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# Entering of natural radionuclides in soil and root crops with fertilizers and their distribution in “soil-plant” system

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## NORMATIVE REFERENCES

In this dissertation work, references are made to the following standards:

ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons, Second edition 2015-08-01, issued by ISO-Geneva (CH), International Organization for Standardization.

Interstate Standard 17.4.4.02-84, 2008. Nature protection. Soils. Methods for sampling and preparation of soil for chemical, bacteriological, helmintological analysis (In Russian)

Interstate Standard 5180-84, 2005. Soils. Laboratory methods for determination of physical characteristics (In Russian).

Interstate Standard 26213-2021. Soils. Methods for determination of organic matter (In Russian).

Interstate standard 26423-85, 1986. Soils. Methods for determination of specific electric conductivity, pH and solid residue of water extract (In Russian).

JCGM 200, 2008. International vocabulary of metrology – Basics and general concepts and associated terms.

## LIST OF ABBREVIATIONS

The following symbols and abbreviations are used in this dissertation work:

| | | |
|---|---|---|
| $A_{ab}$,i | - | the activity concentration of radionuclides in aboveground part of vegetable |
| $A_i$ | - | activity concentration of isotope in the sample |
| AN | - | ammonium nitrate |
| $A_{p,i}$ | - | the activity concentration of radionuclides in root vegetable part |
| $A_{r,i}$ | - | the activity concentration of radionuclides in root crop of vegetable |
| $A_{Ra\text{-}226}$ | - | activity concentration of Ra-226 in the sample |
| $A_{s,i}$ | - | the activity concentration of radionuclides in soil |
| $A_{tr}$ | - | activity concentration of isotope in the tracer |
| DSC | - | differential scanning calorimetry |
| DSp | - | double superphosphate |
| $E_n$-score | - | normalized error used to assess the agreement between a participant's measurement result and a reference value in interlaboratory comparisons. |
| HPGe detector | - | high purity germanium detector |
| IAEA-375 | - | Radionuclides and Trace Elements in Soil |
| $k_0$-INAA | - | $k_0$-instrumental neutron activation analysis |
| $m_{Ba\text{-}133\ sample}$ | - | mass of added Ba-133 in the sample |
| $m_{Ba\text{-}133Std}$ | - | mass of added Ba-133 in barium standard disc |
| MF | - | phitomicro fertilizer |
| MPP | - | mono-potassium phosphate |
| $m_s$ | - | mass of the sample |
| $m_{tr}$ | - | mass of added tracer |
| NIST SRM 4359 | - | Seaweed Radionuclide Standard |
| NPK | - | complex mineral fertilizer, including nitrogen (N), phosphorus (P) and potassium (K) |
| OMM | - | organo-mineral mixture |
| $P_{Ba\text{-}133\ sample}$ | - | net peak area of Ba-133 in the sample |
| PF | - | peat fertilizer |
| Ph | - | phosphoric fertilizer |
| $P_i$ | - | net peak area of isotope |
| $P_{Ra\text{-}226}$ | - | peak area of Ra-226 |
| $P_{tr}$ | - | net peak area of tracer |
| QA/QC | - | quality assurance / quality control |
| RBC | - | root barrier coefficient |
| $R_{chem}$ | - | radiochemical yield (recovery) |
| REEs | - | rare earth elements |
| SP | - | superphosphate |
| STA | - | simultaneous thermal analysis |

| | | |
|---|---|---|
| $t_{\text{Ba-133 sample}}$ | - | time of the sample measurement |
| $t_{\text{Ba-133Std}}$ | - | time of measurement of Ba-133 in barium standard disc |
| TF | - | transfer factor |
| TG | - | thermogravimetric analysis |
| $t_{\text{Ra-226}}$ | - | time of measurement of the sample |
| $\varepsilon_{\alpha\ \text{det}}$ | - | efficiency of an alpha detector |
| $\zeta$-*score* | - | standard performance statistic for proficiency testing |

# INTRODUCTION

## General description of the work

The thesis is devoted to the influence of the application of different fertilizers during cultivation of *D.carrota* (carrot) and *R.Sativus* (radish) to natural radionuclides uptake by root vegetables. The determination of activity concentration of natural radionuclides in fertilizers, soil, and root vegetable was performed in the frame of the research. Evaluation of distribution of natural radionuclides in geochemical fractions of soil was performed in order to determine the effect of application of fertilizers to redistribution of radionuclides among geochemical fractions. The transfer of natural radionuclides to vegetative organs of carrot was investigated. In addition, activity ratios of natural radionuclides was evaluated in soil and root crop of carrot samples.

## The relevance of the work

The increasing demand for food products due to the overpopulation of our planet has led to the intensification of agriculture. Despite the benefits of using fertilizers in agriculture, application of the also leads to contamination of soil by different pollutants including radionuclides [1-2]. In addition, application of fertilizers could change the chemical speciation of radionuclides, which could lead to the enhancement of their mobility and bioavailability [3-4].

Vegetables cultivated on fertilized agricultural lands can uptake radionuclides via the root system, and radionuclides can reach the human body through the food chain and accumulate, causing internal exposure [5]. Therefore, understanding the behaviour of natural radionuclides in soil-plant environmental system is essential for building the scientific knowledge of the migration and bioavailability of natural radionuclides under effect of fertilization. In addition, the evaluation of the release of radionuclides into the environment is an important issue to protect public health [6]. The uptake of radionuclides from soil to vegetables was widely investigated all over the world, however transfer of radionuclides could vary significantly depends on vegetable type, soil characteristics and the environmental changes. These factors are reasonable to evaluate transfer factor locally, since there might be fluctuation between them. In addition, effects of using fertilizer are not always considered. The application of fertilizers may alter the physicochemical properties of soil, including changes in pH and water retention, among others [7].

Therefore, gathering the new data of effect of application of fertilizer to transfer of natural radionuclides will enable recommendations of use of different fertilizers on regional level with respect to investigated radionuclides. In addition, local research [8-9] related to the transfer of radionuclides in soil-plant system, was mostly been devoted to artificial radionuclides. This motivates to carry out this study with the aim of determining the effect of fertilizers to transfer of natural radionuclides from soil to agriculture crop as there are no previous studies have been performed.

In the frame of current research, the soil-to-root vegetable transfer factor for the U-234, U-238, Th-230, Th-232 and Ra-226 were calculated according to the

determined activity concentration in soil and root vegetables (*D.carrota, R.Sativus*) cultivated on soil fertilized with different fertilizers in a pot experiment. For the estimation of the influence of fertilizer on the mobility of natural radionuclides in soil, U-234, U-238, Th-230, Th-232 and Ra-226 geochemical fractionation in soil was investigated. The activity ratios of U-234/U-238, Ra-226/U-234, Ra-226/U-238, Th-230/U-238 were calculated based on obtained activity concentration of natural radionuclides in soil and *D.carrota,* and *R.Sativus* samples.

**Purpose of the work** is to establish influence of application of fertilizers on accumulation ability of radionuclides in root vegetables *D.carrota,* and *R.Sativus.*

**The tasks of the thesis:**

- to select the fertilizers commonly used in agricultural practices of Kazakhstan;
- to perform experiments of cultivation of *D.carrota* (carrot) and *R.Sativus* (radish) on soils which will be enriched by different type of fertilizers;
- to determine the activity concentrations of natural radionuclides of uranium and thorium series in fertilizers, soil samples and vegetative organs of *D.carrota* (carrot) and *R.Sativus* (radish);
- to evaluate the soil-to-root vegetable transfer of natural radionuclides for *D.carrota* (carrot), and *R.Sativus* (radish) cultivated with application of various fertilizers;
- to evaluate the effect of fertilizers on distribution of geochemical forms of natural radionuclides in soil;
- to evaluate the effect of fertilizers on activity ratio of natural radionuclides in the studied samples.

**The object of the study** are fertilizers, soil, and vegetative organs of *D.carrota* (carrot), and *R.Sativus* (radish).

**The subject of the study** is influence of fertilizer to distribution of natural radionuclides in geochemical fractions of the soil, soil-to-root vegetable transfer factor of natural radionuclides and activity ratios of natural radionuclides.

**Research methods:** In the frame of the dissertation work following methods were applied:

1. Alpha–particle spectrometry utilizing PIPS semiconductor detectors (Alpha Analyst, Canberra, USA) for the determination of alpha-emitting radionuclides;
2. $k_0$ – instrumental neutron activation analysis (conducted on a TRIGA MARK II nuclear reactor, with subsequent gamma-ray spectrometric measurements using an absolutely calibrated coaxial HPGe detector, for multi-elemental quantification);
3. Simultaneous thermal analysis (TGA/DSC) for preliminary evaluation of water soluble and organo soluble fractions of fertilizers.

**The scientific novelty of the thesis**

The scientific novelty of this work lies in a comprehensive study of the processes of entering of natural radionuclides the soil and carrot through fertilizers and their distribution in the soil-plant system. For the first time, analysis of the effect of

various fertilizers on the mobility and bioavailability of natural radionuclides in the soil of the Almaty and Turkestan regions has been conducted. The bioavailability of radionuclides for root crops was estimated by sequential extraction depending on used fertilizer. Fertilizers that have the most significant effect on the mobility and bioavailability of radionuclides have been identified. Results allow for proposing recommendations on use of fertilizers to minimize the radiation exposure due to consumption of root vegetables.

**Validity and reliability of the obtained results.**

The scientific validity and reliability of the obtained results were ensured through the application of standardized analytical methods and appropriate statistical treatment of the data. The accuracy of radionuclide measurements was confirmed by analysing certified reference materials.

**Theoretical significance.** The results of the thesis expanded the understanding of the behaviour of natural radionuclides in soil-plant environmental system which is essential for building the scientific knowledge of the migration and bioavailability of natural radionuclides under effect of fertilization.

**Practical significance.** The obtained results serve as a basis for developing recommendations on the use of certain types of fertilizers during cultivation of root vegetables with respect to analysed radionuclides.

**The main provision for the defence:**

1. The total activity concentration of U-234, U-238, Th-230, Th-232, and Ra-226 in monopotassium phosphate, ammonium nitrate, superphosphate, double superphosphate, phosphoric, organo-mineral mixture, NPK fertilizer, microfertilizer, peat fertilizer did not exceed limit value of 1000 Bq/kg according to the Technical Regulations of the Eurasian Economic Union "On requirements for mineral fertilizers";
2. The application of monopotassium phosphate to soil samples from Baiterek village (Almaty region) increases the proportion of mobile uranium and leads to increase in the accumulation of uranium in the edible root of *R.Sativus*;
3. The application of double superphosphate to soil samples from Kyzemshek village (Turkestan region) significantly increases the transfer and accumulation of uranium isotopes (U-234, U-238) and Ra-226 in the edible root of *D.carrota*, compared to unfertilized soils.

**The main results of the study:**

1. The activity concentration of investigated fertilizers is relatively low and did not exceed required value of 1000 Bq/kg according to the Technical Regulations of the Eurasian Economic Union "On requirements for mineral fertilizers. Among the investigated fertilizer the highest activity concentration of U-234, U-238, Th-230, Ra-226 was determined for phosphoric fertilizer and equal to 146±11 Bq/kg, 148±13 Bq/kg, 238±15 Bq/kg, 169±4 Bq/kg, respectively. The highest concentration of Th-232 was determined for double superphosphate and equal to 42±5 Bq/kg.

2. The highest activity concertation of natural radionuclides was determined for root crop of carrot cultivated with application of double superphosphate (Kyzemshek village, Turkestan region) and equal to 56 Bq/kg for U-234, 55 Bq/kg for U-238, 77 Bq/kg for Th-230, 6.5 Bq/kg for Th-232, 79 Bq/kg for Ra-226.
3. Application of monopotassium phosphate led to increase of transfer factor of U-234, U-238, T-230 for radish cultivated on soil from Baiterek village, Almaty region.
4. The application of double superphosphate fertilizer resulted in an increased transfer factor for uranium (U-234, U-238), thorium (Th-230, Th-232), and radium (Ra-226) isotopes in the root crop of carrot cultivated on soil from Kyzemshek village, Turkestan region. The transfer factor exceeded one for U-234, U-238, and Ra-226, indicating their active transfer from soil to the edible part of the crop, suggesting enhanced bioavailability of these radionuclides under fertilization conditions.
5. The U-234/U-238 ratio remained close to unity in both soil and root crop samples, indicating equilibrium and suggesting that fertilizer application has minimal impact to uranium isotope fractionation.

**Relation of the thesis with research and government programs.** The dissertation was carried out within the framework of a scientific project of the Ministry of Education and Science of the Republic of Kazakhstan, "Influence of application of mineral fertilizers on accumulation ability of radionuclides and heavy metals in root vegetables" grant number AP08052224, 2020 – 2022.

**The personal contribution of the author** of the study consists in the analysis of scientific literature data related to the theme of the thesis, carrying out the vegetation experiment, performing radiochemical separation procedure for simultaneous determination of isotopes of natural radionuclides with following measurement on alpha-spectrometry system (Alpha Analyst, Canberra, USA), evaluation and interpretation of obtained results.

**Approbation of work.** The results of the thesis were presented and discussed at international scientific conferences, such as International Birimzhanov Conference, Almaty, Kazakhstan, 2019, 2021; International Scientific and Practical Conference "Innovative development and potential of modern science", Prague, Czech Republic, 2020; International Conference "XII Toraigyrov readings", Pavlodar, Kazakhstan, 2020; International scientific and practical conference of the agro-industrial complex, including veterinary medicine, Belgorod, Russia, 2020; 8th International k0-Users' Workshop 6 – 10 June 2022 Ljubljana, Slovenia.

**Publications**. The main results on the theme of the thesis are presented in 10 publications, including:

- One article in an international peer-reviewed journal with non-zero impact factor (IF=1.9, Q3, SJR 0.621) according to the Web of Science database (.A. Nursapina, B.A. Shynybek, I.V. Matveyeva, Sh.N. Nazarkulova, M. Strok , L. Benedik, O.I. Ponomarenko. Effect of mineral fertilisers application on the transfer of natural radionuclides from soil to radish (Raphanus sativus L.) //

Journal of Environmental Radioactivity 247 (2022) 106863 https://doi.org/10.1016/j.jenvrad.2022.106863 - conducting experiments, data processing, drafting the initial manuscript, and editing in collaboration with co-authors);

- Three articles in scientific journals recommended by the Committee for Quality Assurance in the Field of education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (1. R. Jaćimović1, B.A. Shynybek, I.V. Matveyeva, Sh.N. Nazarkulova, N.A. Nursapina, O.I. Ponomarenko. Assessment of minor and trace elements in mineral fertilizers purchased in Almaty city, Kazakhstan, using k0-INAA // International Journal of Biology and Chemistry 13, No 2, 130 (2020) https://doi.org/10.26577/ijbch.2020.v13.i2.15 - sample preparation, participation in drafting the initial manuscript, editing, and preparation of responses to reviewers in collaboration with co-authors; 2. Nursapina N.A., Matveyeva I.V., Yarovaya E.Yu., Zlobina E.V., Shynybek B.A., Bakytkan B., Nazarkulova Sh.N., Ponomarenko O.I. Influence of fertilizers application on mobility of metals // Chemical journal of Kazkahstan V. 2, № 78(2022), 48-58 https://doi.org/10.51580/2022-2/2710-1185.64 - sample preparation, analysis of results, participation in drafting the initial manuscript and editing in collaboration with co-authors; 3. N.A. Nursapina, I.V. Matveyeva, Sh.N. Nazarkulova, R. Jaćimović. Determination of impurities in fertilizers purchased in Almaty (Kazakhstan) // International Journal of Biology and Chemistry 17, No 1 (2024). https://doi.org/10.26577/IJBCh2024v17i1-a14 - sample preparation, drafting of the initial manuscript, and editing in collaboration with co-authors);
- Six abstracts at international conferences (conducting experiments, data analysis, and drafting the initial version of the abstract);
- The monograph (The Influence of the Use of Mineral Fertilizers on the Accumulation of Radionuclides and Heavy Metals in Root Crops: Monograph / I.V. Matveeva [et al.]. – Almaty: LEM, 2022. – 112 p. ISBN 978-601-239-698-0 - Literature review, conducting of the experimental part, data analysis).

**Volume and the structure of the thesis**

The thesis is consisting of introduction, three sections, conclusions, and a list of references. The work is presented on 107 pages, contains 40 figures, 13 tables, and 176 bibliographical references.

# LITERATURE REVIEW

## 1.1 Characteristics of soils of Kazakhstan

Kazakhstan is the largest land-locked country in the world with massive land area of $2.725 \cdot 10^6$ km and with continental climate [10]. Kazakhstan has three basic ecosystems such as desert areas, grassland, mountains, and foothills. The territory of Kazakhstan is located between the Siberian Taiga in the north and the Central Asia deserts in the south, the Caspian Sea in the west and the mountain range of the Tien-Shan and Altay in the east. Three natural category resources such as rain-fed land, irrigated land, and pasture form agriculture system of Kazakhstan [11].

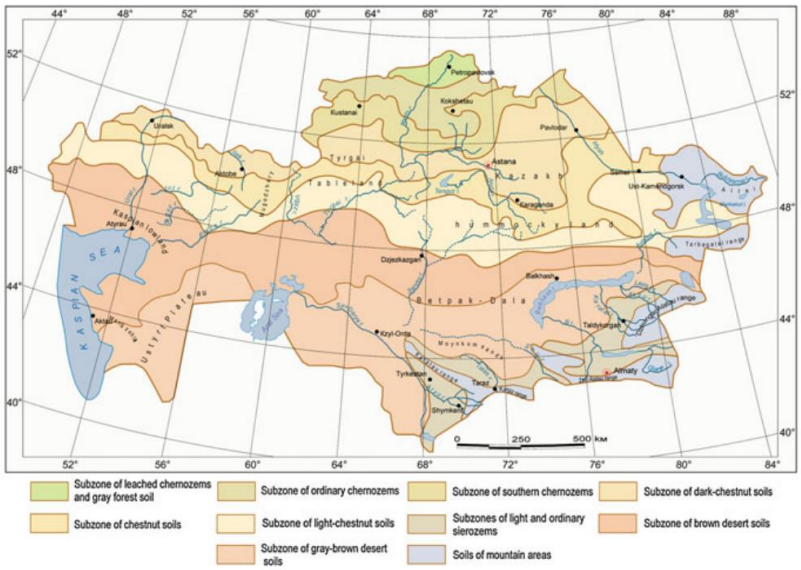



Figure 1. Kazakhstan's soil zones [12]

According to the United Nation Development Program (UNDP) Report 2004 [13], classification of soils of Kazakhstan mostly undergo by zones and altitudes. The geographic soil zones in Kazakhstan from north to south are forest-steppe, steppe, desert-steppe, and desert, where zones are classified according to the types of soil (Figure 1.) [12]. The chernozem (approximately 10 % of the total area) zone mostly belongs to the north part of the republic: bleached chernozem of the forest steppe zone, common chernozem and southern chernozem of moderately arid steppe.

To the south of the republic, chernozem is replaced by chestnut soils (approximately 33 % of the total area) such as dark-chestnut soils of the arid steppe zone, chestnut soils typical for the arid steppe, and light-chestnut soils of semi-deserts. Further to the south there is zone of brown soils.

In the south of the flat part of the republic there is a zone of grey-brown soils. The territory of brown and grey-brown soils covers approximately 45 % of total area of country.

In the foothills of West and North Tien Shan, grey and grey-chestnut soils of mountain plains and foothills prevail. The soils of piedmont plains and mountains occupy 12.4 % of the territory of the country.

In present work, soils of two region of Kazakhstan (Almaty and Turkestan region) were investigated. The foothill zone of the Almaty region is represented by dark chestnut soils with a humus content of 6-9 % in the horizon and a pH value of 6.8-7.7. Meanwhile the foothill desert steppe zone of the Almaty region is represented by light chestnut, ordinary grey soils, as well as meadow-grey soils. Soil pH varies from 7.5 to 8.4. The main soils of the Turkestan region are represented by mountain meadows, ordinary chernozems, grey-brown soils of high desert plains, salt marshes and sands. The lowest content of humus is determined in grey-brown soils of high desert plains. Soil pH varies from 8.2 to 8.6 [14].

Particular interest belongs to Turkestan region due to its close location to the uranium mining industry. Attention should also be paid to one of the main cities of Kazakhstan, Almaty which is located in Almaty region, with the largest population, where level of environmental pollution has high rates in the country [15-17]. It has to be mentioned also significant contaminations in certain regions with radionuclides as a result of mining and processing of uranium ores [18-24].

According to the other research [25], the irrigated areas of Southern Kazakhstan are heavily polluted with boron, fluorine, lead and copper. For instance, in south region of Kazakhstan (Karatau-Zhambyl industrial complex) increased fluorine content in soils (17-30 mg/kg) were identified due to the emission of chemical enterprises of the phosphorus industry and long-term use of mineral fertilizers and chemical meliorants in irrigation fields.

In the last decade, Kazakhstan has occupied a leading position in the extraction of uranium ore in the world. It is widely known that 13 % of Kazakhstan territory is contaminated with artificial and technogenically enhanced natural radionuclides as a result of the activities of nuclear test sites and the uranium industry. It is possible that areas with increased radioactivity due to the presence of high concentrations of natural radionuclides of the uranium and thorium series can be formed near enterprises that produce and process uranium ore. Considering the radioecological situation in uranium producing countries [26-27] where uranium ore was mined and processed, as well as on the basis of single measurements carried out by a number of agencies in Kazakhstan, it can be stated that the area, especially soil, around the operating uranium facilities can be contaminated with natural radionuclides.

### 1.2 Natural radionuclides in soil

Natural radionuclides occur naturally in soil environment from the paedogenic processes [28-29].

The major naturally occurring radionuclides present in soil structure are K-40 and radionuclides of uranium and thorium series (Figure 2).

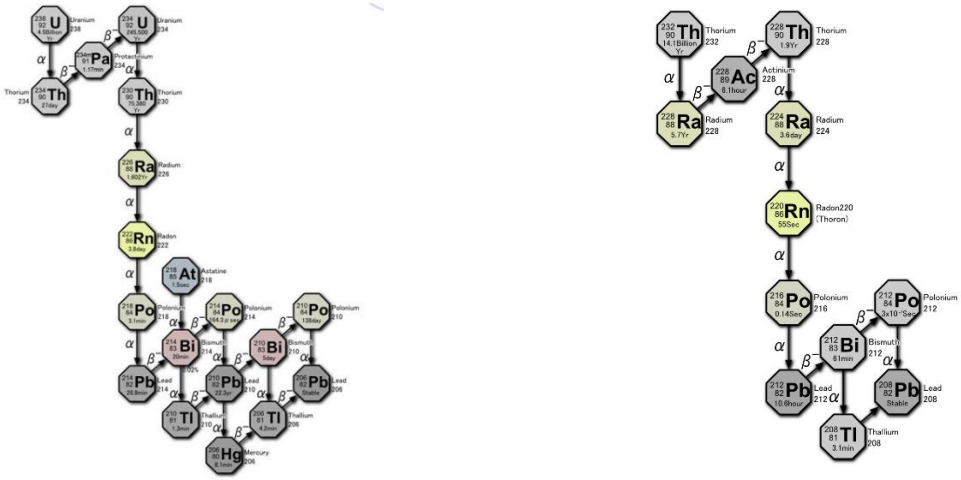


Figure 2. Uranium and thorium decay chain [30]

Radionuclides of primordial (radioisotopes which have half-lives comparable to the age of the Earth $4.5 \cdot 10^9$ years) origin that initiate natural radioactive decay series (Th-232, U-238 and U-235) are of major importance, as most of the natural radioactivity detected on Earth and its related dose results from radionuclides belonging to these decay series. Uranium series contain Ra-226 and its decay products which are responsible for a major fraction of the radiation dose received by inhalation and ingestion pathways [31]. The annual effective dose for this series according to the United Nations Scientific Committee on the Effect of Atomic Radiation (UNSCEAR) has been estimated as 1.34 mSv, with a contribution from external and internal exposure of 0.10 and 1.24 mSv, respectively [32]. Meanwhile, thorium series generates an annual effective dose of 0.34 mSv, of which 0.16 mSv is caused by external exposure and 0.18 mSv is an internal dose resulting from ingestion and inhalation [32]. Thorium is one of the highly radiotoxic elements because it decays to a number of other α -, β- and/or γ-emitting progenies (Mahmood and Mohamed, 2010). Th-232 (alpha emitting) and Th-230 (alpha emitting from U-238 decay chain) are particularly important due to their relatively long half-lives, high natural abundance and α -particle radiation.

Radionuclides are not uniformly distributed in soil and varies from region to region, depending on the anthropogenic activities, geological and geographic features of each region [33]. Soil is a dynamic layer, which can be contaminated by different contaminants through the emissions from various sources, including atmospheric deposition, mining, disposal of high concentrated wastes from industrial sector, pesticides, application of mineral fertilizers, wastewater irrigation, etc. [34-36]. Natural radionuclides in the soil are responsible for the background radiation exposure of the population [37]. According to the UNSCEAR report, the radiation dose coming from natural sources is equal on average to 2.4 mSv/year, whereas from artificial sources it is equal to 0.8 mSv/year worldwide [38]. However, for Kazakhstan the radiation dose coming from natural sources is equal on average to 3.1 mSv/year, in addition 1.1 mSv/year coming from artificial sources (medical procedures) [39].

The major radiation exposure from soil comes from upper layer of the soil [40]. The terrestrial component of the natural background radiation is dependent on the compositions of the soils and rocks, which contain natural radionuclides [41]. Relatively increased radioactivity is associated with igneous rocks, meanwhile low activity belongs to sedimentary rocks. However, there are some exceptions: for example, shales and phosphates demonstrate relatively high content of radionuclides [42].

Uranium and thorium tend to form in alkaline rocks and its concentration mostly increase in silica [43]. According to the research [44], terra-rossa (red soil) type of soil, mostly contains primordial radionuclides, and the main contributors are 35 % K-40, 50 % Th-232 series and 15 % U-238 series. Th distribution in soil is more homogeneous and it has a higher concentration in alluvial soils. In case of tetravalent thorium, the mobility of thorium increases with organic matter content, due to formation of strong organic complexes [45]. U and Th are usually present in the soil in the valences states of VI+ and IV+, respectively.

### 1.2.1 Uranium mobility and bioavailability in soil

Isotopes of uranium are widely distributed in Earth's crust with average uranium concentration of 2.7 mg/kg [46]. Concentration of uranium varies depending on rock type, for instance, the lowest content of uranium is found in basalts, meanwhile the highest concentration is in phosphate rocks [47].

The behaviour of uranium in soil is complex due to existence of several species of uranium and different factors affecting its behaviour. Uranium occurs in two predominant oxidation states: the reduced form U(IV) and the oxidized form U(VI), with the latter being considerably more soluble and mobile in the environment. The redox conditions in the soil strongly influence the transformation between these forms. Under reducing conditions, U(IV) is stable and considered relatively immobile due to the formation of poorly soluble minerals such as uraninite ($UO_2$). In contrast, U(VI) exists predominantly in the form of the uranyl ion ($UO_2^{2+}$) and forms soluble complexes, particularly under oxidizing and alkaline conditions, enhancing its environmental mobility.

Between pH values of 4.0 and 7.5—which are typical for most of soils, U(VI) primarily exists in hydrolyzed forms. In solution, uranium exists mainly in the form of $UO_2^{2+}$ (uranyl ion) and soluble carbonate complexes $(UO_2)_2CO_3(OH)_3^-$, $UO_2CO_3^\circ$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ and possibly as $(UO_2)_3(CO_3)_6^{6-}$ (Figure 3) [48-49]. Notably, in slightly alkaline environments (pH 7–8), uranium predominantly forms stable carbonate complexes such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$, which significantly reduce its sorption to soil components and increase its mobility.

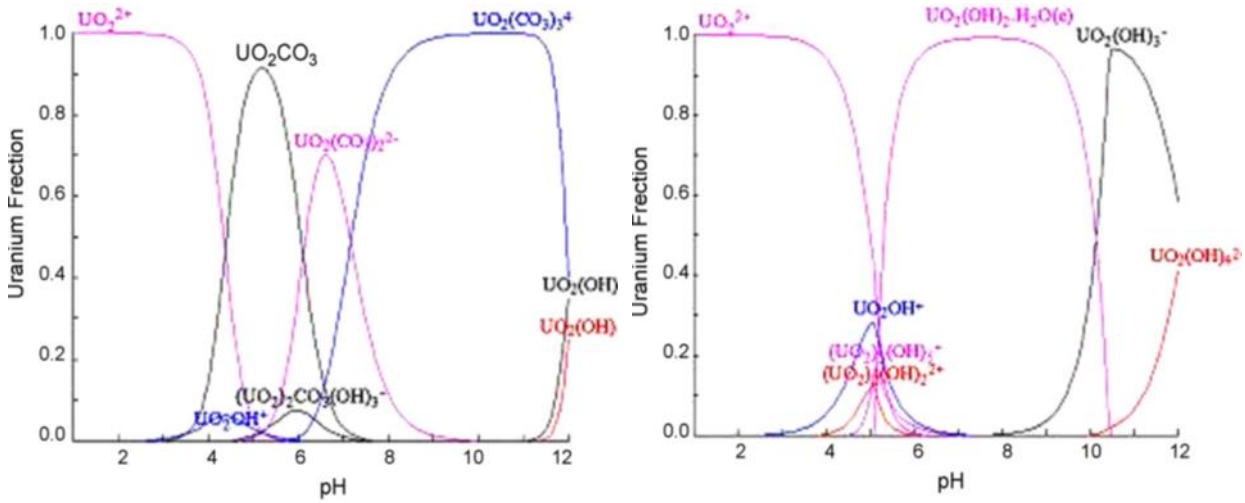



Figure 3 - Dependence of the forms of uranium on pH [48]

In the presence of both carbonates and phosphates, uranyl-phosphate complexes such as [$UO_2HPO_4^0$] and [$UO_2PO_4^-$] are also formed, influencing uranium retention in the soil matrix (Figure 4) [50].

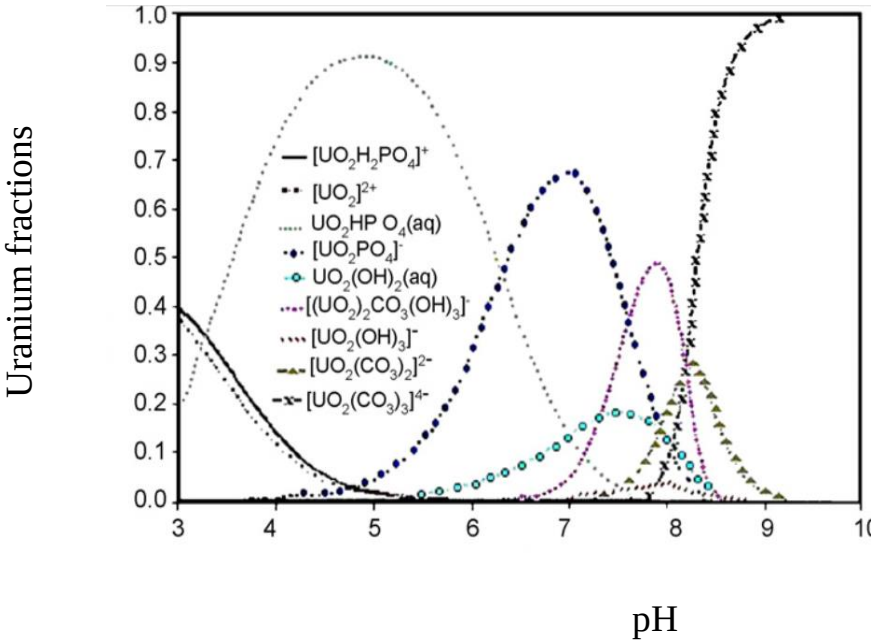



Figure 4 – Calculated speciation of uranium in the system $UO_2$-$PO_4$-$CO_3$-OH-$H_2O$, under the condition of supersaturation [50]

Mobility of uranium mostly depends on sorption and complexation processes on inorganic an organic component of the soil such as organic matter, humic substances, clay minerals, Fe/Mn oxides, etc. [51].

Positively charged uranyl ions interact with negatively charged surfaces of these soil constituents through various sorption mechanisms, including adsorption, ion exchange, and chemisorption. Hydroxylated groups (–SiOH and –AlOH) on the surfaces of clay minerals and metal oxides also provide active sites for sorption of uranyl species. Sorption in these variable-charge sites is highly pH-dependent; at

low pH, protons ($H^+$) compete with U(VI) for sorption sites, forming positively charged surfaces ($–SOH_2^+$), whereas at higher pH, uranyl ions displace $H^+$ and bind to deprotonated hydroxyl groups.

It should be noted that uranium-carbonate complexes tend to remain in solution even near neutral pH, limiting their sorption and enhancing mobility in soil. Sorption of these anionic complexes is limited, particularly in the presence of high carbonate concentrations, where uranyl-carbonate complexes dominate. Furthermore, carbonate and sulphate complexes of uranium are generally water-soluble, thus facilitating the long-range transport of uranium via soil water, uptake by plants, or redistribution through evaporation processes [52].

