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EFFECTS OF LONG-TERM FERTILIZATION ON STRONTIUM (SR) AND VANADIUM (V) IN AGRICULTURAL SOILS OF PRIMORYE IN RUSSIA UNDER CLIMATE CHANGE

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Strontium (Sr) and Vanadium (V) are potentially dangerous for the natural environment. Little is known about the accumulation and mobility thought soils profiles of different Sr and V forms. Several studies of Sr and V distribution in soils have demonstrated strongly fixation of elements by different soil properties. Climate change and, respectively, soils redox cycles changes can affect the main soil properties and of their associated elements. In current work, contents and the main factors controlling the vertical distribution and accumulation of total, "pseudo-total" and water soluble forms of Sr and V in the agricultural soils formed under long-term fertilizer application were studied. Total Sr and V contents increased to 10% and 2% respectively with adding fertilizer. The contents of "pseudo-total" Sr and V forms increased to 20%. The concentrations of water soluble Sr and V forms increased to 65%. The contents of Sr and V were manly controlled by soil acidity levels and organic C content in studied soils. Additionally, Sr was associated with Ca-, P-, Mn-containing compounds and V with Al-, Si-, Fe- containing compounds. Knowledge of the chemical behavior of the Sr and V in the agricultural soils creates a scientific basis for risk assessment and remediation strategies.

Keywords: *agricultural soils; fertilizer application; strontium; vanadium; soil properties, climate change.*

Introduction

One of the most important scientific and practical problems is the stability of the soil to excessive heavy metals input. Extensive areas of land are contaminated with heavy metals [15, 21]. The content, distribution and accumulation such heavy metals as Zn, Pb, Ni, Cd, Cr and Cu were studied in detail in soils of different regions of the Russian Federation. At the same time, attention to such elements as Sr and V is not enough to have a real understanding of the background content of these elements in soils. The features of the interaction of elements with the basic soil properties and migration of Sr and V in soil-plant system are poorly studied. Strontium and V are potentially dangerous for the natural environment [21]. The toxic Sr level for biota has not been completely established because of insufficient evidence about deleterious effects on biota of the high levels of stable Sr in the biosphere. Strontium has a similar action to Ca and Sr plays a similar role in many cellular metabolic possesses [2, 8]. Concentration of V above 2 ppm (for some bush beans above 13 ppm) in plants and above 140 ppm in the soil solution is toxic for the plants as high concentrations of V causes chlorosis and growth limit [7, 8].

Based on published data, in agricultural soils of Sweden and Japan the average concentration of V is 69 and 180 mg kg^{-1}, respectively, Sr is 163 and 190 mg kg^{-1}, respectively [8]. One of the most common sources of input of the studied elements is the use of phosphorus fertilizers in the arable soil. The content of Sr and V varies from 25 to 500 mg kg^{-1} and from 2 to 180 mg kg^{-1}, in phosphate rock, superphosphate, ammophos and other phosphorus-containing fertilizers, respectively [8, 9]. At present time there are no regulatory documents that determine the permissible content of Sr and V in fertilizers on the territory of the Russian Federation. On the Primorsky Krai territory there is a state development program and the area of land used in the agricultural production of the region is increased. At the same time, the amount of fertilizers adding in this area is not controlled and causes a change in the elemental composition of the soil [14].

The aim of the current work was to assess the influence of long-term mineral and organo- mineral fertilizers application on the content of different Sr and V forms in arable soils of Primorsky Krai.

Materials and methods

The objects of this study were soils formed in the territory of agrochemical station of Primorye Research Institute of Agriculture Far Eastern Branch of Russian Academy of Sciences. The experience of applying different types of fertilizers has been carried out for 77 years. The investigated type of soil is characterized by high content of humus (to 4%) and clay and silt particles (80–85%). Soils are formed on lake-alluvial deposits. These soils occupy more than 50% of agricultural land of Primorsky Krai [4].

8 full rotations of 9-full crop rotation had been completed by the time of the research. During this time, $N_{2020}P_{3385}K_{2465}$ adding as part of mineral fertilizers, 320 t ha^{-1} of manure and 41.6 t ha^{-1} of lime. Applied fertilizer amount was calculated with replacement of cultures. In period from 2000 to 2009, additional experience was carried out with higher (from 3 to 5 times) doses of fertilizers and different methods of soil treatment [5].

The experiment was carried out in the field on plots in 3-fold repetition, with each of which a mixed soil sample was taken to the depth of the arable horizon (n=18). The plot area is 150 m^2. The experimental variants selected – without fertilizer (control), with the adding of mineral (NPK) and organo-mineral fertilizers (PK+manure+lime).

