ABSTRACT
thesis for the degree of Doctor of Philosophy (Ph.D.)
on specialty «8D05301 – Chemistry»

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

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 (U-234/U-238, Ra-226/U-234, Ra-226/U-238, Th-230/U-238) were 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. However, alongside these advantages, the use of fertilizers poses certain risks, including soil contamination by various components, notably natural radionuclides. In addition, application of fertilizers could change the chemical speciation of radionuclides, which could lead to the enhancement of their mobility and bioavailability.

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. Therefore, understanding the behavior 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. 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.

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 researches 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.

Purpose of the work is to establish the 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 the comprehensive investigation of the entry of natural radionuclides into soil and root vegetable crops through fertilizer application, and their subsequent distribution within the soil–plant system. For the first time, the effects of various fertilizers on the mobility and bioavailability of natural radionuclides in the soils of the Almaty and Turkestan regions have been analysed. The bioavailability of radionuclides to root crops was assessed through sequential extraction, with differentiation based on the type of fertilizer applied.

Fertilizers that most significantly influence radionuclide mobility and bioavailability have been identified. The results provide a basis for developing fertilizer use recommendations aimed at minimizing radiation exposure from the 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 this thesis contribute to a deeper understanding of the behavior of natural radionuclides in the soil–plant environmental system, which is essential for advancing scientific knowledge on their migration and bioavailability under the influence 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 includes the analysis of scientific literature relevant to the thesis topic, the implementation of vegetation experiments, the performance of radiochemical separation procedures for the simultaneous determination of natural radionuclide isotopes, followed by measurements using an alpha spectrometry system (Alpha Analyst, Canberra, USA), as well as the evaluation and interpretation of the 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 k_0-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).

Contribution to scientific publications writing: investigation, data analysis, methodology, writing – original draft, review and editing with co-authors.

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 106 pages, contains 40 figures, 13 tables, and 176 bibliographical references.