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CONTENT OF NUTRIENTS AND HEAVY METALS AND QUALITY OF TOMATOES ON RECLAIMED SUBSTRATES

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Abstract

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Intensive development of mining and processing industry leads to a continuous reduction of arable and non- fund land. These adverse facts impose to proceed to the use for agricultural purposes of the land that is restored after a reclamation activities, regardless of their low fertility.

The aim of this study was to determine the effect of culture medium on substrate reclaimed by the content of nutrients and heavy metals in the vegetative mass of tomatoes as well as on the quality of the fruit.

Experiment is set on four reclamation substrate taken by technical and biological reclaimed dumps built in iron ore (Lokorsko) and coal (Moshino). For convenience in the work materials used in the experiment will be marked as:

Object 1 – reclamation of organic substrate rehabilitated dump near Moshino, horizon 0–30 cm;
Object 2 – reclamation substrate technical rehabilitated dump in the area of Moshino;
Objectt 3 – reclamation of organic substrate rehabilitated dump near Lokorsko, horizon 0–30 cm;
Object 4 – reclamation substrate technical rehabilitated dump near Lokorsko.

It was found that fertilizer rate applied in experience ($N_{800}R_{600}K_{757}$) is adequately selected in terms of N-fertilization, while PK-fertilization have formed a significant residual in the soil of these elements. High residual concentration of mobile phosphorus fertilization variants Objects 1-3 associated with low phosphorous content in plant tissues and in three subjects of the experiment indicate a disturbing factor in the uptake of phosphorus by tomato plants. The content of potassium in crop production experiment is displayed within the optimal range, while plants fertilized with $(NH_4)_2SO_4$ was higher than those fertilized with NH_4NO_3. The content of oligo-and trace elements Ca, Mg, Zn, Cu, Mn in plant tissues of plants tomatoes ranges indicated it is optimal. As extremely tolerant to pollution culture tomatoes have significant potential for phytoremediation of contaminated land. The values of plastid pigments in the vegetative mass of tomato plants Objects 1-3 fertilized with NH_4NO_3, were significantly higher than those of variants with $(NH_4)_2SO_4$. Fruits of plants fertilized with NH_4NO_3, of Objects 2 and 3 have a higher content of vitamin "C", lycopene common dyes and sugars.

Key words: soil destruction, soil reclamation, heavy metals, tomatoes

Introduction

Intensive development of mining and processing industry leads to a continuous reduction of arable and non-fund land. Total annual loss of agricultural land worldwide is estimated at 15 million ha. If the process of destruction of the land continues soon every person will have about only 0.1–0.2 ha of arable land (Banov and Atanassov, 2011).

These adverse facts impose to proceed to the use for agricultural purposes of the land that is restored after a purposeful reclamation activities, regardless of their low fertility. For this purpose, there are conducted a lot of in-depth research

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on monitoring of degraded soils (Dinev and Nikova, 2008). An important element of soil fertility is the assessment and maintenance of soil carbon (Katsarova and Koutev, 2011; Tsolova et al., 2011; Filcheva et al., 2012).

As a rule, the reclaimed absorbed by the direction of their biological reclamation (agricultural, forestry, etc.) (Banov et al., 2011), but under certain circumstances related to social and economic reasons it is possible reclaimed areas to be used for production of plants production, strictly monitoring its quality.

The aim of this study was to determine the effect of culture medium on substrate reclaimed by the content of nutrients and heavy metals in the vegetative mass of tomatoes as well as on the quality of the fruit.

Materials and Methods

Experiment is set on four reclamation substrate taken by technical and biological reclaimed dumps built in iron ore (Lokorsko) and coal (Moshino). For convenience in the work materials used in the experiment will be marked as:

■ Object 1 – reclamation of organic substrate rehabilitated dump near Moshino, horizon 0–30 cm;

■ Object 2 – reclamation substrate technical rehabilitated dump in the area of Moshino;

■ Objectt 3 – reclamation of organic substrate rehabilitated dump near Lokorsko, horizon 0–30 cm;

■ Object 4 – reclamation substrate technical rehabilitated dump near Lokorsko.

Table 1 shows the values of agrochemical indicators characterizing the surveyed reclamation substrates. Soil reaction in Objects 1, 2 and 3 is slightly alkaline – pH_{KCl} varies from 6.8 to 7.0. Humus content in the Object 1 is average – 3.99%, while in Object 2 (0.93%) and 3 (1.14%) is low. The content of mineral nitrogen in reclaimed substrates Object 1 averaged (53.9 $mg.kg^{-1}$) and at Objects 2 (28.4 $mg.kg^{-1}$) and 3 (14.5 $mg.kg^{-1}$) – low. Content of mobile phosphorus in Object 2 is low and in sites 1 and 3 – medium. Regarding the content of K_2O three objects showed to be very well preserved.

