and open extraction of uranium ore and zonal soil types and bottom sludge from adjacent gullies and rivers in the area of the 30 sites in the forests of Bulgaria, were studied. The content of natural radionuclides was determined (^{238}U, ^{226}Ra, ^{232}Th, ^{40}K) in the 157 samples from the Stara Planina massif, in the 92 samples from the Rila-Rhodope massif and in the 38 samples from the Transko Kraishte.

The reaction of the soil solution is defined according to ISO 10390.

Statistics10 and Excel10 were used for Statistical Data Processing and Result Visualization.

Results and Discussion

The main factor, which affects the geochemical reactions associated with radionuclides and explains their mobility in the soil, is the pH. Knowing the relationships between the pH and the contents of major radionuclides is important and it depends on both the technology of uranium mining and on a set of interrelated indicators. This reflects on the assessment of the risk of radioactive contamination of the environment and planned reclamation activities.

The linear model for the object Buhovo - mine "V shaft", which describes the activity of ^{232}Th depending on the pH, is the most accurate between 320 and 930 Bq.kg^{-1}, therefore the forecast coincides with approximately 16% of the data (Fig. 1). From the analysis of the dependencies between the main radionuclides, it can be seen that in the higher contents of ^{232}Th the corresponding content of ^{40}K is lower and vice versa. The ^{232}Th content from the section "west" is lower, so the prediction by the model is increased, except for a sample of 850 Bq.kg^{-1} measured in the established lowest pH 4.2. The forecast covers more precisely the experimentally established values at the section "east" where the content of the radioactive isotope is higher. The exception for the peak values is most likely due to the exported in mining ore nuggets rich(the except for the peak values most likely due to exported in mining ore nuggets rich ^{232}Th.

The established Relationship between the content of ^{232}Th and soil pH is negative (R = -0.40). Therefore, the increase in the acidity results in an increase in the predictive activity of ^{232}Th with 104 Bq.kg^{-1}.

The differences found in the forecasts for both sections (west and east) are the result of differences in the technology, the timing and the duration of uranium mining. The ground relief of the technogenic forms resulting from human activities facilitates the translocation of the radioactive pollutants through the location and the manner of landfilling of mining waste (pic. 1 and pic. 2).

The analysis showed specific differences between the two areas, which again stressed the need for micro-locally study and modelling of the ongoing processes.

These processes are related to the behavior of the natural radionuclides and the environmental risk in the object Buhovo - mine "V shaft" (Photo 1 & 2), which is located in the east-northeast direction about 25 km by air from the central parts of Sofia.

The "Ribaritsa" mine is located near the village Ribaritsa (just over 10 km as the crow flies in the southern direction) to the border of the National Park "Central Balkan". The landfilled mining waste falls within the borders of the site "Tsentralen Balkan bufer" and that includes two protected areas from the European ecological network Natura 2000 (the Habitats Directive BG0001493 Natura 2000 and The Birds Directive BG0002128).

The function that describes the ^{238}U content depending on the soil pH represents the most accurate prediction in the range of 100 to 1100 Bq.kg^{-1} and the experimental data match is about 23% (Fig. 2). The Fig. shows that the samples with higher content of the model radionuclide are in the site No 1. Conversely, the values of site No 2 are lower,

so the model's predictions are too high. The forecast covers more precisely the experimentally established values at the site No 1, except for one peak value (1941 $Bq.kg^{-1}$). This is most likely due to the exported and deposited uranium-rich ore fragments at the sampling site.

The determined negative dependence (R = -0.48) between ^{238}U and the soil pH results in the predicted increase in acidity to reflect on an increase in the predicted levels of ^{238}U with 760 $Bq.kg^{-1}$. This forecast shows a high risk of uranium contamination in the environment.

The study presented significant differences between the two sites due to the various stages of mining waste disposal from uranium mining. The established lower uranium concentrations are the result of ongoing active surface processes of weathering and allowing (without transport) the disaggregation products of weathering in place.

From natural point of view, the knowledge of the behavior of the natural radionuclides contained in the uranium mined waste discharged after is important because of the significance of the territory.