Soil organic substances, particularly humic acids, also influence uranium mobility. At pH around 5, humic acids form soluble uranium complexes. However, the presence of $Fe^{3+}$ ions can limit the mobility of uranium by promoting sorption of uranyl-humate complexes onto colloidal particles of humic matter. This reduces uranium's availability for leaching or uptake by plants [53].

The presence of phosphate in soils, particularly from phosphorus-containing fertilizers, plays a significant role in uranium immobilization. In acidic soils, phosphate ions ($H_2PO_4^-$), and in alkaline conditions $HPO_4^{2-}$, promote the formation of low-solubility uranium-phosphate minerals. Fertilization with phosphate sources can therefore lead to a reduction in uranium solubility and mobility [54].

Understanding factors affecting the mobilization or immobilization of uranium is essential for predicting uranium transport in soil systems and further transfer to plant system, especially in the context of uncontrolled use of fertilizers and environmental contamination.

### 1.2.2 Thorium mobility and bioavailability in soil

The geochemical properties of thorium differ from those of uranium. The intensity of thorium removal from the crust by weathering and its migration capacity in the aquatic environment is significantly less than that of uranium and does not depend on the redox conditions of the environment. Thorium has different isotopes with high radiotoxicity and with +4 oxidation state which is of importance in geochemistry [55]. Thorium is widely distributed in earth's crust with average concentrations of 8-12 mg/g and with average concentration in soil 6 mg/g.

Thorium is mostly present in the insoluble residue of carbonate rocks (clay materials). In most soils thorium is immobile. According to [56], at pH 6.5 the adsorption of thorium on clays, oxides, and organic matter increases. At pH values > 3, Th (IV) undergoes extensive hydrolysis with formation of monomeric and oligomeric species with following formation of polymeric complexes of colloidal proportions [57].

Thorium belongs to the group of hydrolyzing elements, the compounds of which are unstable in diluted aqueous solutions of the active water exchange zone due to intensive hydrolysis. In aqueous solutions at pH above 3, thorium undergoes hydrolysis forming various hydroxocompounds. Based on the calculated data [58] on the distribution of thorium species depending on pH, shown in Figure 5, the non-

complexed $Th^{4+}$ ion is the dominant ion at pH values lower than 3.5. With the increase of pH, the dominating species become hydroxocompounds $Th(OH)_2^{2+}$, $Th(OH)_3^{+}$, and $Th(OH)_4^{0}$.

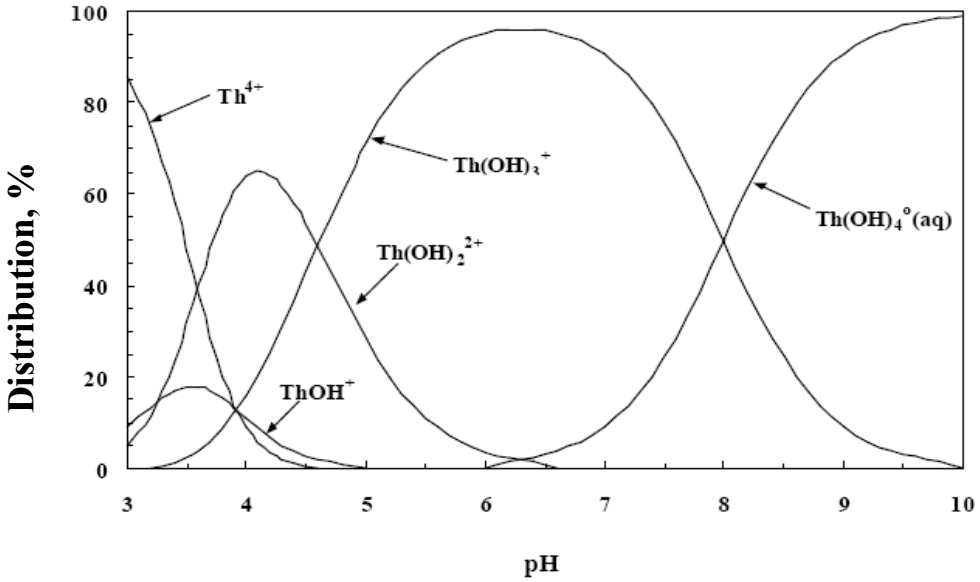



Figure 5. Estimated speciation of thorium distribution as a function of pH []

Humic acids, which forms a major part of soil organic matter, affect thorium adsorption on different minerals due to large surface area [59-60]. According to [61], complexation of thorium with humic acids increases with increasing pH value.

In addition, organic complexes of thorium have a significant influence on its mobility in the "soil–water" system. For example, the authors [58] investigated the process of complex formation of thorium with citrate ($C_6H_5O_7^{3-}$), oxalate ($C_2O_4^{2-}$), and EDTA ($C_{10}H_{12}O_8N_2^{4-}$) ions in order to determine the possible role of organic complexing agents in the mobility of thorium in natural waters. They concluded that thorium–organic complexes dominate over inorganic ones in soils and waters, which is rich in organic substances.

The concentration of total dissolved thorium in soil can be increased by the formation of various aqueous complexes. These complexes can be formed with inorganic anions such as dissolved carbonate, fluoride, phosphate, chloride and nitrate [62].

### 1.2.3 Radium mobility and bioavailability in soil

Radium is the radioactive divalent element with 25 isotopes, four of which found in nature (Ra-223, Ra-224, Ra-226, Ra-228), with chemical properties similar to barium and calcium. Ra isotopes (Ra-223, Ra-224, Ra-226, Ra-228) are generated in naturally occurring radioactive series of U, Ac and Th and are therefore widely distributed in the Earth's crust. Various rock types contains different amount of Ra, for instance the highest concentration of Ra is present in shale, bitumen slate and volcanic and phosphate rocks. The average worldwide population weighted value

for Ra-226 concentration in soil of 32 Bq/kg was reported based on data from the UNSCEAR, meanwhile for Kazakhstan this value is equal to 35 Bq/kg [63].

In soil, Ra mostly behaves as other elements of alkaline earth group. Generally, radium is strongly retained by soil. Retention processes is mostly controlled by sorption on clay minerals and organic matter. At pH ≥ 7, the radium is readily absorbed by clays and mineral oxides present in soils [64]. Several research [65-66] reported that radium accumulates in soil with organic-rich horizon.

Radium is present in soil solution in trace concentrations. The conditions where radium migration may occur in soil solution, are in case of low pH, low redox potential, however the competition between other divalent cations may occur [51]. According to [67], the sum of water-soluble, exchangeable, and acid-soluble fractions of soil, which belongs to the mobile one, radium species content is equal to 40 %.

### 1.3 Fertilization as a source of naturally occurring radioactive material

Nitrogen, phosphorus, and potassium belongs to the primary essential nutrients for plants for their higher yield and good health. Nitrogen is available for plants mostly in form of cations and anions such as $NO_3^-$, $NH_4^+$, meanwhile phosphorus is available in form of anion as $H_2PO_4^-$, $HPO_4^{2-}$. Potassium is available in form of cation such as $K^+$. Two types of fertilizers are used in agriculture: inorganic (mineral) and organic. Inorganic fertilizers are classified into three categories: straight, complex, and mixed fertilizers. Straight fertilizers contain only one primary nutrient, meanwhile complex fertilizers are multi-nutrient.

The main differences between inorganic fertilizers and organic fertilizers are the chemical elements contained in them. In the case of mineral fertilizers, elements containing in the fertilizer are directly absorbed by plants after application to the soil. Meanwhile organic fertilizers need to be firstly decomposed with microbiological processes, and after that, their derivatives are absorbed by plants [68].

Soil fertilization is the widespread and important method to increase efficiency and to obtain product with better quality in agricultural activities. In recent years, fertilizer consumption increased exponentially throughout the world, which can cause serious environmental problems. Most fertilizers have complicated compositions and, in addition to the intended elements and nutrients, can include contaminants which accumulates in agriculture soil [69].

The application of excess amount of mineral fertilizers has the following negative consequences [68]:

1. change the physico-chemical characteristics of soil. The use of certain types of fertilizers increases the acidity of soils, which leads to significant losses of humus;
2. the excess application of nitrate fertilizers leads to contamination of soils, agricultural products and fresh water with nitrates;

3. long-term use of mineral fertilizers has a significant impact on the soil microbiota, which can lead to an increase in the number of bacteria and fungi in soils.

Potential source of soil contamination by natural radionuclides is fertilizer industry. Wastes from fertilizers production can contain a large variety of the heavy metals and natural radionuclide like U-238, Th-232. The predominant source of contaminants are P-containing fertilizers due to production from phosphate ores. Phosphate ores can be of sedimentary origin, which represents about 85 % of the phosphate rocks, which were formed mainly from organic residue, the remaining parts of the phosphate rocks. Uranium and its decay products typically accumulate in phosphate deposits of sedimentary origin, therefore when rock is processed into phosphate fertilizer, radionuclides come into fertilizers. Since phosphate fertilizers contain excess amounts of radionuclides, their long-term and extensive use can lead to significant contamination [2].

### 1.3.1 Natural radionuclides in mineral fertilizers

Long term use of fertilizer cause accumulation of metals in soil. There exists large range of commercial fertilizers, which can contain different contaminants. Fertilizers contain naturally occurring radionuclides, such as U-238 and Th-232, their decay products, as well as K-40. The concentration of radionuclides depends on production method and raw material that is used during the manufacture of fertilizer [70].

Phosphate rock is the main source of phosphate for fertilizer industry. The various phosphate rocks are known for their elevated level of radionuclides. The majority of phosphate is produced from sedimentary marine deposits (approximately 75 %), followed by igneous and weathered deposits (approximately 15-20 %), while biogenic resources only account for 1-2 % of production. Primary phosphate minerals include fluorapatite ($Ca_{10}(PO_4)_6F_2$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and carbonate hydroxyapatites ($Ca_{10}(PO_4, CO_3)_6(OH)$). The phosphate ores can contain various toxic elements, such as fluor (F), cadmium (Cd), arsenic (As), mercury (Hg), chromium (Cr) and lead (Pb), along with radionuclides such as U-238, Ra-226 and Th-232 [71-72]. The concentration of uranium isotopes in phosphate deposits of sedimentary origin is about 1500 Bq/kg [73]. Therefore, during the production of fertilizers from this type of rocks, radionuclides can end up in fertilizer.

Phosphoric acid is used during the production of the triple superphosphate, double single superphosphate, ammonium phosphate fertilizers, NPK fertilizers and di-calcium phosphate. Ammonium phosphate fertilizers are produced by reacting directly phosphoric acid with different amounts of ammonium. Triple superphosphate, double single superphosphate, and NPK fertilizers are obtained by reacting phosphoric acid with phosphate rock and ammonium, meanwhile single superphosphate is obtained by reacting phosphate rock with sulphuric acid. During the reaction of phosphate rock with sulphuric acid, the radioactive equilibrium between U, Th and their decay products is disrupted, and the radionuclides migrate

according to their solubility. Uranium isotopes mostly form highly soluble compounds with phosphate ions, while Ra isotopes, Pb-210 and Po-210 remain in phosphogypsum [74-75].

According to the data [76] presented in Table 1, radionuclides in phosphate fertilizer belonging to Th-232 and U-238 decay series, and also K-40 are the major contributors of outdoor terrestrial natural radiation. By contrast, organic fertilizers generally contain low uranium concentration with maximum concentration not exceeding 12 mg/kg [77].

Table 1. Radioactivity levels in phosphate products (Bq/kg) [76].

| **Product** | **U-238** | **Ra-226** | **Th-232** |
|---|---|---|---|
| Phosphoric acid | 1200–1500 | 300 | — |
| Normal superphosphate | 520–1100 | 110–960 | 15–44 |
| Triple superphosphate | 800–2160 | 230–800 | 44–48 |
| Mono-ammonium phosphate | 2000 | 20 | 63 |
| Diammonium phosphate | 2300 | 210 | <15 |
| Dicalcium phosphate | — | 740 | <37 |
| PK fertilizers | 410 | 370 | <15 |
| NP fertilizers | 920 | 310 | <30 |
| NPK fertilizers | 440–470 | 210–270 | <15 |

According to the research [78], the average total concentration of radionuclides of 33 analysed samples of fertilizers from Vojovodina region (Serbia) were higher than acceptable level of 370 Bq/kg [79]. Meanwhile, in research [80] the level of natural radioactivity in 43 samples of seven fertilizer types, which were collected from the farmers and the market of Upper Egypt, were as follows single superphosphate > nitrogen potassium fertilizer > golden fertilizer > nitrogen phosphorus > urea improved > ammonium nitrate. The fertilizer with the least natural radioactivity was ammonium nitrate. A study [81] showed that superphosphate, triple superphosphate, and phosphogypsum had high activity concentration of radionuclides which equals to 400 Bq/kg. Phosphate fertilizers from Pakistan had the uranium activity concentration of 799 Bq/kg. Activity concentrations of U-238 and Ra-226 in phosphogypsum produced by various fertilizer industries in India were equal to 1000 Bq/kg [82].

### 1.4 Natural radionuclides in plants: factors and processes involved in transfer of natural radionuclides in soil-plant system

Root vegetables, such as *D.carrota* (carrot) and *R.sativus* (radish), were selected in the frame of this research due to their environmental sensitivity, physiological characteristics, and their relevance in the diet of the local population. These crops are widely cultivated and consumed across Kazakhstan, forming an essential part of the national food basket [83].

From a radioecological standpoint, root vegetables are particularly suitable for evaluating the transfer of natural radionuclides from soil to plant, as they are grown directly in contact with the soil matrix, where radionuclides such as Ra-226, Th-232, and K-40 are naturally present.

Numerous studies have demonstrated that root vegetables tend to accumulate higher levels of natural radionuclides in their edible parts compared to other crop types, making them reliable indicators in radioecological assessments [84 - 87]. Although potatoes, cucumbers, and lettuce have also shown significant radionuclide accumulation in some contexts, root vegetables remain the most direct models for soil–plant transfer due to their immediate and continuous interaction with the soil environment.

The uptake of radionuclides and nutrients by plants occurs primarily via the root system, through three key mechanisms: mass flow, diffusion, and root interception [88].

Mass flow involves the transport of dissolved ions with water toward the roots during transpiration. Essential nutrients such as calcium, magnesium, and nitrogen are typically transported through this process.

Diffusion refers to the passive movement of ions along a concentration gradient to the root surface and is the primary mechanism for elements such as phosphorus and potassium.

Root interception occurs when growing roots come into direct contact with soil particles or colloids, enabling the absorption of associated ions.

The root–soil interface, known as the rhizosphere, plays a critical role in influencing radionuclide mobility. One of the important processes occurring in this zone is acidification, which results from the release of protons ($H^+$) and organic acids by plant roots. This can enhance the solubility and bioavailability of certain radionuclides and metals [89–91]. For example, nitrogen nutrition influences rhizosphere pH: uptake of ammonium ($NH_4^+$) leads to rhizosphere acidification, whereas nitrate ($NO_3^-$) uptake can result in a slight pH increase due to proton consumption. Additionally, an imbalance between the uptake of cations (e.g., $K^+$) and anions may also affect the proton balance, further altering rhizosphere pH [92].

Plant roots also exude various low-molecular-weight organic compounds, such as organic acids, which act as natural chelators. These compounds can complex with metal ions and increase their solubility in the soil solution, thereby enhancing the uptake of certain radionuclides [93]. Furthermore, the presence of water-soluble chelating agents contributes to the mobilization of metals by increasing their concentrations in the soil aqueous phase [94].

Phosphorus (P) availability in soil is another critical factor affecting the mobility and uptake of radionuclides, particularly uranium. In soils, phosphorus is

mainly present in the form of negatively charged anions—$H_2PO_4^-$ under acidic conditions and $HPO_4^{2-}$ under alkaline conditions. These anions can react with uranium to form insoluble uranium phosphate complexes, which are geochemically stable and thus less available for plant uptake. Consequently, phosphorus fertilization can reduce uranium bioavailability and its transfer from soil to plants [95].

In summary, the selection of *D.carrota* and *R.sativus* as test plants is justified by both their physiological traits—specifically, their root architecture, interaction with the soil environment, and capacity for contaminant accumulation—and by their practical importance as staple vegetables in Kazakhstan. Studying these crops within the soil–plant system allows for a realistic assessment of radionuclide transfer pathways and potential radiological risks to the population through ingestion.

### 1.4.1 Uranium plant uptake

Uranium has no essential biological function to the plant, nevertheless a wide range of terrestrial plant uptake it from the soil. Uranium, present in soil, enters the plants through roots and is distributed in different parts of the plants [96].

The rapid uptake of uranium by plant roots may be explained by its interaction with the outer cellular structures, where uranium can precipitate or become adsorbed onto the components of the cell wall. Similar to other heavy metals, uranium enters plants primarily through root uptake, while direct deposition onto aerial parts from the atmosphere contributes only minimally to overall accumulation. Uranium cations (primarily $UO_2^{2+}$) are believed to be taken up by root cells via transport pathways shared with essential elements such as calcium ($Ca^{2+}$), iron ($Fe^{2+}/Fe^{3+}$), and magnesium ($Mg^{2+}$). These pathways include specific ion carriers and non-selective cation channels in root cell membranes, which facilitate the entry of uranium due to its similar chemical properties [97].

Plant uptake and translocation of uranium is specific for different soil type and plant. Plants can not recognize which radionuclides are absorbing, so then uptake isotopes in the ratios present in soil solution. Bioavailable form of uranium is present mostly in form of soluble carbonate complexes with uranium in hexavalent oxidation state.

According to [98], in the investigated species of plants *Strumarium, Phragmites communis, Artemisia nitrosa and Artemisia serotina*, which was collected from the territories contaminated by uranium industry of Kazakhstan, the concentration of uranium, thorium isotopes and Ra-226 was higher in root system compared to aboveground part.

The process of intake of U-238 in plants occurs continuously throughout the entire vegetation period, and plants accumulate the radionuclide per unit mass in the earlier phases of their development more than in later phase [99]. When U-238 enters the plants, it mostly accumulates in the root system, which serves as a barrier to the transport of the radionuclide into the aboveground part [100]. However, according to [101] uranyl cation, uranyl carbonate complexes and negatively charged uranyl

phosphate anion are predominant forms which are absorbed by plant roots with further relocation into shoots.

### 1.4.2 Thorium plant uptake

Thorium is, similar as uranium, non-essential element for plants; in addition, it is relatively less mobile than uranium. The chemical toxicity of actinides may be similar to that of heavy metals, however, radiotoxicity associated with radioactive decay can result in additional toxic effects on a plant [102]. However, according to [103], Th plant accumulation has not affected the plant biomass. On the other hand, young wheat seedlings which was germinated in thorium nitrate solution had decreased calcium content in all parts of the seedlings, which can pose negative effect to the plant.

Thorium soil-to-plant transfer factor is less for finer textured soil. While according to the [104] research, TF (transfer factor) value of thorium was less in case of clay soil. The analysis of soil group effects at the plant group level showed few significant differences (all cereals and fodder only) with clay soils showing significantly lower TF values than sand and loam soils. According to the IAEA reports [105], the highest TF value was observed for pasture, then fodder crops and fruits. There were differences between the crop groups, for instance, the lowest TF value was for tubers and equal to $2.0 \times 10^{-4}$, significantly different from that for fodder ($4.8 \times 10^{-3}$) and leafy vegetables ($1.2 \times 10^{-3}$).

As in case of uranium, thorium translocation is limited and thorium is mostly accumulated in root of the plant [106]. According to the research [102], during the investigation of wheat, the fining was that the content of thorium isotopes in root was substantially greater than that in leaves.

### 1.4.3 Radium plant uptake

Radium migration in soil solution can be caused by high content of total dissolved solids, such as Be, Mg, Ca, Ba, Sr [107]. Radium is a member of the alkaline earth metals, a group which contain important elements for plant nutrition, such as calcium and magnesium. Based on range of research [108-109], there is evident that exist correlation between calcium content in the plant species and radium transfer from soil. For instance, according to [109], during the investigation of different vegetables species, it was determined that highest radium levels were in vegetables with the highest calcium content, i. e. beans.

Radium behaves as other radionuclides and mostly accumulate in root part of the plants [110]. However, compared to uranium and thorium, radium is more mobile due to different solubilities of the elements with oxidation state +2 [111-112].

According to the IAEA 2010 report, the radium transfer factor values varied between the crops type and soil type. Based on the research [113], during the investigation of 108 species of plant, which were collected from different parts of France, radium concentration varied in the range over five orders of magnitude with mean (min–max) of $1.66 \pm 0.03$ (0.020–113) Bq/kg. Investigated plant species show

coherent and decreasing soil-to-plant transfer factor values in the following order: roots > bark > branches and stems ≈ leaves. In research [114], the soil-to-plant transfer factor for radium isotopes (Ra-226, Ra-228) for different crops (cabbage, cucumber, pepper, zucchini, kale) was within the range of that reported by the IAEA 2010. However, among the investigated vegetables, cucumber and cabbage samples shows maximum value of transfer factor for Ra-226, which was equal to 0.07. Determined mean transfer factors for Ra-226 during the pot experiment for five types of plants cultivated on contaminated soil, which was collected from Syrian oilfield were $1.6 \cdot 10^{-3}$ for *Atriplex halimus L.* (quinoa), $2.1 \cdot 10^{-3}$ for *Atriplex canescens* (willow white), $2.5 \cdot 10^{-3}$ for *Atriplex Leucoclada Bioss*, $8.2 \cdot 10^{-3}$ for *Bermuda grass*, and the highest value was $1.7 \cdot 10^{-2}$ for *Alfalfa* [115]. While it was observed that TFs were increasing along with time of planting, as the concentrations of relevant radionuclides in the second and the third harvests were higher than those in the first harvest.

### 1.5 Soil-to-root vegetable transfer factor (TF)

The soil-to-root vegetable transfer factor is commonly used for the evaluation of the ability of plants to uptake of natural radionuclides from the soil, also allowing estimation of internal radiation dose because of food ingestion [116].

The TF of various radionuclides is dependent on many factors, such as: the form in which the activity enters or is present in soil (e.g. as particles, aerosol or solution); the physicochemical properties of the radionuclide; the type of soil and the physicochemical characteristics of the soil (including soil properties such as texture, pH, exchangeable K and Ca and organic matter); the type of crop; crop management practices (irrigation, application of fertilizers) and the degree of preparation of the plant material, such as peeling root crops, washing, etc. [117]. These factors are reasonable to evaluate transfer factor locally since there might be fluctuation between them.

The TF was calculated according to the following equation [118]:

$$TF = A_{p,i} / A_{s,i} \quad (1)$$

where $A_{p,i}$ is the activity concentration of radionuclides in root vegetable part (Bq kg-1), expressed per dry mass, $A_{s,i}$ is the activity concentration of radionuclides in soil (Bq kg-1), expressed per mass and i is the radionuclide index in a sample [136-137].

### 1.6 Root barrier coefficient

In order to establish the root barrier, the root barrier coefficient (RBC) was calculated as the ratio of activity of radionuclide in aboveground parts to the activity of radionuclide in root of the plant [119].

The RBC was calculated according to the following equation [120]:

$$RBC = A_{ab,i} / A_{r,i} \quad (2)$$

where $A_{ab}$,i is the activity concentration of radionuclides in aboveground part of vegetable (Bq kg-1), expressed per dry mass, $A_{r,i}$ is the activity concentration of radionuclides in root crop of vegetable (Bq kg-1), expressed per dry mass and i is the radionuclide index in a sample.

### 1.7 Radioactivity ratio

Radioactivity ratio such as U-234/U-238, Ra-226/U-234, Ra-226/U-238, and Th-230/U-238 serve as geochemical and radiological indicators in assessing the behaviour, mobility, and source differentiation of natural radionuclides in environmental compartments, particularly within the soil–plant system.

The activity ratio U-234/U-238 in soil typically deviates from secular equilibrium (1.0) due to alpha-recoil effects and preferential leaching of U-234.

In soils, the Ra-226/U-238 ratio is mostly below unity (0.2–0.8) because Ra-226 is more mobile and can be leached [121]. However, in root vegetables, Ra-226 tends to accumulate more efficiently than uranium, leading to Ra-226/U-238 ratios more than 1 [122]. The Ra-226/U-234 ratio follows a similar trend, with higher values in plants due to Ra-226's bioavailability [101].

Th-230 is relatively immobile in soils due to its strong adsorption to mineral surfaces. Consequently, the Th-230/U-238 ratio in soils is often close to equilibrium (~1.0) in undisturbed systems [123]. However, root vegetables could demonstrate much lower Th-230/U-238 ratios (0.01–0.1) because thorium is poorly translocated into plants compared to uranium [124].

# 2 EXPERIMENTAL PARTS

## 2.1 Sampling of the soil

Soil samples were sampled in May 2019, 2020, and 2021 from the territory of Almaty region (Baiterek, located about 40 km from Almaty (2019), Koklaisai village, 25 km away from Almaty city (2020) and Turkestan region (Kyzemshek village, Suzak district (2021). Kyzemshek is a village, which was formed as a settlement of miners of the Uvanas uranium deposit.

Soil was chosen considering the fact that vicinity of chosen area was not affected by mineral fertilizers.

Approximately 100 kg of soil was collected from five points and mixed into one representative sample [125-126]. The soil of the Almaty region according to [12] belongs to subzones of light and ordinary sierozems, meanwhie soil of Turkestan region belongs to meadow-sierozem saline soils.

Investigated samples were placed into polythene bags, labelled, and transported to the Laboratory of Radiation Ecology (al-Farabi Kazakh National University, al-Farabi 71/23, Almaty, Kazakhstan). In the laboratory, the soil was air dried, sieved (d = 2 mm) and used for vegetation experiments [127].

## 2.2 Pedological soil properties

*Soil organic matter*

Soil organic matter was determined following gravimetric method for determining organic matter [128]. The gravimetric method is based on determining the mass of the ash residue of soil sample after calcination of the sample at temperature of 525 °C. The loss of mass during calcination is taken as a mass fraction of organic matter.

*pH of soil*

The pH of the investigated soil was determined in the water extract according with GOST 26423-85 [129]. An air-dried soil sample, with a mass of 10.00 ± 0.01 g was placed into a beaker, and 25 mL of distilled water was added (soil-to-water ratio of 1:2.5). The mixture was stirred thoroughly and left to stand for 30 minutes with occasional stirring. After settling, the pH value was measured in the supernatant using a glass electrode and a potentiometric pH meter calibrated with standard buffer solutions.

## 2.3 Selection of the seeds of the root vegetables

The seeds of the root vegetable *D.carrota* (Carrot “Nantes”, Agro-firm AILITA, Russia Federation) was purchased in the local market and grown on soils from the Almaty region and South Kazakhstan (closed to uranium mine). In the

frame of current research, *D.carrota* was chosen according to the food basket of population of Kazakhstan [80].

The seeds of the root vegetable *R. sativus* (Radish "Rubin", Scientific Production Enterprise "INVENT+", village Zatobolsk, Kostanay region, Kazakhstan) were purchased in the local market and grown on soil from the Almaty region (2019).

### 2.4 Vegetation experiment

The soil from Baiterek village, collected in 2019, was fertilised with two different mineral fertilisers: ammonium nitrate (AN) and mono-potassium phosphate (MPP).

The soil (Koklaisai 2020, Kyzemshek 2021) was fertilised with nine different fertilisers to investigate effect of different fertilizers on transfer of natural radionuclides from soil to plant system. Fertilizers chosen were that, which are commonly used in Kazakhstan and can be purchased in specialized shops in Kazakhstan (Table 2).

Table 2 - General information about fertilizers given by producers

| № | Type of fertilizer | $P_2O_5$ / % | $K_2O$ / % | N / % | Producer |
|---|---|---|---|---|---|
| 1 | Ammonium nitrate (AN) | - | - | 33 | "Fasko+", Russian Federation |
| 2 | Mono-potassium phosphate (MPP) | 50 | 33 | - | "Bujskij Himicheskij Zavod", Russian Federation |
| 3 | Organo-mineral mixture (OMM) | 5 | 8 | - | "Kemira", Russia Federation |
| 4 | NPK (LZ) | 12 | 15 | 10 | "RusAgroHim", Russia Federation |
| 5 | Superphosphate (SP) | 30 | - | 9 | "Garden Retail Service", Russia Federation |
| 6 | Double superphosphate (DSp) | 41 | - | 5 | "Garden Retail Service", Russia Federation |
| 7 | Phosphoric fertilizer (Ph) | 20 | - | 8 | "Garden Retail Service", Russia Federation |
| 8 | Peat fertilizers (PF) | 3 | 3 | 1 | "AgroSnabRetail", Russia Federation |
| 9 | Phitomicro fertilizer (MF) | - | - | 1 | Scientific production and |

| | | | | | |
|---|---|---|---|---|---|
| | | | | | technical center "Zhalyn", Kazakhstan |

*"-" – information not given by the producer*

The vegetation experiment was carried out according to classical agrochemical reference [126]. Two-litre plastic pots were used for cultivation of *R. sativus* (Figure 6). At the same time, *D.carrota* was cultivated in 6 litre plastic pots. *D.carrota* are root vegetables that grow deep, requiring more space for root development compared to *R. sativus*. A 6-liter pot provides sufficient space for the proper growth of the *D.carrota* root system, allowing the root to develop to the desired size.

Pieces of glass were prewashed with hydrochloric acid and then placed as drainage in 2/3 of the bottom of the pot, afterwards, those pots were filled with soil.



Figure 6. Cultivation of root vegetables under open conditions

Seeds were pre-treated by washing with 1 % formalin solution with purpose of disinfection from any microorganism on the surface of seeds, after that they were rinsed with distilled water. The germination of seeds was carried out on a filter paper moistened by water and placed a Petri dish. After germination, the planting of sprouts into pots was carried out (Figure 7).



Figure 7. Germination of seeds of root vegetables

The vegetation experiment was carried out under open environment conditions. Plants were cultivated in ten pots. Fertilizers were added according to

the recommendation of their usage. The soil samples were mixed with a certain amount of fertilizer and placed into pots. The last pot was without mineral fertiliser. From two to ten vegetable plants were cultivated per pot. Plants were watered depends on dryness of the soil, except on rainy days, with similar amounts of water, equalling to 400 mL per watering per pot [126]. Root vegetable was cultivated in June and harvesting was carried out at the beginning of October.

### 2.5 Sample pre-treatment

After vegetation experiment, the soil from each pot was air dried (Figure 8). Then it was sieved through a 1 mm sieve and homogenised. A subsample of 5 g was taken from each soil sample. These subsamples were ashed at 650°C for four hours to remove organic matter.



Figure 8. Pre-treatment of soil samples

Vegetative organs of root vegetables were separated and washed with distilled water. After that, plant samples were crushed into small pieces, air dried and homogenized (Figure 9). The plant samples were ashed at 650°C for four hours. The temperature was raised gradually, at the beginning with intervals of 20–30°C up to 150°C. At this temperature, samples stayed for one hour to prevent the burning of the samples.