Mechanical composition studied substrates are heavy sandy loam to light clay (Figure 1).

The content of micro elements and heavy metals (Table 2) is within the bounds of ppermissible of Order № 3 for limit values of harmful substances in the soil, prom. SG . №. 71 of August 12, 2008, with the exception of the high levels of concentration in terms of lead and copper at Object 4 (Nikolov and Zlatareva, 1999; Zlatareva and Nikolov, 1999).

The four sites during the first ten days of April bet experience with hybrid tomatoes' „Nikolina-F1". For the purposes of the study were used containers holding 4 kg soil, each experiment contains four repetitions.

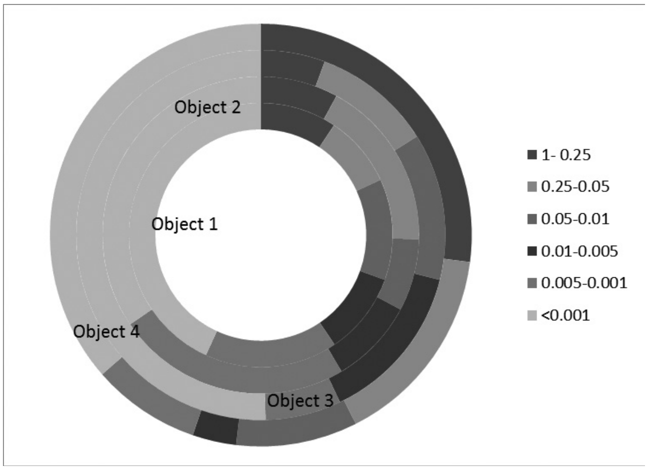

Fig. 1. Mechanical composition of the reclamation substrates in% of the air-dry state

Table 2
Output content of trace elements and heavy metals in reclamation substrates

Object	Cu	Ni	Pb	Zn	Cd	Fe
	$mg.kg^{-1}$					%
Object 1	47.0	38.5	49.0	53.5	0	38700
Object 2	45.5	8.0	97.5	73.0	0	21400
Object 3	49.5	20.0	51.5	84.0	0	37000
Object 4	535.0	34.0	2575.0	312.5	0	88200

Table 1
Agrochemical characteristics of the reclamation substrates

Object	pH		NH_4N+NO_3-N	P_2O_5	K_2O	Humus
	H_2O	KCl	$mg.kg^{-1}$	$mg.100g^{-1}$		%
Object 1	7.2	6.8	53.9	7.5	61.4	3.99
Object 2	7.7	7.0	28.4	1.3	57.5	0.93
Object 3	8.1	7.0	14.5	5.6	36.8	1.14
Object 4	8.1	7.5	26.1	11.4	29.1	0.47

Scheme of the experiment

- Controlled variant – without fertilization – 1
- Fon $P_{600}K_{757} + N_{400+400}$ – $(NH_4)_2SO_4$ – 2
- Fon $P_{600}K_{757} + N_{400+400}$ – NH_4NO_3 – 3

The scheme of the test includes: 1: Controlled variant (without fertilization) and variants 2 and 3: by entering mineral fertilizers. Option 2 nitrogen is introduced into the standard 800 mgN.kg^{-1} soil as $(NH_4)_2SO_4$. In variant 3 nitrogen fertilization in the same rate, but in the form of NH_4NO_3. Phosphorus and potassium fertilization and background are made by depositing KH_2PO_4 still in the preparation of the soil substrates in standard 600 mgP.kg^{-1} soil and 757 mgK.kg^{-1} soil. Nitrogen rate was paid twice – 400 mgN.kg^{-1} soil in preparation of soil substrates with phosphorus and potassium fertilization. The other half of the nitrogen rate is paid one week after planting the plants in pots. The choice of ammonium nitrate and ammonium sulfate, as a physiologically acidic fertilizer (Gorbanov, 2010; Mengel and Kirkby, 1982; Merkel, 1973) is related to alkaline soil reaction.

Tomato plants in containers take out from and put into 4 pcs. In phase 1–2 true leaf stage (phase "cross"). In Object 4 (substrate reclamation technical rehabilitated dump near Lokorsko) regardless of repeated replanting seedlings in containers, the plants did not survive in any of the options and the object dropped from the study.