The object "Ribaritsa" also falls into the Central Balkan Biosphere Reserve, and under the Seville strategy these sites are an iconic place, an example of a harmonious co-existence between man and nature and they demonstrate good practices and policies. They are part of the UNESCO World Wide Web Reserve. All this calls for measures to reduce the risk to the environment in the Ribaritsa mine.

Yavorovets mine is located in about 1 km southwest of the village Yavorovets, Maglizh Municipality.

The analysis of site data indicates that the function describing the ^{40}K content in relation to soil pH (R = -0.86) is the most accurate in the range of 190 to 920 $Bq.kg^{-1}$ on the site No 2 content of ^{40}K is higher than the content of ^{40}K on the site No 1 (Fig. 3). The active soil reaction is neutral to slightly alkaline on site No 1, and on site No 2 the pH varies in the acidic range of 4.8 to 5.4, which also determines the higher values of ^{40}K. In general, the model shows that 75% of experimental data are the same as predicted. In this case, the forecast is over 95% correct on site 2.

The predicted acidification of the environment leads to an increase of 195 $Bq.kg^{-1}$. This increase in quantities may be due to the extraction of the radioactive isotope from the sand fraction. The environmental risk is significant as the site is in close proximity to a river.

The modelling of the dependence between the ^{232}Th content and the pH of the environment found the most accurate estimate in the range of 14 to 51 $Bq.kg^{-1}$, and the match to the experimental data is 57%. The determined negative linear regression is represented by the equation: $^{232}Th = 97.797 - 9.8126 \times pH$.

Similarly to the content of ^{40}K and here concentrations of ^{232}Th are on the site No 2 are higher than those on the site No 1. At site No 1, the model's forecast is higher, with the exception of the three samples with a lower forecast, as two of which are in the 0 - 20 cm layer.

The observed negative correlation between ^{232}Th and pH (R = -0.76) predetermines the increase in the predicted ^{232}Th by about 10 $Bq.kg^{-1}$ in acidification of the environment by one pH unit. The environmental risk is similar to the one with ^{40}K.

"Selishte" mine is located in about 2 km south-southeast of the town of Lucky and falls into two protected areas of the Natura 2000 network (BG0002073 Dobrostan under The Birds Directive and the Habitats Directive BG0001031 Rodopi – Sredni).

The analysis of the regression linear model, which describes the content of ^{40}K in relation to pH, exhibited the greatest match in the range of 480 to 950 $Bq.kg^{-1}$ (Fig. 4). The established dependence is negative (R=-0.65). The large variation of the values determines the 42% match of the forecasts with the observed data. Acidification of the environment with one pH

unit results in an estimated increase in the content of the radioactive isotope by about 290 $Bq.kg^{-1}$.