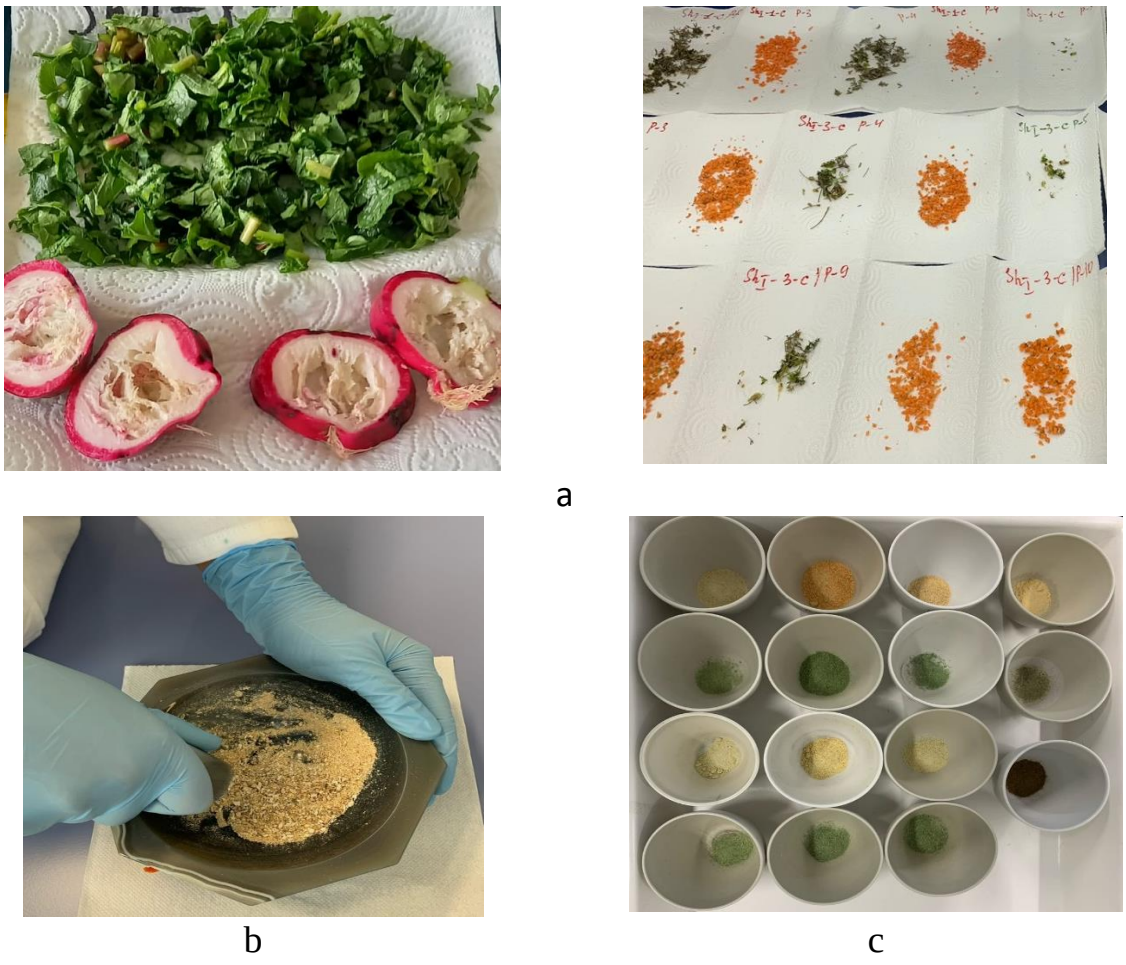


Figure 9. Pre-treated root vegetable samples: a – air drying of samples, b – homogenization of samples, c – preparation for ashing

### 2.6 $k_0$-INAA analysis

For $k_0$-INAA, a known aliquot of solid (190 mg - 240 mg) and liquid (2.6 g - 2.9 g) fertilizer was sealed in a polyethylene ampoule.

For determination of intermediate/median and long-lived radionuclides, the samples together with an Al-0.1 % Au standard (ERM-EB530A alloy) were stacked together, fixed in a polyethylene vial and irradiated for 12 hours in the carousel facility of a TRIGA Mark II reactor (Neutron Activation Analysis group, Jožef Stefan Institute, Ljubljana, Slovenia) with a thermal neutron flux of $1.1 \times 10^{12}$ $cm^{-2}$ $s^{-1}$ [130].

After irradiation, the aliquot was measured after 4, 8 and 23 days of cooling on absolutely calibrated HPGe detectors (40 % and 45 % relative efficiency). For peak area evaluation, the HyperLab program was used [131]. The values $f$ = 22.54 (thermal to epithermal flux ratio) and $\alpha$ = –0.0075 (epithermal flux deviation from the ideal 1/E distribution) in the chosen irradiation channel of the carousel facility were used to calculate mass fractions. For mass fractions and effective solid angle calculations, the software package Kayzero for Windows V3 [132] was applied, where the $k_0$-database from the year 2020 was used [133].

For QA/QC purposes for $k_0$-INAA, the certified reference material BCR-320R channel sediment was irradiated together with the samples. In order to prove the reliability of the results the calculation of $E_n$-score was done. The data (Figure 10) were evaluated using their $E_n$-score [134] and were within $|E_n| \leq 1.0$, indicating the successful performance of the $k_0$-INAA method.

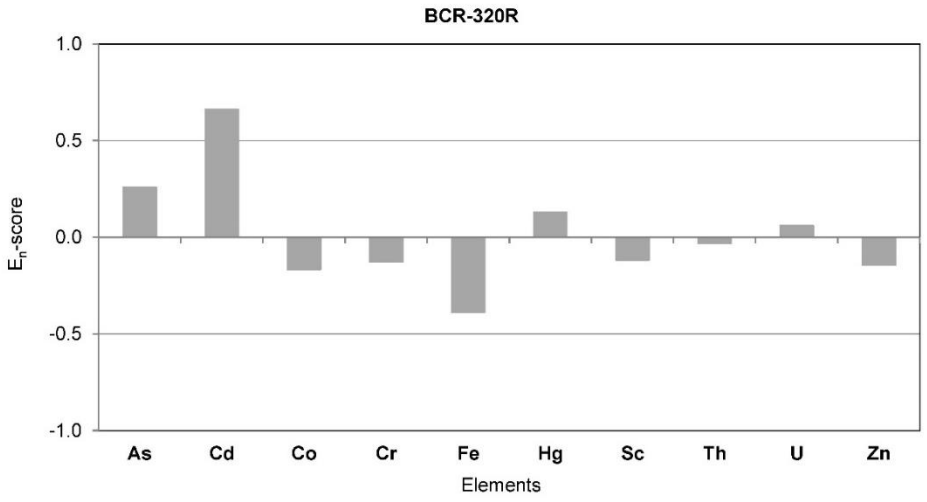



Figure 10. Evaluation of $k_0$-INAA data by $E_n$-score for BCR-320R channel sediment

### 2.7 Determination of radionuclides: sample digestion procedure

The sample digestion was carried out according to [135].

The approximately 1 g of investigated samples and lithium borates in a 1:1.5 ratio and U-232, Th-229 and Ba-133 tracers were added to a platinum crucible and dried at 90°C. After that, the completely dried sample was placed in Claisse LeNeo furnace (Malvern Panalytical, U.K.) (Figure 11).

The fusion was carried out at 1050°C for 30 minutes. The obtained glass, after fusion, was immediately poured into stirred distilled water (100 mL) in a Teflon beaker. The contents of the Teflon beaker were transferred into a glass beaker. After that, the beaker was placed on a hot plate with temperature $125^0$C ± 10°C with stirring, and 10 mL of concentrated nitric acid was added for dissolution of obtained glass. When the volume of solution was reduced to 50 mL, the temperature had to be decreased to 90°C. After the cooling of the sample, 1 mL of 0.2 M polyethylene glycol was added for removing silicates and stirring was applied for 1 hour. The solution was left overnight. Then solution was prepared for simultaneous separation of uranium, thorium and radium.




Figure 11. The sample digestion using Claisse LeNeo furnace

### 2.7.1 Radiochemical separation procedure for simultaneous determination of U-234, U-238, Th-232, Th-230 and Ra-226

The radiochemical separation procedure is described elsewhere [136].

Extraction chromatography TEVA resin was used for separation of Th isotopes, and UTEVA resin was used for U isotopes, while the rest of the sample, which passed through the second column, was used for Ra-226 analysis (Figure 12). TEVA and UTEVA resin were pre-treated with 10 mL of distilled water, 10 mL of 1 M $HNO_3$ and 10 mL of 3 M of $HNO_3$ before the radiochemical separation.

The sample was filtered through a quantitative filter paper before loading on the TEVA and UTEVA columns, which were stacked together in tandem as shown on Figure 12. After solution passed through the resin, columns were washed with 30 mL of 3 M $HNO_3$ for elution of Ra, while Th was retained on TEVA resin and U on UTEVA resin.

Columns were then separated and treated separately. UTEVA column was washed with 5 mL of 9 M HCl and 20 mL of 5 M HCl – 0.05 oxalic acid to remove residual of thorium and other impurities. After that, uranium was desorbed from UTEVA with 15 mL of 1 M HCl. For micro-co-precipitation of uranium, 0.1 mL of 0.5 mg/mL Nd carrier, 1 mL of 15 % of $TiCl_3$ and 1 mL of concentrated HF were added to solution. Obtained solution was placed into the ice bath for 30 minutes for effective co-precipitation. Preparation of counting source was carried out with filtration of micro-precipitate using 0.1 μm filter (Eichrom, USA). Finally, the filter was glued to Al disc and dried under heating lamp.

TEVA column was washed with 20 mL of 9 M HCl and 5 mL of 6 M HCl to desorb thorium. Collected solution was evaporated until the dryness. The residue was dissolved with 15 mL of 1 M HCl and 0.1 mL of 0.5 mg/mL Nd carrier and 1 mL of concentrated HF were added to the solution, and then placed into the ice bath for 30 minutes. Then Preparation of counting source was carried out with filtration of micro-precipitate using 0.1 μm filter (Eichrom, USA)..Finally, the filter was glued to Al disc and dried under heating lamp.

1 mL of concentrated $H_2SO_4$ and 1 mL of 50 mg/mL of $Pb(NO_3)_2$ were added to radium containing solution to co-precipitate radium and barium with $PbSO_4$. After

the 10 min of stirring, the sample was centrifuged for 5 min at 3000 rpm. The precipitate was washed with distilled water until the neutral pH of supernatant. After that, precipitate was dissolved with addition of 5 mL of 0.1M EDTA/0.5M NaOH and usage of ultrasound bath (Elma, Germany). Then 0.3 mL of 0.3 mg/mL of barium carrier and 1 drop of liquid pH indicator were added. In order to adjust pH of solution between 3-4, 1:1 acetic acid was added. For forming $Ba(Ra)SO_4$ precipitate, 4 mL of saturated $Na_2SO_4$ were added. Then 0.3 mL of 0.125 mg/mL of $BaSO_4$ substrate were added. After the 30 minutes, counting source was prepared by filtering of the solution through 0.1 μm filter (Eichrom, USA). Finally, the filter was glued to Al disc and dried under heating lamp.



Figure 12. Tandem radiochemical separation of Th, U and Ra

### 2.7.2 Alpha–particle spectrometry

For the measurement of alpha-particles of U-238, U-234, Th-232, Th-230 and Ra-226, an alpha-spectrometry system (Alpha Analyst, Canberra, USA) with PIPS semiconductor detectors was used. Data analyses were performed using Apex Alpha spectroscopy system software. The alpha-emitting source was measured until a statistically sufficient number of counts were acquired (Figure 13). The count time was from 72 to 120 hours.

Chemical recovery of Ra-226 was measured on coaxial HPGe gamma-spectrometry (Canberra, USA) by measurement of added Ba-133 tracer relative to the Ba-133 standard.

QA/QC procedure included regular background and calibrating sources measurement for checking instrument performance. Combined standard uncertainty evaluations of the activity concentrations of U-234, U-238, Th-230 and Th-232 were done according to guide to the expression of uncertainty in measurement [137].

Calculation of activity concentration of uranium and thorium isotopes were done according to the following equations (3-6):

$$A_i = \frac{P_i \cdot m_{tr} \cdot A_{tr}}{P_{tr} \cdot m_s} \ [Bq/kg] \qquad (3)$$

where:
$P_i$ - net peak area of isotope
$A_i$ - activity concentration of isotope in the sample in Bq/kg
$A_{tr}$ - activity concentration of isotope in the tracer in Bq/kg
$m_{tr}$ - mass of added tracer (g)
$P_{tr}$ - net peak area of tracer
$m_s$ - mass of the sample (kg)

Combined standard uncertainty evaluations of the activity concentrations were done according to guide to the expression of uncertainty in measurement [137] and expressed as following:

$$u_{A_i} = A_i \cdot \sqrt{\left(\frac{u(P_{tr})}{P_{tr}}\right)^2 + \left(\frac{u(m_{tr})}{m_{tr}}\right)^2 + \left(\frac{u(A_{tr})}{A_{tr}}\right)^2 + \left(\frac{u(P_i)}{P_i}\right)^2 + \left(\frac{u(m_s)}{m_s}\right)^2} \quad (4)$$

Expanded uncertainty is obtained by multiplying combined standard uncertainty with a coverage factor of 2.

Calculation of Ra-226 activity concnetration was done according to the following equations:

Sample recovery calculation: determinination of recovery is obtained by gamma-ray spectrometry

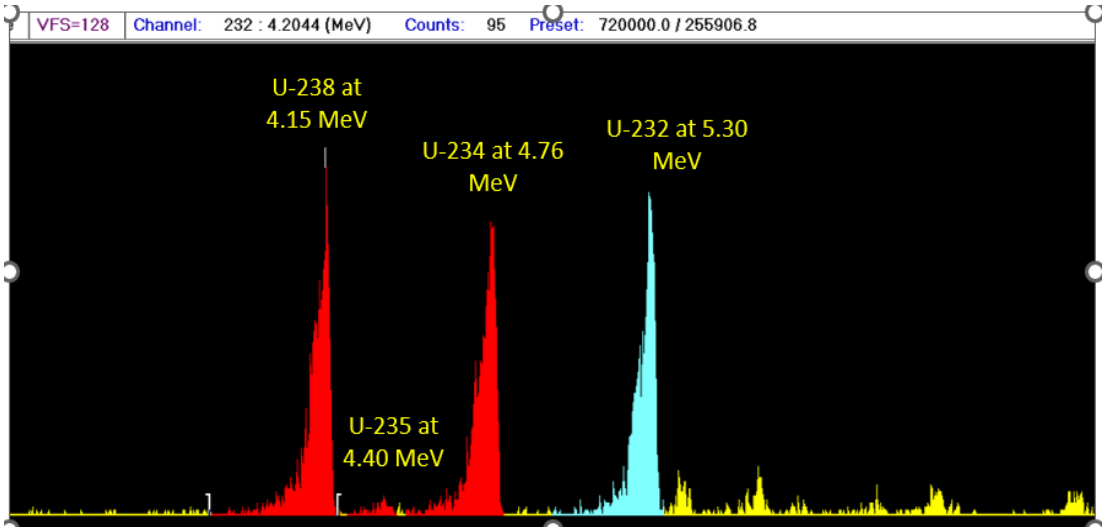
$$R_{chem} = \frac{P_{Ba-133_{sample}}}{t_{Ba-133_{sample}} \cdot m_{Ba-133_{sample}}} \cdot \frac{t_{Ba-133_{std}} \cdot m_{Ba-133_{std}}}{P_{Ba-133_{std}}} \quad (5)$$

where:
$R_{chem}$ - radiochemical yield (recovery)
$P_{\text{Ba-133 sample}}$ - net peak area of Ba-133 in the sample
$t_{\text{Ba-133 sample}}$ - time of the sample measurement (s)
$m_{\text{Ba-133 sample}}$ - mass of added Ba-133 in the sample (g)
$t_{\text{Ba-133Std}}$ - time of measurement of Ba-133 in barium standard disc (s)
$P_{Ba-133_{std}}$ - net peak area of Ba-133 in the standart
$m_{\text{Ba-133Std}}$ - mass of added Ba-133 in barium standard disc (g)

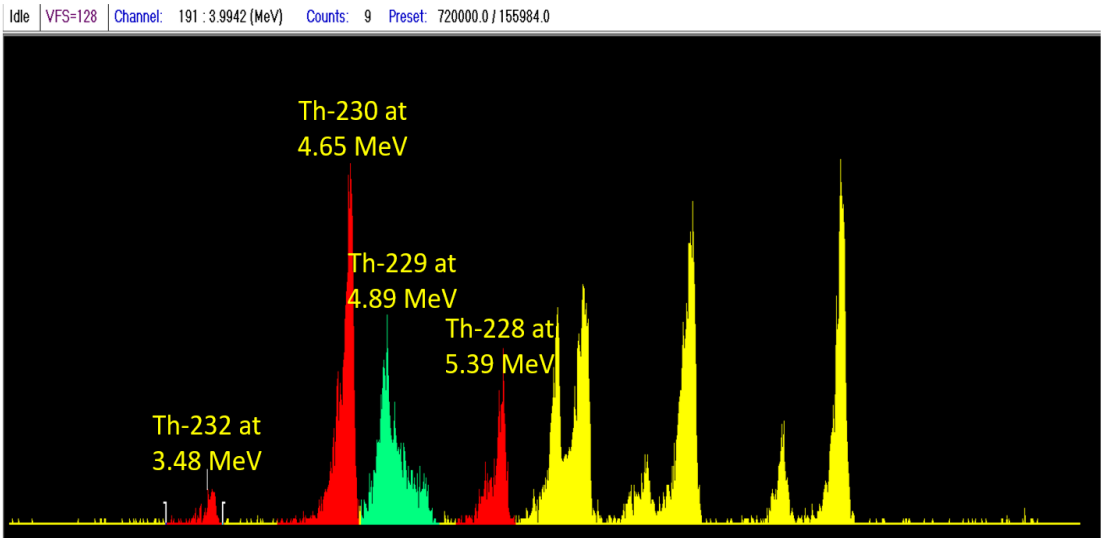
Activity concentration of Ra-226 in the sample

$$A_{Ra-226} = \frac{P_{Ra-226}}{t_{Ra-226} \cdot \varepsilon_{\alpha_{det}} \cdot m_{sample} \cdot R_{chem}} \quad (6)$$

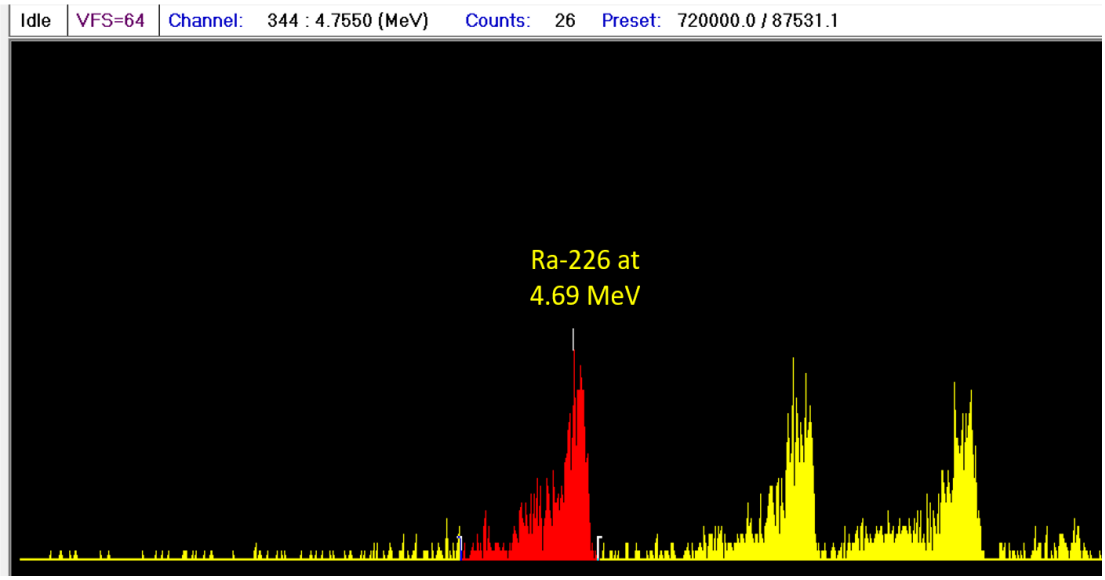
where: $A_{\text{Ra-226}}$ - activity concentration of Ra-226 in the sample in (Bq/kg)
$P_{\text{Ra-226}}$ - peak area of Ra-226
$t_{\text{Ra-226}}$ - time of measurement of the sample (s)
$m$ -mass of the sample (kg)
$\varepsilon_{\alpha\ \text{det}}$ - efficiency of an alpha detector
$R_{\text{chem}}$ - radiochemical yield (recovery)




a. Uranium isotopes




b. Thorium isotopes




c. Ra-226

Figure 13. Typical alpha – spectrum of uranium isotopes, thorium isotopes and Ra-226

### 2.7.3 Method validation

A standard reference material NIST SRM 4359 (Seaweed Radionuclide Standard) and a reference material IAEA-375 (Radionuclides and Trace Elements in Soil) were used as quality control samples.

Table 3 - Comparison of certified and measured activity concentrations (Bk/kg) obtained by alpha- spectrometric determinations in reference materials.

| Reference material | Radionuclide | Certified value[a] | Information value | Measured value[b] |
|---|---|---|---|---|
| NIST SRM 4359 | U-238 | 8.67 ± 0.54 | | 7.99 ± 0.64 |
| | U-235 | 0.400 ± 0.047 | | 0.41 ± 0.24 |
| | U-234 | 9.5 ± 1.1 | | 8.69 ± 1.68 |
| | Ra-226 | | 5.7 | 5.54 ± 0.64 |
| | Th-230 | | 3.3 | 4.18 ± 1.26 |
| | Th-232 | 2.40 ± 0.30 | | 2.72 ± 0.36 |
| IAEA-375 | U-234 | | 25 ± 8 | 24.9 ± 0.48 |
| | U-238 | | 24.4 ± 5.4 | 23.8 ± 0.56 |
| | Th-232 | 20.5 ± 1.3 | | 19.8 ± 2.4 |
| | Ra-226 | 20 ± 2 | | 20.2 ± 4.8 |

The obtained results (Table 3) showed good agreement between the assigned and measured values.

[a] – From the certificate, uncertainty values given as combined expanded

uncertainties (k=2)

[b] – The values are presented as averages with standard deviations (3 replicates)

In order to prove the reliability of the results the calculation of $E_n$-number was done.

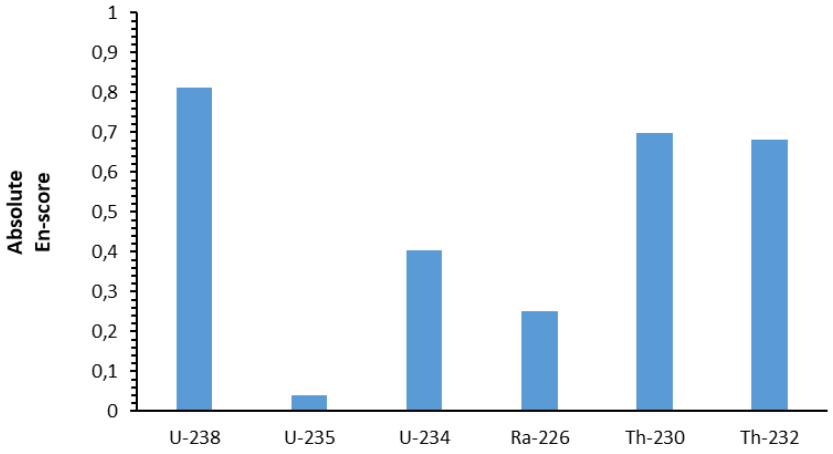



Figure 14. Evaluation of alpha-spectrometry data by *E*n-score for NIST SRM 4359 Seaweed

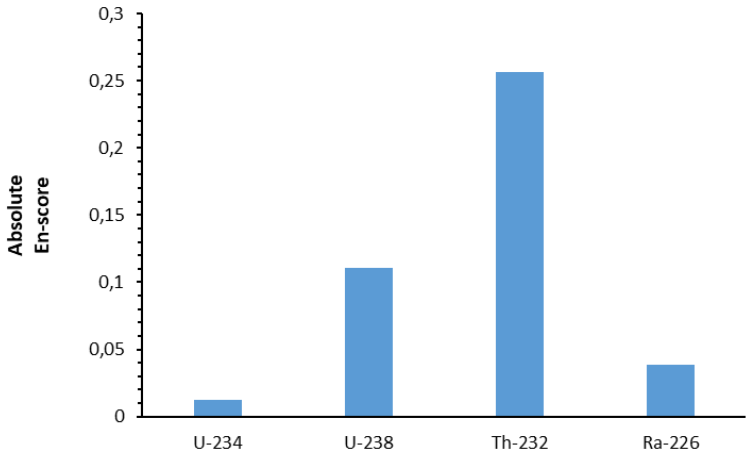



Figure 15. Evaluation of alpha-spectrometry data by $E_n$-score for IAEA-375 (Radionuclides and Trace Elements in Soil

The data (Figure. 14, 15) were evaluated using their $E_n$-score [138] and were within $|E_n| \leq 1.0$, indicating the successful performance of the alpha-spectrometry method.

### 2.8 Sequential extraction

To analyse the fractionation and bioavailability of uranium, a sequential extraction protocol was applied [139]. The geochemical phases of each extraction step with extracting solution are presented in Table 4. The analytical procedure

includes extraction of radionuclides using different extraction solutions. Four grams of soil sample were mixed with each extracting solution; the solid-to-liquid ratio was 1:10. After centrifugation, samples were filtered through the paper filter.

Table 4 - The reactants and conditions of sequential extractions

| Step | Soil fractions | Corresponding minerals | Used reactant | Procedure |
|---|---|---|---|---|
| 1. | Water-soluble F0 | - | MilliQ-water | Shaken for 2 h; centrifuged at 4000 rpm for 30 min |
| 2. | Exchangeable F1 | - | 1 M $NH_4Ac$ (pH 8.2) | Shaken for 2 h; centrifuged at 4000 rpm for 30 min |
| 3. | Bound to carbonates F2 | Carbonates (calcite, etc.) | 1 M $NH_4Ac$ adjusted to pH 5.0 with HOAc | Shaken for 2 h; centrifuged at 4000 rpm for 30 min |
| 4. | Bound to Fe-/Mn-oxides F3 | Oxides of iron and manganese (goethite, hematite, perrolusite) | 0.04 M $NH_2OH{\cdot}HCl$ in 25 % (v/v) HOAc | 80 °C; shaken for 5 h; centrifuged at 4000 rpm for 30 min |
| 5. | Bound to organic matter F4 | Organic substances (humus, etc.) | 30 % $H_2O_2$ in 0.02 M $HNO_3$ (pH 2) | 80 °C; shaken for 5 h; centrifuged at 4000 rpm for 30 min |
| 6. | Strongly bound F5 | Clay minerals (chlorite, kaolinite, etc.) | 4 M $HNO_3$ (pH 2) | 80 °C; shaken for 6 h; centrifuged at 4000 rpm for 30 min |

The fractions obtained after sequential extraction were evaporated and residue dissolved in 3 M $HNO_3$ to convert for suitable conditions for further radiochemical separation and measurements of radionuclides as described in chapters 2.7.1 and 2.7.2.

## 2.9 Simultaneous thermal analysis

The simultaneous thermal analysis is based on the decomposition of the main components of the soil absorbing complex during stepwise heating at different temperatures, accompanied by changes in the mass of the analyzed samples.

Sample preparation included the homogenization of samples with pestle and mortar crushing. Samples were placed in corundum crucibles and analyzed on NETZSCH STA 449 F3A-0372- M with NETZSCH Proteus software. The identical

empty corundum crucible was put with the analyzing sample as a reference. The temperature grew from 30 to 800°C. The heating rate was equal to 20° K/ min. The atmosphere of the analysis was nitrogen gas with purity of 99.99 %.

# 3 RESULTS AND DISCUSSIONS

## 3.1 Activity concentration of natural radionuclides in fertilizers

Fertilizers showed a wide range of uranium, thorium, and radium concentrations, which are presented in Table 5. In general, the activity of investigated fertilizers is relatively low; according to the Technical Regulations of the Eurasian Economic Union "On requirements for mineral fertilizers" [140], activity concentrations of investigated fertilizers have not exceeded 1000 Bq/kg, while according to the Technical regulations of Kazakhstan "Requirements for the safety of fertilizers" [141], the specific activity of natural radionuclides for phosphorus fertilizers and soil-improving substances should not exceed 4000 Bq/kg.

Table 5 - Content of natural radionuclides in fertilisers with expanded standard uncertainties (k = 2)

| Fertilizers | Activity concentration, Bq/kg (dry weight) | | | | |
|---|---|---|---|---|---|
| | U-234 | U-238 | Th-230 | Th-232 | Ra-226 |
| NPK fertilizer | 24 ± 2 | 24 ± 3 | 27.5 ± 3.8 | 19 ± 3 | 15 ± 1 |
| Organo mineral mixture (OMM) | 19.8 ± 1.5 | 19 ± 2 | 25.7 ± 1.5 | 7.3 ± 0.6 | 11 ± 1 |
| Superphosphate (SP) | 143 ± 11 | 144 ± 14 | 89 ± 14 | 30 ± 6 | 14 ± 1 |
| Mono-potassium phosphate (MPP) | 3.9 ± 0.4 | 2.0 ± 0.3 | 28 ± 2 | 3.0 ± 0.6 | 0.6 ± 0.1 |
| Ammonium nitrate (AN) | 2.2 ± 0.3 | 1.7 ± 0.2 | 36 ± 1 | 4.7 ± 0.4 | 1.0 ± 0.1 |
| Double superphosphate (DSp) | 97 ± 7 | 96.2 ± 8.6 | 109 ± 11 | 42 ± 5 | 24 ± 2 |
| Phosphoric fertilizer (Ph) | 146 ± 11 | 148 ± 13 | 238 ± 15 | 11.5 ± 1.1 | 169 ± 4 |
| Peat fertilizer (PF) | 0.02 ± 0.002 | 0.02 ± 0.007 | 0.22 ± 0.03 | 0.03 ± 0.01 | 0.09 ± 0.02 |
| Phytomicro-fertilizer (MF) | 0.01 ± 0.001 | 0.007 ± 0.004 | 0.14 ± 0.03 | 0.009 ± 0.006 | 0.02 ± 0.008 |

Among the investigated phosphate containing fertilizers (superphosphate, mono-potassium phosphate, double superphosphate, phosphoric fertilizer), U-234 concentration varied from 3.8 to 146 Bg/kg, U-238 concentration ranged from 1.9 to 148 Bq/kg, Th-230 concentration varied from 0.14 to 238 Bq/kg, Th-232 concentration varied from 0.009 to 42 Bq/kg, and Ra-226 concentration varied from 0.9 to 169 Bq/kg.

In several research [142-144] it has been reported that the activity of phosphate containing fertilizers (especially for U-238 content) correlates well with their phosphate content. The highest concentration of U-234, U-238, and Ra-226

was determined in phosphoric fertilizer (with 20 % of $P_2O_5$ content), meanwhile lowest concentration in mono-potassium phosphate (with 50 % of $P_2O_5$), the good correlation previously reported is not presented in our case, the same trend was reported in [2] research. This can be related with usage of different raw phosphate ore and production process which was applied.

Among the other fertilizers, which includes organic fertilizers (peat fertilizer, phitomicro-fertilizer, organo-mineral mixture) and mineral fertilizer (ammonium nitrate, NPK fertilizer), activity concentrations of uranium, thorium and radium isotopes are relatively low. The highest concentration of all isotopes among the afore-mentioned fertilizers was determined in LZ fertilizer, which belongs to NPK fertilizers. Determined high concentration of radionuclides in LZ fertilizer can be explained by its processing method, phosphate rocks can be used as initial raw material, according to given information by producer LZ contain 12 % of $P_2O_5$.

It is worth noting that organic fertilizer organo-mineral mixture showed higher activity concentration of uranium, thorium, and radium isotopes in comparison to phosphate containing fertilizer, for instance mono-potassium phosphate.

### 3.2 Content of major, minor and trace elements in fertilizers

Most fertilizers have complicated compositions and, in addition to the intended elements and nutrients, can include contaminants [145], such as radionuclides and rare earth elements (REEs) [146-150]. $k_0$-instrumental neutron activation analysis ($k_0$-INAA) was applied to determine the mass fractions of major, minor and trace elements (Table 6) in fertilizers obtained from the local market in Almaty city and hence are used by locals for improvement of quality of crops.