The content of macro-and micronutrients in the soil is determined by standard methods (Arinushkina, 1970). Ammonium and nitrate nitrogen were determined colorimetrically. Mobile forms of phosphorus and potassium – a method of Ivanov (1984). Mobile forms of trace minerals – EDTA extract and pH in H_2O and KCL – potentiometric.

In plants, the total nitrogen determined by Kjeldahl method by digestion with concentrated H_2SO_4 and 30% H_2O_2. Other macro- and micronutrients were determined by "dry" burned in muffle furnaces and subsequent dissolution in 20% HCl considering the atomic absorption spectrophotometer (Mincheva and Brashnarova, 1975).

The study determined the chlorophyll in fresh mass spectrophotometry to extract by 80% acetone by the method of Vernon, 1960. From plant samples of tomato fruits after drying at 60°C prior to fixation is determined dry matter (% SDA) – weight. The content of total sugars has been determined by refractometer – (%) (Digital refractometer – 32 145). The content of total acid, and ascorbic acid was determined on an apparatus RQ flex plus 10 Merck. Lycopene and common dyes are defined in the filtrate from acetone – spectrophotometry.

Results and Discussion

Content of macro, trace elements and heavy metals in tomato plantsMeasured at the end of the study pH values (Table 3) showed no tendency to acidification of the soil by fertilization with $(NH_4)_2SO_4$, as might be expected from fertilization with physiologic acid fertilizers. Differences in pH values at fertilization with $(NH_4)_2SO_4$ and NH_4NO_3 in test objects are insignificant and do not differ significantly from baseline soil reaction. Estimating residual content of mineral nitrogen in the versions of Objects 1 – 3 can be concluded that the fertilizer rate ($N_{800}P_{600}K_{757}$) proved adequate in relation to nitrogen fertilization as a result of phosphorus and potassium fertilization have formed significant residual concentration of these elements in the soil, at the end of the experiment. As may be presumed in accordance with the larger biomass formed during embodiments of ammonium nitrate fertilizer, the end of the study, the residual concentration of inorganic nitrogen in the versions with NH_4NO_3 are smaller than those fertilized with $(NH_4)_2SO_4$. In Object 3 formed where yields are highest residual mineral nitrogen contents are the lowest compared to other sites. In respect of mobile forms of phosphorus and potassium contents residual significant, especially phosphorous. In Object 1 phosphorus content in the soil at the end of the experience is over 12 times

Table 3
Nutrient content in the soil substrate at the end of the study

	Variant	pH		Mineral N	P_2O_5	K_2O	Humus
		H_2O	KCl	mg.kg^{-1}	mg.100g^{-1}	mg.100g^{-1}	%
Object-1	1. checking	7.6	7.0	16.7	5.2	35.4	4.41
	2. $(NH_4)_2SO_4$	7.6	7.0	27.1	64.0	40.3	4.57
	3. NH_4NO_3	7.6	7.0	24.8	65.6	37.5	4.26
Object-2	1. checking	8.1	7.1	17.9	12.0	32.2	1.03
	2. $(NH_4)_2SO_4$	7.8	6.9	19.0	68.4	25.7	1.31
	3. NH_4NO_3	7.5	6.9	14.4	68.3	26.7	0.99
Object-3	1. checking	8.3	7.5	13.2	4.2	19.3	0.36
	2. $(NH_4)_2SO_4$	8.0	7.6	10.5	67.7	33.7	0.16
	3. NH_4NO_3	8.0	7.7	8.6	68.1	43.4	0.49

Table 4
Nutrient content in stems of tomatoes at the end of the study

Object	Variant	Total N	P	K	Ca	Mg	Zn	Cu	Ni	Fe	Mn	Pb	Cd
		%					ppm						
	1. checking	0.5	0.27	2.1	0.93	0.30	86	9	16	134	13	0	0
Object -1	2. $(NH_4)_2SO_4$	1.0	0.19	2.5	1.13	0.11	25	2	13	73	13	18	0
	3. NH_4NO_3	1.3	0.13	2.1	1.19	0.14	19	2	8	91	16	13	0
	1. checking	0.5	0.13	1.6	0.63	0.30	82	8	8	40	5	0	0
Object -2	2. $(NH_4)_2SO_4$	1.1	0.13	2.1	0.91	0.21	35	4	10	71	11	23	0
	3. NH_4NO_3	1.4	0.13	1.9	0.89	0.17	37	4	10	69	13	14	0
	1. checking	0.4	0.42	2.0	0.56	0.32	77	8	7	78	9	0	0
Object -3	2. $(NH_4)_2SO_4$	1.1	0.18	2.2	0.70	0.25	19	2	11	66	17	16	0
	3. NH_4NO_3	1.2	0.17	2.0	0.79	0.31	28	2	5	63	23	1	0