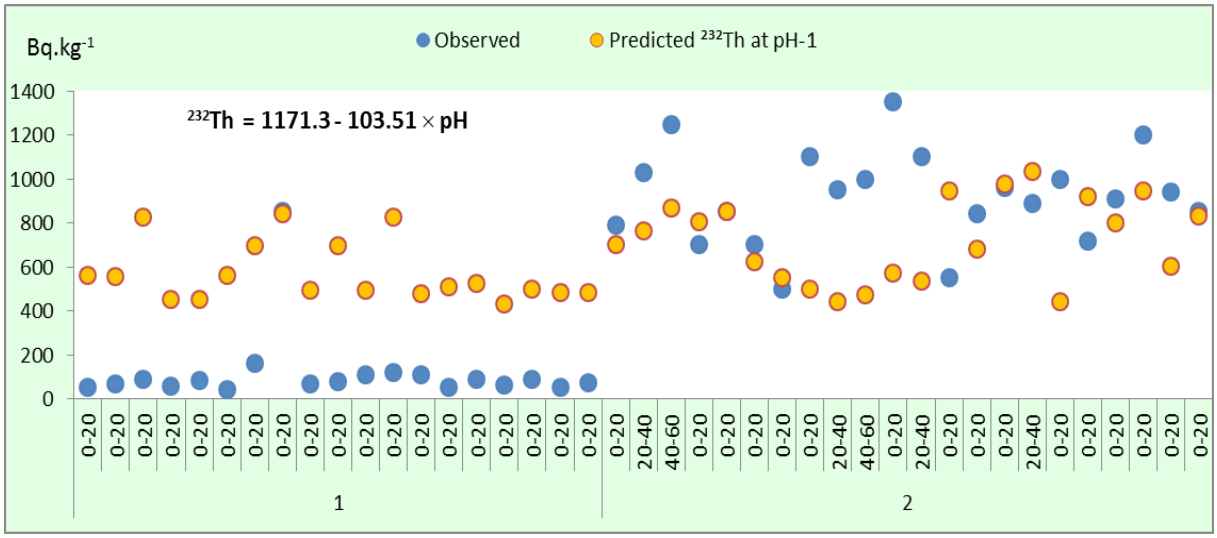

Fig. 1. Modelling the activity of ^{232}Th depending on the soil pH for the object Buhovo (site west – No 1; site east – No 2).

Photo. 1. Object Buhovo - section "V shaft" mine, site west (Photo: Rossitsa Petrova).

Photo 2. Object Buhovo - section "V shaft" mine, site east (Photo: Rossitsa Petrova).

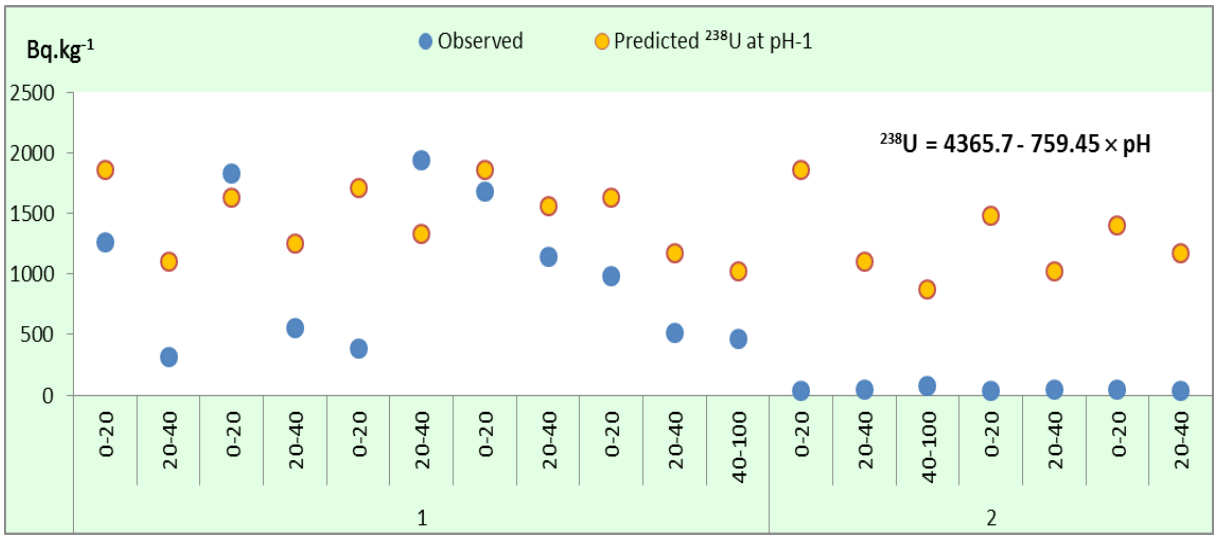

Fig. 2. Modelling the content of ^{238}U depending on the soil pH for the object Ribaritsa (site No 1, site No 2).