Table 6 - The mass fractions of elements obtained by $k_0$-INAA with combined standard uncertainty for studied fertilizers are given in mg/kg [151-152].

| El. | Superphosphate[a] | OMM[a] (Fert Ika) | Monopotassium phosphate[a] | Ammonium nitrate[a] | NPK | Double superphosphate[a] | Phosphoric [a] | Peat | Microfertilizer |
|---|---|---|---|---|---|---|---|---|---|
| K | 3185±620 | 64360±2277 | 285650±10052 | 7.85±1.60 | 140100±4986 | 1400 ± 80 | 82700 ± 2900 | < 12[b] | 6.21 ± 0.33 |
| Ca | 89000±4641 | 104050±3747 | < 897[b] | 121±20 | 139450±7548 | 184600 ± 6500 | 194500 ± 7000 | 85.8 ± 4.1 | < 3.2[b] |
| Ba | 248±15 | 42.5±2.5 | < 21[b] | 5.25±0.26 | 125±5 | 51.2 ± 3.9 | 91.9 ± 5.6 | 0.800 ± 0.044 | < 0.078[b] |
| Cs | 0.391±0.027 | 0.329±0.013 | < 0.044[b] | < 0.004 [b] | 0.188±0.013 | 0.356 ± 0.015 | 0.597 ± 0.022 | 0.00130 ± 0.00011 | < 0.0005 [b] |
| Na | 3268±116 | 1991±70 | 1744±62 | 15.2±0.8 | 27180±1111 | 1524 ± 53 | 4273 ± 150 | 430 ± 15 | 2.73 ± 0.10 |
| Rb | 12.1±0.9 | 7.52±0.31 | 33.8±1.3 | < 0.17[b] | 46.4±1.8 | 8.86 ± 0.37 | 23.0 ± 0.8 | 0.0301 ± 0.0056 | < 0.017[b] |
| Sr | 6153±218 | 296±13 | < 30[b] | 30.9±1.3 | 4767±174 | 1205 ± 43 | 866 ± 32 | 2.40 ± 0.12 | < 0.20[b] |
| Cr | 19.0±1.0 | 11.4±0.5 | < 1.3[b] | 0.685±0.172 | 3.86±174 | 12.9 ± 0.5 | 19.9 ± 0.7 | 0.0734 ± 0.0030 | < 0.0046[b] |
| Fe | 3766±136 | 3443±132 | < 17[b] | 52.7±2.3 | 1475±54 | 2630 ± 100 | 12470 ± 440 | 22.6 ± 0.8 | < 0.39[b] |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Co | 1.49±0.06 | 2.22±0.08 | < 0.021[b] | < 0.009 [b] | 0.538±0.021 | 1.00 ± 0.04 | 17.0 ± 0.6 | 0.00993 ± 0.00043 | < 0.0007[b] |
| Zn | 33.1±1.5 | 12.4±0.6 | 1.52±0.21 | 0.223±0.057 | 11.0±0.6 | 24.4 ± 0.9 | 46.2 ± 1.7 | 0.428 ± 0.018 | 0.131 ± 0.007 |
| Hg | 0.57± | < 0.125[b] | < 0.42[b] | < 0.017 [b] | < 0.18 [b] | < 0.23[b] | < 0.07[b] | < 0.0021[b] | < 0.0013[b] |
| As | 2.26±0.33 | 0.792±0.045 | < 0.63[b] | 0.0126±0.0023 | < 1.5[b] | 1.57 ± 0.07 | 10.8 ± 0.4 | 0.0139 ± 0.0009 | < 0.0008[b] |
| Sb | 0.256±0.019 | 0.0852±0.0051 | 0.309±0.014 | 0.00757±0.00040 | 0.088±0.015 | 0.172 ± 0.008 | 0.325 ± 0.013 | 0.00401 ± 0.00016 | < 0.00011[b] |
| Se | 1.8± | < 0.32[b] | < 0.99[b] | < 0.031[b] | < 0.51[b] | < 0.55[b] | < 0.39[b] | 0.00380 ± 0.00054 | < 0.0023[b] |
| Ce | 1087±38 | 25.9±1.7 | < 1.5[b] | 0.0358±0.0075 | 241±9 | 194 ± 7 | 43.1 ± 1.5 | 0.0301 ± 0.0013 | < 0.002[b] |
| Eu | 18.6±0.7 | 0.498±0.031 | < 0.0057[b] | < 0.001[b] | 5.95±0.22 | 4.72 ± 0.17 | 0.849 ± 0.036 | 0.000421± 0.000088 | < 0.00003[b] |
| La | 651±23 | 17.0±1.0 | < 0.028[b] | 0.0176±0.0039 | 136±5 | 112 ± 4 | 20.1 ± 0.7 | 0.0128 ± 0.0005 | < 0.0002[b] |
| Nd | 423±15 | 10.7±1.0 | < 4.8[b] | < 0.053[b] | 111±4 | 85.1 ± 3.0 | 18.7 ± 0.9 | < 0.0001[b] | < 0.002[b] |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sc | 0.829±0.031 | 1.17±0.05 | 0.0105±0.0006 | 0.00283±0.00021 | 0.157±0.010 | 0.647 ± 0.023 | 2.43 ± 0.09 | 0.00514 ± 0.00018 | < 0.00004[b] |
| Sm | 63.1±2.2 | 1.60±0.08 | < 0.081[b] | 0.00404±0.00053 | 18.1±0.7 | 14.8 ± 0.5 | 4.00 ± 0.14 | 0.00254 ± 0.00009 | < 0.00006[b] |
| Tb | 6.26±0.22 | 0.238±0.011 | < 0.018[b] | < 0.0012[b] | 2.16±0.08 | 1.84 ± 0.06 | 0.533 ± 0.019 | 0.00037 ± 0.00004 | <0.00016[b] |
| Yb | 7.32±0.26 | 1.16±0.04 | < 0.10[b] | 0.00353±0.00044 | 2.84±0.10 | 3.94 ± 0.14 | 1.44 ± 0.05 | < 0.00067[b] | < 0.00001[b] |
| Th | 17.4±0.6 | 2.36±0.09 | < 0.10[b] | 0.00420±0.00057 | 8.48±0.32 | 8.76 ± 0.29 | 1.76 ± 0.06 | 0.00489 ± 0.00021 | < 0.0003[b] |
| U | 12.0±0.5 | 0.977±0.036 | < 0.54[b] | 0.00574±0.00075 | 1.82±0.10 | 8.37 ± 0.29 | 12.8 ± 0.5 | 0.00139 ± 0.00011 | 0.000899 ± 0.000047 |

a – mass fractions are given on air dry mass basis.

b – limit of detection (LD) calculated as LD=2.706+4.653 √B , where B is the background level in the gamma energy region of the signal peak in question.

Among the investigated fertilizers, the high concentration of calcium, potassium and sodium was determined in solid fertilizers.

Most elements in the liquid organic fertilizers (peat and microfertilizer) were insignificant, except for iron, an essential micronutrient, the content of which was 57 times higher in the case of peat fertilizer in comparison to microfertilizer. Although iron is an essential component for plants, its high concentration may lead to decreased P availability due to the formation of iron-phosphate salts and, therefore, can indirectly harm plants [153]. Iron content was 5, 8.4, 3.6, 3.3, 236.6 times higher in phosphoric fertilizer than in double superphosphate, NPK fertilizer, OMM, superphosphate, ammonium nitrate, respectively.

The highest concentration of strontium was determined in superphosphate and NPK fertilizers. Elevated amount of Ba was determined in all fertilizers, except monopotassium phosphate and microfertilizer. Although strontium and barium can replace calcium in biological systems due to their chemical similarity, their uptake by plants is strongly dependent on the relative abundance of calcium in soil and fertilizers. Calcium is typically present in much higher concentrations than Sr and Ba, the competitive inhibition by Ca often limits the plant uptake of these elements. On other hand, Ba could affect to Ra distribution in soil profile due to formation of Ba(Ra)SO4.

Among the rare earth elements, the content of Ce, Eu, La, Nd, Sm, Tb, and Yb in superphosphate was highest in comparison to other fertilizers. Interestingly, that double superphosphate and phosphoric fertilizer produced by the same producers, has significant differences in REEs content. The content of Ce, Eu, La, Nd, Sm, Tb, and Yb in double superphosphate was 4.5, 5.6, 5.6, 4.5, 3.7, 3.5, and 2.7 times higher than the Phosphoric mineral fertilizer. Only the content of Sc was 3.8 times higher in the case of Phosphoric fertilizer. It could be explained by the producer using different raw materials, i.e., the differences in REEs content in solid fertilizers might indicate the different origins of the raw materials, or different proportion of added raw materials containing REEs. For example, it has been shown that apatite carbonate minerals are more enriched in REEs [154-157]. In the case of double superphosphate and superphosphate, the raw material used for its production could be apatite carbonate minerals.

In monopotassium phosphate and microfertilizer, most of the analyzed components, except for macro-nutrients, were found in concentrations below the detection limit. These fertilizers may be considered for use by the local population; however, such recommendations should be made only after a comprehensive assessment of the background levels of these elements in local soils, as well as an evaluation of the cumulative input from fertilizer application in accordance with the manufacturer’s prescribed usage rates.

### 3.3 Simultaneous thermal analysis of fertilizers

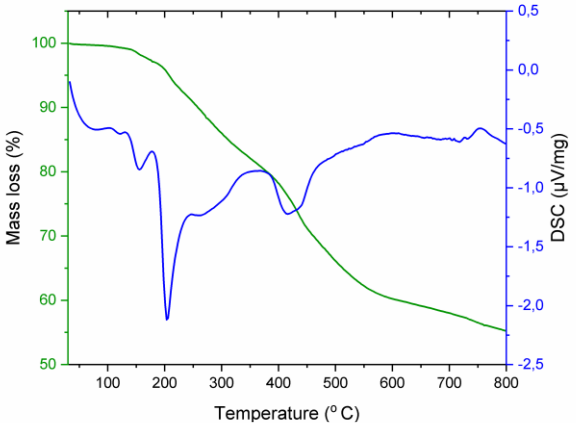
*Results presented based on the published conference paper: Matveyeva I.V., Nursapina N.A., Bakhadur A., Nazarkulova Sh.N., Shynybek B.A., Ponomarenko O.I. Simultaneous thermal analysis of mineral fertilizers purchased in Almaty // BIO WEB of Conference, 2nd International symposium "Innovations in Life Science", 22 April, 2021.*

In order to predict the potential mobility of fertilizer components, simultaneous thermal analysis (STA) was used as fast and simple method to analyze seven solid fertilizers, such as, superphosphate, double superphosphate, monopotassium phosphate, ammonium nitrate, phosphoric, organo-mineral mixture.

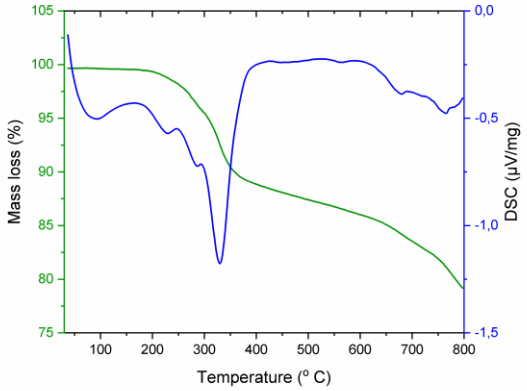
Simultaneous thermal analysis (STA), comprising thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), was applied to evaluate decomposition, evaporation, and ignition processes, as well as to estimate the solubility forms (e.g., water-soluble or organo-soluble), which determine the migration potential of contaminants (especially radionuclides) in the soil-plant system.

This section was based on published results [158] on Conference Paper.

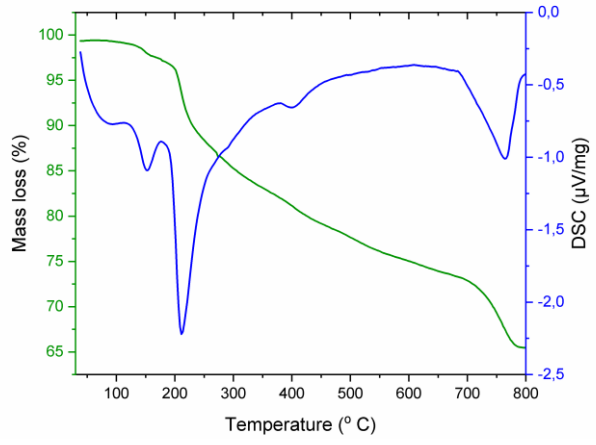
Among the analyzed samples, fertilizers such as superphosphate, double superphosphate, and phosphoric showed significant mass loss (Figure 16) (ranging from 20.9 % to 44.8 %) within the temperature range of 100 to 800°C, indicating the presence of both adsorbed and crystallized water. Their thermal stability is associated with inorganic phosphate compounds that decompose at elevated temperatures. The presence of crystal hydrates may decrease the migration ability of radionuclides; however, their soluble nature suggests that migration is potentially still possible.




*a* – superphosphate



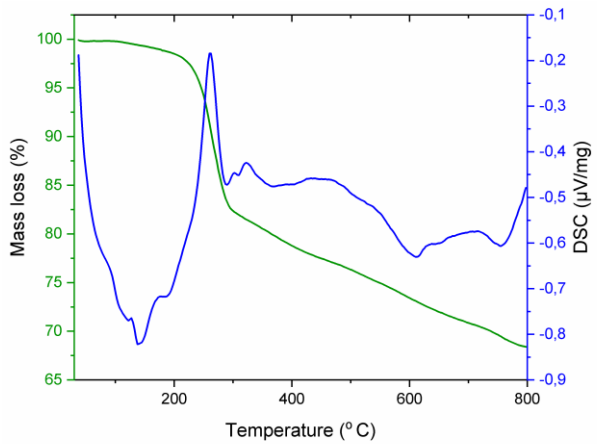

*b* – phosphoric



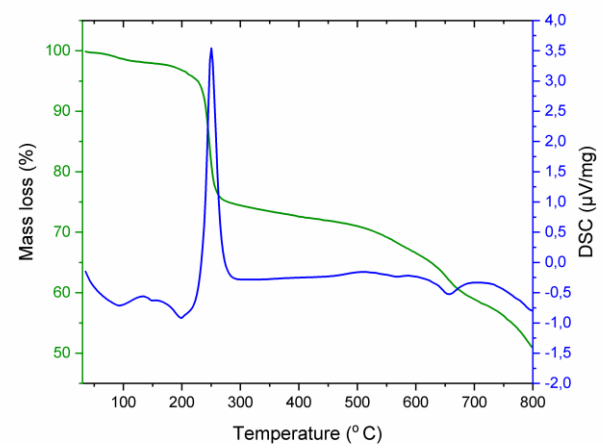
*c* – double superphospahte

Figure 16. TG/DSC curve of superphosphate, phosphoric, double superphosphate fertilizers

Organo-mineral fertilizers such as organo-mineral mixture and NPK fertilizer demonstrated pronounced exothermic effects in the 200–300°C range, related to the combustion of organic matter (Figure 17). This indicates a substantial presence of organo-soluble components, which is aligned with information given by producers.



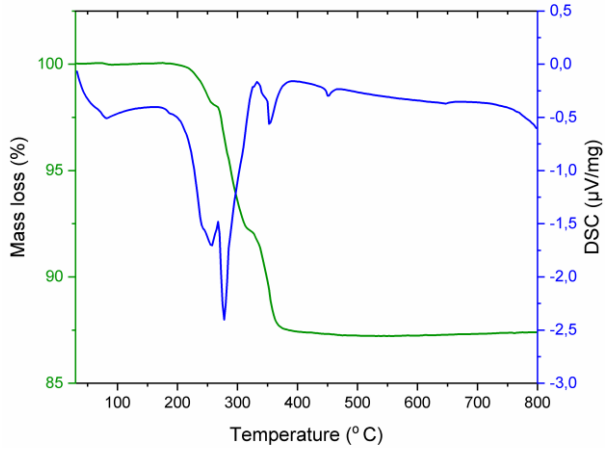

*a* – NPK fertilizer



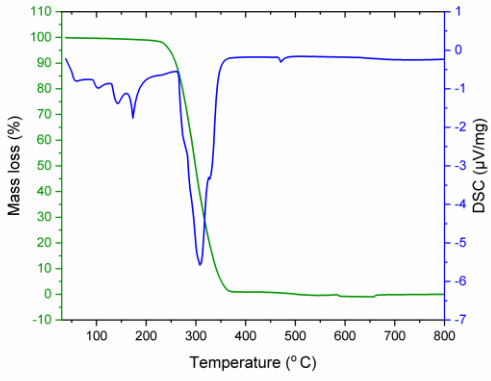

*b* – organo-mineral mixture

Figure 17. TG/DSC curve of NPK fertilizer and organo-mineral mixture fertilizer

Monopotassium phosphate and ammonium nitrate demonstrate almost complete decomposition and evaporation of active components at the early stages of heating (Figure 18). For ammonium nitrate fertilizer, a mass loss of up to 97.8 % was observed due to thermal decomposition of the main component. The high solubility of their components indicates a potentially rapid migration of any present contaminants upon application to soil.




*a* – monopotassium phospahte




*b* -ammonium nitrate

Figure 18. TG/DSC curve of monopotassium phosphate and ammonium nitrate

Based on thermal analysis results, it could be concluded that fertilizers could be classified by their soluble fractions, for instance monopotassium phosphate and ammonia nitrate are containing inorganic water-soluble compounds, which allow to predict high potential of migration ability of components of fertilizers in that water-soluble fraction. Components of organo-mineral mixture and NPK fertilizer mostly belongs to organo-soluble fraction, which could be potentially mobile.

### 3.4 Pedological parameters of the soil

Physicochemical parameters of the investigated soil samples (Almaty Region; Turkestan Region) are shown in Table 7.

Table 7 - Physicochemical parameters of the investigated soil (arithmetic mean values with standard deviations of three replicates)

| Fertilized soil sample | Pedological parameter | | | | | |
|---|---|---|---|---|---|---|
| | Koklaisai village, Almaty region, | | Kyzemshek village, Turkestan region, | | Baiterek village, Almaty region | |
| | Organic matter, [%] | pH | Organic matter, [%] | pH | Organic matter, [%] | pH |
| Unfertilized soil | 4 ± 0.6 | 7.3 ± 0.1 | 3 ± 0.6 | 7.9 ± 0.04 | 7.4 ± 0.07 | 8.01± 0.04 |
| Superphosphate | 5 ± 0.2 | 7.6 ± 0.1 | 4 ± 0.6 | 6.6 ± 0.02 | n/d | n/d |
| Fertika (organo-mineral mixture) | 6 ± 0.5 | 7.7 ± 0.09 | 3 ± 0.4 | 7.9 ± 0.04 | n/d | n/d |
| Mono-potassium phosphate | 3 ± 0.5 | 7.7 ± 0.1 | 3 ± 0.3 | 7.4 ± 0.03 | 7.5 ± 0.01 | 8.06± 0.02 |
| Ammonium nitrate | 3 ± 0.5 | 7.1 ± 0.09 | 3 ± 0.2 | 7.5 ± 0.04 | 7.8 ± 0.19 | 8.03 ± 0.03 |
| NPK fertilizer | 2.7 ± 0.57 | 7.8 ± 0.06 | 2 ± 0.1 | 7.8 ± 0.03 | n/d | n/d |
| Double Superphosphate | 3 ± 0.3 | 7.9 ± 0.07 | 3 ± 0.4 | 7.8 ± 0.03 | n/d | n/d |
| Phosphoric | 5 ± 0.5 | 7.8 ± 0.09 | 2.5 ± 0.3 | 7.2 ± 0.02 | n/d | n/d |
| Peat fertilizer | 5 ± 0.5 | 7.9 ± 0.07 | 2.5 ± 0.2 | 7.5 ± 0.03 | n/d | n/d |
| Phitomicro-fertilizer | 5 ± 0.4 | 7.9 ± 0.13 | 2 ± 0.2 | 7.6 ± 0.03 | n/d | n/d |

**n/d – no data*

As it can be seen from Table X, application of fertilizer during the cultivation period leads to change in soil pH value. Soil factors such as pH and organic matter are likely to be more appropriate predictors for radionuclide mobility. The adsorption of radionuclides on soil is mostly affected by soil pH and soil organic matter. The transfer of metals between the easily available and less-available phases is significantly influenced by the competition of other cations (especially $H^+$) on the organic matter surface [53]. The application of mineral fertiliser for soil from village Baiterek, Almaty Region during the cultivation period leads to an insignificant increase in soil pH. At an alkaline pH, the mobility and bioavailability of uranium are higher due to the domination of anionic uranyl complexes [159-160], which leads to its transfer into the soil-root system [161].

### 3.5 Activity concentration of natural radionuclides in soil samples

The activity concentrations of U-234, U-238, Th-230, Th-232 and Ra-226 in soil from Almaty region (Baiterek village) were obtained by alpha-particle spectrometry. The results are presented in published research article - Nursapina N.A., Shynybek B.A., Matveyeva I.V., Nazarkulova, Sh.N., Štrok M., Benedik L, Ponomarenko O.I. Effect of mineral fertilisers application on the transfer of natural radionuclides from soil to radish (Raphanus sativus L.) // Journal of Environmental Radioactivity, V.247, 2022. 10.1016/j.jenvrad.2022.106863.

Activity concentration of natural radionuclides in fertilized soil fluctuated in comparison to unfertilized soil. From these results, the activity concentrations of U-234 and U-238 in MPP mineral fertiliser were slightly higher than in AN, whereas the contents of Th-230, Th-232 and Ra-226 in AN were slightly higher than in MPP. Considering the amount of fertiliser applied (for radish plant experiment), the activity added with mineral fertiliser was negligible. Nevertheless, mineral fertiliser could change the chemical speciation of radionuclides, which could lead to the enhancement of their mobility and bioavailability.

The activity concentrations of U-234, U-238, Th-230, Th-232 and Ra-226 in soil from Almaty region (Koklaisai village) were obtained by alpha-particle spectrometry. The results are presented in Table 8.

Table 8 - Content of natural radionuclides in soil from Almaty region (Koklaisai village) with expanded uncertainties (k = 2)

| Sample | Added fertilizers | Activity concentration Bq/kg (dry weight) | | | | |
|---|---|---|---|---|---|---|
| | | U-234 | U-238 | Th-230 | Th-232 | Ra-226 |
| Soil from Almaty region | Without fertilizer | 28 ± 2 | 29 ± 4 | 52 ± 6 | 55 ± 6 | 39 ± 3 |
| | Superphosphate | 31 ± 1 | 32 ± 2 | 61 ± 3 | 67 ± 3 | 44 ± 3 |
| | Organo-mineral mixture | 34 ± 3 | 33 ± 1 | 60 ± 1 | 66 ± 3 | 38 ± 2 |
| | Mono-potassium phosphate | 30 ± 1 | 30 ± 1 | 50 ± 2 | 54 ± 2 | 44 ± 2 |
| | Ammonium nitrate | 30 ± 1 | 30 ± 1 | 55 ± 2 | 56 ± 2 | 38 ± 2 |
| | NPK fertilizer | 29 ± 1 | 30 ± 1 | 52 ± 2 | 53 ± 2 | 43 ± 2 |
| | Double Superphosphate | 31 ± 1 | 32 ± 1 | 45 ± 2 | 48 ± 2 | 45 ± 2 |
| | Phosphoric | 30 ± 1 | 30 ± 1 | 57 ± 2 | 61 ± 2 | 45 ± 2 |
| | Peat fertilizer | 30 ± 1 | 30 ± 1 | 46 ± 1 | 48 ± 2 | 41 ± 2 |
| | Phitomicro-fertilizer | 30 ± 1 | 31 ± 1 | 50 ± 2 | 52 ± 2 | 40 ± 2 |

The activity concentration of natural radionuclides in fertilized soils of Almaty region (Koklaisai village) insignificantly fluctuated in comparison to unfertilized soil. However, have to note that addition of fertilizer could lead to change of chemical form of radionuclides.

Considering the amount of fertiliser applied (for carrot plant experiment), the percentages of total activity added to soil before the cultivation experiment varied from 0.075 to 1.65 %, depending on applied fertilizer.

In order to assess the potential impact of fertilizer to radionuclide accumulation in soil, the zeta-score was applied according to ISO 13528 [162]. Zeta-score was applied to evaluate how significantly the activity concentration of radionuclides in fertilized soil differs from unfertilized soil. The results of zeta-score presented in Table 9.

Table 9 - The result of absolute zeta-score for fertilized soil samples from Koklaisai village, Almaty region.

| *Radionuclide* | *SP* | *OMM* | *MPP* | *AN* | *LZ* | *DSP* | *Ph* | *PF* | *MF* |
|---|---|---|---|---|---|---|---|---|---|
| | *ζ-score* | | | | | | | | |
| U-234 | *1.34* | *1.66* | *0.89* | *0.89* | *0.45* | *1.34* | *0.89* | *0.89* | *0.89* |
| U-238 | *0.67* | *0.97* | *0.24* | *0.24* | *0.24* | *0.73* | *0.24* | *0.24* | *0.49* |
| Th-230 | *1.34* | *1.32* | *0.32* | *0.47* | *0* | *1.11* | *0.79* | *0.99* | *0.32* |
| Th-232 | *1.79* | *1.64* | *0.16* | *0.16* | *0.32* | *1.11* | *0.95* | *1.11* | *0.47* |
| Ra-226 | *1.17* | *0.35* | *1.38* | *0.35* | *1.11* | *1.67* | *1.67* | *0.56* | *0.28* |

*If the $|\zeta| > 2$ – the difference is statistically significant at 95% confidence.*
*If the $|\zeta| < 2$ – the difference is not statistically significant.*

According to Table X., the difference in activity concentration of natural radionuclides in fertilized and unfertilized soil is within statistical uncertainties. Based on ζ-score it can be concluded that the application of fertilizer did not significantly affect the activity concentration of natural radionuclides in soil. However, application of fertilizer could alter the chemical forms of radionuclides, potentially increasing their mobility and availability to plant.

The activity concentrations of U-234, U-238, Th-230, Th-232 and Ra-226 in soil from Turkestan region were obtained by alpha-particle spectrometry. The results are presented in Table 10.

Table 10 - Content of natural radionuclides in soil from Turkestan region (near the uranium production) with expanded combined standard uncertainties (k = 2)

| **Sample** | **Fertilizers** | **Activity concentration Bq/kg (dry weight)** | | | | |
|---|---|---|---|---|---|---|
| | | **U-234** | **U-238** | **Th-230** | **Th-232** | **Ra-226** |
| Soil Turkestan region | Superphosphate | 37 ± 3 | 36 ± 6 | 208 ± 16 | 24 ± 2 | 101 ± 5 |
| | Fertika (organo-mineral mixture) | 37 ± 3 | 36 ± 4 | 224 ± 15 | 23 ± 2 | 99 ± 5 |
| | Mono-potassium phosphate | 38 ± 3 | 34 ± 5 | 197 ± 15 | 20 ± 3 | 125 ± 15 |
| | Ammonium nitrate | 36 ± 3 | 35 ± 3 | 206 ± 16 | 18 ± 2 | 100 ± 4 |
| | NPK fertilizer | 40 ± 3 | 42 ± 6 | 258 ± 42 | 19 ± 5 | 134 ± 18 |
| | Double Superphosphate | 40 ± 3 | 41 ± 4 | 222 ± 12 | 22 ± 2 | 96 ± 8 |
| | Phosphoric | 41 ± 4 | 40 ± 5 | 242 ± 16 | 22 ± 2 | 98 ± 8 |
| | Peat fertilizer | 38 ± 4 | 39 ± 3 | 220 ± 17 | 22 ± 3 | 97 ± 10 |
| | Phitomicro-fertilizer | 41 ± 3 | 42 ± 5 | 237 ± 16 | 21 ± 2 | 118 ± 11 |
| | Without fertilizer | 31 ± 7 | 32 ± 2 | 255 ± 47 | 23 ± 4 | 117 ± 15 |

Table 11 - The result of absolute zeta-score for fertilized soil samples from Kyzemshek village, Turkestan region.

| *Radionuclide* | *SP* | *OMM* | *MPP* | *AN* | *LZ* | *DSP* | *Ph* | *PF* | *MF* |
|---|---|---|---|---|---|---|---|---|---|
| | *ζ-score* | | | | | | | | |
| U-234 | *1.18* | *1.18* | *1.31* | *1.05* | *1.84* | *1.58* | *2.48* | *1.24* | *1.71* |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| U-238 | *0.63* | *0.89* | *0.37* | *0.83* | *1.58* | *2.01* | *2.41* | *1.94* | *1.86* |
| Th-230 | *1.99* | *0.63* | *1.5* | *0.99* | *0.05* | *0.68* | *0.26* | *0.7* | *0.36* |
| Th-232 | *0.61* | *0.73* | *1.05* | *1.33* | *1.06* | *0.85* | *0.85* | *0.82* | *0.97* |
| Ra-226 | *1.96* | *1.14* | *1.98* | *1.11* | *1.41* | *1.41* | *1.47* | *1.11* | *0.05* |

*If the* $|\zeta| > 2$ *– the difference is statistically significant at 95% confidence.*
*If the* $|\zeta| < 2$ *– the difference is not statistically significant.*

According to Table 11, the difference in activity concentration of natural radionuclides in fertilized and unfertilized soil is within statistical uncertainties. Based on ζ-score it can be concluded that the application of fertilizer did not significantly affect the activity concentration of natural radionuclides in soil.

Considering the amount of fertiliser applied (for carrot plat experiment), the percentages of total activity added to soil before the cultivation experiment varied from 0.075 to 1.65 %.

Despite the fact that application of fertilizers did not lead to dramatic increase of concentration of radionuclides in soil, it could result in change of geochemical speciation of radionuclide, which could lead to the enhancement of their mobility and bioavailability [163].

### 3.6 Natural radionuclide fractionation in fertilized soil from Baiterek village, Almaty region

To assess to which fraction uranium is bound, a sequential extraction protocol was applied. The first five fractions of the applied sequential extraction protocol were defined as mobile and potentially mobile. Uranium fractionation in fertilized soil from Baiterek village, Almaty region is presented in published research article - Nursapina N.A., Shynybek B.A., Matveyeva I.V., ;Nazarkulova, Sh.N., Štrok M., Benedik L, Ponomarenko O.I Effect of mineral fertilisers application on the transfer of natural radionuclides from soil to radish (Raphanus sativus L.) // Journal of Environmental Radioactivity, V.247, 2022. 10.1016/j.jenvrad.2022.106863. Based on published data, MPP fertilised soil has higher content of uranium distributed in mobile and bioavailable fractions (water soluble, exchangeable, bound to carbonate) compared to AN fertilized soil.

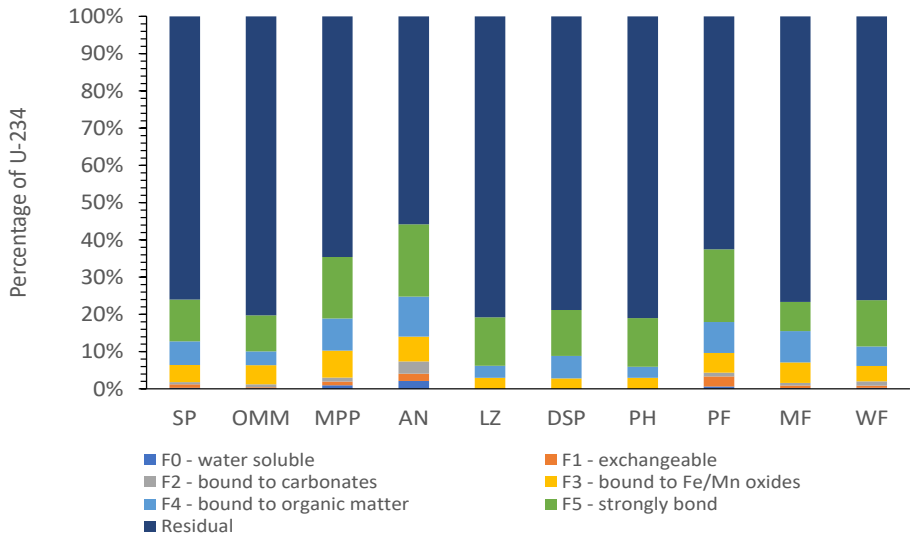
### 3.7 Natural radionuclide fractionation in fertilized soil from Koklaisai village, Almaty region

*Distribution of uranium isotopes*

To assess to which fraction isotopes of uranium is bound, a sequential extraction protocol was applied.

The first five fractions of the applied sequential extraction protocol were defined as mobile and potentially mobile; however, if the physicochemical condition of the soil is changed, it will directly affect the mobility of natural radionuclides. Figure X shows

results of sequential extraction protocol for U-234for fertilized and unfertilized soil. Uncertainties, which are calculated as expanded uncertainties, are not shown on the bar graph for better clarity.




*a*

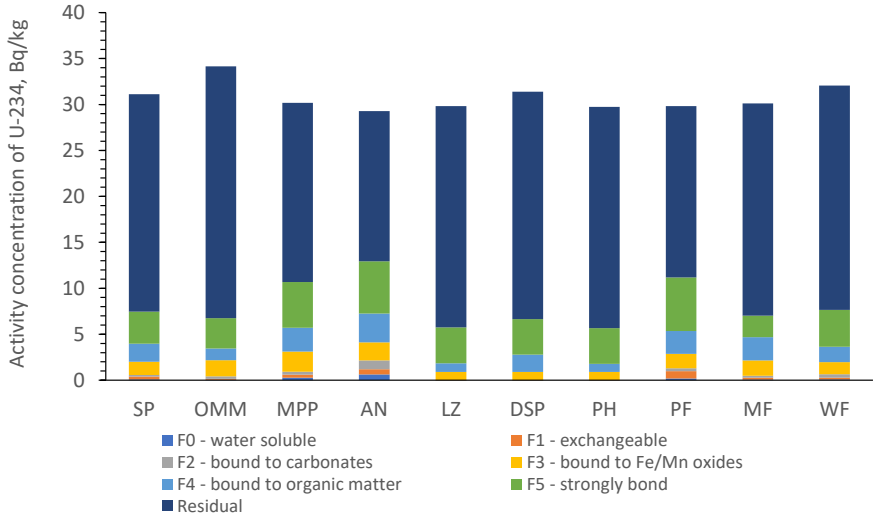



Figure 19 - Comparison of U-234 content in geochemical fractions of unfertilized and fertilized soil from Almaty region: a – percentage of U-234; b – activity concentration of U-234

U-234 is mostly distributed in residual fraction (Figure 19), accounting for nearly 80-90 % of the total U-234, where radionuclide can be fixed in crystal lattice of the clay minerals, such as chlorite and kaolinite.