Table 5
Nutrient content in the leaves of tomato at the end of the study

Object	Variant	Total N	P	K	Ca	Mg	Zn	Cu	Ni	Fe	Mn	Pb	Cd
		%					ppm						
	1. checking	0.98	0.28	2.2	3.99	0.73	44	12	16	210	39	4	0
Object-1	2. $(NH_4)_2SO_4$	0.99	0.18	3.7	2.60	0.44	46	6	4	310	45	0	0
	3. NH_4NO_3	1.0	0.18	3.5	3.50	0.52	43	7	10	439	63	32	0
	1. checking	0.81	0.16	2.0	3.63	0.74	42	12	18	371	50	3.5	0
Object-2	2. $(NH_4)_2SO_4$	1.1	0.14	3.5	3.44	0.79	45	7	14	244	33	13	0
	3. NH_4NO_3	1.3	0.17	2.9	2.05	0.53	43	6	7	275	34	0	0
	1. checking	0.92	0.43	1.7	3.55	1.40	23	9	3	175	55	2	0
Object-3	2. $(NH_4)_2SO_4$	1.3	0.18	3.3	2.15	0.82	43	5	5	254	58	56	0
	3. NH_4NO_3	1.3	0.17	2.7	2.36	0.90	31	4	14	230	70	21	0

more than non-fertilized option in Object 2 – more than 21 times, while Object 3 – more than 11 times.

In Tables 4 and 5 it is showen the contents of nutrients and heavy metals in the biomass (stalks and leaves) of tomato. The data for total nitrogen content in the leaves and stems of tomatoes showed optimal values. When cited in the literature optimal contents of the order of 0.5–1.5% for leaves (Mitova, 2007; Myths and Dinev, 2011; Neubert et al., 1970), the variations in the experience of total nitrogen content is between 0.81–1.3% for leaves and 0.4–1.4% of the stems. Taking into account the residual amount of mineral nitrogen in the soil at the end of the growing season, it may be said that the attached nitrogen rate is adequately selected for the feeding of the plants by the end of vegetation. Missing a noticeable difference in the absorption of mineral nitrogen between the versions with $(NH_4)_2SO4$ and NH_4NO_3 in the three experimental sites, but there is a slight trend that is absorbed total nitrogen is more available with NH_4NO_3 (Objects 1 and 2).

The study phosphorus and potassium values were chosen based on previous studies with tomatoes (Mitova, 2007; Myths and Stoykov, 2008), which recommended optimal rates of fertilization with these elements relative to the stage of development of culture. In the experience of the content of phosphorus in plant samples from tomatoes is low and ranges from 0.14 to 0.43% in the leaves and from 0.13 to 0.42% of the stems. Despite the high rate of fertilization – 600 mgP.kg^{-1} of soil and plants in the control variant with higher phosphorus content in their tissues, as compared with tomatoes fertilization. On the other hand, in Table 3, which shows the residual content of phosphorus in the movable end of the study it appears that these quantities range from 1.2 in the control embodiment of the Object – 2 and 68.4 mgP.kg^{-1} soil with the same object. High residue levels of mobile phosphorus in soil fertilization variants of the three experimental sites associated with suboptimal content in plant tissues of plants fertilization showed the existence of a disturbing factor entry and uptake of phosphorus by plants. The connection between nitrogen form and receipt of phosphorus in tomato plants. When nitrate feeding plants used relatively little phosphorus in comparison with ammonium – fed cultures (Yanishebskiy and Krishtenko, 1988). The state of "nitric stress" occurs when in nitrate nitrogen source in the nutrient medium, the plants are not absorbed by the phosphor phosphate fertilizers (Yanishebskiy and Krishtenko, 1988). In the displayed experience, however, nedoimachnoto phosphorus nutrition is observed in plants fertilized with $(NH_4)_2SO_4$, so that N – form can not be determined in this case as the only factor inhibits the absorption of phosphorus by plants.