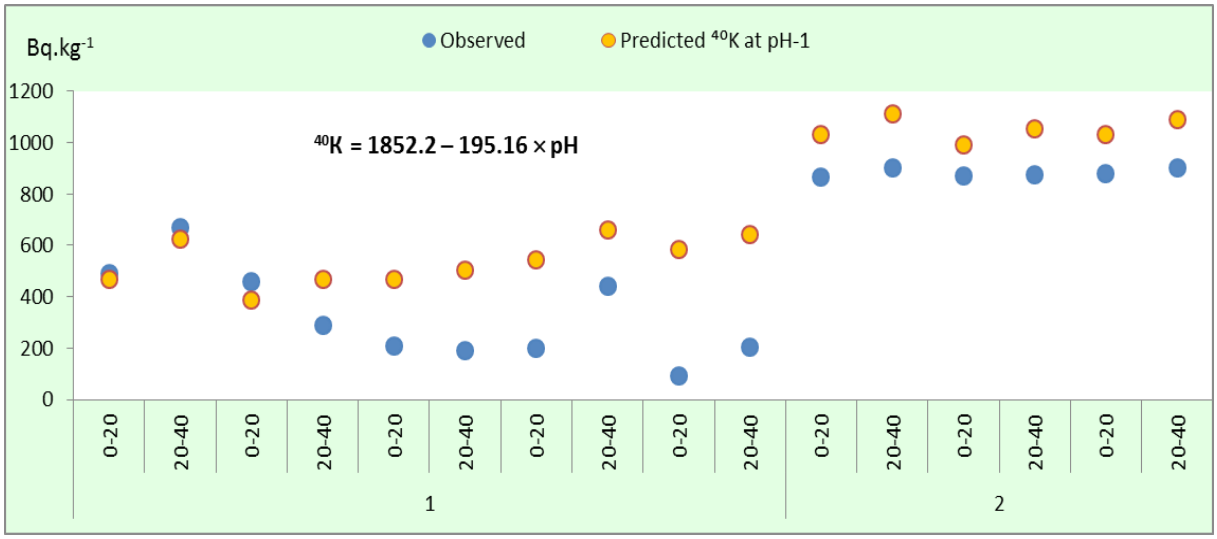

Fig. 3. Modelling the content of ^{40}K depending on the soil pH for the object Yavorovets (site No 1, site No 2).

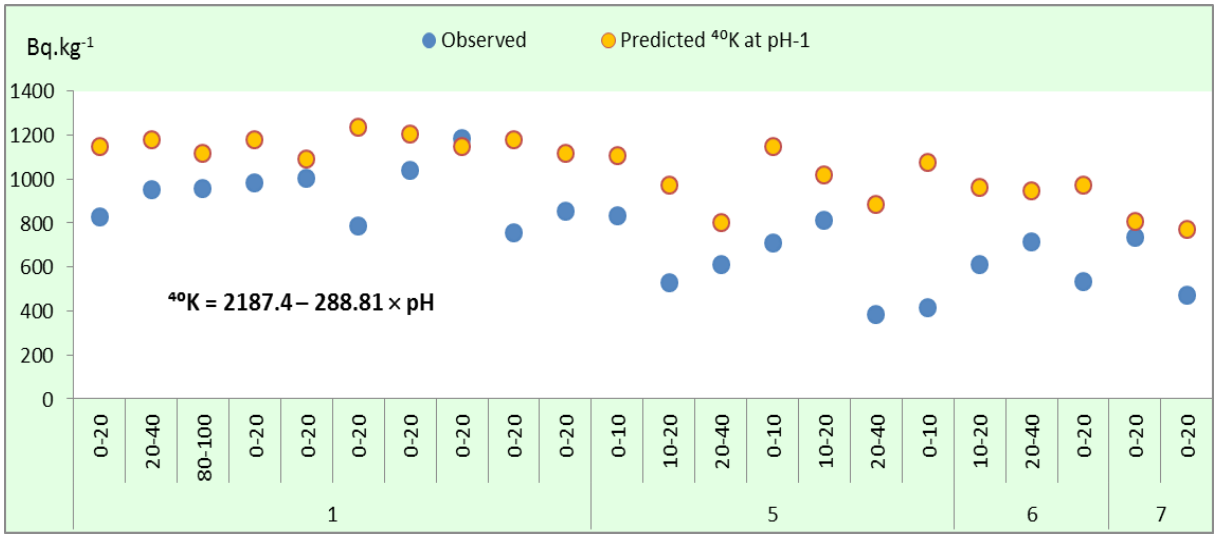

Fig. 4. Modelling the content of ^{40}K depending on the soil pH for the object Selishte (site No 1, site No 5, site No 6, site No 7).

For an object known as Settlement mine, the model established in the ^{226}Ra content, which depends on the pH, is most resistant in the range of 1000 to 5700 Bq.kg^{-1}. The model is used at pH up to 5.53 unit. Amounts of the radioactive isotope in site No 1 are significantly higher than those in other sites. The large variation in data leads to the model describing approximately 37% of the values.