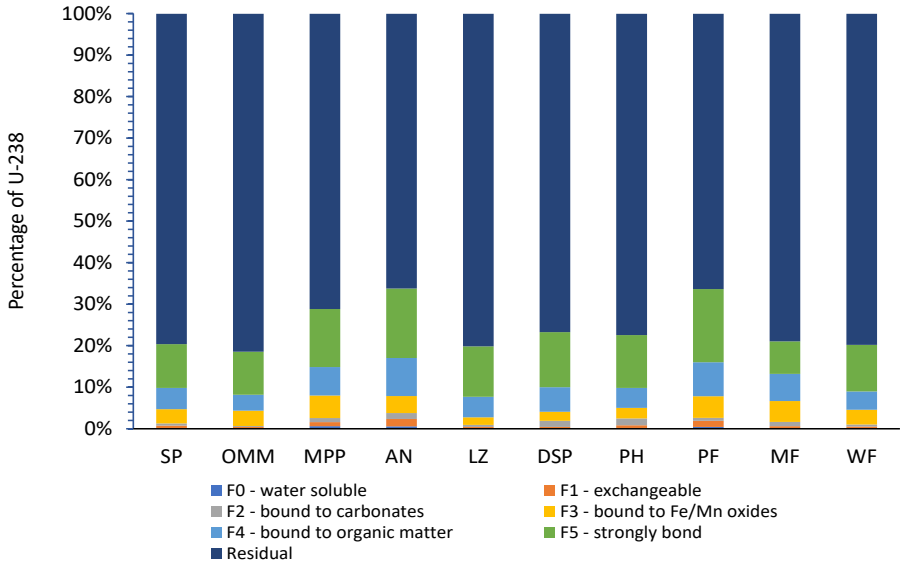
Nevertheless, fluctuation of uranium isotopes content can be seen between different fractions for differently fertilized soil in comparison to unfertilized soil.

Fertilized soils (microfertilizer, peat fertilizer, ammonium nitrate, monopotassium phosphate) show slightly higher proportions of mobile and potentially mobile forms of U-234, which are distributed in exchangeable, bound to carbonates, bound to Fe/Mn oxides, and bound to organic matter fractions compared to the unfertilized soil.

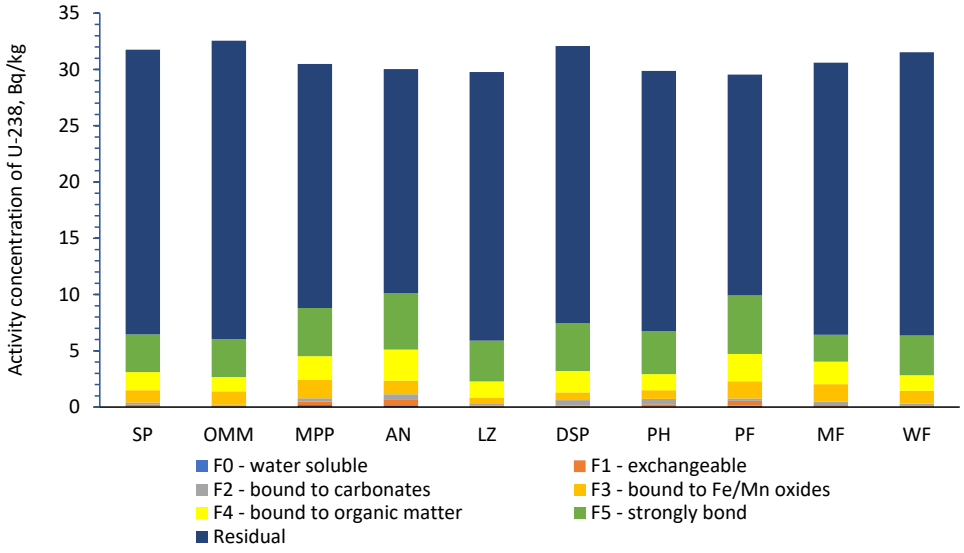
Application of ammonium nitrate led to change in the distribution of U-234, the amount of mobile and potentially mobile fractions increased 2.6 times in comparison to unfertilized soil. It could be explained by slight soil acidification (Table 7), which led to dissolving carbonate-bound forms of U-234, releasing it into the soil solution and following re-distribution.

The addition of liquid organic fertilizer (microfertilizer, peat fertilizer), which contains amino and phenolic acids, could lead to partial dissolution of uranium in residual fraction, following redistribution between the other fractions, mainly in bound to organic matter fraction. According to research [164], uranium could form complexes with different amino acids on cell surfaces (plant, bacteria, fungi) over a wide pH range, which could lead to increasing uranium concentration in bound to organic matter fraction.

Figure 20 shows results of sequential extraction protocol for U-238 for fertilized and unfertilized soil. Uncertainties, which are calculated as expanded uncertainties, are not shown on the bar graph for better clarity.




*a*




*b*

Figure 20 - Comparison of U-238 content in geochemical fractions of unfertilized and fertilized soil from Almaty region: *a* – percentage of U-238; *b* – activity concentration of U-238

Similar to U-234, U-238 is also mostly distributed in residual fraction (Figure 20), accounting for nearly 80 % of the total U-238, where radionuclide can be fixed in crystal lattice of the clay minerals, such as chlorite and kaolinite.

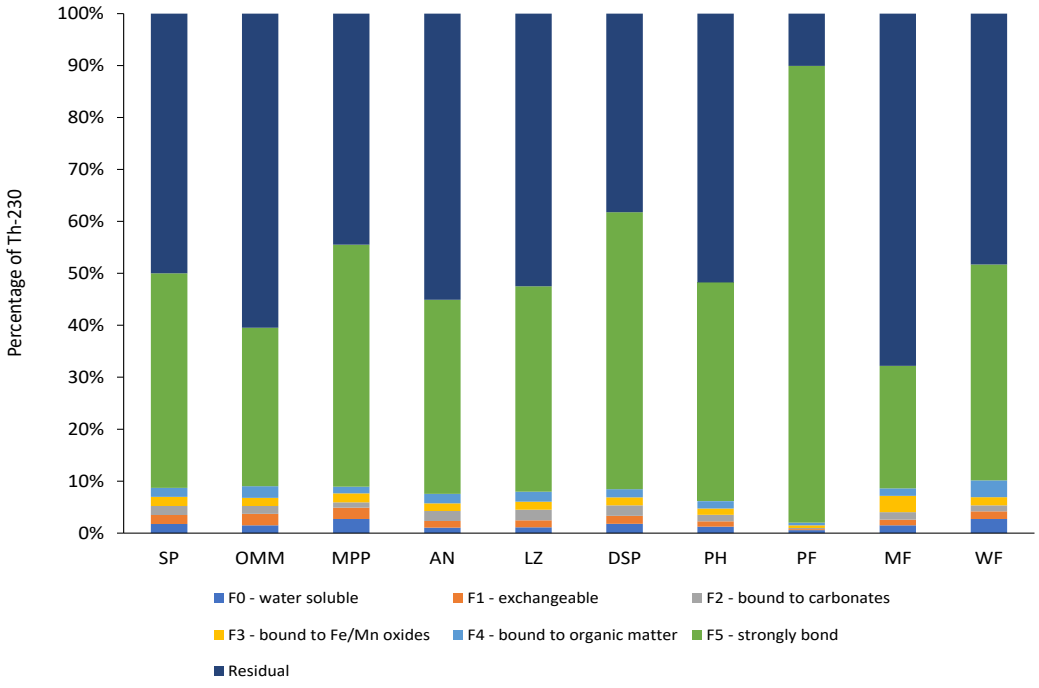
Up to 20 % of U-238 is distributed in mobile and potentially mobile fractions (first five fractions). Application of microfertilizer, peat fertilizer, monopotassium phosphate, and ammonium nitrate lead to slightly increase of bioavailable and mobile form of U-238 (as in case of U-234) compared to unfertilized soil.

Addition of liquid organic fertilizers (microfertilizer and peat fertilizer) which contain weak organic acids, could lead to dissolution of resistant minerals, which reduced the amount of strongly bond fraction. According to research [164], uranium could form complexes with different amino acids on cell surfaces (plant, bacteria, fungi) over a wide pH range, which could lead to increasing uranium concentration in bound to organic matter fraction. On the other hand, the addition of humic acid with negative charges could increase the adsorption of uranium ions onto the amorphous oxides due to static electronic affinity, and forming ternary surface complexes through carboxyl and hydroxyl [60], which resulted in the increase of amount of bound to Fe/Mn oxides fraction.

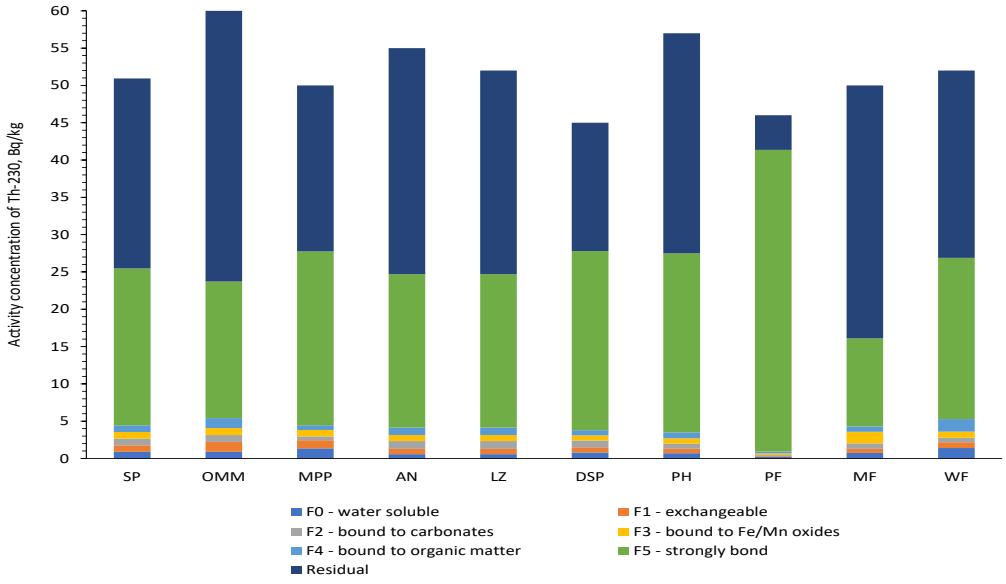
Overall, uranium isotopes are mainly distributed in strongly bound and residual fractions, which belong to the immobile fractions. Despite that, the application of certain fertilizers leads to the release of uranium from stable soil fractions into more bioavailable and leachable forms, increasing its potential uptake by plants. This highlights the need for responsible fertilizer management and mitigation strategies, such as soil amendments or buffer application, to minimize environmental and health risks associated with radionuclide mobility in fertilized soils.

*Distribution of thorium isotopes*

Distribution of thorium isotopes in geochemical fraction of soil (fertilized, unfertilized) from Almaty region is presented in Figure 21. Uncertainties, which are calculated as expanded uncertainties, are not shown on the bar graph for better clarity.




*a*




*b*

Figure 21 - Comparison of Th-230 content in geochemical fractions of unfertilized and fertilized soil from Almaty region: *a* – percentage of Th-230; *b* – activity concentration of Th-230

It can be noted from Figure 21., that Th-230 across the investigated samples was mostly distributed in strongly bond and residual fraction (over 90 %), which belongs to immobile and most stable fractions, where Th-230 is most likely fixed in crystal lattice of different minerals, such as quartz and aluminosilicates, due to high affinity of thorium for adsorption onto mineral surfaces [165]. This indicates that Th-230 is predominantly immobile in soil.

The unfertilized soil has comparable amount of Th-230 in mobile fractions to fertilized soil, with a slight difference in bound to Fe/Mn oxide and bound to organic matter fractions across the investigated soil samples. This could be explained by natural processes, such as organic matter decomposition or oxide formation, which could lead to redistribution of Th-230 into mobile forms in the absence of fertilizers.

According to Figure X., distribution of Th-230 increase in residual fraction of peat fertilized soil in comparison to unfertilized soil. Addition of the fertilizer lead to increase of the pH of soil (Table 7), which according to the research [166] could promote $Th(OH)_4(aq)$ to form $Th(OH)_4$ and $ThO_2$ precipitation. Have to note that, application of peat fertilizer, which contain humic and fulvic acids, according to the [167] could promote to form strong complexes of Th with carboxylic and phenolic functional groups of FA/HA on the different mineral surfaces.

The distribution of Th-230 in mobile and potentially mobile fractions is consistently low (< 10 %) in all investigated samples compared to the residual and strongly bound fractions.

Despite that, application of certain fertilizers leads to redistribution of Th-230 between the mobile and potentially mobile fractions. Addition of NPK fertilizer and ammonium nitrate fertilizers lead to an increase of amount of bound to carbonate fraction to two times in comparison to unfertilized soil. It could be explained by several reasons:

a) Application of NPK fertilizer, which belongs to the NPK fertilizer, could promote increase of carbonate precipitation since it contains calcium as a secondary nutrient (Table 6);
b) Ammonium nitrate supply ammonium ($NH_4^+$) and nitrate ($NO_3^-$) ions, and other nutrients, such as potassium ($K^+$) and phosphorus (P). These ions can compete with thorium for adsorption sites on soil particles (e.g., clays, Fe/Mn oxides). When adsorption sites on Fe/Mn oxides (bound to Fe/Mn oxide fraction) and organic matter (bound to organic matter fraction) are occupied by these competing ions, Th-230 possibly could be redirected to bind with carbonates (bound to carbonate fractions).

Application of organic mineral mixture and monopotassium phosphate fertilizers leads to increase of amount of exchangeable fraction to 1.5 and 1.3 times respectively in comparison to unfertilized soil.

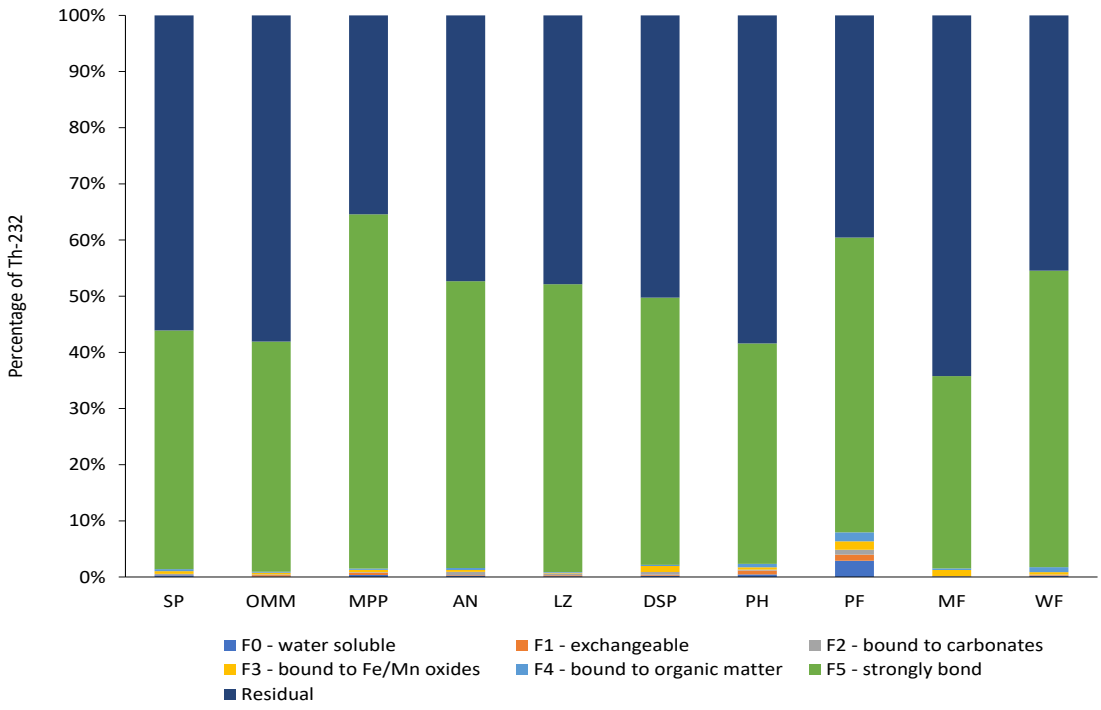
Organic mineral mixture fertilizer contains organic matter (according to the information given by production) that could promote an increase of the cation exchange capacity (CEC) of the soil. Organic matter provides negatively charged sites on humic substances and other organic molecules, which can bind positively charged ions like $Th^{4+}$ in an exchangeable form. This leads to a higher proportion of Th-230 in the

exchangeable fraction. Application of monopotassium phosphate which predominantly contains $K^+$ (Table 6) ion could possibly affect the competition of $K^+$ and $Th^{4+}$ for exchangeable sites in soil. However, this competition leads to the displacement of other cations, resulting in an increase in the exchangeable fraction of Th-230.

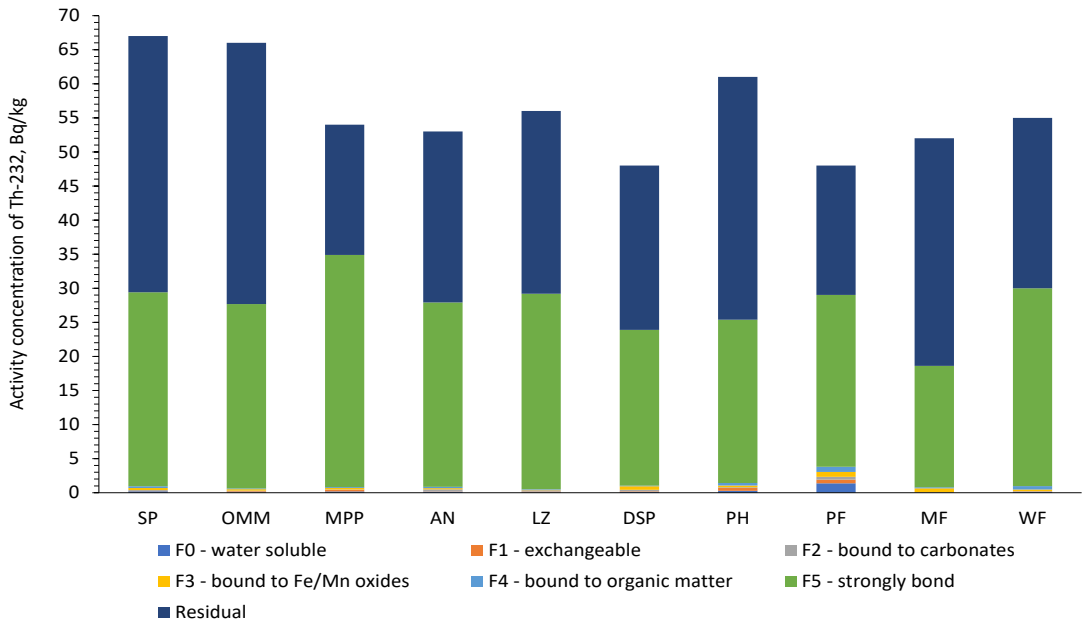
Application of microfertilizer, which belongs to the organic fertilizer, leads to increase of amount of bound to Fe/Mn oxide fraction to two times in comparison to unfertilized soil. Humic acid with negative charge, containing in organic fertilizer, could increase the adsorption of thorium ions onto the amorphous oxides due to static electronic affinity, and forming ternary surface complexes through carboxyl and hydroxyl [60], which resulted in the increase of amount of bound to Fe/Mn oxides fraction.

Overall, Th-230 is predominantly distributed in strongly bond and residual fractions, which are immobile. Despite that, redistribution of Th-230 between the different geo-chemical fractions occurs in fertilized soil samples. These changes highlight the critical role of fertilizer composition in influencing the mobility, bioavailability, and environmental behavior of Th-230 in soils.

Figure 22 shows results of sequential extraction protocol for Th-232 for fertilized and unfertilized soil. Uncertainties, which are calculated as expanded uncertainties, are not shown on the bar graph for better clarity.




*a*




*b*

Figure 22 - Comparison of Th-232 content in geochemical fractions of fertilized and unfertilized soil from Almaty region: a – percentage of Th-232; b – activity concentration of Th-232

The residual fraction consistently dominates the Th-232 distribution across all investigated samples, ranging from 50 % to 70 %. It reveals that the Th-232 is strongly bound within mineral matrices and suggests that the majority of Th-232 remains immobile.

The water soluble fraction, representing the mobile and bioavailable Th-232, shows variation among the investigated samples. Distribution of Th-232 in water soluble fraction is higher in peat fertilized soil (2.9 %) in comparison to unfertilized soil (0.17 %). This specifies that certain fertilizers may affect the mobility of Th-232.

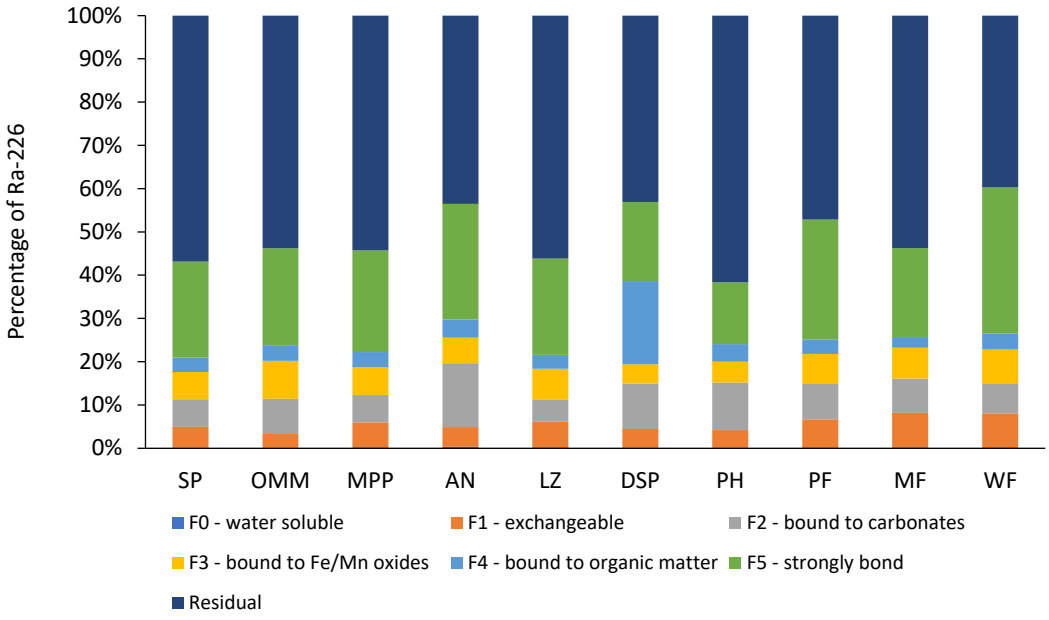
Exchangeable, bound to carbonate, bound to Fe/Mn oxide, and bound to organic matter fractions contribute collectively to less than 10 % of the total Th-232 distribution. These fractions show slight increases in soil fertilized with peat fertilizer, phosphoric fertilizer, and micro fertilizer in comparison to unfertilized soil, suggesting that certain fertilizers may slightly increase the mobility and bioavailability of Th-232.

According to the Figure 22, application of organic fertilizers tend to enhance the mobility of Th-232, increasing its presence in bioavailable forms. In contrast, mineral-based fertilizers primarily retain Th-232 in residual and strongly bond fractions, which belongs to immobile fractions.

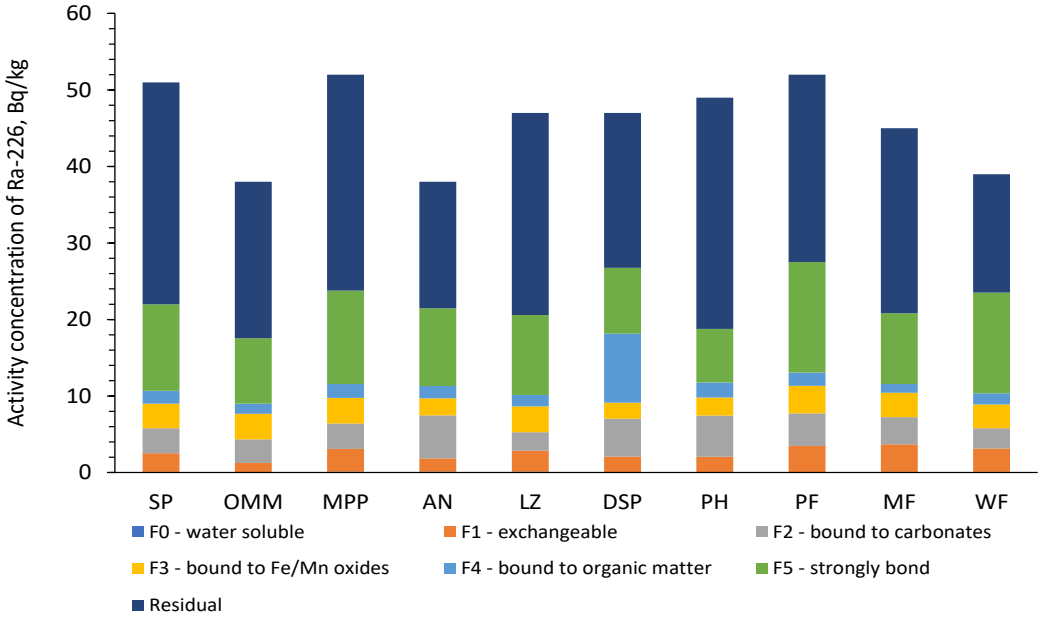
Overall, Th-232 is mostly present in immobile fractions, where Th-232 can be fixed in crystal lattice of different minerals, such as quartz and aluminosilicates. Therefore, the transfer of Th-232 from soil to plant system is minimized.

*Distribution of Ra-226*

Distribution of Ra-226 in geochemical fraction of the soil from Almaty region is presented in Figure 23. Uncertainties, which are calculated as expanded uncertainties, are not shown on the bar graph for better clarity.




*a*




*b*

Figure 23. Comparison of Ra-226 content in geochemical fractions of fertilized and unfertilized soil from Almaty region: *a* – percentage of Ra-226; *b* – activity concentration of Ra-226

Distribution of Ra-226 in strongly bond and residual fractions varied significantly across all investigated samples

At the same time, distribution of Ra-226 in mobile and potentially mobile fractions increased by 12 % for double superphosphate fertilized soil compared to unfertilized soil. Addition of double superphosphate, where the main component is $Ca(H_2PO_4)_2 \cdot H_2O$, could lead to an increase of concentration of calcium in soil. Ca can occupy ion exchange sites thus displacing Ra which could lead to redistribution between the fractions.

Application of ammonium nitrate led to an increase of amount of bound to carbonate fraction from 7 % (unfertilized soil) to 15 % (ammonium nitrate fertilized soil). Ammonium nitrate is a nitrogen-based fertilizer that can acidify the soil during nitrification processes. This slight change in soil pH (acidification) may promote the dissolution of Ra-226 from residual fractions, leading to its redistribution into the bound to carbonate fraction

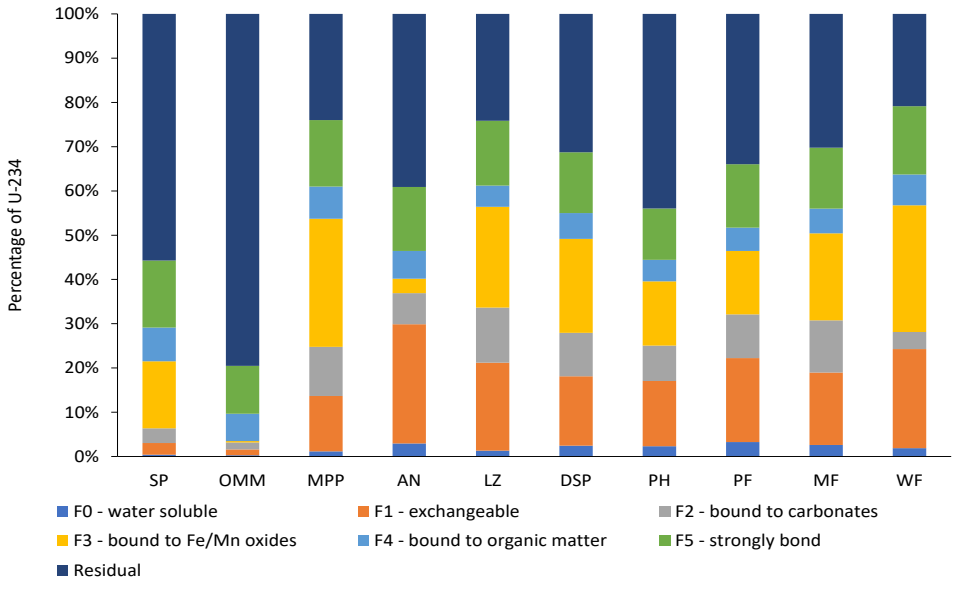
Application of fertilizers alters the distribution of Ra-226 across soil fractions, with double superphosphate and ammonium nitrate having the most pronounced effect on mobilizing Ra-226.

### 3.8 Natural radionuclides fractionation in fertilized soil from Kyzemshek village, Turkestan region

*Distribution of uranium isotopes*

To assess to which fraction radionuclides are bound, a sequential extraction protocol was applied.

The first five fractions of the applied sequential extraction protocol were defined as mobile and potentially mobile; however, if the physicochemical condition of the soil is changed, it will directly affect the mobility of natural radionuclides. Figure 24 shows results of sequential extraction protocol for U-234 for fertilized and unfertilized soil. Uncertainties, which are calculated as expanded uncertainties, are not shown on the bar graph for better clarity.



*a*

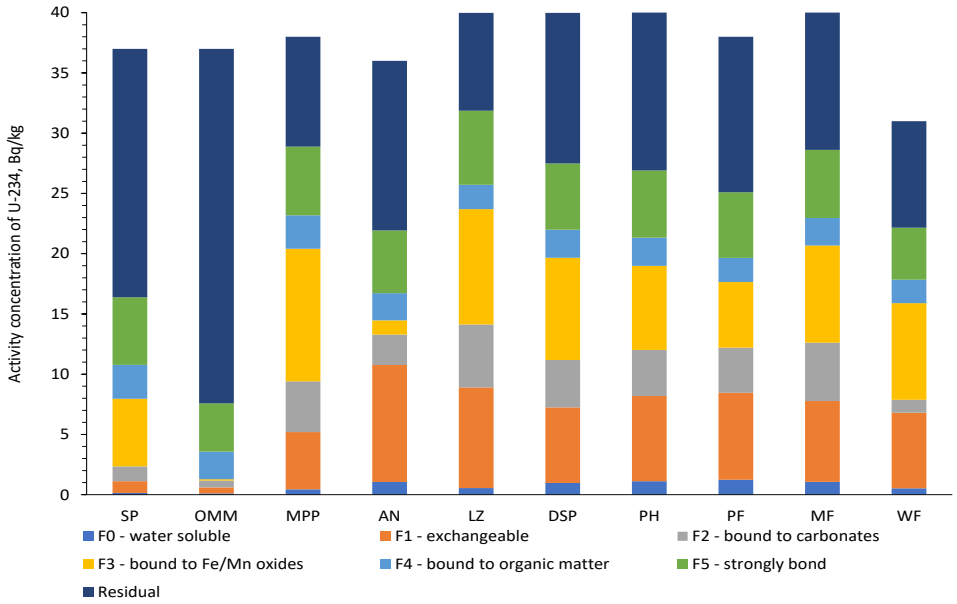



Figure 24 - Comparison of U-234 content in geochemical fractions of fertilized and unfertilized soil from Turkestan region: *a* – percentage of U-234, *b* – activity concentration of U-234

The distribution of U-234 in residual and strongly bond fractions increased with application of fertilizers. This indicates that a significant portion of U-234 is strongly retained and not easily mobilized.

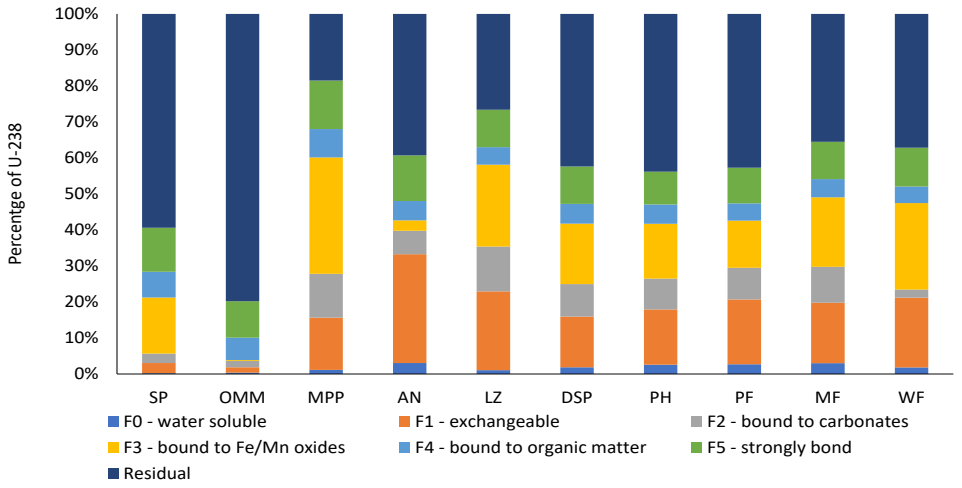
Fertilization of soil with superphosphate and organo-mineral mixture led to strong immobilization of U-234 since 70 % and 90 % (SP and OMM) of U-234 is distributed in strongly bond and residual fractions.