Analysis of soil samples was carried out at the center for collective use of Biotechnology and Gene Engineering of the FSC Biodiversity FEB RAS. Total SiO_2, Al_2O_3, Fe_2O_3, MnO, P_2O_5, CaO, Sr and V contents were determined via energy dispersive X-ray fluorescence spectroscopy (EDX) using a Shimadzu EDX- 800HS-P instrument (Shimadzu EUROPA GmbH) equipped with a rhodium X-ray tube (settings: vacuum, voltage 50 kV, current 100 mA, detection time 300 s, dead time 20%, and a collimator of 10 mm). Data were analyzed using PCEDX Shimadzu software. The elements were measured by K-line emission. Eight certified reference standard soil samples. Validation of calibration curves constructed for elements present in the standards was performed through analysis of standard reference materials. One standard soil sample (2499–83) was included for every five unknown samples.

The Sr and V potentially plant-available forms extracted with a mixture of fluoric and nitric acids according to the methods described by Pansu M. and Gautheyrou J., named "pseudototal", according to research by Nesterova et al. [10, 11]. Water-soluble forms of elements were extracted with water extraction (soil : water – 1 : 10) [16]. The elements concentration in acidic and water extracts was measured using the atomic absorption spectrometry method, on the AA-7000, Shimadzu atomic absorption spectrophotometer.

The humus content was determined by the method of Tyurin [17]. The soil acidity was determined by potentiometric method in accordance with the standard recommendations [6].

Strontium and V concentrations in the studied samples compared with the established mean concentrations of elements in the surface horizons of the European soils, agricultural soils of Japan and soils of the world [8].

Results and discussion

The average abundance of total Sr in the soils of different variants of the experiment was as follows: organo-mineral fertilizers > mineral fertilizers > control. Pseudototal and water-soluble forms of Sr and all study forms V have same distribution range: fertilizer > organic fertilizer > control.

Comparison of the Sr and V content in the studied soils with relevant literature data about mean values of elements in soils of Japan, Europe and the world indicates the presence of some excess of the established values. The concentration of total Sr forms was below the average content of this element in the soils of Japan and in the soils of the world and higher than the average level of the element content in the soils of Europe. Total V in the studied soils was 1.5 times higher than the average content of this element in the soils of Europe. In the soils of the control variants of the experiment, the concentration of total forms of Sr varied from 143 to 151 mg kg^{-1}. According to Kabata-Pendias, the Sr content in the agricultural soils of Japan varied from 32 to 130 mg kg^{-1}; in the arable soils of Sweden from 112 to 258 mg kg^{-1} [8]. The total Sr in the soils increased by 10%, the content of pseudototal and water-soluble forms Sr increased by 20% and 70%, respectively, when adding fertilizers. The content of total V in the control varied from 96 to 107 mg kg^{-1}. Arable soils of Sweden are characterized by a V content ranging from 28 to 111 mg kg^{-1}; in the agricultural soils of Japan it varied from 94 to 250 mg kg^{-1}. Adding of organo-mineral and mineral fertilizers did not significantly increase of the total V content in the soils (up to 2%). The increase of the concentration of water-soluble and pseudototal forms V were at 75% and 19%, respectively [8] (Table 1).

Total Sr largely dependent on the soil acidity and Ca–, P–, Mn– content in the soils of the control variants and this correlation increased by applying mineral and organo-mineral fertilizers. Pseudototal Sr significantly correlated with the humus content and Al–, Fe–, Si– containing phases. Significant correlations observed between concentration of water-soluble forms Sr and Al–, Fe–, Si– content in the control variants. The distribution and accumulation of water-soluble forms Sr controlled by soil acidity with adding of organo-mineral fertilizers. The mineral fertilizers adding increased the relationship between total Sr– and Si– content. Pseudototal forms Sr find

Table 1

The content of Sr and V different forms in soils, studied experience variants (mg kg^{-1})

	Total forms		Pseudototal forms		Water soluble forms	
	Sr	V	Sr	V	Sr	V
Control experience variaints	146.80	102.63	87.09	69.94	0.02400	0.00075
Organo-mineral fertilizers adding	161.83	104.18	105.61	80.14	0.07150	0.00145
Mineral fertilizers adding	153.22	104.62	107.68	85.90	0.07600	0.00295
World-soil average	175	129	-	-	-	-
Agricultural soils of Japan	190	180	-	-	-	-
Top soils of Europe	130	68	-	-	-	-

Table 2

The correlation coefficients between the contents of Sr and the physical-chemical properties of soils

	Total Sr			Pseudototal Sr			Water soluble Sr		
	Control	Organo-mineral fertilizers adding	Mineral fertilizers adding	Control	Organo-mineral fertilizers adding	Mineral fertilizers adding	Control	Organo-mineral fertilizers adding	Mineral fertilizers adding
Al_2O_3	–0.82	–0.91	–0.98	0.95	0.22	0.86	0.50	–1.00	0.87
SiO_2	–0.82	–0.93	1.00	–0.95	–0.22	0.31	–0.50	1.00	0.98
P_2O_5	0.82	0.92	0.87	0.65	–0.33	0.09	0.87	–0.80	0.92
CaO	0.82	0.92	0.84	0.66	–0.28	–0.28	0.86	–0.83	–0.97
MnO	0.82	0.91	0.93	–0.66	0.30	–0.71	–0.87	0.82	–0.96
Fe_2O_3	–0.84	–0.93	–0.98	–0.66	0.30	–0.75	–0.87	0.82	–0.95
Humus	–1.00	–0.99	–0.72	–0.66	0.32	0.10	–0.87	0.80	–0.82
pH KCl	1.00	0.99	–1.00	0.68	–0.27	0.09	0.85	–0.84	0.91

a significant correlation with the humus content. The distribution and accumulation of water-soluble forms of Sr controlled by the humus and Al–, Fe– content, and the soil acidity (Table 2).