Optimal potassium content in leaves of tomatoes is between 2.5 and 6.65% (Mitova, 2007; Myths and Dinev, 2011; Neubert et al., 1970). In the experience of the plants only non-fertilized embodiments are less than optimal contents. In all three sites the plants fertilized with $(NH_4)_2SO_4$ with higher potassium content. In general, however, regardless of the starting potassium that the availability is very good, the content of potassium in the leaves and stems in the lower part of the optimum.

The calcium content in the leaves varies between 2.05 and 3.99%, while in the stem between 0.56 and 1.19%. In literature as optimal calcium content in tomato vegvtativna table indicating values from 2.5 to 7.15%. The calcium content in the leaves as opposed to the stalk, however, in all three items was highest in the control embodiment. The cottage – 1 and 3 of the calcium content in the variant with NH_4NO_3 is higher compared to plants fertilized with $(NH_4)_2SO_4$.

Magnesium content in the foliage of the test plants varies between 0.44 and 1.4%, and within the boundaries of that as optimum (0.6–0.9) in the literature (Kurwits and Kirkby, 1981).

Of the trace elements and heavy metals zinc reported in the leaves is within the optimal range (20–200 ppm) and in the study varied between 23 and 46 ppm. The plants fertilized with ammonium sulphate have gained more zinc in their tissues than those of ammonium nitrate, which corresponds to the increased information content of Zn in the tissues of plants with predominantly ammonium meal (Yanishevskiy and Krishtenko, 1988).

The copper content in the leaves of the plants of the masses experience is between 4 and 12 ppm in the optimal values of between 8 and 15 ppm. All three objects plants in the control options are the highest contents of Cu.

An optimal manganese content in the plants between 35 and 240 ppm, in the test the content of Mn is in the lower part of the optimum – between 33 and 70 ppm. Plants fertilized with ammonium nitrate with higher manganese content of the fertilizing with ammonium sulphate.

The iron content in the foliage varies between 175 and 439 ppm with optimum levels of 150 to 300 ppm. The Objects 1 and 2 plants NH_4NO_3 have a high iron content, while Object 3 dependence is reversed. In operation Yanishebskiy and Krishtenko (1988) specifies data hydroponic experience (not show in soil culture) for increased synthesis of Fe as a result of ammonium nutrition and domatovi cucumber plants.

In hygienic standard for lead in the plant tissues of tomatoes is from 4.0 mg.kg^{-1}, a significant proportion of the variants of the experience content exceeds permissible. In the embodiment of the sheet with the object of NH_4NO_3 – 1 is the content of lead (32 mg.kg^{-1}) – 8 times, as well as variants with $(NH_4)_2SO_4$ by the Object 2 (13 mg.kg^{-1}) – 3 times the above limit. In Object 3 in both species fertilization contents of Pb is much higher than permissible – in plants fertilized with $(NH_4)_2SO_4$ (56 mg.kg^{-1}) – 14 times, and in the version with NH_4NO_3 (21 mg.kg^{-1}) – 5 times.

When allowed norm for cadmium in the pany mass is 0.1 mg.kg^{-1} (Nikova et al., 2011) in the leaves and stems of tomatoes at the end of the study was not detected Cd. The nickel content in the tomato foliage was between 3 and 18 ppm, and in the stem between 7 and 16 ppm in sanitary than 0.5 ppm. In stems and leaves (Object 2) export of Ni variants with $(NH_4)_2SO_4$ is greater than in plants with NH_4NO_3.

Physiological and biochemical parameters in tomato on reclaimed substrates

The content of plastid pigments is important underlying index and an indicator of the overall development of the plant body. Analysis of chlorophyll content in leaves (Figure 2). Plant phase formation tied first inflorescence definitely shows higher values of chlorophyll "a", chlorophyll "b", chlorophyll "a + b", and carotenoids in the foliage of the plants fertilized with NH_4NO_3. The ratio of Ch „a"/Ch „b" in the embodiments of the experiment varied between 1.81 and 2.34 and is in the range indicated as optimal (Berova and others., 2007). As the biometric measurements, reflecting the growth and development of plants under different nitrogen fertilizer sources, presented in another work of authors (Mitova et al., 2013), plants fertilized with NH_4NO_3 have better development, which is expressed not only by yields and biometrics, but also to general visual assessment, which is the