The percentage of distribution of U-234 in exchangeable fraction of AN fertilized soil increased to 5 % compared to unfertilized soil. At the same time the amount of bound to Fe/Mn oxide fraction decreased. Application of ammonium nitrate as a nitrification agent is a source of protons in soil. Possibly uranium cations are released from soil matrix by the exchange cation $H^+$, whereas oxides, hydroxides react with $H^+$ to form free cations, which resulted in decreasing the amount of bound to Fe/Mn oxide fraction and following redistribution of uranium to another fractions [168]. Increase of U-234 distribution in exchangeable fraction could led to mobility and phyto-availability of U-234.

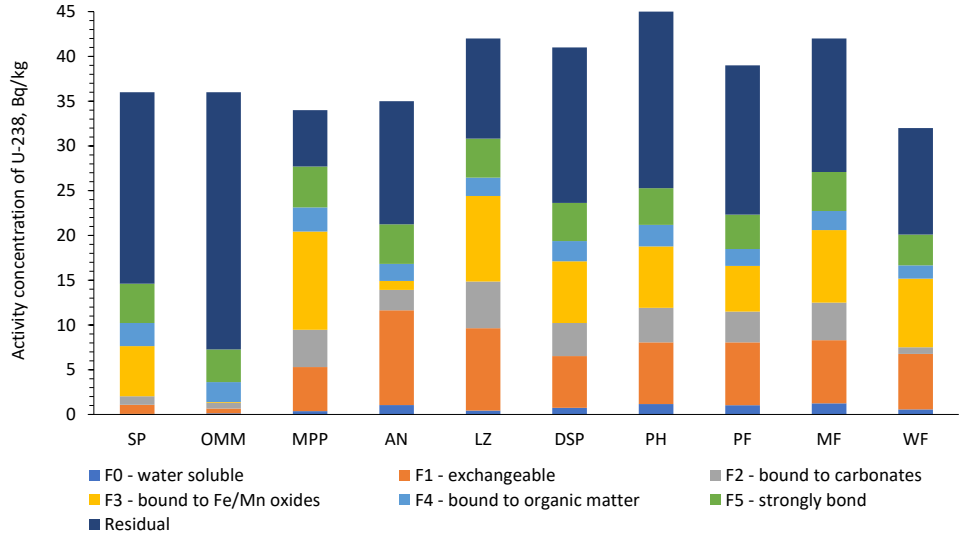
Application of all fertilizers, except for superphosphate and organo-mineral mixture, led to gradual increase of amount of bound to carbonate fraction compared to unfertilized soil. Fertilizers could change soil pH, at slightly alkaline condition, uranium could form carbonate complexes, which resulted in an increase of amount of bound to carbonate fraction. Uranium-carbonate complexes could enhance the mobility of uranium in soil profile and be phytoavailable for plant. In addition, phosphate containing fertilizers could participate in the formation of complexes, such as uranyl

monoacid biphosphate, triuranyl diphosphate, which could lead to mobilization of uranium [169].

Distribution of U-238 in geochemical fractions of soil (fertilized, unfertilized) from Turkestan region are presented in Figure 25. Uncertainties, which are calculated as expanded uncertainties are not shown on the bar graph for better clarity.




*a*




*b*

Figure 25 - Comparison of U-238 content in geochemical fractions of fertilized and unfertilized soil from Turkestan region: *a* – percentage of U-238, *b* – activity concentration of U-238

U-238 is mostly distributed in strongly bound and residual fractions. Application of monopotassium phosphate and NPK fertilizers led to change in distribution of U-238 between the fractions compared to unfertilized soil. The amount of mobile and potentially mobile fractions increased from 52 % for unfertilized soil to 68 % and 63 % for MPP and LZ fertilized soil, respectively.

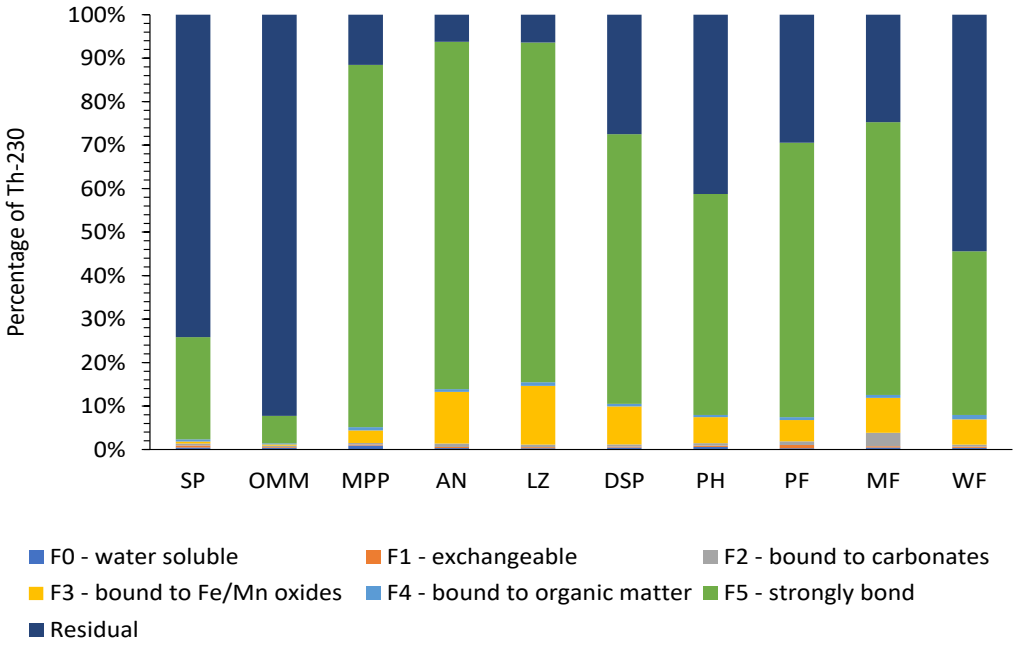
Increased distribution of U-238 in bound to carbonate fraction compared to unfertilized soil was observed across all samples, with the exception of soil fertilized with superphosphate and organo-mineral mixture.

The results could be explained by the change of the pH of the soil due to the application of fertilizers. At alkaline conditions, uranium could form carbonate complexes, which resulted in an increase of amount of bound to carbonate fraction. Uranium-carbonate complexes could enhance the mobility of uranium in soil profile and be phytoavailable for plant. In addition, phosphates containing NPK fertilizer, could participate in the formation of complexes, such as uranyl monoacid biphosphate, triuranyl diphosphate, which could lead to mobilization of uranium [169].

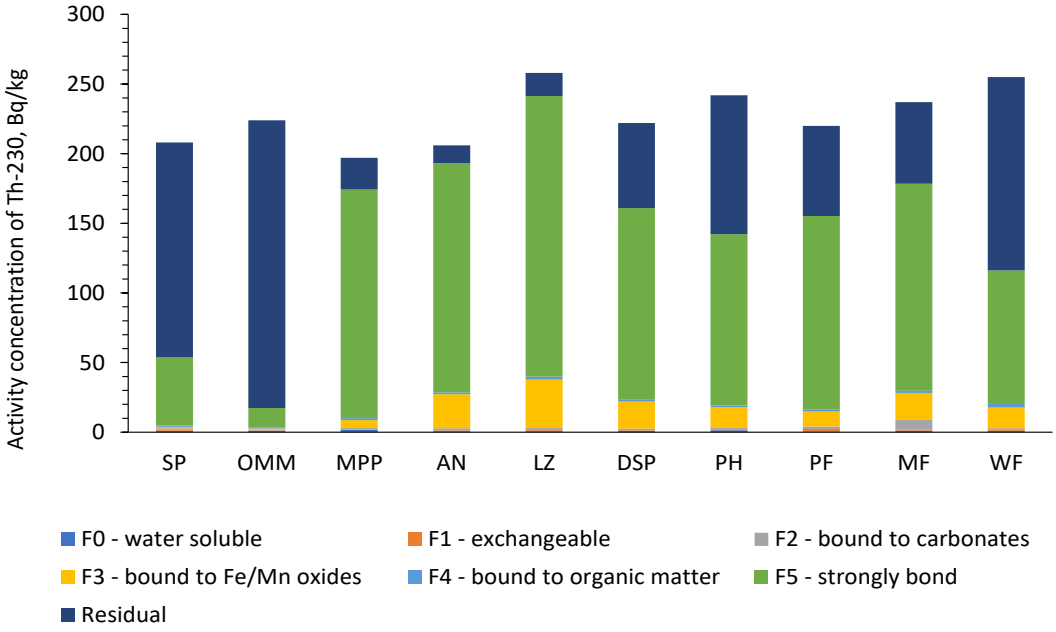
Noticeable change in distribution of U-238 in exchangeable fraction is observed for AN fertilized soil, where percentage of distribution of U-238 increased from 19 % in unfertilized soil to 30 % of AN fertilized soil. Application of ammonium nitrate as a nitrification agent is a source of protons in soil, reducing soil pH. Lower pH increases uranium solubility, shifting more U-238 into the exchangeable fraction [168]. Since exchangeable fraction belongs to the mobile and phytoavailable fraction, application of AN fertilizer could promote transfer of U-238 from soil to plant.

*Distribution of thorium isotopes*

Distribution of Th-230 in geochemical fractions of soil (fertilized, unfertilized) from Turkestan region is presented in Figure 26. Uncertainties, which are calculated as expanded uncertainties, are not shown on the bar graph for better clarity.




*a*




*b*

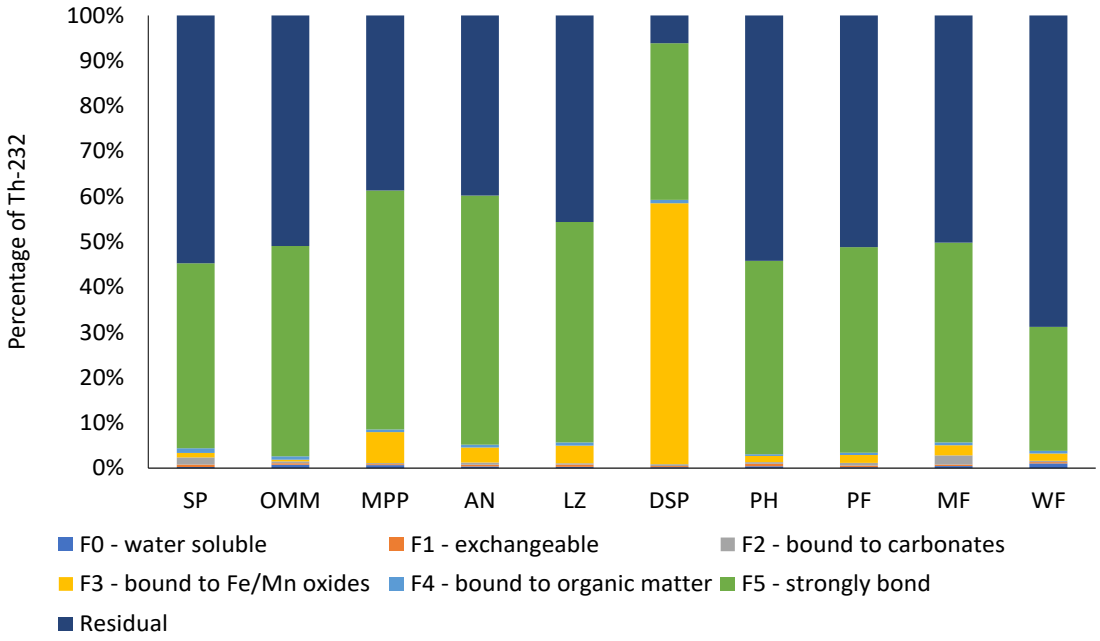
Figure 26 - Comparison of Th-230 content in geochemical fractions of fertilized and unfertilized soil from Turkestan region: *a* – percentage of Th-230, *b* – activity concentration of Th-230

Th-230 is mostly distributed in residual and strongly bound fractions. Application of fertilizers, according to Figure 26, lead to re-distribution of Th-230 between the fractions.

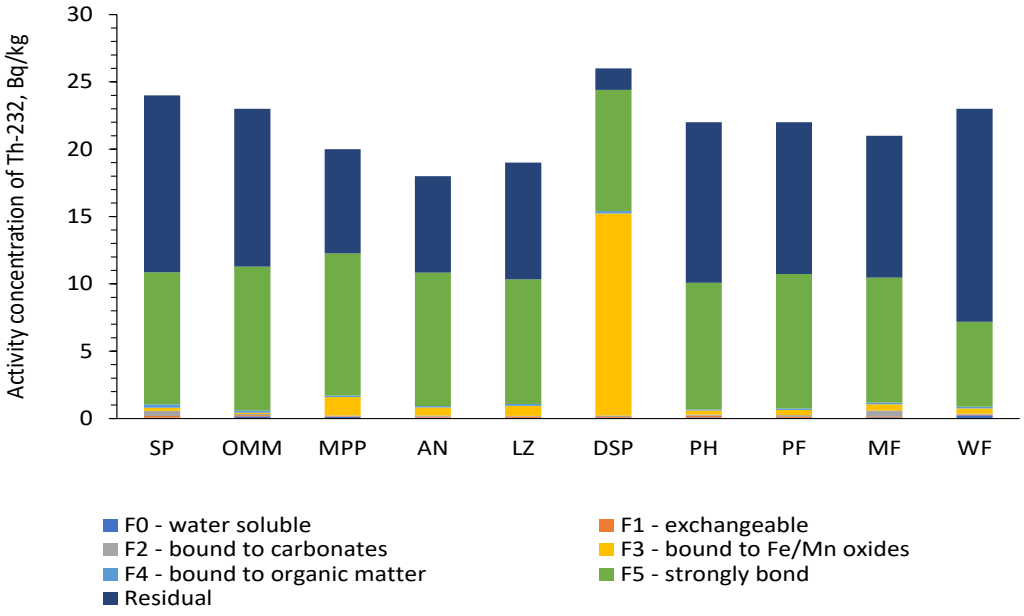
The percentage of distribution of Th-230 in bound to Fe/Mn oxide fraction increase from 6 % in unfertilized soil to 12 % and 13 % in AN and LZ fertilized soil, respectively.

Noticeable change in distribution of Th-230 in mobile and potentially mobile fractions is observed for AN, LZ, DSP, MF fertilized soil, where the percentage of distribution of Th-230 increased from 8 % for unfertilized soil to 14 % for AN, 15 % for LZ, 11 % for DSP, and 13 % for MF. The presence of iron and manganese in the fertilizers could promote the formation or enhancement of Fe/Mn oxides. In addition, alterations in soil pH and redox conditions possible due to application of fertilizers, enhance the solubility of Fe and Mn and favour their precipitation as oxides capable of binding Th-230.

Distribution of Th-232 in geochemical fractions of soil (fertilized, unfertilized) from Turkestan region are presented in Figure 27. Uncertainties, which are calculated as expanded uncertainties are not shown on the bar graph for better clarity.




*a*




*b*

Figure 27 - Comparison of Th-232 content in geochemical fractions of fertilized and unfertilized soil from Turkestan region: *a* – percentage of Th-232, *b* – activity concentration of Th-232

More than 90 % of Th-232 is distributed in strongly bound and residual fractions through all investigated samples, except for DSP fertilized soil, where 49 % of Th-232 is distributed in strongly bound and residual fractions.

Application of certain fertilizer led to a change of distribution of Th-232 between the fractions. Noticeable change in distribution of Th-232 in mobile and potentially mobile fractions is observed for MPP, AN, LZ, and MF fertilized soil compared to

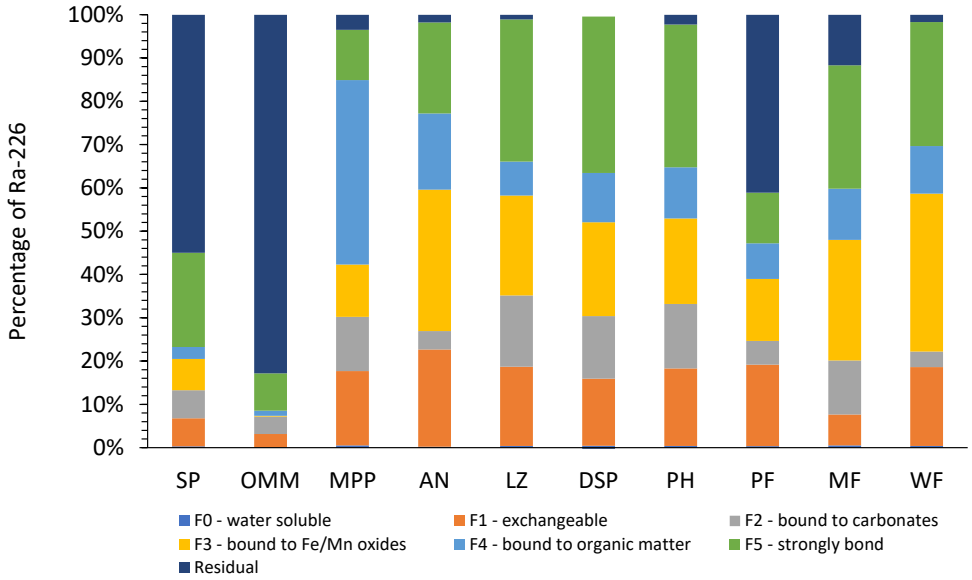
unfertilized soil, where the percentage of distribution of Th-232 increased from 3 % in unfertilized soil to 9 % for MPP, 5 % for AN, 6 % for LZ, and 6 % for MF.

Significant increase of percentage of distribution of Th-232 was observed for DSP fertilized soil in mobile and potentially mobile fractions, where percentage of distribution of Th-232 increased from 3 % in unfertilized soil to 59 % in DSP fertilized soil. Among the mobile and potentially mobile fractions, 58 % of Th-232 is distributed in bound to Fe/Mn oxide fraction. Addition of fertilizer lead to change in the pH of the soil to slightly alkaline condition (pH 7.8, Table 7), which could potentially result in increase of $Th(OH)_n^{4-n}$, which enhanced the sorption and coprecipitation of thorium with Fe/Mn oxide and hydroxide.

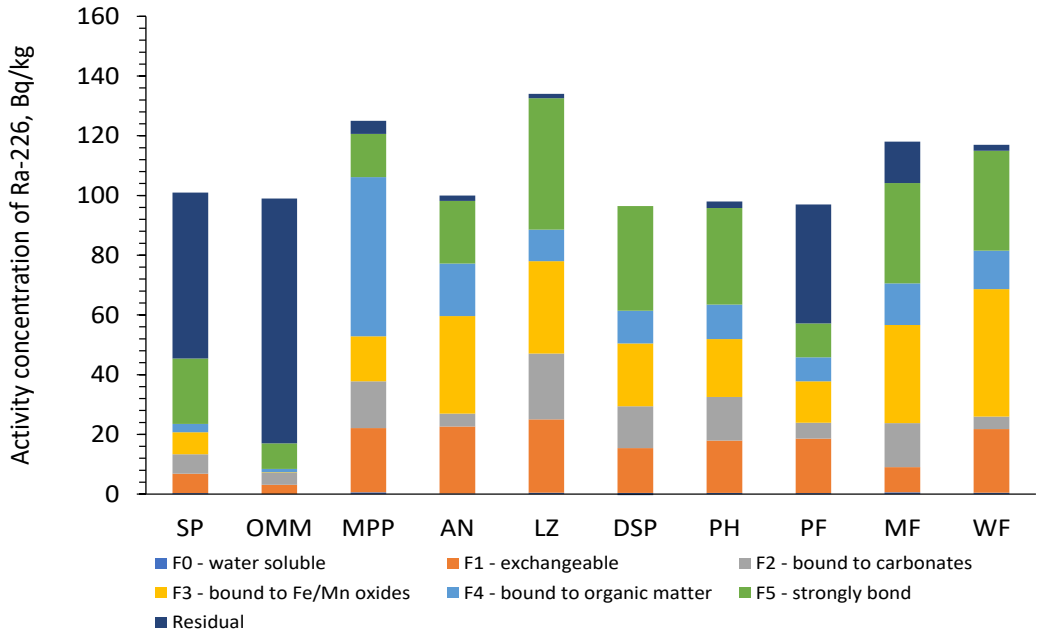
In summary, Th-232 is mostly distributed in residual and strongly bound fractions, which is immobile. Application of certain fertilizers, such as MPP, LZ, AN, and DSP leads to change in the distribution of Th-232 between the fractions, making it more mobile and potentially more available for plant uptake or transport in the soil-plant system.

*Distribution of Ra-226*

Distribution of Ra-226 in geochemical fractions of soil from Turkestan (fertilized, unfertilized) region are presented in Figure 28. Uncertainties, which are calculated as expanded uncertainties are not shown on the bar graph for better clarity.




*a*




*b*

Figure 28 - Comparison of Ra-226 content in geochemical fractions of fertilized and unfertilized soil from Turkestan region: *a* – percentage of Ra-226, *b* – activity concentration of Ra-226

Ra-226 in unfertilized soil is mostly distributed in mobile and potentially mobile fractions. Application of fertilizers lead to redistribution of Ra-226 between the fractions.

Application of fertilizers leads to an increase of percentage of distribution of Ra-226 in residual fraction for soil fertilized with superphosphate, organo-mineral mixture, peat fertilizer, and microfertilizer. Significant effect to the distribution of Ra-226 into strongly bond and residual fractions compared to unfertilized soil was found for application of SP and OMM. Possibly, superphosphate immobilizes Ra-226 through phosphate precipitation, due to formation of Ra-phosphate precipitates, shifting it to the residual fraction. Organo-mineral mixture enhances Ra-226 adsorption on Fe/Mn oxides and organic matter, increasing its presence in strongly bound and residual fractions.

Slight increase of amount of mobile fractions, such as water soluble, exchangeable, and bound to carbonate fractions, due to application of MPP, AN, LZ, DSP, and PH fertilizers is observed compared to unfertilized soil. Among the mobile fractions, a noticeable increase of distribution of Ra-226 is observed for bound to carbonate fractions, where the percentage of distribution of Ra-226 in unfertilized soil (4 %) increased for 8 % for MPP, 12 % for PH, and DSP, 11 % for LZ, 9 % for MPP, and 4 % for SP.

Phosphate-based fertilizers (SP, DSP, PH, MPP) and LZ (NPK fertilizer), introduce significant amounts of calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), and carbonate ($CO_3^{2-}$) ions into the soil. Fertilizer-derived $Ca^{2+}$ and $Mg^{2+}$ compete with $Ra^{2+}$ for exchangeable sites on clay minerals and Fe/Mn oxides, which resulted in decrease of

amount of bound to Fe/Mn oxide fraction for PH, DSP, LZ, MPP, and SP fertilized soil compared to unfertilized soil, with following redistribution of Ra-226 into bound to carbonate fraction [170-171].

In addition, some fertilizers, particularly DSP, SP, PH, and MPP, contain carbonates or lead to the formation of bicarbonates ($HCO_3^-$) upon dissolution. This increases the availability of $CO_3^{2-}$ ions, promoting the co-precipitation of $RaCO_3$ with $CaCO_3$. As calcium phosphates would be expected to dissolve in the weak acid of the carbonate fraction reagent (ammonium acetate), any co-precipitating Ra-226 would also be recovered in this fraction.

Increase in distribution of Ra-226 in mobile fraction could result in transfer of Ra-226 from soil to plant system.

Among the investigated samples, distribution of Ra-226 increased in mobile and potentially mobile fraction for MPP and AN fertilized soil from 70 % in unfertilized soil to 77 % and 85 % for AN and MPP fertilized soil, respectively. For the rest of the samples, a slight decrease is observed.

### 3.9 Comparative conclusion of sequential extraction of investigated soils

Based on the results of sequential extraction of soil from different sites of Kazakhstan fertilized by nine different fertilizers evaluation of distribution of natural radionuclides in geochemical fraction of soil was done. Soil from Baiterek village showed the highest mobilization potential of uranium under monopotassium phosphate application, where uranium was predominately found in mobile fractions such as water soluble, exchangeable, and bound to carbonate fraction. In contrast, ammonium nitrate application resulted in decreased uranium mobility.

Koklaisay soils showed moderate uranium mobilization, with U-234 and U-238 mostly retained in residual fractions. However, the use of microfertilizer, peat fertilizer, monopotassium phosphate, and ammonium nitrate lead to slightly increase of bioavailable and mobile form of uranium isotopes. Organic fertilizers (peat, microfertilizers) could lead to promotion of complexation of uranium with organic matter, enhancing its redistribution. Thorium and radium mobility increased slightly in response to fertiliser application, particularly those fertilizers that alter pH and promote iron/manganese oxide formation. Compared to soil from Baiterek village, soils from Koklaysai village were less sensitive to fertiliser-induced mobilisation.

In soil from Kyzemshek village (Turkestan region), application of superphosphate and organomineral mixture resulted in strong immobilisation of uranium and thorium isotopes. However, AN application resulted in increases of distribution of U-234, U-238 in exchangeable fraction, suggesting potential environmental risks under slightly acidic conditions. Monopotassium phosphate and ammonium nitrate having the most pronounced effect on mobilizing Ra-226, distribution of Ra-226 increased in mobile and potentially mobile fraction for MPP and AN fertilized soil from 70 % in unfertilized soil to 77 % and 85 % for AN and MPP fertilized soil, respectively.

Based on the results obtained, it could be concluded that the study highlights that both soil characteristics and fertilizer type affect the geochemical behavior of natural radionuclides. The results highlight the importance of site-specific fertilizer management strategies to reduce environmental and radiological risks in agricultural lands.

### 3.10 Activity concentration of natural radionuclides in *R.Sativus* edible part grown on soil from Baiterek village, Almaty region

The results are presented in published research article - Nursapina N.A., Shynybek B.A., Matveyeva I.V., Nazarkulova, Sh.N., Štrok M., Benedik L, Ponomarenko O.I. Effect of mineral fertilisers application on the transfer of natural radionuclides from soil to radish (Raphanus sativus L.) // Journal of Environmental Radioactivity, V.247, 2022. 10.1016/j.jenvrad.2022.106863.

Based on published data, the highest activity concentration of natural radionuclides was found for radish growing on soil, which was fertilised by MPP, while the concentration of natural radionuclides in radish cultivated on AN-fertilised soil was slightly lower compared to plants grown without fertiliser.

### 3.11 Activity concentration of natural radionuclides in *D.Carrota* samples grown on soil from Koklaisai village, Almaty region

The activity concentration (Bq/kg, dry weight) with expanded uncertainties for selected radionuclides in carrot samples (root, shoot) grown in soil from Koklaisai village, Almaty region is presented in Table 12.

Table 12 - Content of natural radionuclides in carrot samples with expanded uncertainties ($k$=2)

| Fertilizer | Carrot | U-234, Bq/kg | U-238, Bq/kg | Th-230, Bq/kg | Th-232, Bq/kg | Ra-226, Bq/kg |
|---|---|---|---|---|---|---|
| Without fertilizer | Root | 0.38±0.03 | 0.38±0.12 | 1±0.3 | 0.32±0.16 | 2.1±0.4 |
| | Shoot | 1.63±0.12 | 1.56±0.23 | 0.6±0.04 | 0.34±0.03 | 5±0.5 |
| Organo-mineral mixture | Root | 0.39±0.03 | 0.34±0.1 | 1.6±0.3 | 0.9±0.2 | 2±0.4 |
| | Shoot | 1.4±0.1 | 1.2±0.2 | 2.4±0.4 | 2.3±0.4 | 4.3±0.5 |
| Monopotassium phosphate | Root | 5.7±0.3 | 5.5±0.3 | 12±3 | 3.4±0.5 | 5.8±0.8 |
| | Shoot | 3.8±0.3 | 3.6±0.2 | 4.5±0.6 | 4.65±0.6 | 6.7±0.8 |
| Ammonium nitrate | Root | 4.6±0.3 | 3.8±1.5 | 10 ± 3 | 2.9±1.8 | 4.4±2.05 |
| | Shoot | 3.3±0.2 | 3±0.5 | 4±0.6 | 4±0.6 | 6±1 |
| NPK fertilizer | Root | 0.18±0.01 | 0.15±0.03 | 0.6±0.1 | 0.2±0.05 | 1.4±0.2 |
| | Shoot | 1.6±0.1 | 1.6±0.2 | 3±0.5 | 3±0.5 | 7.5±0.7 |
| Double superphosphate | Root | 0.23±0.02 | 0.22±0.06 | 0.5±0.1 | 0.13±0.07 | 2.5±0.3 |
| | Shoot | 1.3±0.2 | 1.3±0.2 | 2±0.3 | 2±0.3 | 4.5±0.5 |
| Phosphoric | Root | 0.32±0.02 | 0.34±0.06 | 0.7±0.1 | 0.16±0.07 | 2.6±0.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Shoot | 1.3±0.1 | 1.4±0.2 | 2.5±0.4 | 2.2±0.3 | 4.7±0.5 |
| Peat fertilizer | Root | 1.4±0.1 | 1.5±0.4 | 4±1 | 1±0.5 | 5.4±1.3 |
| | Shoot | 2.5±0.2 | 2.4±0.3 | 4±0.5 | 4±0.5 | 5.6±0.6 |
| Microfertilizer | Root | 3.4±0.3 | 2.1±0.9 | 9±3 | 3.6±0.2 | 5±0.2 |
| | Shoot | 2.2±0.2 | 2±0.3 | 1.8±0.2 | 1.8±0.2 | 5.8±0.7 |

Actinides tend to absorb to the outer layer of root vegetables since they do not have any essential function for plants [172]. The range of concentrations in root crop of carrot grown on soil from Almaty region with application of different fertilizers were between 0.18 ± 0.01 to 4.6 ± 0.3 Bq/kg for U-234, 0.15 ± 0.03 to 3.8 ± 1.5 Bq/kg for U-238, 0.5 ± 0.1 to 11 ± 3 Bq/kg for Th-230, 0.13 ± 0.07 to 3.6 ± 2 Bq/kg for Th-232 and 1.4 ± 0.2 to 5.4 ± 1.3 Bq/kg for Ra-226.

From Table X. it is observed that the variation of activity concentration of natural radionuclides in carrot samples depends on application of different fertilizers. The concentration of uranium isotopes in root crop of carrot which was grown on soil fertilized by NPK or double superphosphate was lower than in unfertilized soil. The same trend was observed for thorium isotopes. This could be explained by immobilization of uranium isotopes due to the application of fertilizers.

No notable change in activity concentration of uranium isotopes in root crop of carrot in comparison to unfertilized soil is observed for soil fertilized by phosphoric fertilizer and organo-mineral mixture.

For measured uranium isotopes, the concentration in root crop of carrot grown by application of ammonium nitrate, monopotassium phosphate, peat fertilizer, and microfertilizer, was an order-of-magnitude higher than in root crop of carrot grown in unfertilized soil. The maximum concentration among the investigated root crop samples was determined in root crop of carrot grown on monopotassium phosphate fertilized soil. Based on results of sequential extraction, it could be concluded that the application of monopotassium phosphate led to formation of more mobile and phytoavailable species of uranium isotopes, which resulted in high concentration of isotopes in root crop of carrot.

The concentration of thorium isotopes in root crop of carrot was also an order-of-magnitude higher in aforementioned fertilizers, including organo-mineral fertilizer. This may be attributed to formation of phyto-available form of natural radionuclides due to application of fertilizers.For instance, on the results of sequential extraction analysis of fertilized soils (microfertilizer, peat fertilizer, ammonium nitrate, monopotassium phosphate) shows slightly higher proportions of bioavailable forms of U-234, U-238, compared to unfertilized soil. The same trend is observed for Th-230.

The concentration of Ra-226 in root crop of carrot, which was grown on soil fertilized by NPK fertilizer, was lower than in unfertilized soil. Increase of Ra-226 concentration in comparison to unfertilized soil is observed for root crop of carrot which was grown with application of monopotassium phosphate, ammonium nitrate, microfertilizer, and peat fertilizer. No notable change in activity concentration of Ra-226 in root crop of carrot in comparison to unfertilized soil was observed for soil fertilized by organo-mineral mixture, double superphosphate and phosphoric fertilizer.

The range of concentrations in shoot of carrot grown on fertilized and unfertilized soil from Koklaisai village were between 1.3 ± 0.1 to 3.3 ± 0.2 Bq/kg for U-234, 1.2 ± 0.2 to 3 ± 0.5 Bq/kg for U-238, 0.6 ± 0.04 to 5 ± 0.7 Bq/kg for Th-230, 0.34 ± 0.03 to 7 ± 1 Bq/kg for Th-232 and 4.5 ± 0.5 to 7.5 ± 0.7 Bq/kg for Ra-226.

No change in concentration of uranium isotopes was observed for shoot of carrot grown on monopotassium, double superphosphate, organo-mineral mixture, and NPK fertilizer fertilized soil in comparison to unfertilized soil. For other investigated samples of shoot, concentration of uranium isotopes was slightly increased than in shoot grown without application of fertilizer.