The Sr– content in soils is often associated with calcium and phosphorus because of the similarity of geochemical characteristics, and it concentrated in Mn–containing minerals under natural environmental conditions [8]. The main part of Sr pseudototal forms was incorporated to the organic-mineral soil complex and mineral phase of soils. Most of the previous studies have demonstrated that Sr is strongly fixed by organic matter in soils [8]. However, a recent study has shown that Sr formed non-stable complexes with organic matter and that in acid soils, Sr transported by the soil solution throughout the soil profile [3]. The results obtained from the soils of the control variants of the experiment do not confirm this trend. The absence of a significant relationship between the content of Sr water-soluble forms and the humus content in soils of the control variants indicated a strong fixation of the element with organic matter of the soil. Additional doses of Sr in the variants of experiment with the application of organo-mineral fertilizers accompanied by the formation of easily mobile Sr compounds with Ca–, P–, Mn– containing phases and the element is actively transferred to the soil solution. Strontium sorbed on the surface of Al and Fe compounds as part

Table 3

The correlation coefficients between the contents of V and the physical-chemical properties of soils

	Total V			Pseudototal V			Water soluble V		
	Control	Organo-mineral fertilizers adding	Mineral fertilizers adding	Control	Organo-mineral fertilizers adding	Mineral fertilizers adding	Control	Organo-mineral fertilizers adding	Mineral fertilizers adding
Al_2O_3	–0.60	0.86	–0.12	–0.74	–0.52	0.98	–0.50	1.00	0.87
SiO_2	–0.60	0.89	–0.07	0.74	0.52	0.87	0.50	–1.00	0.33
P_2O_5	0.60	–0.88	–0.55	–0.98	0.01	0.74	0.01	0.80	0.11
CaO	0.60	–0.88	–0.59	–0.98	–0.04	–0.85	0.00	0.83	–0.29
MnO	0.60	–0.87	0.31	0.98	0.02	–1.00	0.00	–0.82	–0.72
Fe_2O_3	–0.57	0.89	–0.12	0.98	0.02	–1.00	0.00	–0.82	–0.75
Humus	–0.12	1.00	0.73	0.98	–0.01	–0.59	0.00	–0.81	0.09
pH KCl	0.12	–1.00	0.11	–0.97	–0.05	0.74	–0.03	0.84	0.11

of soluble complexes and migrates beyond the soil profile when applying mineral fertilizers [1, 18].

The distribution and accumulation of total and pseudototal forms of V controlled by the content of Ca–, P–, Mn– phases in the control variants soils of experience. Additionally, the contents of V pseudototal forms controlled by the soil acidity. Water-soluble forms V have a low level of correlation with the soil acidity. The distribution and accumulation of total and water soluble forms of V controlled by the humus and Fe–, Al–, and Si– content by fertilizers adding. Concentration of the V pseudototal forms correlated with the soil acidity (Table 3).

Numerous studies indicated that V fixed in the composition of poorly soluble complexes with polyvalent cations, such as bivalent calcium [19]. Additional intake of V with fertilizers leads to active fixation of the element in the organic-mineral soil complex and soil minerals containing Fe and Al, but this relationship is not strong and the element easily migrated into the soil solution. According to van der Weijden and van der Weijden [20], V in soils is frequently co-associated with Fe [12, 13, 20]. Water-soluble forms are compounds available to plants, easily migrating along the soil profile. The most mobile form of V in soils is VO^{2+}, which prevails in acidic soils and forms stable complexes with soil organic matter. Anionic forms of this metal are VO^{3-}, VO_4^{2-} and H_2VO^{4-} more often prevail under neutral and alkaline conditions of soil solution [8, 13].

Conclusions

With long-term fertilization, the content of total forms of Sr increased by 10%; pseudototal forms Sr by 20%; water soluble forms of Sr 70%, in comparison with the control variants. When additional doses of Sr in the composition of fertilizers added, the level of the element's relationship with Ca–, P–, Mn– and Si–containing phases increased. When applying mineral fertilizers, the main sources of water-soluble Sr compounds are Al and Fe-containing compounds and humus.

A significant increase in the concentration of total forms of V when fertilizer was not installed, however, the content of water-soluble and pseudototal forms of V increased by 75% and 19%, respectively. In soils of the control variants of the experiment, the V concentration controlled by Ca–, P–, Mn – content. The additional input of V with fertilizers leads to the element fixation in the composition of the organic-mineral soil complex and in the composition of soil minerals, where the V predominant forms are pseudototal and water soluble forms.

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