The negative relationship between the natural radionuclide content and the pH of the environment (R = -0.61) is the reason for the predicted acidification by one pH unit and it is expected to increase the amount of ^{226}Ra by about 2610 Bq.kg^{-1} (Fig. 5). Acidification of the environment will lead to the danger of extracting the radioactive isotope from the surface of the ore.The model for a Selishte mine which presents the predicted ^{232}Th content, depending on the, pH, is the most stable in the range of 26 to 97 Bq.kg^{-1}. Variation of the data means that the model describes approximately

34% of the values. The determined linear regression is represented by the equation: $^{232}Th = 284.3 - 43.724 \times pH$.

The established negative relationship (R = -0.58), is the reason for in case of acidification by one pH unit that there might be an increase to the contents of ^{232}Th to about 44 $Bq.kg^{-1}$. The presented forecast shows the risks of extracting the natural radionuclide from ore exported to the surface.

The estimated content of ^{238}U is in range of 260 to 6510 $Bq.kg^{-1}$. But for one point, the contents of the radioactive isotope on site No 1 exceed those on the other sites. The model describes approximately 34% of the values resulting from the large variation in isotope content. The determined negative linear dependence (R = -0.58) is represented by the equation: $^{238}U = 28708 - 5162.7 \times pH$.

Predicting the contents of the model is in a pH range of not less than 5.53 unit.

With the predicted acidification of the environment, the ^{238}U content is expected to increase by about 3253 $Bq.kg^{-1}$. The acidification of the environment leads to the extraction of the studied radionuclides from surface ore particles and to the pollution of the environment.

The "Zdravetz" mine is situated in about 4 km west of the village Dobralak, Kuklen Municipality, Plovdiv district. The object falls into protected areas according to the two directives for the Natura 2000 network (BG0002073 Dobrostan under the Birds Directive and the Habitats Directive BG0001031 Rodopi – Sredni).

The model of the content of alpha specific activity in relation to pH, operates within a range of 1525 to 23882 $Bq.kg^{-1}$ (Fig. 6). A strong negative relationship is established (R = -0.70). Similarly to the model describing the content of ^{226}Ra and in this case two very high levels of alpha specific activity on site No 1 were established. As a result of this variation, the calculated model describes about 49% of the values. Again, the prognosis is higher at the low contents on the site No 4.

The predicted acidification of the environment with one pH unit predicts an increase in the specific activity level of about 5200 $Bq.kg^{-1}$.

The estimated content of ^{226}Ra, depending on the pH for the Zdravetz object, indicates that the model can be used in an interval between 122 and 3403 $Bq.kg^{-1}$. The determined linear relationship is represented by the equation: $^{226}Ra = 5234 - 763.03 \times pH$. The two very high contents found on site No 1 lead to the model describing about 47% of the observed values. The forecast is increased with low content in the site No 4.

The predicted acidification of the environment results in an increase in the content of ^{226}Ra by 763 $Bq.kg^{-1}$, due to a negative relationship between the radionuclide content and the environment pH (R = -0.69).

The higher environmental risk must be reduced to acceptable levels by applying a set of measures for reclamation of the sites. In the case of higher contents of ^{226}Ra in the soil ("Selishte" mine and "Zdravetz" mine), the instance of the re-cultivation of the "Kurilo" mine - section "Iskra" and the section "V shaft" can be used.

Conclusions

The modelling of the specific activity of the studied natural radionuclides as a function of pH has once again demonstrated the complexity of ongoing processes in systems influenced by human activity. The models specific to each object were identified. They are particularly important for assessing the degree of contamination and the risk to human health and to the environment from the geological exploration and mining of uranium ore which were carried out in the past.

The petrographic and the mineral differences, the climate conditions, the specific features of the technogenic relief, and the extended period of exposure to the Earth's surface are the main factors that influence the modelling of natural radionuclide behavior.

The analysis found out that the risk to the environment was significant, due to the stimulation of the processes of weathering and release of pollutants into the environment.

All of the presented results show increased risks of radiation as a result of the anthropogenic impact and the extraction of rock pieces uranium ore.