For measured thorium isotopes, the concentration in shoot of carrot for all applied fertilizers was an order-of-magnitude higher than that in root crop of carrot grown in unfertilized soil.

Ra-226 concentration in most of analyzed shoot samples was comparable with concentration of shoot of carrot grown on unfertilized sample. Except for shoot of carrot grown on NPK fertilized soil, where concentration of Ra-226 was 1.5 times higher than in shoot of carrot grown on unfertilized soil.

### 3.12 Activity concentration of natural radionuclides in *D.Carrota* samples grown on soil from Kyzemshek village, Turkestan region

The activity concentration (Bq/kg, dry weight) with expanded uncertainties for selected radionuclides in carrot samples (root, shoot) grown in soil from Turkestan region are presented in Table 13.

Table 13 - Content of natural radionuclides in carrot samples with expanded uncertainties ($k$=2) grown on soil from Turkestan region

| Fertilizer | Carrot | U-234, Bq/kg | U-238, Bq/kg | Th-230, Bq/kg | Th-232, Bq/kg | Ra-226, Bq/kg |
|---|---|---|---|---|---|---|
| Without fertilizer | Root | 0.35±0.03 | 0.25±0.05 | 0.2±0.1 | 0.1±0.01 | 1.8±0.2 |
| | Shoot | 3.42±0.26 | 3.17±0.42 | 3.6±0.4 | 2.8±0.3 | 7.8±0.8 |
| Superphosphate | Root | 0.98±0.07 | 0.79±0.13 | 2.2±0.2 | 0.3±0.1 | 4.9±0.4 |
| | Shoot | 2.36±0.18 | 2.37±0.28 | 3.5±0.3 | 1.9±0.2 | 13±1 |
| Organo-mineral mixture | Root | 0.6±0.04 | 0.5±0.09 | 0.6±0.1 | 1±0.1 | - |
| | Shoot | 3.5±0.3 | 3±0.3 | 3.5±0.7 | 2±0.5 | 8±0.8 |
| Monopotassium phosphate | Root | 6.8±0.5 | 6.4±0.7 | 17±2 | 0.8±0.2 | 22±2 |
| | Shoot | 5.0±0.4 | 5 ± 0.8 | 15±1 | 2±0.3 | 49±4 |
| Ammonium nitrate | Root | 21±2 | 21±2 | 26±2 | 1±0.2 | 31±2 |
| | Shoot | 23±2 | 22±2 | 25±3 | 2.4±0.5 | 65±5 |
| NPK fertilizer | Root | 12.5±0.9 | 12±1 | 14±2 | 0.7±0.2 | 29±3 |
| | Shoot | 15 ±1 | 15±2 | 24±2 | 1.6±0.3 | 72±6 |
| Double superphosphate | Root | 56±4 | 55±8 | 77±7 | 6.5±1.4 | 79±7 |
| | Shoot | 22±2 | 21±2 | 10±1 | 1.5±0.2 | 26±2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Phosphoric | Root | 10±1 | 10±1 | 9±1 | 0.4±0.2 | 22±2 |
| | Shoot | 13±1 | 14±2 | 8±1 | 3±0.4 | 25±2 |
| Peat fertilizer | Root | 26±2 | 26±3 | 12±1 | 0.9±0.1 | 32±3 |
| | Shoot | 17±1 | 18±2 | 8±1 | 2.1±0.3 | 51±5 |
| Microfertilizer | Root | 19±1 | 19±2 | 8±1 | 0.5±0.1 | 17±2 |
| | Shoot | 33±3 | 33±3 | 14±2 | 2.5±0.5 | 31±3 |

The range of concentrations in root crop of carrot grown on fertilized and unfertilized soil from Turkestan region were between 0.35 ± 0.03 to 56 ± 4 Bq/kg for U-234, 0.25 ± 0.05 to 55 ± 8 Bq/kg for U-238, 0.2 ± 0.1 to 77 ± 7 Bq/kg for Th-230, 0.1 ± 0.01 to 6.5 ± 1.4 Bq/kg for Th-232 and 1.8 ± 0.2 to 79 ± 7 Bq/kg for Ra-226.

The concentration of natural radionuclides in root crop of carrot grown by application of fertilizers was an order-of-magnitude higher than in root crop of carrot grown in unfertilized soil. It could be explained, based on the results of sequential extraction, that application of fertilizers led to increase of bound to carbonate fraction, which belongs to the potentially mobile and phytoavailable fraction. The highest concentration of natural radionuclides was determined in root crop of carrot grown with application of double superphosphate. High concentrations of natural radionuclides in root crop of carrot could be possibly explained from the results of sequential extraction, where, for example, notable change in distribution of Th-232 was observed with application of double superphosphate where amount of strongly bond fraction decreased from 97 % in unfertilized soil to 49 % in fertilized soil, which could promote isotope transfer from soil to plant. In case of Ra-226, amount of bound to carbonate fraction, which is potentially phyto-available fraction, increased gradually for superphosphate, monopotassium phosphate, NPK fertilizer, double superphosphate, microfertilizer, phosphoric fertilized soil samples, which resulted in increase of Ra-226 in root crop of carrot.

The range of concentrations in shoot of carrot grown on fertilized and unfertilized soil from Turkestan region were between 2.36 ± 0.18 to 33 ± 3 Bq/kg for U-234, 2.37 ± 0.28 to 33 ± 3 Bq/kg for U-238, 3.5 ± 0.3 to 25 ± 3 Bq/kg for Th-230, 1.5 ± 0.2 to 3 ± 0.4 Bq/kg for Th-232 and 7.8 ± 0.8 to 65 ± 5 Bq/kg for Ra-226. For measured uranium isotopes, the concentration in shoot of carrot grown by application of fertilizers was an order-of-magnitude higher than in shoot of carrot grown in unfertilized soil, except for superphosphate and organo-mineral mixture.

Content of Th-230 in shoot of carrot grown with application of investigated fertilizers increased an order-of-magnitude, except for superphosphate and organo-mineral mixture, where results were comparable to Th-230 content in shoot of carrot grown on unfertilized soil. Meanwhile, content of Th-232 slightly decreased in shoot of carrot grown by application of superphosphate, double superphosphate and NPK fertilizers. In all other investigated samples, the content of Th-232 in shoot of carrot was comparable to Th-232 content in shoot of carrot grown in unfertilized soil.

The content of Ra-226 in shoot of carrot grown by application of organo-mineral mixture was comparable with the content of Ra-226 in shoot of carrot grown on

unfertilized soil. For all other shoot samples, the content of Ra-226 was an order-of-magnitude higher compared to shoot of carrot, which was grown on unfertilized soil.

### 3.13 Soil to root vegetable transfer factor (TF)

*Soil from Baiterek village, Almaty region*

The results are presented in published research article - Nursapina N.A., Shynybek B.A., Matveyeva I.V., Nazarkulova, Sh.N., Štrok M., Benedik L, Ponomarenko O.I. Effect of mineral fertilisers application on the transfer of natural radionuclides from soil to radish (Raphanus sativus L.) // Journal of Environmental Radioactivity, V.247, 2022. 10.1016/j.jenvrad.2022.106863.

Based on published results, the soil to root vegetable transfer factor was higher than 1.0 for U-234, U-238 and Th-230 for radish that was grown on soil fertilised with MPP. The results show that the TF values of the Th-230 and Th-232 are higher than those for Ra-226 in all cases. This was the opposite of what was found by Azeez et al. (2019) [6]], where Th-230 and Th-232 isotopes were found to be less mobile than Ra-226. Therefore, the TF of radionuclides depends on the metabolic nature of each plant and the availability of radionuclides [118]. Meanwhile, in the case of radish cultivated on AN-fertilised soil and soil without fertiliser, the TF values were below 1.0. The results show that all calculated TF values for natural radionuclides in investigated samples were higher than the mean values for U ($8.4 \times 10^{-3}$), Th ($8.0 \times 10^{-4}$) and Ra ($7 \times 10^{-2}$) reported so far for root crops [118].

*Soil from Koklaisai village, Almaty region*

The results of the soil to root vegetable transfer factor (TF) for uranium isotopes are presented in Figure 29. The results varied depending on the used fertilizer. The highest TF value among the investigated samples was determined for root crop of carrot grown on soil fertilized by ammonium nitrate, monopotassium phosphate, peat fertilizer, and microfertilizer. The TF value of U-234 and U-238 for root crop of carrot grown with application of ammonium nitrate, monopotassium phosphate, peat fertilizer and microfertilizer was 13, 19, 5, 12 and 15, 18, 5, 7 times higher in comparison of TF value of root crop of carrot grown on unfertilized soil. Since TF is the function of the available uranium soil concentration [173], this finding suggests that application of forementioned fertilizers increased bioavailability of uranium isotopes in soil from Almaty region. Despite that application of fertilizers could lead to the change of the geochemical distribution of natural radionuclides in soil, the TF value was not more than 1.

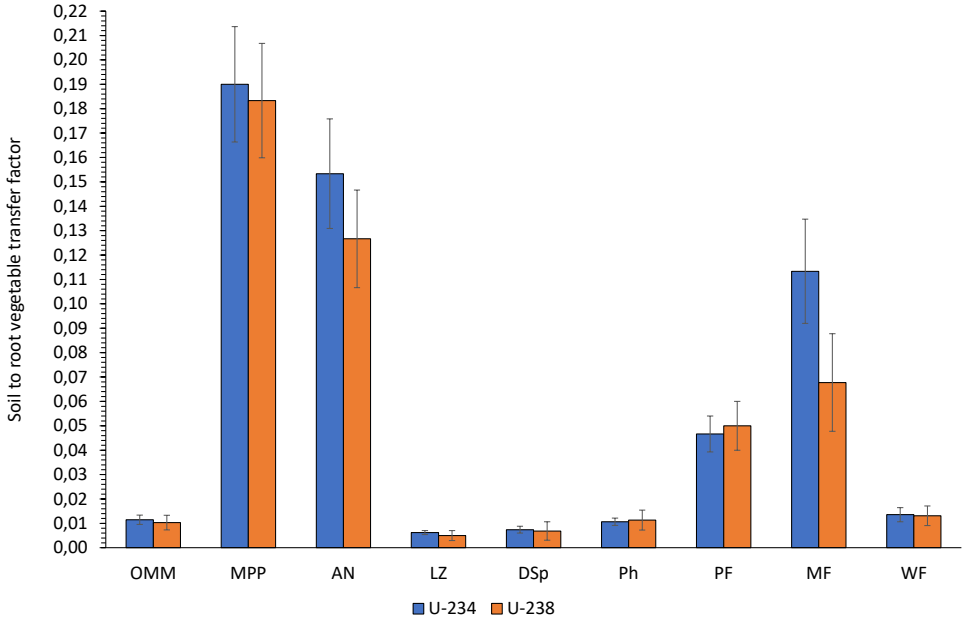



Figure 29 - Soil-to-root vegetable transfer factor of uranium isotopes for carrot cultivated on soil from Almaty region fertilised by different fertilizers (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

The results of the soil to root vegetable transfer factor (TF) for thorium isotopes are presented in Figure 30. The results varied depending on the used fertilizer. The highest TF value of thorium isotopes was determined for carrot samples grown with application of ammonium nitrate, phosphoric fertilizer, peat fertilizer and microfertilizer.

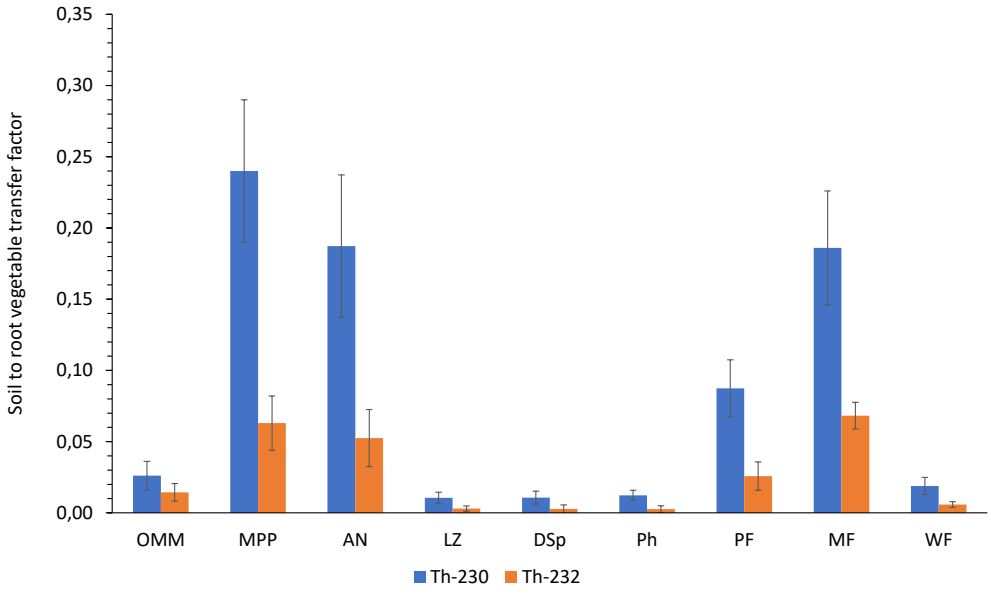



Figure 30 - Soil-to-root vegetable transfer factor of thorium isotopes for carrot cultivated on soil from Almaty region fertilised by different fertilizers (with expanded

uncertainties with a coverage factor *k*=2, corresponding to a confidence level of approximately 95%)

The TF value of Th-230 and Th-232 for root crop of carrot grown with application of ammonium nitrate, monopotassium phosphate, peat fertilizer and microfertilizer was 5.3, 12, 2.5, 5 and 4, 6, 2, 5 times higher in comparison of TF value of root crop of carrot grown on unfertilized soil. This funding suggests that application of forementioned fertilizers increased bioavailability of thorium isotopes for soil from Almaty region. Despite that application of fertilizers could lead to the change of the geochemical distribution of natural radionuclides in soil, the TF value was not more than 1. The TF value of thorium isotopes for root crop of carrot grown with application of double superphosphate and NPK fertilizer was slightly lower than for carrot grown on unfertilized soil. While for rest of root crop of carrot samples, the TF value was comparable for root crop of carrot grown on fertilized soil. The TF values for Th-230 are significantly higher compared to Th-232. The reason for this is most likely higher content of Th-232 present tightly bound in mineral lattice compared to Th-230, which is produced in U-238 decay chain through two alpha decays, which may recoil Th-230 out of mineral lattice.

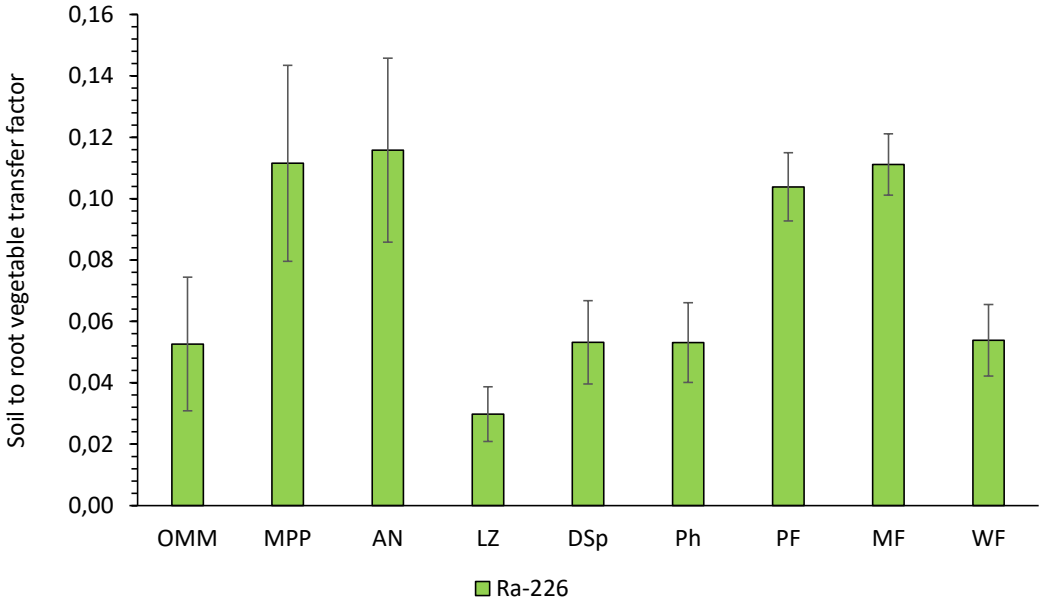



Figure 31 - Soil-to-root vegetable transfer factor of thorium isotopes for carrot cultivated on soil from Almaty region fertilised by different fertilizers (with expanded uncertainties with a coverage factor *k*=2, corresponding to a confidence level of approximately 95%)

The results of the soil to root vegetable transfer (TF) factor of Ra-226 are presented in Figure 31. The results varied depending on the used fertilizer. The highest TF value of Ra-226 was determined for carrot samples grown with application of monopotassium phosphate, ammonium nitrate, phosphoric fertilizer, peat fertilizer and microfertilizer. The TF value of Ra-226 for root crop of carrot grown with application

of monopotassium phosphate, ammonium nitrate, phosphoric fertilizer, peat fertilizer and microfertilizer was 1.6, 1.4, 1.2, 2, 1.8 times higher in comparison of TF value of root crop of carrot grown on unfertilized soil.

The results show that all calculated TF values for uranium and thorium isotopes in investigated samples were higher than the mean values for U ($8.4 \times 10^{-3}$) and Th ($8.0 \times 10^{-4}$) reported so far for root crops (IAEA, 2010). Meanwhile, the TF value calculated for Ra-226 was higher than the mean value for Ra ($7 \times 10^{-2}$) reported by IAEA, 2010 only for carrot samples grown by application of monopotassium phosphate, peat fertilizer and microfertilizer.

*Soil from Kyzemshek village, Turkestan region*

The results of the soil to root vegetable transfer factor (TF) for uranium isotopes are presented in Figure 32. The results varied depending on the used fertilizer.

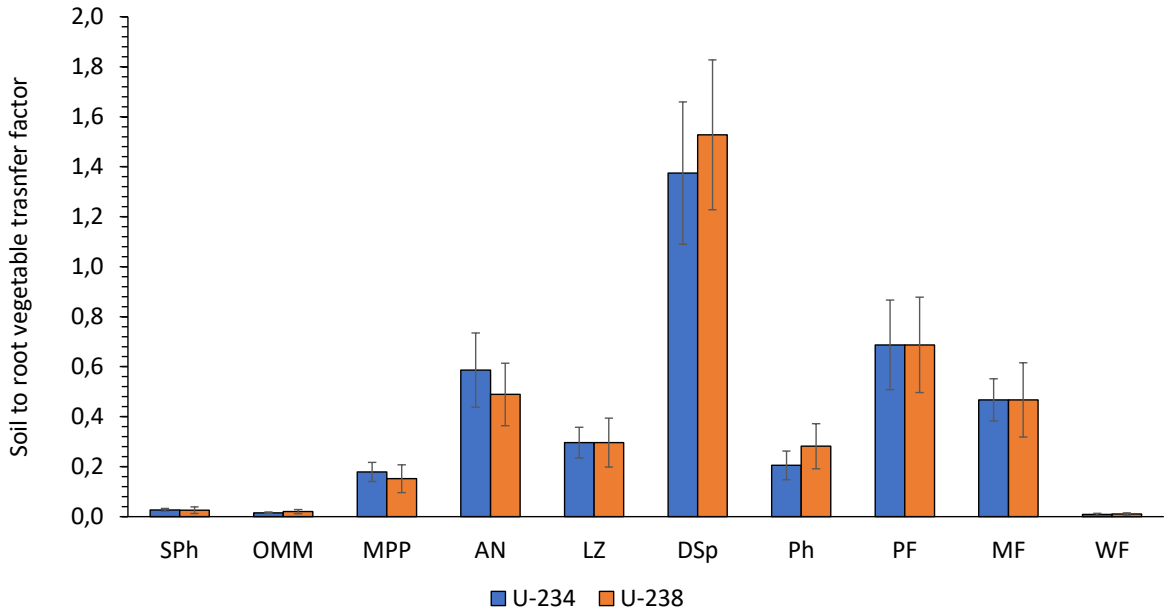



Figure 32 - Soil-to-root vegetable transfer factor of uranium isotopes for carrot cultivated on soil from Turkestan region fertilised by different fertilizers (with expanded uncertainties with a coverage factor *k*=2, corresponding to a confidence level of approximately 95%)

The TF value of U-234 and U-238 for carrot grown with application of superphosphate and organo-mineral mixture (Fertika) was 3 and 2 times higher than the TF value of uranium isotopes for carrot grown on unfertilized soil.

More significant increase of TF value of uranium isotopes was observed for all other investigated samples of carrot in comparison to carrot grown on unfertilized soil.

Application of double superphosphate during cultivation period led to dramatical change of TF value. The TF value of U-234 and U-238 for carrot grown with application of double superphosphate was 137 and 134 times higher than those for

carrot grown on unfertilized soil. Among the investigated samples, the TF value of uranium isotopes was higher than one for carrot grown with application of double superphosphate, which indicate high uptake and accumulation of uranium isotopes in root crop of carrot. Based on results of sequential extraction, it can be seen that application of double superphosphate led to increase of amount of bound to carbonate fraction, which is potentially phytoavailable, for both uranium isotopes in comparison to unfertilized soil. This could be explanation of enhanced uranium isotopes uptake by root crop of carrot grown with application of double superphosphate.

According to the obtained results, it can be seen that application of fertilizers during cultivation period increased bioavailability of uranium isotopes for soil from Turkestan region.

The results of the soil to root vegetable transfer factor (TF) for thorium isotopes are presented in Figure 33. The results varied depending on the used fertilizer.

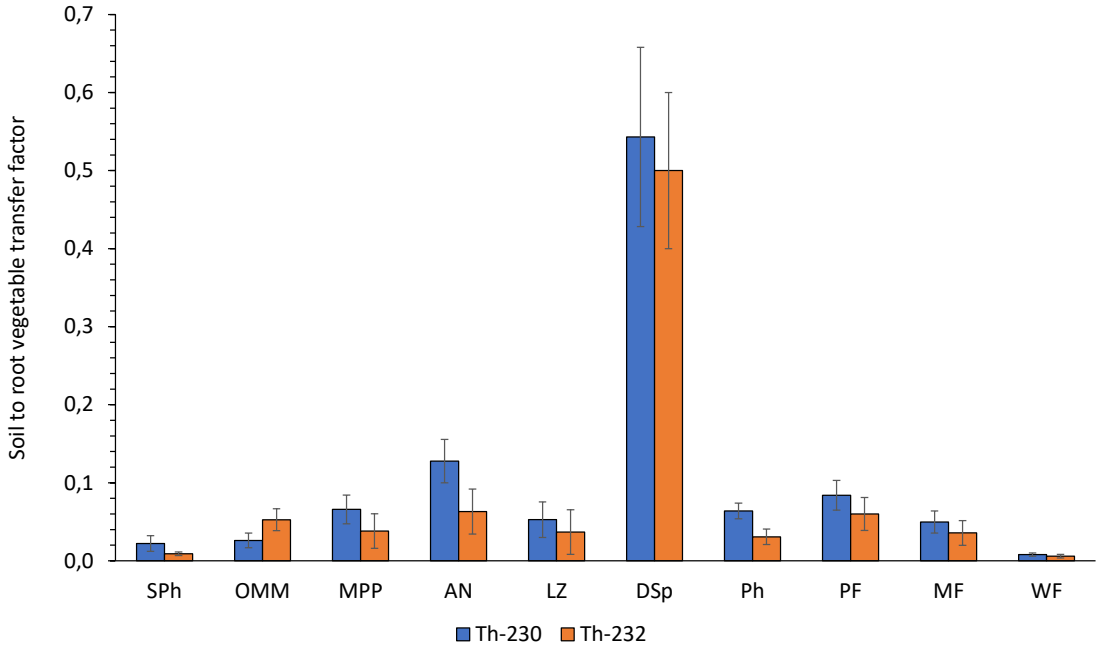



Figure 33 - Soil-to-root vegetable transfer factor of thorium isotopes for carrot cultivated on soil from Turkestan region fertilised by different fertilizers (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

The TF value of thorium isotopes for carrot samples grown with application of fertilizers were an order-of-magnitude higher than for carrot grown on unfertilized soil. Among the calculated TF values, the highest was for carrot grown with application of double superphosphate. TF values of thorium isotopes were not higher than 1 for none of the investigated samples. Addition of double superphosphate enhanced bioavailability of thorium isotopes with consequently increased uptake of thorium isotopes by root crop of carrot. In addition, this was proved by the results of sequential extraction analysis, where dramatical change of distribution of Th-232 was observed.

The percent of Th-232 distributed in strongly bound fraction significantly decreased from 88 % in unfertilized soil to 38 % in double superphosphate fertilized soil.

According to the obtained results, it can be seen that application of fertilizers during cultivation period increased bioavailability of thorium isotopes for soil from Turkestan region.

The results of the soil to root vegetable transfer factor (TF) for Ra-226 are presented in Figure 34. The results varied depending on the used fertilizer.

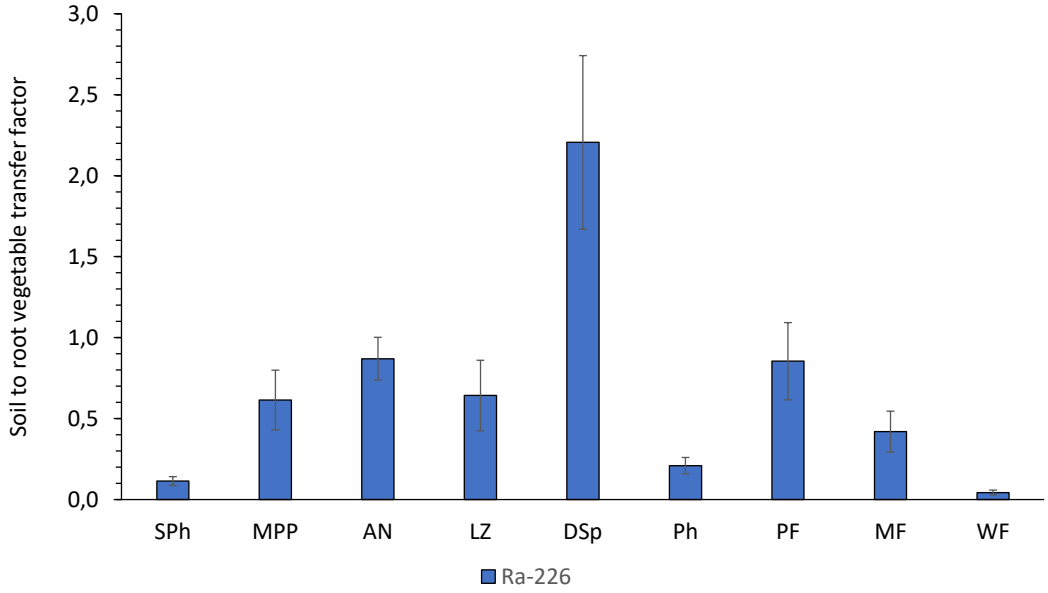



Figure 34 - Soil-to-root vegetable transfer factor of Ra-226 for carrot cultivated on soil from Turkestan region fertilised by different fertilizers (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

The TF value of Ra-226 for carrot samples grown with application of fertilizers were an order-of-magnitude higher than for carrot grown on unfertilized soil, except for carrot cultivated with application of superphosphate, where TF value was comparable to TF value of carrot grown on unfertilized soil. Among the calculated TF values, the highest was for carrot grown with application of double superphosphate, where TF value of Ra-226 was 15 times higher than for carrot grown on unfertilized soil. TF values of Ra-226 were not higher than 1 for none of the investigated samples, except for radish cultivated with double superphosphate. Based on the results of sequential extraction, addition of double superphosphate four times increased amount of bound to carbonate fraction in comparison to unfertilized soil, which promoted the bioavailability of radium species.

According to the obtained results, it can be seen that application of fertilizers during cultivation period increased bioavailability of Ra-226 for soil from Turkestan region.

The results show that all calculated TF values for natural radionuclides in investigated samples were higher than the mean values for U ($8.4 \times 10^{-3}$), Th ($8.0 \times 10^{-4}$), Ra ($7 \times 10^{-2}$) reported so far for root crops [105].

### 3.14 Comparative conclusion of soil to root vegetable transfer factor

A comparative analysis of the soil to root vegetable transfer factor of natural radionuclides for radish and carrot samples showed differences depending on the type of soil and fertilizers used.

For radish samples cultivated on soils from Baiterek village, Almaty region, the maximum TF values for uranium (U-234, U-238) and thorium (Th-230, Th-232) were observed with the use of monopotassium phosphate. The TF value exceeded 1, which indicates accumulation of these radionuclides in root crop of radish.

For carrot cultivated on soil from Koklaisai village, Almaty region, the highest TF values of uranium and thorium were determined for soils fertilized by ammonium nitrate, monopotassium phosphate, peat and micro fertilizers. The TF of uranium increased by 13-19 times compared to the soil without fertilizers, which indicates an increase in the mobility of uranium. However, even under these conditions, TF remained below 1, which indicates a limited transfer of radionuclides to root crop of carrot.

For carrot cultivated on soil from Kyzemshek village, Turkestan region, the application of double superphosphate had the greatest impact on soil to root vegetable transfer factor. TF for uranium, and radium isotopes exceed one, which indicates accumulation of these radionuclides in carrots.

Thus, the most pronounced increase in bioavailability and accumulation of radionuclides was noted for the soil from the Turkestan region. This possibly could relate to the change in the geochemical fraction of soil where radionuclides are distributed.

### 3.15 Root barrier coefficient

*Soil from Koklaisai village, Almaty region*

In order to evaluate the root barrier, the root barrier coefficient (RBC) was calculated as the ratio of activity of radionuclide in aboveground part of carrot to the activity of radionuclide in root of the carrot [119]. The root barrier coefficient of alpha emitting radionuclides for carrot cultivated on soil from Almaty region with application of different fertilizers are presented in Figure 35.

As it can be seen from Figure 35, the root barrier coefficient varied depending on the type of the applied fertilizer, indicating differences in the radionuclide retention within the root system.

The RBC value for carrot grown on unfertilized soil were less than 1 only for Th-230 (0.6) indicating its accumulation in root of carrot. In the case of Th-232, it was equal to 1.1, indicating equal distribution of Th-232 between the root and aboveground

part of carrot. For U-234, U-238, and Ra-226, the RBC value was more than 1, indicating translocation of radionuclides from root to aboveground part of carrot.

The RBC value for uranium isotopes for investigated samples were the highest for carrot samples grown on soil fertilized with NPK fertilizer, and double-superphosphate. The lowest RBC value for U-234 was determined for MF (0.6), MPP (0.7), AN (1.0), and PF (1.8). Application of microfertilizer and monopotassium lead to concentration of U-234 in root of carrot.

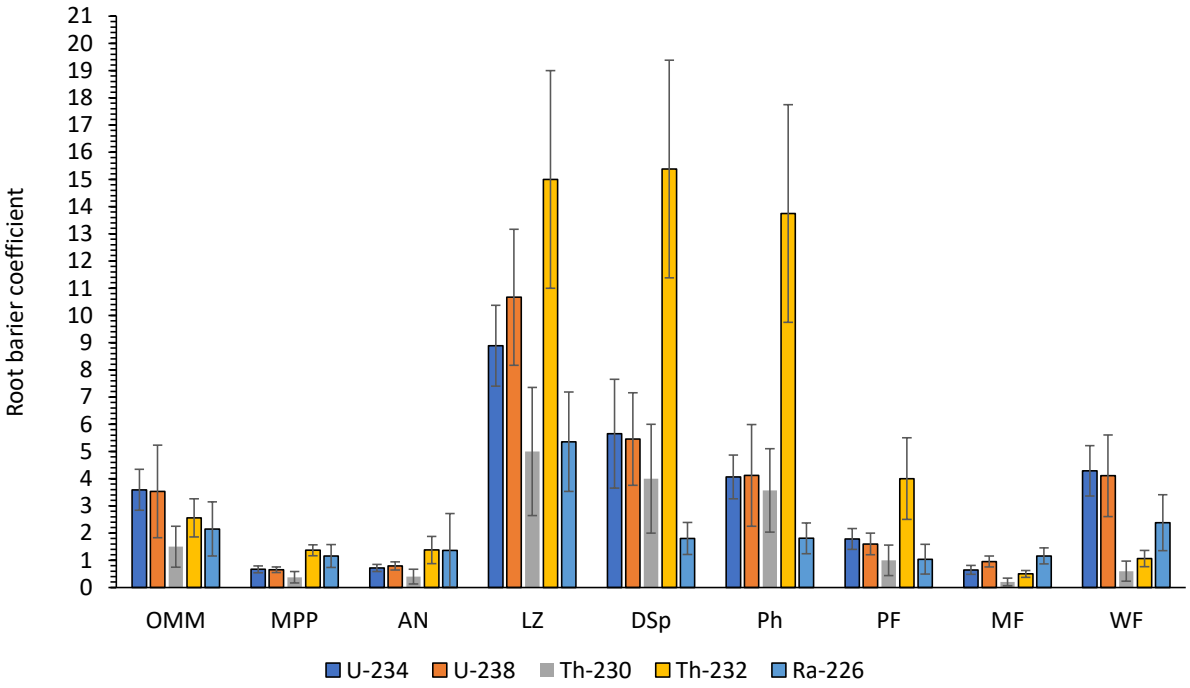



Figure 35 - Root barrier coefficient for natural radionuclides (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

In the case of Th-230, carrot grown with the application of microfertilizer, monopotassium phosphate and ammonium nitrate, RBC values were less than 1 and less than that in unfertilized soil, indicating concentration of Th-230 in root of carrot. The RBC value was more than 1 for carrot cultivated with application of organo-mineral mixture, NPK fertilizer, double superphosphate and phosphoric fertilizer, indicating translocation of Th-230 from root to aboveground part of carrot.