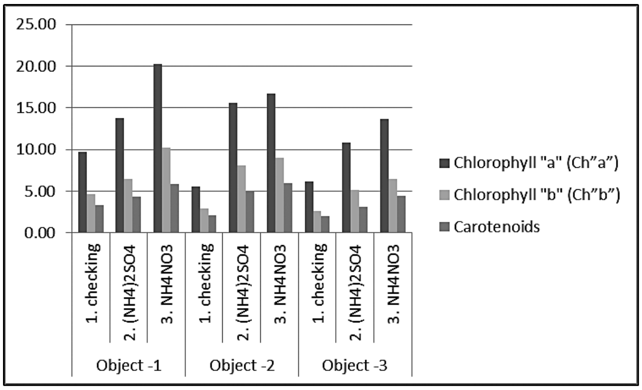

Fig. 2. Content of plastid pigments in fruits of tomato

Table 6
Biochemical composition of tomato fruits

Object	Variant	Vitamin C	Total acids (%)	Lycopene mg %	% B-carotene and other yellow colored pigments	Total dyes	Total sugars (%)	Solids (%)
Object-1	1. checking							
	2. $(NH_4)_2SO_4$							
	3. NH_4NO_3	18.0	0.81	3.66	23.0	4.75	3.72	5.5
Object-2	1. checking							
	2. $(NH_4)_2SO_4$	9.7	0.85	3.35	26.0	4.53	3.17	6.4
	3. NH_4NO_3	10.1	0.71	3.63	23.0	4.71	4.78	5.9
Object-3	1. checking							
	2. $(NH_4)_2SO_4$	13.9	0.80	2.20	25.0	3.28	3.98	4.9
	3. NH_4NO_3	17.8	0.75	3.76	33.0	3.98	5.72	5.1

result of chlorophyll content. Proper selection of the form of nitrogen fertilization is confirmed by the fact that the total content of chlorophyll in plants fertilized with NH_4NO_3 and at three sites was greater than 2 – fold higher than in non-fertilized plants. The content of chlorophyll "a + b" in the version of NH_4NO_3 from Object 1 is 51.3% higher than that of plants with $(NH_4)_2SO_4$, the Object 2 by 8.6%, while Object 3 with 25.9%.

Data for biochemical analysis of the tomato fruits (Table 6) obtained in the assay give an indication of the quality of the reclaimed product on substrates, wherein a feed of different forms of nitrogen fertilizers. The obtained values of the indicators lycopene, total sugars and dyes, absolutely dry matter strictly comparable with those identified as optimal in the literature (Mitova and Dinev, 2011). In non fertilized plants, and in Object 1 in the embodiment 1 with a dung $(NH_4)_2SO_4$ is not formed fruit. In Objects 2 and 3 vitamin „C", lycopene, general dyes and sugars are higher in the fruits of plants fertilized with NH_4NO_3 than those fertilized with $(NH_4)_2SO_4$. The content of total acids was reported to experience slightly higher than that considered optimal, and that the Vitamin „C" – lower, which may be due to varietal characteristics of and „simulated" growing conditions.

Conclusions

The results of soil and plant analyzes made at the end of the vegetation of tomatoes showed that fertilizer rate applied in experience ($N_{800}P_{600}K_{757}$) is adequately selected in terms of N-fertilization, while PK-fertilization have formed a significant residual in the soil of these elements.

High residual concentration of mobile phosphorus fertilization variants Objects 1–3 associated with low phosphorous content in plant tissues and in three subjects of the experiment indicate a disturbing factor in the uptake of phosphorus by tomato plants.

The content of potassium in crop production experiment is displayed within the optimal range, while plants fertilized with $(NH_4)_2SO_4$ was higher than those fertilized with NH_4NO_3.

The content of oligo-and trace elements Ca, Mg, Zn, Cu, Mn in plant tissues of plants tomatoes ranges indicated it is optimal.

As extremely tolerant to pollution culture tomatoes have significant potential for phytoremediation of contaminated land. The content of Fe in the foliage of tomatoes in Objects 1 and 2 slightly exceed the upper limit of the content of elements in crop production. Ni content in the leaves and stems of tomato repeatedly exceed the recommended hygiene standards, in foliage of tomatoes is 3–36 times, and in stems with 10–32 times more. The content of Pb in the leaves of tomatoes from different sites experiments exceeds permissible limits by 3 to 14 times.

The values of plastid pigments in the vegetative mass of tomato plants Objects 1–3 fertilized with NH_4NO_3, were significantly higher than those of variants with $(NH_4)_2SO_4$. Fruits of plants fertilized with NH_4NO_3, of Objects 2 and 3 have a higher content of vitamin "C", lycopene common dyes and sugars.

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