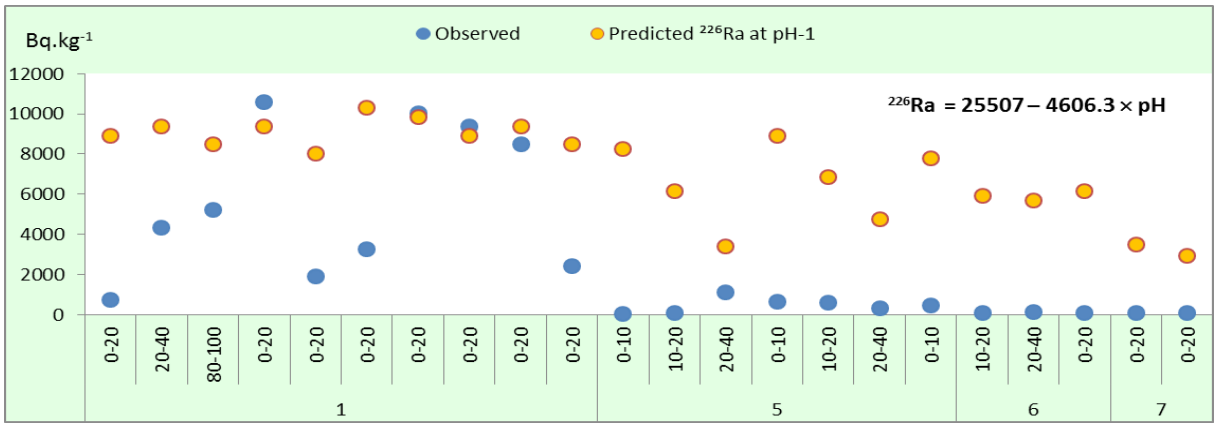

Fig. 5. Modelling the content of ^{226}Ra depending on the soil pH for the object Selishte (site No 1, site No 5, site No 6, site No 7).

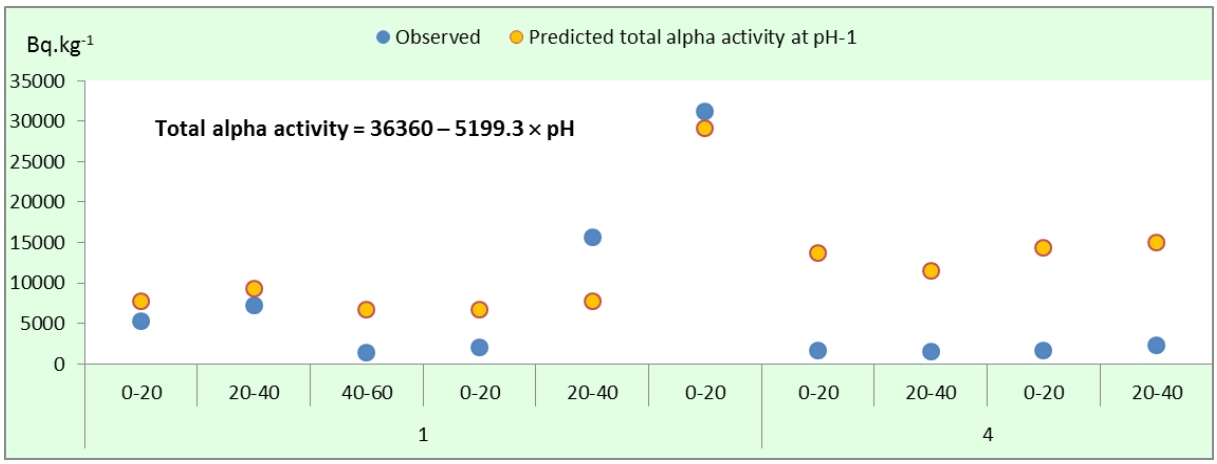

Fig. 6. Modelling the content of Total alpha activity depending on the soil pH for the object Zdravetz (site No 1, site No 4).

In conclusion, all of the studied objects must be reclaimed with a purpose to reduce the risk to the environment and human health. This conclusion is also supported by the importance of sites from a natural point of view, as most of them fall within the European ecological network Natura 2000. All sites fall into forest areas, some of which are in close proximity to large urban areas or health resort villages and are of interest to tourism. Not a small part of the objects are in dangerous proximity to surface water bodies, and all are potentially dangerous to underground water bodies with which they can come into contact when releasing pollutants into the environment.

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