The RBC value of Th-232 for carrot cultivated with microfertilizer was less than in unfertilized soil and less than one indicating retention of Th-232 in root of carrot. For the rest of the investigated samples, RBC value was more than 1, indicating translocation of Th-232 from root to aboveground part of the carrot.

The RBC value of Ra-226 for carrot cultivated with application of NPK fertilizer was equal to 5, which was higher than in carrot cultivated on unfertilized soil. This indicates greater degree of translocation of Ra-226 from root to aboveground part of carrot due to application of NPK fertilizer. For the rest of the investigated samples, the RBC value was less than the RBC value of unfertilized soil, indicating that fertilizers

may promote retention of radionuclide in root, limiting its translocation within the plant system. However, the RBC value was more than 1 for these samples, indicating that despite the variation in translocation rates, Ra-226 was still preferentially transported to the aboveground part of the carrot.

This finding highlights the influence of different fertilizers on radionuclides retention and translocation within the plant system.

*Soil from Kyzemshek village, Turkestan region*

In order to evaluate the root barrier, the root barrier coefficient (RBC) was calculated as the ratio of activity of radionuclide in aboveground part of carrot to the activity of radionuclide in root of the carrot [119]. The root barrier coefficient of alpha emitting radionuclides for carrot cultivated on soil from Almaty region with application of different fertilizers are presented in Figure 36.

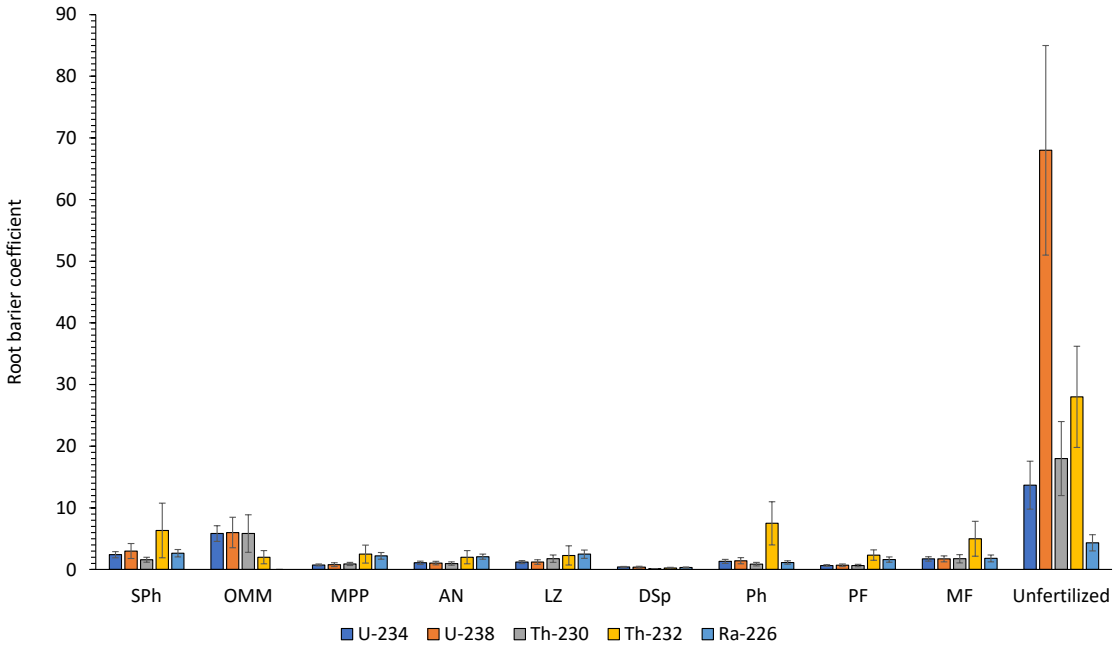



Figure 36 - Root barrier coefficient of natural radionuclides (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

To evaluate the effect of applied fertilizers on radionuclides translocations from root to aboveground part of carrot, each carrot sample cultivated on fertilized soil was compared against carrot samples cultivated on unfertilized soil.

The RBC value for unfertilized soil was the highest for all radionuclides, suggesting that without fertilization, radionuclides has greater translocation level from root to aboveground part of the carrot.

All applied fertilizers significantly reduced the RBC value for U-234, U-238 compared to unfertilized soil, indicating decreasing radionuclide uptake to aboveground part of the carrot and concentration in root. The RBC value of carrot

cultivated with application of double superphosphate show greatest reduction in uranium translocation, reducing it by over 34 (U-234) and 170 (U-238) times compared to carrot cultivated on unfertilized soil, moreover, the RBC value was less than 1. The same trend was observed for the RBC values of carrot cultivated with application of monopotassium phosphate and peat fertilizer. Despite reductions, the RBC values of carrot cultivated with application of superphosphate, ammonium nitrate, NPK fertilizer, phosphoric, micro-fertilizer still had the RBC > 1, meaning that preferential translocation to aboveground part still occurred.

The same trend was observed for thorium isotopes (Th-230, Th-232), where the application of all fertilizers significantly reduces the RBC value of carrot compared to those grown in unfertilized soil. This indicates that fertilization generally enhances the retention of thorium isotopes within the root system, limiting its translocation to the aboveground part. The RBC value of carrot cultivated with double superphosphate shows significant decrease compared to carrot cultivated on unfertilized soil, indicating strong retention effect in root of carrot due to usage of double superphosphate. This finding is in agreement with studies [174-176], where authors show that application of phosphate-based fertilizers reduces solubility and mobility of thorium in soil, leading to its preferential accumulation in root of the plant system. The same trend was observed for the RBC value of carrot for Th-230 cultivated with the application of peat fertilizer, where the RBC was less than 1, indicating retention of Th-230 in root of carrot.

In the case of Ra-226, the application of double superphosphate during cultivation period was more effective at reducing Ra-226 translocation from root to aboveground part of carrot, decreasing the RBC by 14.3 times compared to carrot cultivated on unfertilized soil. All other applied fertilizers decreased translocation of Ra-226 from root to aboveground part of the carrot; however, the RBC was still more than 1, indicating that preferential translocation to aboveground parts occurs.

Application of double superphosphate has been shown to enhance the retention of natural radionuclides in root system of the plant. This occurs due to the possible interactions between phosphates and radionuclides, which lead to the formation of insoluble phosphate complexes that become immobilized in root of the plant. While this retention could be beneficial in reducing translocation to the aboveground part, it may pose potential risk for root crops such as carrots, radish, and other edible root vegetables. Since the root system, in case of root crops, serves as a consumable part, it may increase radiological risk for consumers.

Based on the result of the RBC values of carrot cultivated on two different soils with application of different fertilizers, it can be concluded that fertilization significantly reduces radionuclide translocation in both soil types, with the greatest impact observed in Kyzemshek village soil.

### 3.16 Radionuclide activity ratios

*Soil from Baiterek village, Almaty region*

The results of activity ratios of Ra-226/U-238, U-234/U-238 in soil samples and radish edible part are presented in published research article - Nursapina N.A., Shynybek B.A., Matveyeva I.V., Nazarkulova, Sh.N., Štrok M., Benedik L, Ponomarenko O.I. Effect of mineral fertilisers application on the transfer of natural radionuclides from soil to radish (Raphanus sativus L.) // Journal of Environmental Radioactivity, V.247, 2022. 10.1016/j.jenvrad.2022.106863.

Based on published results, Ra-226/U-238 ratio in radish was consistently below 1, indicating higher uranium accumulation compared to radium. The lowest ratio was determined for radish cultivated with application of monopotassium phosphate, confirming that monopotassium phosphate affects the uranium uptake. U-234/U-238 ratio in radish was greater than 1, indicating that U-234 is more mobile than U-238 due to recoil effect. This finding highlights the role of fertilization in modulating radionuclide uptake.

*Soil from Koklaisai village, Almaty region*

From the activity concentrations, given in Table 12, the activity ratios (Figure 37) of the natural radionuclides were computed for all the fertilized and unfertilized soils and root crop of carrot samples.

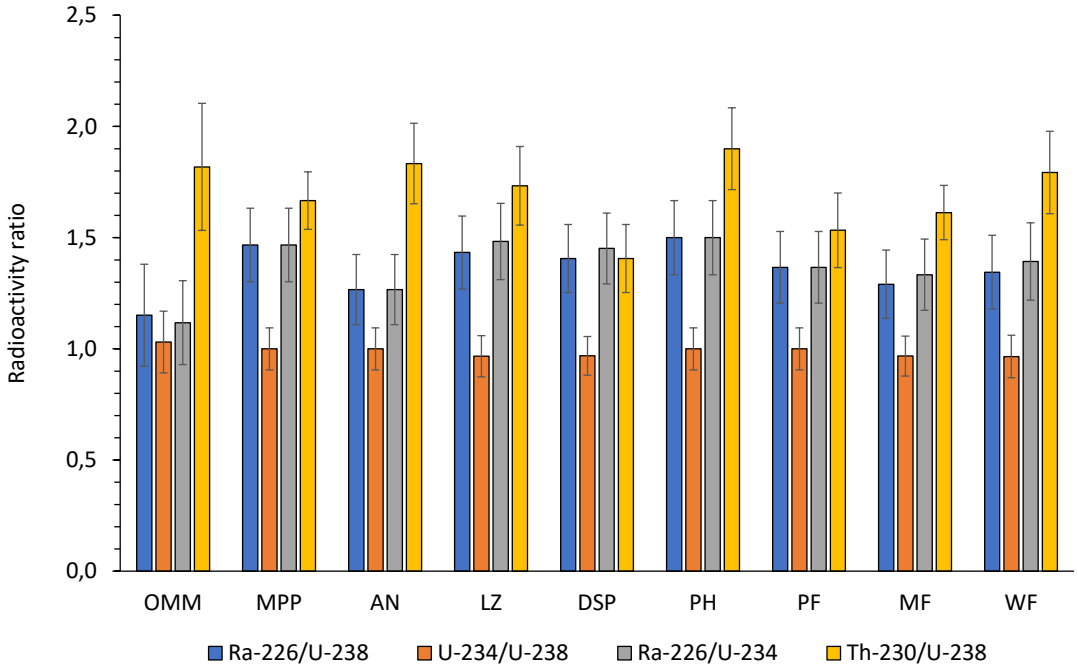



Figure 37 - Activity ratios of Ra-226/U-234, Ra-226/U-238, U-234/U-238 and Th-230/U-238 in fertilized and unfertilized soil samples (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

The U-234/U-238 ratio in soil samples (fertilized and unfertilized) have fluctuated around 1 indicating that the state of equilibrium is most probable. From this

fundings, it can be noted that application of fertilizers did not affect the U-234/U-238 activity ratio. However, the activity ratio of the Ra-226/U-234 and Ra-226/U-238 ranged from 1.12 to 1.5 and from 1.15 to 1.5 respectively, across the investigated soil profile. These finding suggest the relative enrichments of Ra-226, indicating its accumulation in soil compared to uranium isotopes. The higher mobility of U-238 in comparison to Th-230 affects the Th-230/U-238 ratio, which is higher than one for all investigated soil samples.

Activity ratios of Ra-226/U-234 and Ra-226/U-238 in root crop of carrot varied notably across fertilization treatment (Figure 38). Ratio greater than 1 was observed for almost all treatments, except for root crop of carrot cultivated with monopotassium phosphate and ammonium nitrate fertilizer. This indicates preferential accumulation of Ra-226 relative to U-234 and U-238 in root tissues. The lowest ratio was equal to 1 for root crop of carrot cultivated with monopotassium phosphate and ammonium nitrate respectively, indicating balanced uptake of Ra-226 and uranium isotopes.

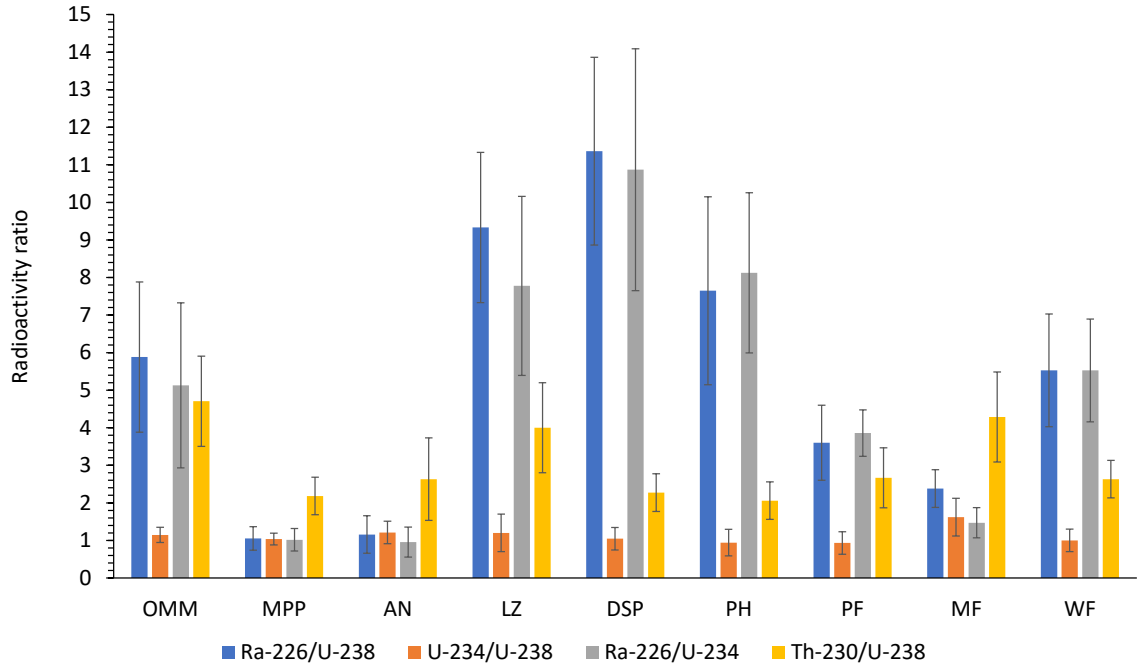



Figure 38 - Activity ratios of Ra-226/U-234, Ra-226/U-238, U-234/U-238 and Th-230/U-238 in root crop of carrot (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

Activity ratios of Ra-226/U-234 and Ra-226/U-238 in root crop of carrot cultivated with application of double superphosphate, NPK fertilizer, and phosphoric fertilizer was higher than in root crop of carrot cultivated on unfertilized soil, indicating stronger Ra-226 accumulation in root crop of carrot as a result of application of fertilizer.

Ra-226/U-238 and Ra-226/U-234 activity ratios showed lower values for root crop of carrot cultivated with ammonium nitrate and monopotassium phosphate than in soil samples. This finding indicates that uranium isotopes were more available for

uptake by root crops of carrot. In addition, for carrot grown with addition of ammonium nitrate and monopotassium phosphate, the TF value for U-234 and U-238 were slightly higher than TF value of Ra-226, indicating greater uranium availability.

The U-234/U-238 activity ratio in root crop of carrot was equal to 1 for almost all investigated samples except for root crop of carrot cultivated with microfertilizer. This indicates that the root crop of carrot accumulated both isotopes of uranium in equal activity concentration except for carrot cultivated with microfertilizer. Application of microfertilizer resulted in enhanced mobility and uptake of U-234.

In order to evaluate radionuclide behaviour in the soil plant-system, activity ratio of radionuclides was compared between root crop of carrot and soil samples.

For all other investigated samples, the Ra-226/U-238 and Ra-226/U-234 activity ratios showed higher values in root crop of carrot than in the corresponding soil samples, which indicate that Ra-226 was more available for uptake by root crop of carrot and preferentially accumulated in root tissue compared to uranium isotopes. This suggests a greater level of uptake of radium by the root of carrot, potentially due to chemical similarity of radium to calcium.

The Th-230/U-238 activity ratio in root crop of carrot samples were higher than in investigated soil samples indicating that Th-230 is more effectively accumulated in the root tissues than U-238. This indicates fractionation between thorium and uranium isotopes during root uptake, influenced by different chemical behaviour and interactions with root tissues.

The obtained results demonstrate that the application of fertilizers can lead to change of activity ratio of radionuclides, resulting in fluctuations in the distribution and behaviour of radionuclides in soil-plant system. This highlights the role of fertilizers as a factor influencing the radionuclide mobility and uptake.

*Soil from Kyzemshek village, Turkestan region*

From the activity concentration given in Table 13, the activity ratios (Figure 39) of the natural radionuclides were computed for all the fertilized and unfertilized soils and root crop of carrot samples.

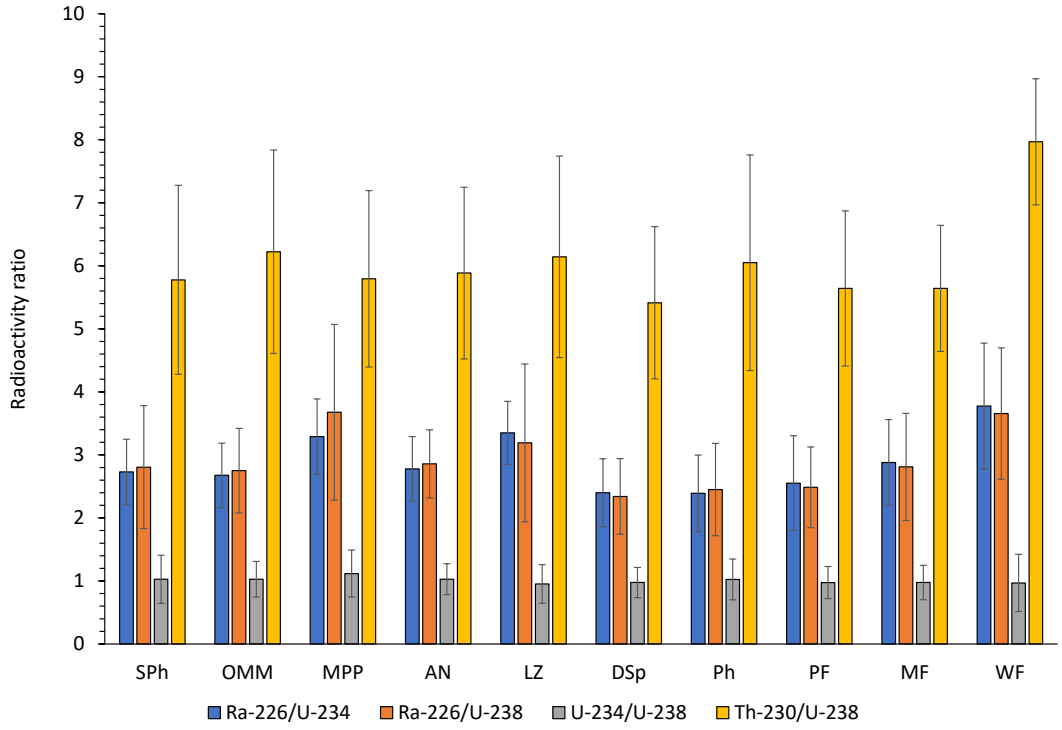



Figure 39 - Activity ratios of Ra-226/U-234, Ra-226/U-238, U-234/U-238 and Th-230/U-238 in fertilized and unfertilized soil samples (with expanded uncertainties with a coverage factor $k$=2, corresponding to a confidence level of approximately 95%)

The U-234/U-238 ratio in soil samples (fertilized and unfertilized) have fluctuated around 1 indicating that the state of equilibrium is most probable. From this fundings, it can be noted that application of fertilizers did not affect to the U-234/U-238 activity ratio as it was in case of soil from Almaty region.

In comparison to unfertilized soil, the application of fertilizers leads to reduction of the activity ratio of Ra-226/U-234, Ra-226/U-238, and Th-230/U-238, indicating that fertilization generally limits accumulation of Ra-226 and Th-230 in root crop of carrot compared to uranium isotopes.

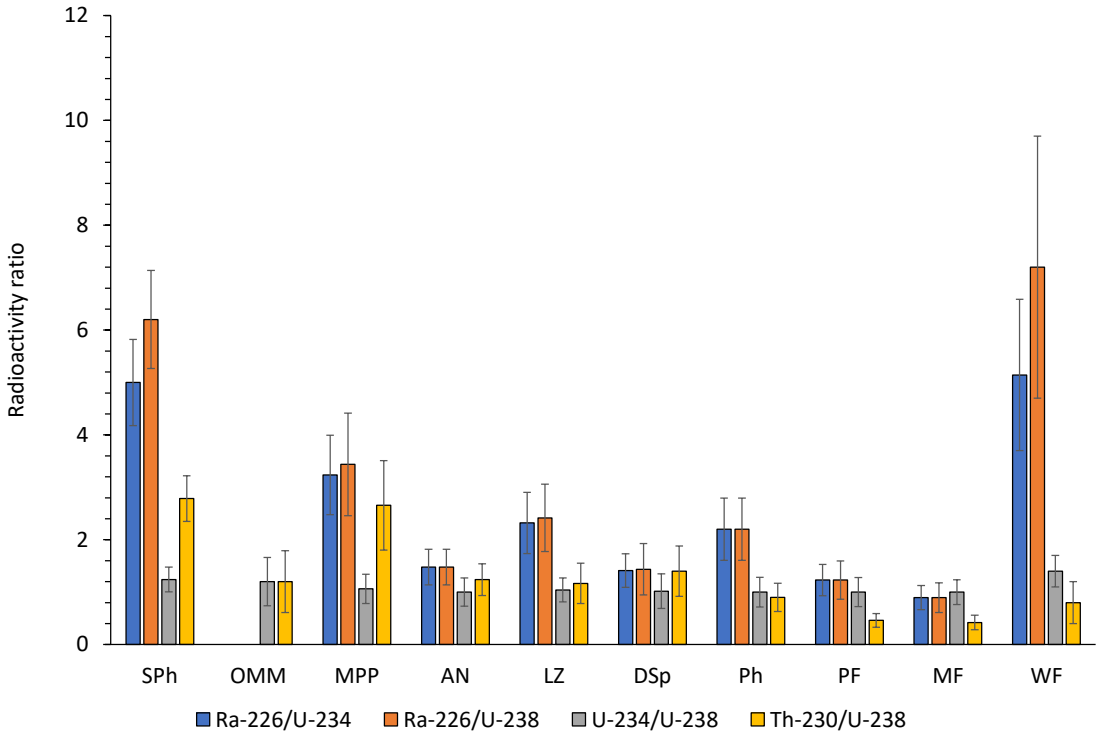



Figure 40 - Activity ratios of Ra-226/U-234, Ra-226/U-238, U-234/U-238 and Th-230/U-238 in root crop of carrot (with expanded uncertainties with a coverage factor *k*=2, corresponding to a confidence level of approximately 95%)

Activity ratios of Ra-226/U-234 and Ra-226/U-238 in root crop of carrot grown with application of fertilizers were lower than in root crop of carrot grown on unfertilized soil indicating decrease of Ra-226 availability due to application of fertilizers.

Activity ratio of Th-230/U-238 in root crop of carrot cultivated on unfertilized soil was equal to 1 indicating balanced uptake of both isotopes under natural soil condition. In comparison, activity ratios of Th-230/U-238 in root crop of carrot cultivated with microfertilizer and peat fertilizer were lower than in unfertilized soil, indicating preferential retention of U-238 in root crop of carrot. Theses may be attributed to the increased mobility and bioavailability of uranium in the presence of these fertilizers. Conversely, for the rest of the investigated samples, activity ratio of Th-230/U-238 is higher than in unfertilized soil, indicating retention of Th-230 in root crop of carrot. These variations demonstrate that the application of different fertilizers resulted in different uptakes of radionuclides due to changes in their chemical forms, solubility, and interactions with root surfaces.

The U-234/U-238 activity ratio for all investigated samples of root crop of carrot were equal to 1 indicating state of equilibrium.

In order to evaluate radionuclide behaviour in the soil plant-system, activity ratio of radionuclides was compared between root crop of carrot and soil samples. Ra-226/U-238 and Ra-226/U-234 activity ratios were higher in soil than in the root crop of carrot for all fertilized soil samples, except in soil fertilized by superphosphate and in the unfertilized soil. This funding indicates that for most of applied fertilizers,

uranium isotopes were more readily absorbed or retained by the root crop, reflecting differences in radionuclides uptake behaviour.

The Th-230/U-238 activity ratio in root crop of carrot samples were lower than in corresponding soil samples, indicating preferential uptake of U-238 by root crop of carrot. This suggests limited Th-230 mobility related to low solubility of Th-230 and possibly strong association with soil particles.

From obtained results it can be seen that the use of fertilizers could lead to change of radionuclide activity ratios and results in such fluctuations. Fertilizers type notable affects radionuclide behaviour in soil-plant system.

# CONCLUSIONS

Based on the results of the study, the following conclusions can be drawn:

Results obtained by alpha-spectrometry analysis of investigated fertilizers, soil and carrot samples revealed that:

- The activity concentration of investigated fertilizers is relatively low and did not exceed limit value of 1000 Bq/kg according to the Technical Regulations of the Eurasian Economic Union "On requirements for mineral fertilizers. Among the investigated fertilizers, the highest activity concentration of U-234, U-238, Th-230, Ra-226 was determined for phosphoric fertilizer and equals to 146 ± 11 Bq/kg, 148 ± 13 Bq/kg, 238 ± 15 Bq/kg, 169 ± 4 Bq/kg, respectively. The highest concentration of Th-232 was determined for double superphosphate and equals to 42 ± 5 Bq/kg.
- Based on ζ-score, calculated for soil from Koklaisai and Kyzemshek village, it can be concluded that the application of fertilizer did not significantly affect the activity concentration of natural radionuclides in soil.
- The highest activity concentration of natural radionuclides was found for *R.Sativus* growing on soil, which was fertilized by monopotassium phosphate.
- The highest activity concentrations of natural radionuclides, cultivated on soil taken from Baiterek village, Almaty region, was determined for root crop of *D.Carrota,* cultivated with application of monopotassium phosphate and equals to 5.7 Bq/kg for U-234, 5.5 Bq/kg for U-238, 12 Bq/kg for Th-230, 3.4 Bq/kg for Th-232 and 5.8 Bq/kg for Ra-226.
- The highest activity concentrations of natural radionuclides, cultivated on soil taken from Kyzemshek village, Turkestan region, was determined for root crop of carrot cultivated with application of double superphosphate and equals to 56 Bq/kg for U-234, 55 Bq/kg for U-238, 77 Bq/kg for Th-230, 6.5 Bq/kg for Th-232 and 79 Bq/kg for Ra-226.

Evaluation of soil-to-root vegetable transfer factors revealed that:

- Application of monopotassium phosphate led to increase of transfer factor of U-234, U-238, T-230 for radish cultivated on soil from Baiterek village, Almaty region.
- Application of monopotassium phosphate, ammonium nitrate, peat fertilizer, microfertilizer lead to an increase of transfer factor of uranium, thorium and radium for root crop of carrot cultivated on soil from Koklaisai village, Almaty region compared to unfertilized soil.
- The application of double superphosphate fertilizer resulted in an increased transfer factor for uranium (U-234, U-238), thorium (Th-230, Th-232), and radium (Ra-226) in the root crop of carrot cultivated on soil from Kyzemshek village, Turkestan region. The transfer factor was higher than 1 for U-234, U-238, and Ra-226, indicating their active transfer from soil to the edible part

of the crop, suggesting enhanced bioavailability of these radionuclides under fertilization conditions.

- The calculated TF values for natural radionuclides in investigated samples were higher than the mean values for U ($8.4 \times 10^{-3}$), Th ($8.0 \times 10^{-4}$), Ra ($7 \times 10^{-2}$) reported so far for root crops.

Based on sequential extraction of fertilized and unfertilized soil from Almaty and Turkestan region, it can be concluded that:

*Koklaisai village, Almaty region*

- The notable change in distribution of uranium isotopes was observed for soil fertilized with ammonium nitrate, where the amount of mobile and potentially mobile fractions increased 2.6 times (U-234) compared to unfertilized soil due to slight soil acidification, which led to dissolution of carbonate-bound forms of U-234, releasing it into the soil solution and following re-distribution.
- Thorium isotopes remain mostly immobile for all investigated samples. Certain fertilizers, especially those containing organic components, can affect their distribution within soil fractions, thereby influencing their potential availability for plant uptake.
- Application of ammonium nitrate led to an increased amount of bound to carbonate fraction of Ra-226 from 7 % (unfertilized soil) to 15 % (ammonium nitrate fertilized soil).

*Kyzemshek village, Turkestan region*

- Application of monopotassium phosphate, ammonium nitrate, double superphosphate, phosphoric, peat fertilizer, microfertilizer leads to increase of uranium isotopes in bound to carbonate fraction compared to unfertilized soil.
- Noticeable change in distribution of Th-230 in mobile and potentially mobile fractions was observed for ammonium nitrate, NPK fertilizer, double superphosphate and microfertilizer fertilized soil, where the percentage of distribution of Th-230 increased from 8 % for unfertilized soil to 14 % for ammonium nitrate, 15 % for NPK fertilizer, 11 % for double superphosphate, and 13 % for microfertilizer.
- Noticeable change in distribution of Th-232 in mobile and potentially mobile fractions was observed for monopotassium phosphate, ammonium nitrate, NPK fertilizer, and microfertilizer fertilized soil compared to unfertilized soil, where the percentage of distribution of Th-232 increased from 3 % in unfertilized soil to 9 % for monopotassium phosphate, 5 % for ammonium nitrate, 6 % for NPK fertilizer, and 6 % for microfertilizer.
- Application of double superphosphate fertilizer significantly increased the mobile and potentially mobile fraction of Th-232 from 3 % (unfertilized soil)

to 59 %, with 58 % in bound to Fe/Mn oxides. This shift is attributed to higher soil pH (7.8), enhancing Th sorption onto Fe/Mn oxides through formation of hydroxide complexes.

- Noticeable increase of distribution of Ra-226 is observed for bound to carbonate fractions, where the percentage of distribution of Ra-226 in unfertilized soil (4 %) increased for 8 % for monopotassium phosphate, 12 % for phosphoric, and double superphosphate, 11 % for NPK fertilizer, 9 % for monopotassium phosphate, and 4 % for superphosphate.

Evaluation of activity ratio of isotopes of natural radionuclides revealed that:

*For Almaty region, Baiterek village:*

- The lowest Ra-226/U-238 ratios were observed in radish grown on monopotassium phosphate fertilized soil, corresponding to higher uranium accumulation, supported by the elevated Ra-226/U-238 ratios in the corresponding soil-indicating enhanced uranium mobility due to monopotassium phosphate application.
- The U-234/U-238 ratio in radish exceeded 1, indicating preferential uptake of U-234, attributed to its greater mobility from recoil effects.
- The U-234/U-238 ratio remained close to unity in soil samples, indicating equilibrium and suggesting that fertilizer application has minimal impact to uranium isotope fractionation.

*For Almaty region, Koklaisai village:*

- The U-234/U-238 ratio remained close to unity in both soil and root crop samples, indicating equilibrium and suggesting that fertilizer application has minimal impact to uranium isotope fractionation.
- The activity ratio of Th-230/U-238 in all fertilized soil samples were higher in comparison to unfertilized soil, indicating increase of Th-230 accumulation in soil due to application of fertilizers.
- Application of double superphosphate, NPK fertilizer, monopotassium phosphate during the cultivation period increased activity ratios of Ra-226/U-234 and Ra-226/U-238 in fertilized soil in comparison to activity ratios of Ra-226/U-234 and Ra-226/U-238 in unfertilized soil.

*For Turkestan region, Kyzemhsek village:*

- The U-234/U-238 ratio remained close to unity in both soil and root crop samples, indicating equilibrium and suggesting that fertilizer application has minimal impact to uranium isotope fractionation.
- Under most fertilization treatments, the Ra-226/U-234 and Ra-226/U-238 activity ratio were generally higher in soil than in root crop of carrot, indicating preferential uptake of uranium isotopes.

- The Th-230/U-238 activity ratio in root crop of carrot samples were lower than in investigated soil samples indicating U-238 availability for root crop.

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